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# Efectul levigării asupra betonului – partea I: caracterizarea evoluției degradării chimice a zonei de tranziție inter facială

## Leaching effect on concrete - part I: characterization of chemical degradation evolution of ITZ

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### Abstract

The study of the durability of concrete subjected to leaching requires knowledge of the mechanisms of chemical degradation of cement paste and of cement paste/aggregate bond. The Interfacial Transition Zone (ITZ), the portion of cement paste in contact with aggregates, is a vulnerable zone in the context of chemical degradation due to its high degree of solubility and diffusivity. In order to evaluate the leaching kinetics as well as the chemical dissolution of bulk cement paste and of the ITZ, parallelepiped cement paste samples and cement paste/aggregate composites were produced and submitted to accelerated leaching. The measurement of the degraded depth was carried out by image analysis of the cross sections of the cement paste and of the interface. The degradation kinetics of the bulk cement paste is proportional to the square root of time. On the other hand, that of the ITZ initially follows the same trend, but slightly accelerates after a critical threshold. Chemical analyses were performed by Energy Dispersive Spectroscopy (EDS) to measure the Ca/Si molar ratios of ITZ and cement paste for a single degradation time. The greater drop of the Ca/Si ratio at the ITZ reveals a significantly greater dissolution of the portlandite than in the bulk cement paste.

Studiul durabilității betonului supus levigării necesită cunoașterea mecanismelor de degradare chimică a pastei de ciment și a legăturii pasta/agregat. Zona de tranziție inter facială (ITZ), porțiunea de pastă de ciment aflată în contact cu agregatele, este o zonă vulnerabilă în contextul degradării chimice datorită gradului ridicat de solubilitate și difuzivitate. Pentru a evalua cinetica de levigare, precum și amploarea disoluției chimice a pastei de ciment propriu zise și a ITZ, s-au produs eșantioane paralelipipedice din pastă de ciment și compozite paste / agregate de ciment. Ulterior, acestea au fost supuse levigării accelerate. Măsurarea grosimii degradate a fost efectuată ca urmare a analizei imaginii secțiunilor transversale ale pastei de ciment și ale interfeței. Cinetica de degradare a pastei de ciment propriu zise este proporțională cu rădăcina pătrată a timpului. Pe de altă parte, cea a ITZ urmează inițial aceeași tendință, dar se accelerează ușor după un prag critic. Analizele chimice au fost efectuate prin spectroscopie energetică dispersivă (EDS) pentru a măsura raporturile molare Ca / Si la nivelul ITZ și al pastei de ciment pentru o singură perioadă de degradare. Scăderea mai mare a raportului Ca / Si la nivelul ITZ indică o amploare a disoluției a portlanditei semnificativ mai mare decât la nivelul pastei de ciment propriu-zise.

**Key words:** concrete, ITZ, leaching, leaching kinetics, dissolution

## 1. Introduction

Concrete is a composite material formed by a cementitious matrix (cement paste) and a granular skeleton (aggregates). Cement paste is obtained following the hydration of the anhydrous cement and acts as a binder between aggregates. It is formed by several chemical species, the most important one being hydrated calcium silicates (C-S-H), and other significant ones being portlandite and ettringite. C-S-H, a poorly crystallized chemical species with variable stoichiometry (Ca/Si molar ratios between 1.2 and 2.3 [1]), are the main contributors to the development of the material mechanical strength.

The Interfacial Transition Zone (ITZ) is the portion of the cement paste that is adjacent to the aggregates and has particular properties. Generally, in the hydrated final state, ITZ has a higher porosity and a

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higher content of chemical species that have weak cohesive properties (portlandite and ettringite) [2], [3].

Concrete leaching occurs following contact of concrete with a chemically aggressive solution, such as water, which is relatively acidic compared to the interstitial solution in concrete. Subsequently, water diffuses into the interstitial solution and changes its concentration of basic ions. Therefore, in order to ensure the chemical equilibrium between interstitial solution and cement paste, a progressively dissolution of the Calcium occurs in the cement paste.

After leaching, the Calcium dissolution from cement paste (bulk and ITZ) produces an increase of porosity and thus a drop of mechanical properties. The leaching process is manifested by the complete dissolution of portlandite that occurs rapidly and the gradual decalcification of C-S-H [4]. ITZ can affect the durability of leached concrete by two mechanisms related to chemical degradation:

- local acceleration of chemical degradation due to its higher porosity and its higher diffusivity
- more important dissolution at the ITZ with respect to the bulk cement paste. This is due to the higher concentration of fully soluble chemical species (portlandite) of ITZ in sound state.

In the context of the study of leaching effect on concrete mechanical behaviour, the results in literature come mainly from macroscopic studies which permitted the deduction of ITZ role rather indirectly. At the macroscopic scale of concrete, the ITZ effect on the leaching kinetics is small, because the slowing effect due to the tortuosity induced by the aggregates prevails over the acceleration induced by the higher diffusivity of the ITZ [5], [6]. On the other hand, following leaching, a greater increase in porosity has been noticed at the ITZ with respect to the bulk cement paste, and was attributed to a significant chemical dissolution [7]. In fact, the greater chemical degradation of ITZ was considered to be the reason why for the same global extent on chemical degradation, the loss of compressive strength of the mortar samples is greater than the loss of compressive strength of the cement paste samples [8].

Therefore, we conclude that prior studies managed to identify the mechanisms by which ITZ affect the durability of concrete on a macroscopic scale. However, numerical models of concrete managed to take into account the ITZ in order to simulate its mechanical behaviour at sound state [9]. These kind of models is likely to be used also on degraded materials, since ITZ effect need to be considered in order to perform correct prediction of the concrete structures lifetime. In this context, an experimental protocol was developed at LMGC to assess the mechanical behaviour of the concrete at local scale of the cement paste/aggregate bond [10]. In the perspective to analyse the mechanical behaviour of the degraded material, chemical degradation characterisation of cement paste and ITZ is necessary. The present study aims to evaluate the leaching kinetics and the magnitude of the chemical dissolution of ITZ by direct measurements. The necessary assessments were performed on cement paste and cement paste/aggregate composite samples.

## **2. Materials and methods**

### **2.1. Materials**

The materials that were used to manufacture the samples are cement paste (CEM I, water/cement ratio of 0.4) and limestone aggregates. The two types of parallelepiped samples, cement paste ones (Figure 1 a) and cement-aggregate composites (Figure 1 b) were obtained following casting in flexible latex samples [11]. The total dimensions of the samples are 10x10x30 mm<sup>3</sup> with a tolerance of ±0.1 mm. The composite sample consist of one half aggregate (10x10x15 mm<sup>3</sup>) and one half cement paste (10x10x15 mm<sup>3</sup>). They were obtained following casting of cement paste onto the aggregate which was previously cut and adjusted to the desired dimensions and allowed the creation of a cement paste/aggregate bond. This cement paste/aggregate bond allow the presence of the same phenomenon that generates the creation of ITZ in real concrete, the wall effect. In fact, the present geometry is well suited for measuring the degraded depth of the (bulk) cement paste and of ITZ.

After casting, the samples were kept in their mould for 24 hours at 100% RH. Then, after demoulding, they were stored in a water lime saturated solution for 40 days in order to allow an optimum cement hydration and avoid any accidental leaching that could occur following preserving samples in water. After 40 days of hydration, the samples were submitted to leaching in order to allow the study of the properties of the degraded material. Concrete leaching is a very long process compared to the time of the laboratory studies. It has been shown that for an ordinary Portland cement paste with a water/cement ration of 0.4, it is necessary to wait 300 years to reach a degraded depth of 4 cm of a macroscopic

sample in water [12]. Therefore, for laboratory specimens, it is then necessary to use specific techniques to accelerate this phenomenon.

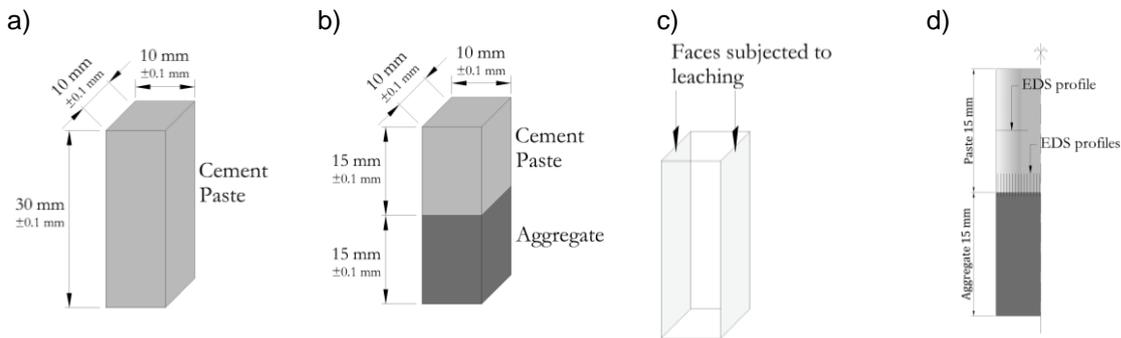


Figure 1 Cement paste (a) and composite sample (b); leaching configuration (c); chemical profiles location (d) *Forma eșantioanelor din pastă de ciment (a) și compozit (b); configurația degradării (c); locația profilurilor chimice (d)*

## 2.2. Accelerated leaching procedure

The chosen degradation method was to use an ammonium nitrate solution instead of water as aggressive agent. The ammonium nitrate solution allows to accelerate the degradation due to high solubility of the hydrates [13]. Consequently, for the same extent of the degraded region, the necessary leaching time is 100 to 300 times lower with ammonium nitrate solution than with pure water. Another advantage of the method is the similarity of the dissolution processes with respect to the reference leaching scenario in water. The concentration of ammonium nitrate solution is similar to that used by other authors [5], [11]: 6 moles / litre which corresponds to 480 grams of ammonium nitrate for 1 litre of water.

Before plunging the samples into aggressive solution, four faces were isolated in order to leave only two opposite longitudinal faces in contact with the aggressive solution on their entire height (Figure 1 c). The samples thus underwent unidirectional chemical degradation which propagates perpendicularly to the attacked faces. The samples were leached for several degradation times: 0.75; 2; 4; 8; and 12 days.

## 2.3. Analysis of leaching kinetics

In order to measure the degraded depth, optical observations can be used following a well-defined contrast between sound and degraded zones. Several authors [14], [15] have used optical observations coupled with chemical analyses to locate the degradation fronts and thus to measure the degraded depth.

Therefore, we decided to use optical measurements coupled with Energy Dispersive X-ray Spectrometry EDS chemical analyses in order to study the degradation kinetics, expressed by the variation of the degraded depth in time. The available tool, optical scanner, allows measurement of grey levels (between 0 and 255) with resolutions that can reach  $2\mu\text{m}$ . A sufficient contrast between grey level of the sound zone and that of the degraded one allowed measurement of degraded depth. For every leaching time, degraded depth was measured on 5 cement pastes and 5 composite samples.

## 2.4. Analysis of the chemical dissolution

Microstructure analyses by Scanning Electron Microscopy (SEM) require a sufficient flatness of the surface that is obtained by polishing. In order to make the polishing possible, the sample was embedded in resin. Chemical analyses of dissolution were carried out for a single degradation period - 4 days on 3 composite samples.

SEM principle consists in the injection of an electron beam on the surface of the sample which gives rise to an interaction volume. The EDS detector, by quantifying the X-rays emitted by the interaction volume, allows the access to the punctual chemical elementary concentrations. Therefore, concentration profiles lines and mappings can be obtained by one-off measurement sets.

Therefore, in this study linear chemical concentration profiles obtained by EDS were generated to study the chemical gradients that develop at ITZ and at bulk cement paste. These profiles allow to measure the punctual concentrations of all the elements which exists in the punctual interaction volumes ( Figure 2 a). However, in this study we decided to focus on the Calcium and Silicon concentrations, as they are related to the presence of the hydrates (C-S-H, portlandite, ettringite) and to their dissolution. Two types

of chemical concentration linear profiles were realized : ones parallel to the degradation direction and others perpendicular to the interfaces (Figure 1 d). Linear profiles parallel to the degradation direction (Figure 4Figure 2 b) allowed us to measure the degraded depth of the bulk cement paste as they reveal the calcium dissolution in the degraded zone [16]. The degraded depth measured by this method was compared to that obtained by image analysis to validate the measurements of the degraded depth. The other type of linear profiles, that perpendicular to the interface, were made in sound zone and in degraded zone. The analyse of these profiles allowed us to demarcate the ITZ and to compare its dissolution state with the one of the bulk cement paste. The linear profiles perpendicular to interface (Figure 2 b) extend over a length of over 100  $\mu\text{m}$  covering ITZ and bulk cement paste zone. The distance between the measuring points on each profile line is 1  $\mu\text{m}$ . The gap between the profile lines in the direction parallel to interface is 0.1 mm.

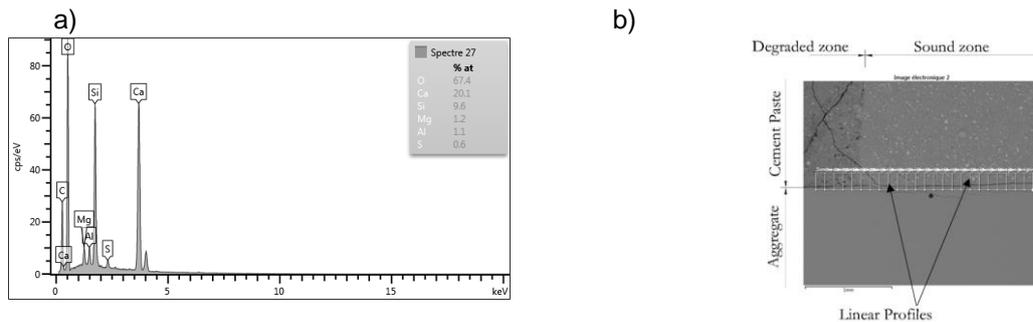


Figure 2 Example of punctual chemical spectrum and associated elementary molar concentrations in cement paste (a) and location of a series of linear profiles perpendicular to the interface (b) *Exemplu de spectru elemental punctual din pasta de ciment și concentrațiile molare elementare asociate (a) și locația unei serii de profiluri liniare perpendiculare pe interfață (b)*

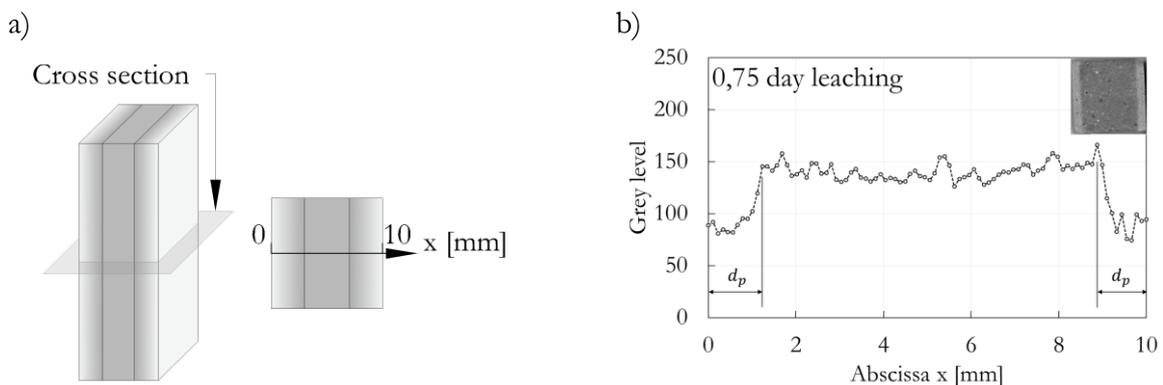
### 3. Results

#### 3.1. Leaching kinetics

The measurement of the degraded depth of cement paste  $d_p$  was made on cross-sections that are perpendicular to the vertical axis of the cement paste and cement paste/aggregate composites samples. The linear dimensions of the square cross sections are 10 mm  $\pm$  0.1 mm. For cement paste samples, images of cross section and grayscale profiles for each degradation time are presented in Figure 3. In this figure, for all degradation times, there is a high grey level in sound zone and a lower grey level in degraded one. In degraded zone, there is an intermediate zone where grey level decay is rapid and varies between the high value found in the sound zone and the reduced value encountered at the end of degraded zone.

The leaching front is the point where mean level of sound zone is reached. Therefore, the degraded depth is equal to the distance between the degradation front and the attacked edge of the sample. position of the main degradation front advances with time toward the centre of the sample.

In order to verify the validity of the degraded depth measurement by image analysis, these results were compared with chemical SEM/EDS analyses. Linear profiles that are parallel to the degradation direction indicate the evolution of molar Ca/Si ratios in the degraded zone and in sound zone of cement paste on a line that starts from the attacked edge of the sample and goes to the sound core. They were made at distances greater than 2 mm from the interface to avoid any influence of the ITZ.



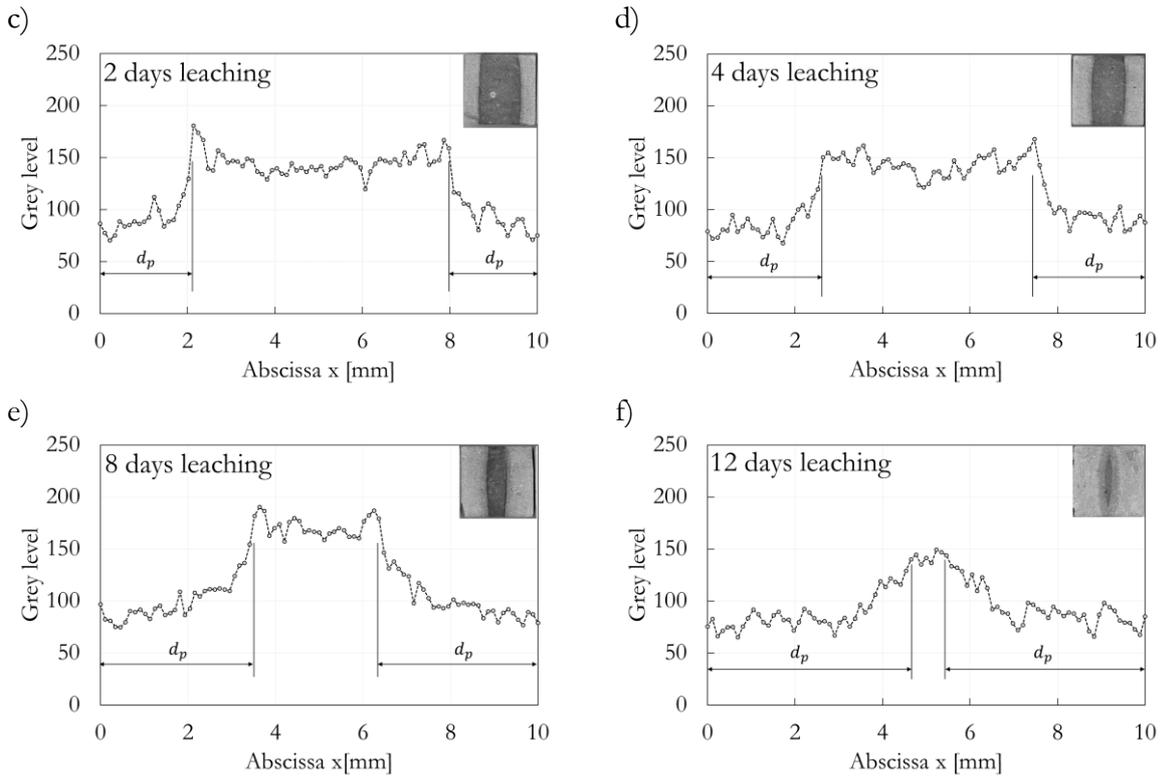


Figure 3 Evolution of the grey level on the median of the cross section of the samples in cement paste. Location of the cross section (a); Cement paste samples after 0.75 day (b), 2 days (c), 4 days (d), 8 days (e) and 12 days (f) of leaching *Evoluția nivelului de gri pe mediana secțiunii transversale a eșantioanelor din pastă de ciment. Locația secțiunii transversale (a); Eșantioane din pastă de ciment după 0,75 zile (b), 2 zile (c), 4 zile (d), 8 zile (e) și 12 zile (f) de levigare*

The Ca / Si molar ratio was chosen as an indicator of chemical degradation because it is directly related to the dissolution of portlandite and the decalcification of C-S-H. Following leaching, calcium (Ca) is dissolved while silicon is unaffected.

In Figure 4, which illustrates the evolution of the Ca/Si molar ratio as a function of the distance from the attacked edge of the sample, we notice, as in the case of image analyses, presence of three zones: the sound zone, an intermediate degraded zone and a highly degraded zone. In the intermediate degraded zone, the decrease of Ca/Si ratio is more pronounced, while in the highly degraded zone the Ca/Si ratio is low and does not present a significant variation. Therefore, in addition to locating the main degradation front, the location of a secondary degradation front between intermediate degraded zone and highly degraded one is also possible. The presence of both leaching fronts has been already observed in the literature[17]. The main front represents the dissolution front of the portlandite while the secondary one represents the decalcification front of the C-S-H [16].

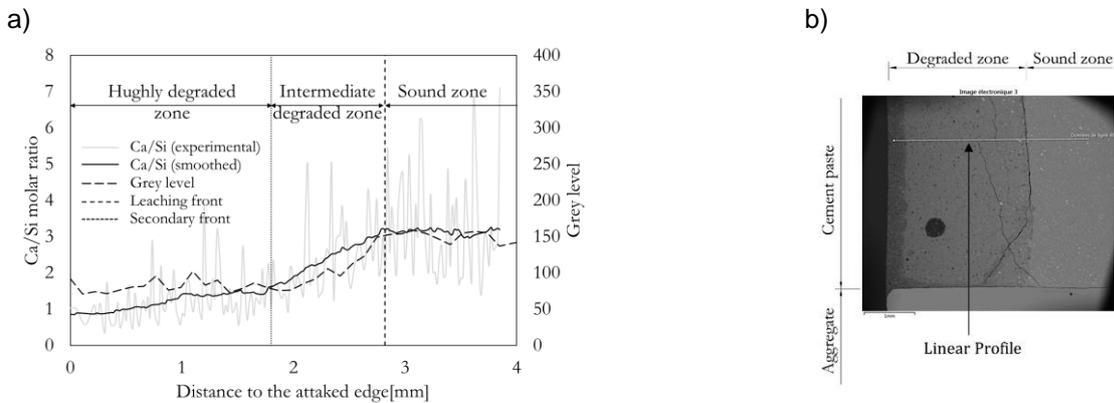


Figure 4 Ca/Si molar ratio in the bulk cement paste as a function of the distance to the attacked edge (a). Location of the linear profile that is parallel to the degraded zone (b) *Raportul molar Ca / Si în pasta de ciment propriu zisă, în funcție de distanța față de latura atacată de soluția agresivă (a). Amplasarea profilului liniar paralel cu direcția degradării (b)*

Besides that, we observed that the mean value of the Ca / Si ratio in the sound zone of 3.2 is similar to that reported by Yuan & Odler [2]. This value is higher than the average Ca/Si ratio of C-S-H (1.7 [18]) due to the coexistence of C-S-H with crystals of portlandite and ettringite, which contain only Calcium and not Silicon. In contrast, the highly degraded zone has Ca / Si ratios between 1 and 1.55 similar to the Ca / Si ratio of decalcified C-S-H ([19], [20]). Therefore, the measurement of the degraded depth made by SEM finds a good agreement with that made by image analysis and validates the latter type of measurement. Once degraded depth measurement obtained by image analysis is validated following the chemical analyses, it was possible to determine the kinetics of the degraded depth. Figure 5 shows that the evolution of the degraded depth is proportional to the square root of time.

This type of leaching kinetics is due to the diffusive nature of leaching phenomenon and has been reported in all the studies that have used accelerated leaching by ammonium nitrate. The proportionality factor  $k$  between degraded depth and square root of time (days) of 1.35 is substantially similar to that obtained by Carde [16] on cement paste cylinders (diameters between 10 and 30 mm) with a similar chemical composition: ordinary Portland cement (CEM I) and  $w/c = 0.4$ . It is lower than that obtained by Jebli [11] (which was equal to 2) who used a similar degradation protocol but on a more diffusive material: CEM II cement paste with  $w/c = 0.5$ .

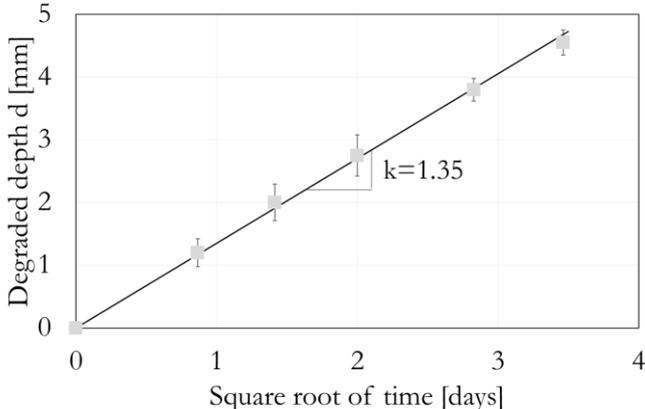
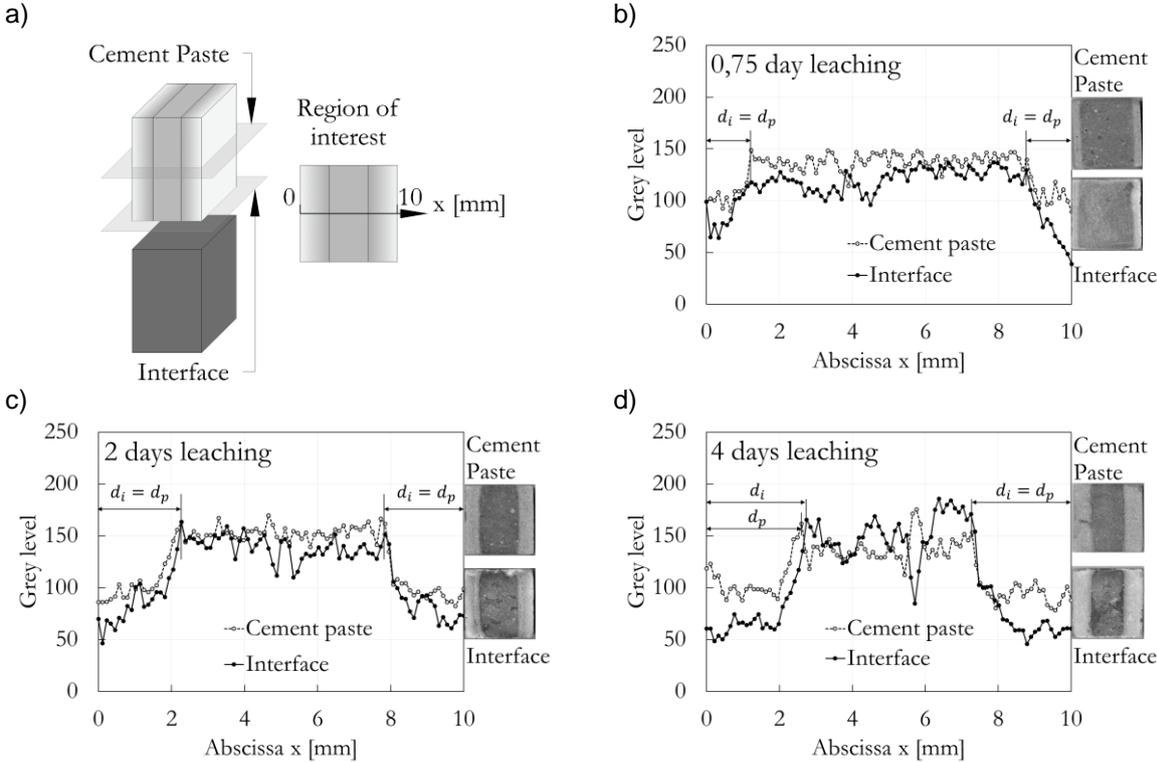


Figure 5 Leaching kinetics of the cement paste *Cinetica levigării pastei de ciment*



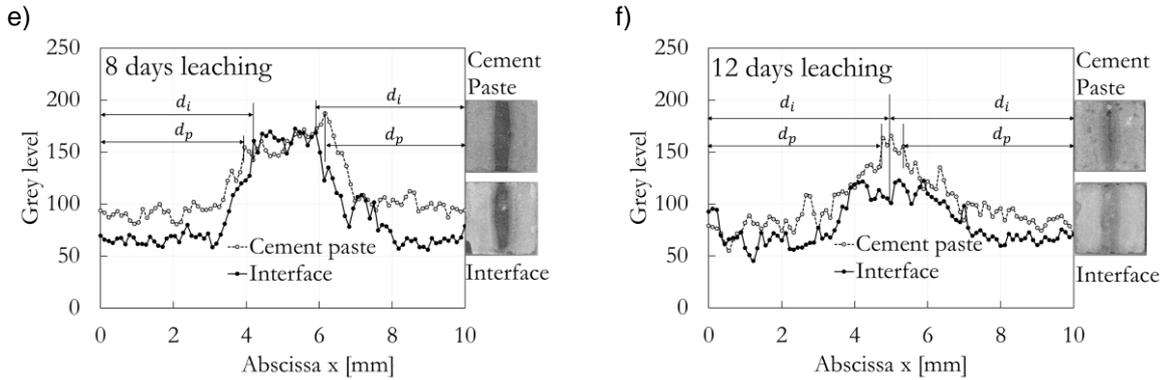


Figure 6 Evolution of the grey level on the median of the cross section of the composite samples, at the interface and at the bulk cement paste . Location of the cross section (a); Composite samples after 0.75 days (b), 2 days (c), 4 days (d), 8 days (e) and 12 days (f) of leaching *Evoluția nivelului gri pe mediane secțiunii transversale a probelor compozite, la interfață și în pasta de ciment propriu-zisă. Locația secțiunii transversale (a); Eșantioane compozite după 0,75 zile (b), 2 zile (c), 4 zile (d), 8 zile (e) și 12 zile (f) de levigare*

In order to compare the leaching kinetics of ITZ, its relative degradation with respect to the bulk cement paste was measured on composite samples following grey level distribution analysis (Figure 6). The samples were allowed to dry for a minimum of 2 days in a 60-70% RH atmosphere to facilitate the detachment of the two parts (cement paste and aggregate) following the drying shrinkage which significantly diminish the adhesion between cement paste and aggregate. Indeed, on this type of samples, the degraded depth was measured at the bulk cement paste and at the cement paste / aggregate interface, on the cement paste side. As in the case of the cross sections of the cement paste samples, the linear dimensions of the square cross section of the interface were  $10 \text{ mm} \pm 0.1 \text{ mm}$ . Consequently, the assumption that measurement of degraded depth made at the interface  $d_i$  is representative for ITZ has been taken into consideration.

In this figure, we observe that the degraded depth of bulk cement paste ( $d_p$ ) and of ITZ ( $d_i$ ) advances simultaneously. However, differences between the degraded depth of ITZ and that of cement paste could be observed after 4 days of leaching.

Taking into account that the degraded depths measured at the bulk cement paste on composite samples and that of the cement paste samples are similar for equal periods of degradation, the evolution of the degraded depth of the ITZ could be compared with that of the cement paste. Subsequently, Figure 7 illustrates the kinetics of degraded depth of cement paste and ITZ.

It has been observed that for leaching times lower than 2 days ( $\sqrt{t} = 1.41 \text{ days}$ ), the degraded depth of the cement paste and that of ITZ coincide. Then, the degradation kinetics of ITZ accelerates with respect to that of cement paste. For a degradation period of 12 days, the ITZ is entirely degraded, while in the bulk cement paste zone a non-degraded portion is still observed. However, the maximum difference between the degraded depth of ITZ and that of bulk cement paste is reduced compared to the degraded depth of cement paste, being 10% of the latter.

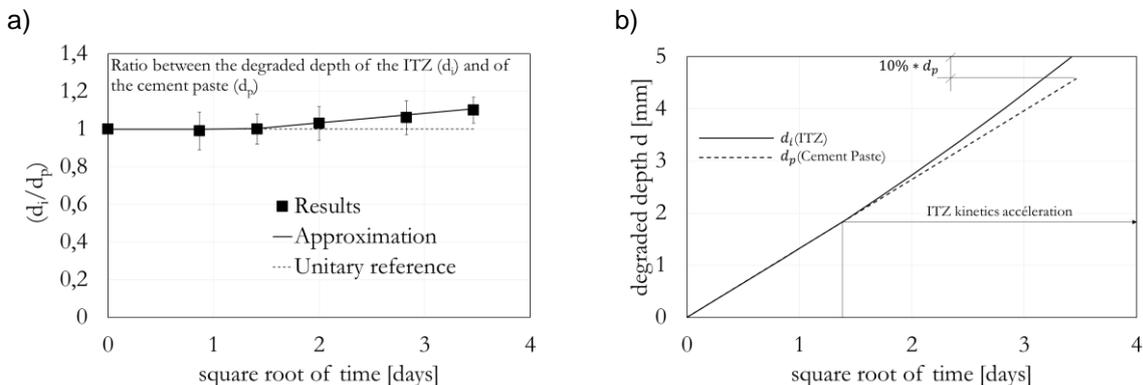


Figure 7 Evolution of the ratio between the degraded depth of ITZ and that of cement paste as a function of square root of time (a) Modelled evolution of the degraded depth of ITZ and cement paste as a function of square root of time (b) *Evoluția raportului dintre grosimile degradate ale ITZ și ale pastei de ciment în funcție de rădăcina pătrată a timpului (a) Evoluția modelată a grosimilor degradate ale ITZ și ale pastei de ciment în funcție de rădăcina pătrată a timpului*

### 3.2. Chemical dissolution

The evaluation of the chemical dissolution of the ITZ and of the paste was realised following the analysis of the elementary chemical molar ratios obtained throughout the linear profiles that are perpendicular to the interface.

First of all, in order to demarcate ITZ from bulk cement paste, the prior determination of the thickness of ITZ was necessary. This objective was achieved by studying the evolution of Ca/Si and Al/Si molar ratios in the sound zone (Figure 8).

The evolution of the Ca/Si average molar ratio in cement paste as a function of distance from the aggregate indicates an area of 15  $\mu\text{m}$  with higher Ca/Si ratios than those recorded further. Beyond 15  $\mu\text{m}$ , the average value of Ca/Si ratio of bulk cement paste is relatively stable around 3.2. The evolution of Al/Si molar ratio is similar to that of Ca/Si ratio, but the values are lower. Indeed, as in the case of Ca/Si ratio, Al/Si ratio has higher values in the 15  $\mu\text{m}$  adjacent to the aggregates and stabilizes for higher distances from the aggregate.

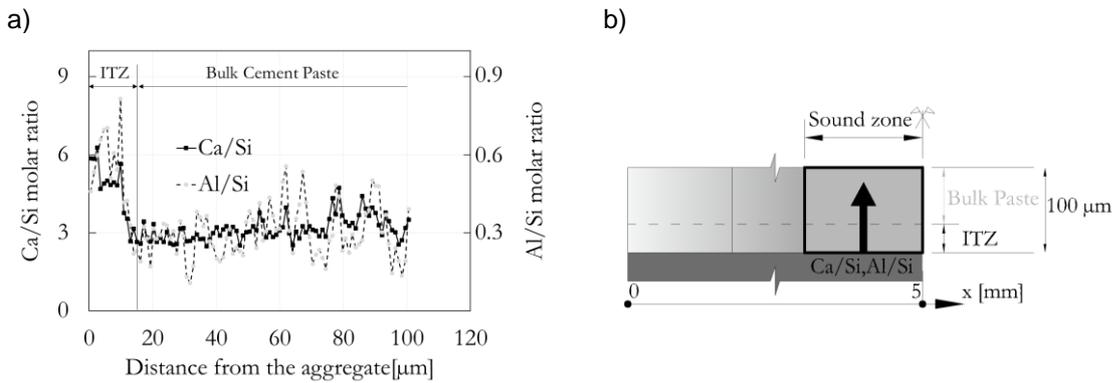


Figure 8 Evolution of the Ca/Si and Al/Si molar ratios in the sound zone as a function of the distance to the aggregate (a); region of interest (b) *Evoluția raporturilor molare Ca / Si și Al / Si în zona nedegradată în funcție de distanța până la agregatul (a); Zona de interes (b)*

Therefore, a distinction was made between the ITZ and the bulk cement paste in perspective of the analysis of degraded zone. ITZ was considered to be the zone with a 15  $\mu\text{m}$  thickness adjacent to the aggregate, while bulk cement paste was considered to be the zone situated beyond this distance.

Subsequently, we studied the evolution of the Ca/Si molar ratio in ITZ and bulk cement paste as a distance from the attacked edge (Figure 9).

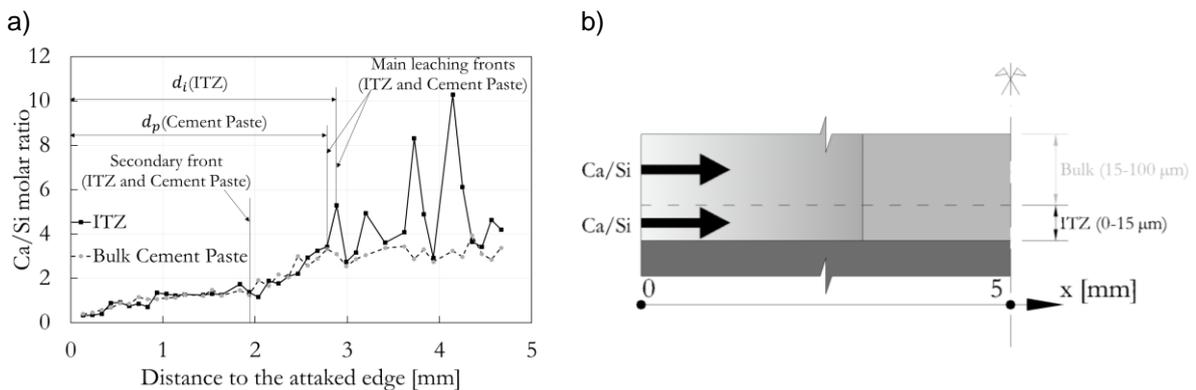


Figure 9 Ca/Si molar ratio profile in the ITZ and in the bulk cement paste in the degradation direction (a); Region of interest (b) *Evoluția raportului molar Ca/Si în ITZ și în pasta de ciment propriu zisă în direcția de degradare (a); Zona de interes (b)*

It can be observed that the Ca/Si ratios in the sound zone of ITZ are higher than those of bulk cement paste. The difference may be justified by the high concentration of portlandite and ettringite in ITZ. In the degraded zone of ITZ and of the bulk cement paste, two zones of different slope can be distinguished: an intermediate zone with a steeper slope and a highly degraded zone with a gentle slope and a reduced value. Throughout the degraded zone, the Ca/Si ratios of ITZ and of the cement paste coincide. With respect to the degraded depth, a 3% degraded difference was observed between the ITZ

and the bulk cement paste, whereas the position of the intermediate degradation front of the ITZ and of the bulk was similar.

Once the three zones of degradation have been demarcated (highly degraded, intermediate degraded and sound), we can compare the mean distributions of the Ca/Si ratios as a function of distance to the aggregate in order to compare the dissolution state of ITZ and bulk cement paste. Figure 10 shows the evolution of Ca/Si ratio in the three zones.

In this figure, we observe in the sound zone the presence of a significant Ca/Si molar ratio gradient at the ITZ, essentially following the presence of portlandite. In the degraded zone (intermediate degraded and highly degraded), this gradient no longer exists as the Ca/Si molar ratios within ITZ and cement paste are similar. This is due to the similarity of residual degradation products: C-S-H in the intermediate zone and decalcified C-S-H in the highly degraded zone, as portlandite is entirely dissolved after leaching [20]. In fact, the greater decrease of the Ca/Si molar ratio within ITZ testifies a greater portlandite dissolution with respect to the bulk cement paste. A similar result was obtained by Burlion et al. [7]. They revealed a sharper increase in the porosity of ITZ that in that of the bulk cement paste which was considered a consequence of the more important dissolution of the ITZ.

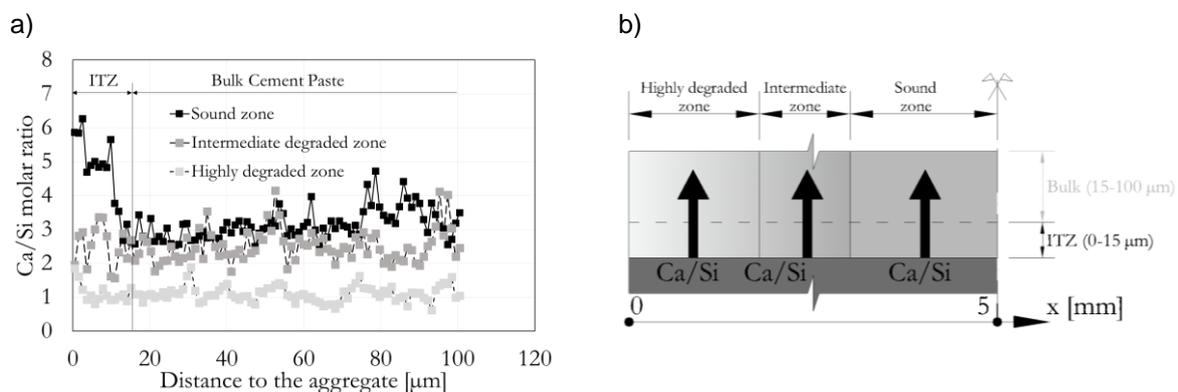


Figure 10 Mean distributions of the Ca/Si mean ratios in the three degradation zones : sound, intermediate degraded and highly degraded (a); region of interest (b) *Distribuțiile raporturilor medii Ca/Si în cele trei zone de degradare: nedegradată, degradată intermediară și puternic degradată (a); zona de interes (b)*

## 4. Conclusion

Microstructural observations were used to determine the leaching kinetics of ITZ and bulk cement paste, and to evaluate the chemical dissolution within ITZ and in bulk cement paste.

Leaching kinetics was expressed by the evolution of the degraded depth in time. The measurement of degraded depth was carried out following analysis of grey levels in the degraded zone of ITZ and of cement paste. The evolution of degraded depth of cement paste is proportional to the square root of time. Regarding the evolution of the degraded depth of ITZ, it initially coincides with that of cement paste. After a critical threshold (2 days of leaching), the leaching kinetics of ITZ accelerates.

The characterization of chemical degradation of ITZ and cement paste was carried out by EDS for a single degradation period - 4 days (degraded depth of 2.75 mm). The area of 15 μm in the vicinity of aggregate with a different chemical concentration (Ca, Si, Al) has been considered ITZ. Thus, the evolution of the Calcium dissolution was studied in the degraded zone of ITZ and of bulk cement paste. Despite the fact that the difference between degraded depth of ITZ and cement paste is reduced for this leaching time (less than 5%), the difference in terms of dissolution is important. The portlandite-rich ITZ undergoes substantially greater dissolution than bulk cement paste following portlandite dissolution. In fact, in the degraded zone, Ca / Si ratios of ITZ and cement are similar following of the existence of same residual chemicals.

In the context of the study of cementitious materials mechanical behaviour, this greater dissolution of ITZ with respect to bulk cement paste could have important repercussions on the mechanical properties of the cement paste/aggregate bond.

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