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Multi-scale approach of the chemical degradation of cementitious materials – Application to the durability of concrete structures

Summary

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Abstract

Key words: Concrete, Leaching, Microstructure, Local Scale, Mechanical Tests

ITZ (Interfacial Transition Zone) is an area formed in the cement paste inside the concrete, around the aggregates, and which displays physical properties that influence the behaviour of the concrete subject to leaching. In order to assess the influence of ITZ on the chemo-mechanical behaviour of sound and degraded concrete at the local scale of the cement paste/aggregate interface, an experimental protocol was used. This protocol is based on cement paste and composite cement paste/aggregate samples with a square section of 10x10 mm² to allow for the measurement of the chemical degradation degree and its impact on the mechanical properties of ITZ. The chemical degradation was carried out in a unidirectional manner, using an aggressive solution of ammonium nitrate. The degradation kinetics, expressed by the evolution of the degraded depth over time, was determined thanks to the digital image analysis on cross sections, following the grey level contrast between the sound and degraded areas. This analysis was supplemented by observations at the microstructure scale, Energy Dispersive X-ray Spectroscopy (EDS) and micro indentation for the analysis of the spatial distribution of chemical dissolution and stiffness in the degraded area. At the local scale, mechanical tensile and shear tests were coupled with the Digital Image Correlation for the calculation of displacement and deformation. Regarding the kinetics of degradation, it has been observed that that of the bulk cement paste is proportional to the square root of time, while that of ITZ is initially similar, but undergoes a slight acceleration after a critical threshold. Chemical and mechanical analyses at the microstructure scale show the presence of a highly degraded zone and an intermediate degraded zone in the bulk cement paste and ITZ. However, the decalcification inside ITZ is more visible than at the level of the paste following the dissolution of the portlandite. At the local scale, mechanical tests on sound samples reveal lower stiffness and resistance of the cement paste/aggregate bond compared to the cement paste, due to the presence of ITZ. Strain measurements are confirmed following the comparison between the results of different types of tests and through a short numerical simulation deriving from experimental results. With regard to the degraded samples, it has been observed that Young's modulus and stress at rupture of the cement paste and composite samples decrease as a function of the chemical degradation rate, but with different amplitudes. The Young's modulus of composite decreases more than the one of the cement paste because of the significant chemical dissolution which occurs at the ITZ level. As far as the tensile stress at rupture is concerned, its decrease accelerates in the case of composites also showing the interfaces become pre-cracked following chemical degradation and before mechanical loading. When ITZ is completely degraded, the loss of adhesion between the cement paste and the aggregate is complete. In contrast, the degraded cement paste is featured by significant stress at rupture, indicating less deep cracking. Thus, overall, it can be observed that the loss of adhesion between the cement paste and the aggregate in the degraded zone occurs following a dissolution process which enhances cracking, without a fundamental effect of the kinetics of degradation. In fact, the experimental protocol outlined in this work has allowed for a global exploration of phenomena that can be further investigated. With a view to extending the field of observation on the mechanical behaviour of sound and degraded concrete at the local scale, new configurations and devices have been proposed or discussed.

Summary

1. Context. Concrete Durability

In the case of structures intended for long lifetimes, concrete is an optimal solution which facilitates the placement and a suitable mechanical behavior in the long term. However, the formulation of the material, as well as its complex microstructure, make it difficult to study its durability, which involves many factors and phenomena of different kinds.

The concept of durability, which aims to guarantee the optimal functioning of structures during the expected lifetime, is threatened by chemical phenomena which have effects on the mechanical behavior of concrete. These are environmental or internal factors which, favored by certain specificities of concrete, generate pathologies which result in the degradation of the material.

Among the most recurring causes of pathologies we can cite carbonation, alkali-aggregate reaction, internal sulphate reaction, leaching. This type of pathology begins at the microstructure level following chemical reactions that modify the internal equilibria existing between the different phases (Adenot, 1992). Their effect is important because, through cracking, they can generate local ruins and, overall, a reduction in the mechanical strength of structures.

For a long time, the mechanical behavior of concrete has been studied mainly at the Representative Elemental Volume (VER) scale. However, concrete is a composite material formed by a granular skeleton embedded in a cement matrix (cement paste), giving rise to an interfacial transition zone (ITZ in English) which forms in the paste around the aggregates (Ollivier et al., 1995; Scrivener, 1996). This zone has characteristics which make the paste / aggregate bond vulnerable to the various pathologies mentioned. In the case of durability, studies at the VER scale are therefore not sufficient, because it is necessary to take into account the behavior of the material at the local scale of the paste / aggregate bond. In this context, an experimental program has been developed at LMGC in Montpellier to model the mechanical behavior of concrete affected by various pathologies, taking into account inter-facial properties (Jebli, 2016). This program is based on a multi-physics and multi-scale approach. It aims to model the mechanical behavior of degraded concrete at the VER scale, by integrating the mechanical properties at the local scale identified experimentally, to ultimately allow structural calculations.

2. Concrete leaching

One of the pathologies mentioned is that produced by leaching which appears following contact of the concrete with a more acidic solution than the basic interstitial solution which occupies the porosity and which is in equilibrium with the cement paste(de Larrard, 2010; Nguyen et al., 2007). Thus, we are witnessing a decalcification which progresses gradually over time and generates the degradation of the mechanical properties of the material following the increase in porosity.

The degradation mechanism takes place through two main phenomena: diffusion and dissolution. The propagation of the leach front and its kinetics are governed by the diffusion of the aggressive solution into the pore solution. Dissolution, especially of Calcium, occurs in the dough to ensure equilibrium with the acidified pore solution.

ITZ is a zone of the cement paste that forms around the aggregates to thicknesses of the order of a few tens of microns, having different physical properties compared to bulk cement paste (Leemann et al., 2010, 2006). Usually this is higher porosity and different chemical species content. These features are of major importance in the context of leaching because they make ITZ a more diffusive environment and more conducive to chemical dissolution. There is therefore an objective risk of a local acceleration of the degradation kinetics, but also of a strong increase in porosity, with a significant effect on the adhesion of the paste to the aggregate.

In the context of studying the behavior of concrete on a local scale, an experimental protocol was set up during Jebli's thesis (Jebli, 2016). This protocol consisted of creating a cement paste / aggregate bond and determining the mechanical properties. Jebli's thesis showed, in general, that the effect of leaching is more noticeable on the mechanical properties of the paste / aggregate bond than on those of the paste. It also showed the need to clarify certain aspects related to ITZ. The main objective was to carry out more localized measurements of its degradation kinetics and mechanical behavior in the interfacial zone, in order to better define the role of ITZ in the degradation mechanism.

3. Experimental study of chemo-mechanical behaviour of concrete at local scale

In order to achieve a quantitative identification of the mechanical parameters of degraded concrete at the local scale, it is necessary to have a good knowledge of its chemo-mechanical behavior. This thesis falls within this framework and aims to assess the influence of ITZ on the chemo-mechanical behavior of the sound and degraded cement paste / aggregate bond, taking cement paste as a reference.

The strategy adopted is to perform chemical analyzes and mechanical tests at the microstructure scale and at the local scale on samples having an appropriate geometry. More specifically, the two avenues of study chosen relate to the degradation kinetics and mechanical properties of concrete at the local scale. In order to be able to study these aspects, a simple geometry, but compatible, has been favored. This involves using cement paste and cement paste / aggregate composite samples with a square cross section. These samples are used to assess the progress of chemical degradation and the overall stress under mechanical loading. The progress of chemical degradation will be measured at the paste and ITZ level to determine their degradation kinetics.

Regarding the mechanical behavior of samples at the local scale, a first part will be dedicated to the healthy state and will involve different configurations and types of mechanical stresses. The evolution of the mechanical properties of degraded samples at the local scale will be analyzed according to the progress of the degradation, in a single configuration. In order to complete the main study pathways, two types of observation will be carried out to support the results and attempt to explain the origin.

These are observations on chemical dissolution and mechanical properties at the microstructural scale. On the one hand, the analysis of the dissolution is necessary to access the spatial evolution of chemical degradation, but also to validate the measurement of degraded depth. On the other hand, the observation of mechanical properties at the level of the microstructure allows comparisons with other observations having common points (either the observation scale or the quantities concerned).

4. Influence of ITZ on concrete behaviour

In order to achieve a quantitative identification of the mechanical parameters of degraded concrete at the local scale, it is necessary to have a good knowledge of its chemo-mechanical behavior. This thesis come within this framework and aims to assess the influence of ITZ on the chemo-mechanical behavior of the sound and degraded cement paste / aggregate bond, taking cement paste as a reference. The strategy adopted is to perform chemical analyzes and mechanical tests at the microstructure scale and at the local scale on samples having an appropriate geometry.

The literature review highlight the physicochemical characteristics of ITZ which have consequences on the mechanical behavior of leached concrete. ITZ's chemical composition has been shown to differ from that of the bulk cement paste paste (Crumbie, 1994; Diamond and Huang, 2001; Scrivener et al., 2004; Yuan and Odler, 1987).

In the fresh state, the presence of anhydrous cement grains is rarefied on contact with the aggregate due to the wall effect and bleeding. Therefore, in the hydrated final state, ITZ differs from the bulk cement paste by a higher porosity and a higher content of chemical species which have weak cohesive properties (portlandite and ettringite) (Larbi, 1991; Monteiro and Mehta, 1985; Monteiro et al., 1985).

Under mechanical stress, the cement paste / aggregate interface often represents a starting point for cracking(Mehta and Monteiro, 2006). However, in the case of high performance concretes, several measures can be taken to improve the mechanical behavior of the cement paste / aggregate bonds. Among these measures, we can cite the reduction of the w / c ratio, the use of micro fillers (especially silica fume), the use of superplasticizers and the choice of limestone aggregates. In the degraded state by leaching, the dissolution of the main chemical element in cement paste, Calcium, produces an increase in porosity and a drop in mechanical properties(Carde, 1996; Carde and François, 1997a). From a chemical point of view, leaching is manifested by the complete dissolution of portlandite and the progressive decalcification of C-S-H(Mainguy et al., 2000; R. Berner, 1988). ITZ can affect the durability of concrete through two mechanisms:

• the local acceleration of chemical degradation due to its higher porosity and therefore its higher diffusivity (Delagrave et al., 1997),

• greater loss of mechanical properties of the paste / aggregate bond compared to the core of the cement paste (Carde and François, 1997b).

This is due to the higher concentration of fully soluble chemical species (portlandite) in the sound state ITZ which results in a greater dissolution with respect to bulk cement paste following leaching. The results in the literature come mainly from studies carried out at the macroscopic scale and show the effect of ITZ on the loss of mechanical properties of concrete (or mortar, which can be considered as a special case of concrete).

In terms of degradation kinetics, the effect of ITZ on macroscopic concrete is insignificant because the slowing due to the tortuosity induced by the aggregates prevails over the acceleration induced by the higher diffusivity of ITZ (Delagrave et al., 1997; Marchand and Delagrave, 1999). In contrast, ITZ undergoes greater chemical dissolution and the interface represents a preferential zone for the appearance of cracking (Burlion et al., 2007; Rougelot et al., 2010). For the same degraded depth (or chemical degradation rate), the loss of compressive strength of the mortar is greater than the loss of compressive strength of the paste, because of the greater dissolution at the ITZ level(Carde and François, 1997b). We therefore note that most studies seem to converge on the influence of ITZ on the durability of concrete. However, observations on the degradation kinetics of ITZ and on the mechanical behavior of the cement paste / aggregate bond are indirectly deduced. They mainly come from analyzes on concrete elements on a macroscopic scale. The present study therefore proposes to experimentally evaluate, from direct measurements at the local scale, the mechanism by which leaching generates the drop in the mechanical properties of concrete. Particular attention will therefore be paid to ITZ and to the paste / aggregate bond. In order to achieve this, a specific experimental protocol has been developed.

5. Materials and methods

As mentioned in chapter 4, the study at the scale of the paste / aggregate bond is needed in order to analyze the complex phenomenology which develops at the ITZ level and influences the mechanical behavior of the concrete. Thus, in order to make such a study possible, an experimental protocol was developed to evaluate the effect of leaching on the mechanical properties of the paste / aggregate bond and on those of the paste. In carrying out this protocol, several experimental methods are used and adapted to the research context. These different experimental methods are related, which also makes verification possible, with comparisons of the results obtained separately by different methods. In order to be able to evaluate the effect of leaching on the mechanical behavior of concrete on a local scale, it is necessary to evaluate the degradation kinetics and the effect of chemical degradation on the mechanical properties of the paste / aggregate bond. and dough. In this sense, samples with specific geometries are used : paralelipiped an reversed Y cement paste and cement paste/composite samples (Figure 1)

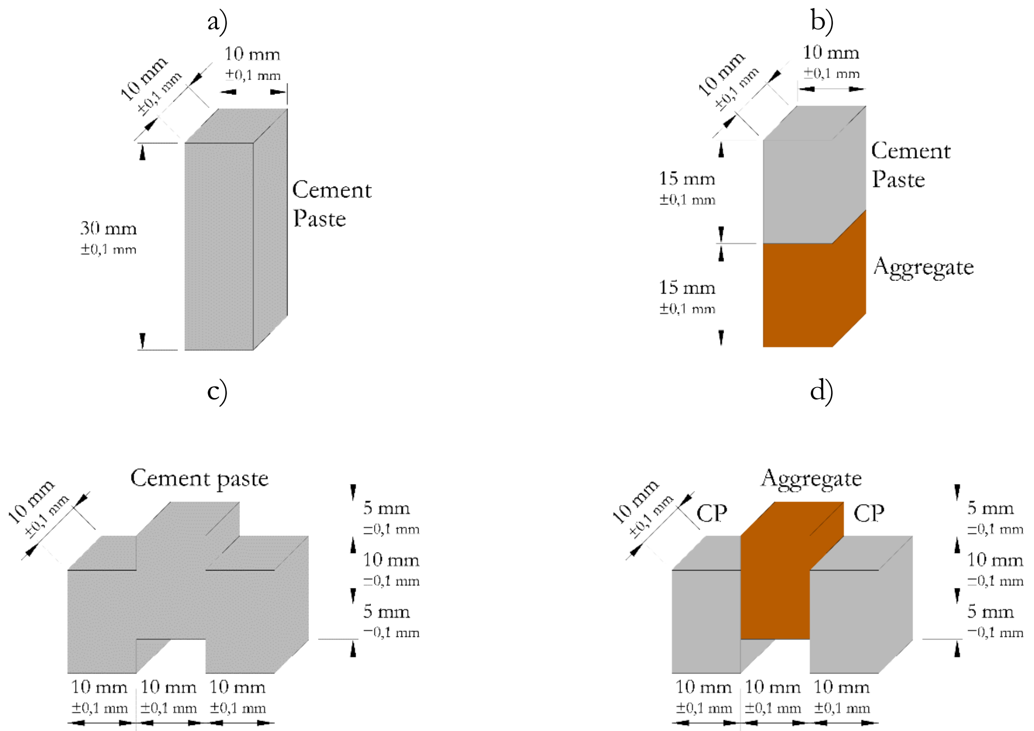

Figure 1 Parallelepiped cement paste a) and composite b) samples; Reversed Y cement paste c) and composite d) samples

As the geometries of these samples are not standardized, sample preparation, especially during manufacture, and the degradation method will be discussed. On these sound and degraded samples, the analyzes performed can be classified into two categories: analyzes at the microstructural scale and mechanical tests at the local scale.

The analyzes at the microstructure scale are mainly oriented towards the characterization of chemical degradation, in order to make possible the interpretation of its effect on the mechanical behavior of concrete at the local scale. The main aspects addressed through these analyzes are degradation kinetics, as well as chemical dissolution and its effect on mechanical properties at the microstructure scale. Mechanical tests at the local level are intended to determine the mechanical properties of the paste / aggregate bond and the paste. In this context, a primordial aspect is represented by the acquisition of displacements and deformations, which are difficult to measure because of their small orders of magnitude. The mechanical tests are therefore carried out in several configurations, in order to be able to verify and compare the results obtained. In the presentation of this protocol, all the experimental methods used are discussed, taking into account that the particular nature of the experimental protocol requires certain specific adaptations. These methods are also useful in the wider context of a research program that deals with the effects of different pathologies on the mechanical behavior of concrete. The mechanical behavior of sound or degraded concrete by leaching is influenced by the existence of ITZ which affects the properties of the paste / aggregate bond. However, the magnitude of this influence is difficult to estimate due to the difficulty of isolating the paste-aggregate bonds to study their properties. However, a more in-depth knowledge of the mechanical properties of these bonds is necessary to appreciate the mechanical behavior of concrete over the long term. Under these conditions, the present experimental protocol was used to analyze the influence of degradation on the mechanical properties of the paste / aggregate bond and on those of the paste.

Actually, in order to assess the mechanical behavior of degraded concrete at the local scale of the paste / aggregate bond, the analysis of chemical degradation is necessary beforehand. As a result, several related aspects have been addressed in order to make the observations possible and representative. The overall aim is to prepare and condition samples with suitable configurations to allow analyzes at the microstructural scale and mechanical tests at the local scale. The analyzes at the microstructure level are intended to determine the degradation kinetics and assess the state of chemical dissolution as well as its effect on mechanical properties. As regards the mechanical tests, they are carried out to analyze the rigidity and resistance of the paste / aggregate bond and of the paste. An adaptation of the test systems at the local level was carried out to extend the field of observation and increase the representativeness of the results. The approach of all these cumulative aspects, of which the individual protocols were adapted during this work, passing through several intermediate versions, demanded a significant part of the total volume of work. The samples used for the analyzes envisaged are of parallelepipedal shape and inverted Y shape, in cement paste and paste / aggregate composites. In the area of interest, their cross sections are squares of 10x10 mm^2, allowing at this level the calculation of the progress of chemical degradation and the state of stress under mechanical stress. These samples were made in flexible silicone molds to facilitate casting and release, but also to minimize the interference of the manufacturing method with measuring the properties of the samples. These arguments made this manufacturing method preferable to conventional variants based on the use of rigid molds. After fabrication, the samples were preserved in a lime-water bath for 40 days to allow optimal hydration and prevent cracking. After the hydration period, a number of samples were individually subjected to accelerated unidirectional degradation in ammonium nitrate solution. The choice of this leaching method is justified by the high degradation rate and by the nature of the degradation scenario generated which is similar to the original scenario.

The chemical degradation of the samples is analyzed by observations at the microstructure level to also make it possible to analyze the effect of leaching on the mechanical properties. The main point of interest of these observations at the microstructure scale is represented by the degradation kinetics, defined by the evolution of the degraded depth as a function of time, determined from the analysis of images of cross sections. The use of image analysis for the measurement of the degraded thickness is facilitated by the contrast between the gray level of the degraded area and that of the sound area (Figure 2).

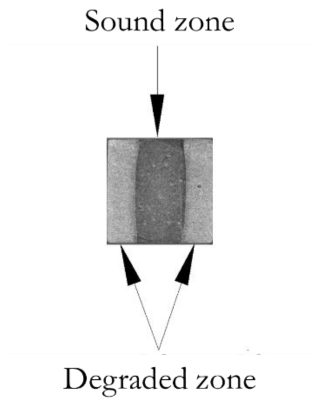

Figure 2 Cross section of degraded sample

Subsequently, the degraded depth values obtained by image analysis are verified by comparison with the results of a chemical analysis by EDS, carried out in a SEM environment, which gives access to point chemical concentrations. Access to the spatial evolution of point chemical concentrations at the ITZ and paste level also offers the possibility of evaluating their dissolution states through linear concentration profiles perpendicular and parallel to interface (Figure 3). These chemical analyzes by EDS are carried out only for a degradation period, because of the rather long time allowed to carry out the polishing necessary to optimize the measurement of the chemical concentrations.

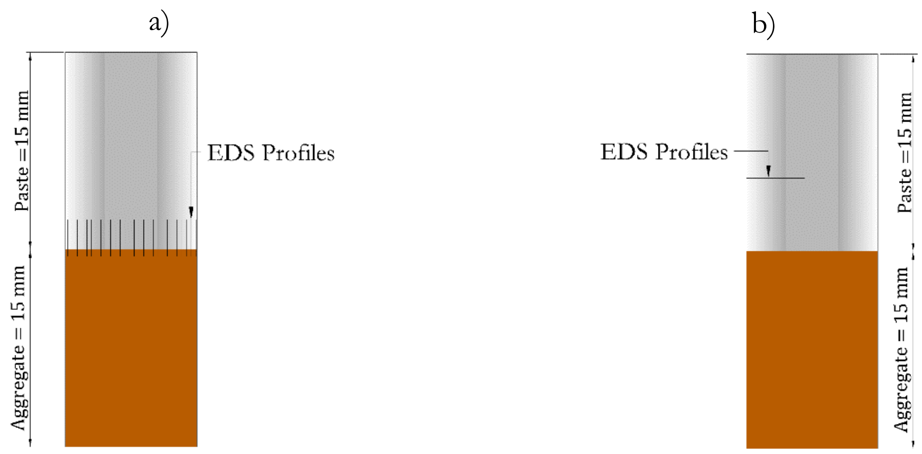

Figure 3 Chemical degradation profiles perpendicular a) and parallel b) to interface

This same polishing was also necessary to make possible the realization of the microindentation observations which were carried out on the same samples as those analyzed by EDS. Micro indentation is used to determine the evolution of Young's modulus at the microstructure scale in degraded and sound areas of the cement paste. The use of this method is justified on the one hand by the possibility of evaluating the effect of chemical degradation on a mechanical property at the scale of the microstructure. On the other hand, it allows a comparison with the values of Young's modulus obtained by mechanical tests at the local scale. These local-scale mechanical tests were performed in three different configurations and coupled with digital image correlation (DIC for the calculation of displacements and strains. The measurement of displacements and strains by CIN was carried out using a high-resolution camera, with the objective of obtaining satisfactory precision of the fields of local and global displacements and strains. Using this method, stress / strain curves are obtained from which the mechanical properties of the samples are determined, as well as displacement and strain fields. Regarding mechanical tests, the main type of test used is tensile tet, which is carried out on parallelepiped samples made of cement paste and composites. The principle of the test is to apply the tensile load to 4 plates glued to 2 opposite sides of the sample, which are perpendicular to that observed by CIN. Particular attention was paid to this tensile test, with the objective of improving and standardizing the experimental loading conditions. The strategy adopted was to control the boundary conditions imposed on the samples by carrying out a gluing assembly device of the loading plates and by using a bi-articulated loading device (Figure 4).

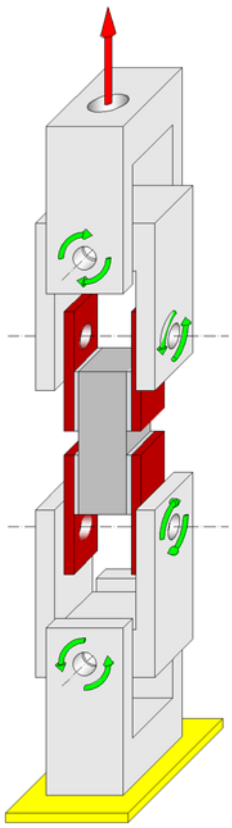

Figure 4 Bi-articulated loading device used for tensile test

The final versions of these two tools were chosen from several drafts. The gluing assembly device was designed to minimize geometric defects and guarantee satisfactory parallelism of the loading axes. Subsequently, the bi-articulation of the loading device helped to even out the distribution of the load to the loading plates, minimizing the effect of geometric defects in the bonding. These two measurements thus allowed a significant improvement in the repeatability of the results. The other two types of test, direct shear and inverted Y-shaped specimen shear, were performed in order to broaden the field of observation and verify the results of the tensile tests. These results concern the effect of ITZ on the mechanical behavior of the paste / aggregate bond, as well as the measurement of deformations by CIN. Regarding the direct shear test, the loading device is the one designed and used during Jebli's thesis (Jebli, 2016), whose shear is obtained between two rigid boxes following the translation of one of them. they. For reversed Y-shaped specimens, the loading device has been designed to ensure satisfactory uniformity of the distributed loads at the two interfaces, located to the right and left of the central block.

So, by summarizing the aspects presented, this experimental protocol has a basic vocation, that of allowing the evaluation of the effect of leaching on the mechanical behavior of concrete on a local scale. However, in the context of an unprecedented experimental scenario, the need to deepen and develop the experimental techniques has generated a secondary vocation. This is an effort to adapt and optimize the experimental methodology, necessary in the larger context of the research program in place at LMGC. This research program explores, at different scales, the mechanical behavior of concrete under conditions of severe environmental stress.

6. Analysis of chemo-mechanical properties of concrete at local scale

The mechanical properties of concrete degraded by leaching depend on the phenomena that occur at the local scale of the paste / aggregate bond. However, an exploration on this scale requires an experimental methodology oriented towards the relationship which exists between the chemical degradation and the mechanical properties of the material. In this sense, an experimental protocol was defined in the previous chapter. Therefore, in this chapter, the results obtained using this experimental protocol will be presented. In order to support these results, and due to a particular experimental methodology, the use of related experimental methods allows the verification of the results obtained. First, the chemical degradation of the samples as well as its effect on mechanical properties are examined through analyzes at the microstructure level. The basic objective is to determine, for several degradation times, the chemical degradation rate of ITZ and cement paste which is a characteristic variable for the progress of degradation. Beyond this aspect, the nature of the chemical degradation is analyzed following the observation of the decalcification level at the ITZ and cement paste. Then, first information on the effect of chemical degradation on the Young's modulus of the cement paste is obtained at the microstructure scale. In order to access the mechanical properties of the paste / aggregate bond and the paste, local mechanical tests are first performed on sound samples. The mechanical properties are obtained through stress / strain curves, while additional information is revealed by the displacement and strain fields. The comparison of the results obtained by the different types of tests also makes it possible to assess the reliability of the results obtained. After this step, the effect of chemical degradation on the mechanical properties of the paste aggregate bond and the paste is evaluated in a single test configuration, in relation to the chemical degradation rate. In this sense, the evolution of mechanical properties as a function of the chemical degradation rate is analyzed with reference to other related aspects, such as chemical dissolution or the appearance of cracking. Therefore, the analysis of the results obtained suggests exploring the link that exists between phenomena of different nature, chemical and mechanical, but also to verify the reliability of the results through the use of several methods.

6.1. Micro structure scale assessements

At the microstructure scale, image analyzes were used to measure the degraded depth of the cement paste and at the interface. The measurements taken at the interface, on the paste side, were considered representative for the ITZ. In total, the degraded depth measurement was carried out for each of the five degradation times on 5 cement paste samples and 5 composite samples. Then, the chemical solutions of the ITZ and the cement paste were evaluated by EDS chemical analyzes, following the measurement of the elementary chemical concentrations. After that, the evolution of Young's modulus in the degraded area of the cement paste was analyzed by micro indentation. The comparison of the results of these three techniques mentioned - image analysis, EDS chemical analysis and micro indentation - made it possible to verify if there exist any correlations between the results obtained. Regarding the analysis of chemical dissolution and micro indentation, they were carried out on 3 composite samples for a single degradation period - 4 days, on polished sections. Observations at the microstructure scale were used to determine the degradation kinetics and chemical dissolution state of paste and ITZ, as well as changes in chemical and mechanical properties in the degraded area.

The degradation kinetics were measured following the analysis of the gray levels in the degraded zone of the ITZ and the cement paste. Measurement of degraded depth of ITZ (at interface) and of cement paste allowed determination of a more characteristic size for degradation state – the chemical degradation rate δ obtained as the ratio between area of sound zone and total area of cross section. The evolution of the chemical degradation depth of cement paste is proportional to the square root of time. At the beginning, the evolution of chemical degradation rate of ITZ coincides with that of cement paste. From a critical threshold (which corresponds to a degradation rate of 40%), the degradation kinetics of ITZ accelerate slightly, in order to reach maximum relative increment of about 10%, probably due to porosity increase following ITZ portlandite dissolution (Figure 5).

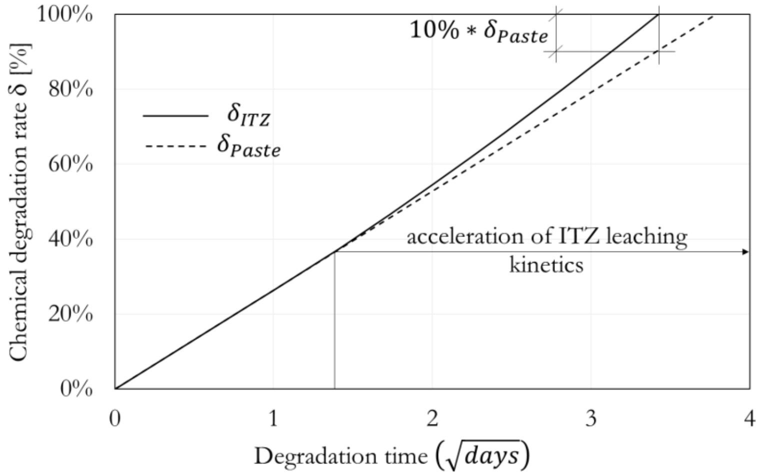

Figure 5 Leaching kinetics of ITZ and Cement Paste

The characterization of the chemical degradation in the ITZ and in the cement paste was carried out by SEM for a single degradation time - 4 days (degradation rate of 56%). In the sound state, the existence of a zone which corresponds to ITZ, with a thickness of approximately 15 μm in the vicinity of the aggregate with a different chemical composition, was revealed. Then, the evolution of the dissolution was studied in the degraded zone of the ITZ and bulk cement paste. Despite the fact that the difference between degraded thickness of ITZ and paste is reduced, the difference in dissolution is significant. The portlandite-rich ITZ is subjected to a significantly greater dissolution than the bulk cement paste. In the degraded part, the Ca / Si ratios are similar in ITZ and in the cement paste due to the existence of the same residual chemicals (Figure 6). Therefore, the fact that chemical dissolution is greater at the ITZ level and therefore; in contact with the aggregate, can have significant repercussions on the mechanical properties of the cement paste / aggregate bond.

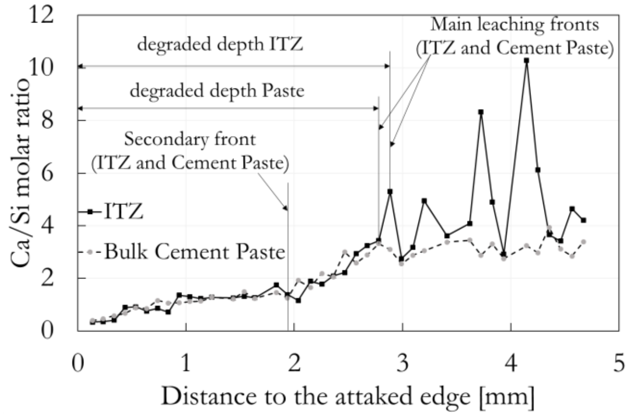

Figure 6 Ca/Si molar ratio profile of cement paste and ITZ degraded to sound zones

Following chemical degradation characterization, micro indentation was used to assess the evolution of Young's modulus of the cement paste in the degraded area. This method demonstrated the existence of two zones in the degraded zone of the paste where the evolution of the Young's modulus is similar to that of the gray levels and the Ca / Si ratio (Figure 7).

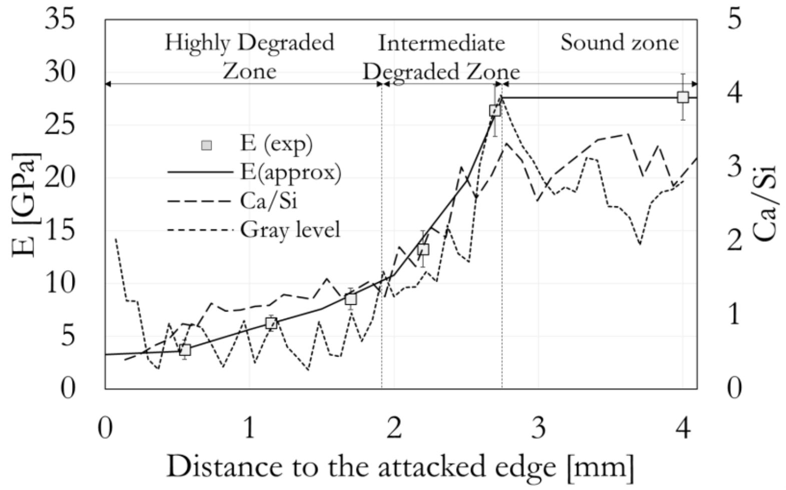

Figure 7 Evolution of Young Modulus, Ca/Si molar ratio and Gray level in degraded zone of cement paste as a function of distance to the attacked edge

Subsequently, correlation between Young Modulus, Ca/Si ratio and gray level, allow extrapolation of existence of highly degraded zone and intermediate degraded zone to all cement paste and cement paste/composite samples. However, loss of rigidity may be greater at cement paste/aggregate bond, since ITZ present significantly higher Calcium dissolution that cement paste.

6.2. Local scale study of mechanical properties of sound material

In this section, we focus on the mechanical behavior of sound samples in cement paste and cement paste / aggregate composites. The mechanical behavior of these samples is reflected in mechanical properties obtained through mechanical tensile and shear tests. Regarding the shear tests, they are carried out in two different configurations, which include a simpler geometry, parallelepipedal and another, more complex, in the shape of reversed Y. The results obtained following the mechanical tests mentioned, on the paste and on the composites, are then compared in terms of modulus of elasticity, tensile stress and strain fields. These tests were carried out using a protocol developed on the basis of an already existing protocol, set up by Jebli (Jebli, 2016). Due to the relatively innovative nature of the approach, particular attention has been focused on protocol development. In this sense, the shaping of the test devices as well as the adaptation of the DIC observation method occupied a significant part of the work volume which extended over 12 months. Within the framework of this experimental protocol, one of the objectives was to obtain sufficient representativeness of the results. In this sense, tensile and shear tests in the reversed Y configuration were performed on 10 different samples for each type of sample (paste and composite cast with 2 different orientations). Indeed, the usefulness of carrying out a minimum of 10 samples for each different type of test was indicated by Lhonneur et al. (Lhonneur et al., 2019). He indicated that this number of tests was necessary to obtain an average value representative of the breaking force in the tensile test. For the reversed Y samples, the same number of tests were performed to allow comparison of the results with those obtained by the tensile test. On the other hand, the shear tests in the parallelepiped configuration were carried out on 3 samples of each type, because through this test only a general observation of the mechanical properties is envisaged.

Tensile tests on cement paste and composite samples allowed comparison in terms of Young Modulus and stress at rupture through stress/strain curves. These curves were obtained by linear approximation of rough noisy signal, as sample behavior was fragile.

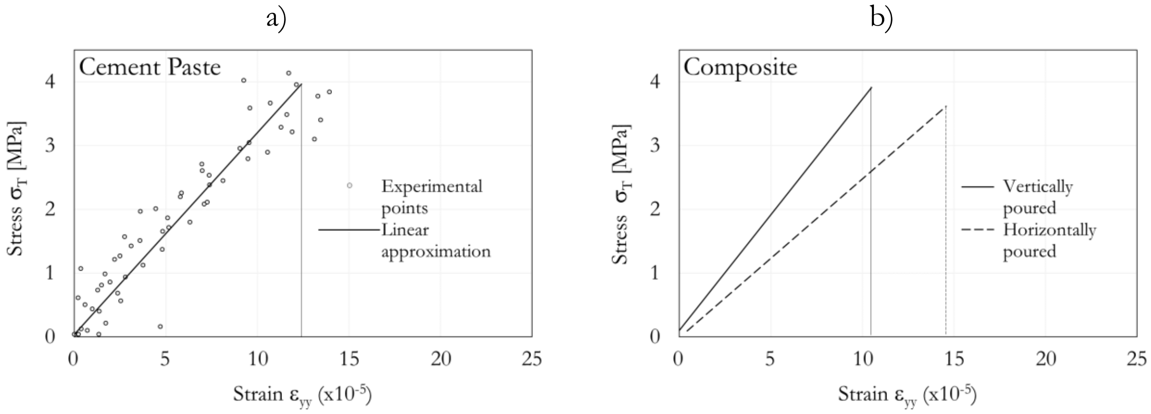

Figure 8 Stress/strain curves obtained following tensile tests on cement paste a) and composite samples b)

As concerns rigidity, the experimental comparison of the Young's modulus of composites with the theoretical one in the case of a perfect bond makes it possible to highlight the influence of the presence of ITZ. The Young's modulus of real composites is lower than that corresponding to the ideal case of a perfect bond. This observation is in agreement with the general idea deduced at the macroscopic scale that the imperfection of the paste / aggregate bond has a negative effect on the global Young's modulus of concrete (Lee and Park, 2008; Sun et al. , 2007). It is also noted that the tensile strengths of composites obtained in the present study are higher than those obtained in other studies which have used similar formulations (Nguyen, 2013; Yuan and Odler, 1987; Zimbelman, 1985). This difference can be explained by the choice of the manufacturing protocol which favors a strong paste / aggregate link, as well as by the effect of scale generated by the smaller dimensions of the samples used in this study compared to the others. A visible difference in modulus of elasticity and tensile stress at rupture was noted between composites casted vertically and composites casted horizontally, following a phenomenology similar to bleeding encountered in real concrete.

As concerns shear tests parallelepiped samples, they highlighted the effect of ITZ on the mechanical properties of the cement paste / aggregate bonds. This effect manifests by lower stiffness and lower strength of the cement paste / aggregate bond. When comparing composites and cement paste, we first notice that the two types of composites have lower stresses at rupture than the cement paste, because of the brittleness of the paste / aggregate bond. It has also been observed that composites casted horizontally exhibit an average stress at break which is approximately one half of that of composites cast vertically, probably due to a phenomenon similar to bleeding. In addition, a softening effect of ITZ on the paste / aggregate bond is shown on horizontally cast composite samples which exhibit shear moduli lower than those of paste.

Indeed, this type of test can be considered representative for the shear strength of composites, because the failure occurs at the interface, in an area where the shear is not disturbed by significant parasitic tension. The shear strength of the vertically casted composite is twice that of horizontally casted composites, showing a strong influence of the pour direction.

In addition to these results, a large dispersion is noticed in the measurement of Young's moduli. This dispersion can be attributed to the measurement of very small displacements which are close to the limit of the method, to the large mesh which can amplify the effect of local defects and to defects in the verticality of the sample. Two types of shear tests were performed on cement paste and cement paste / aggregate composite samples: on parallelepiped and reversed Y-shaped samples. These two types of test reveal a complex stress / strain state where shear remains predominant.

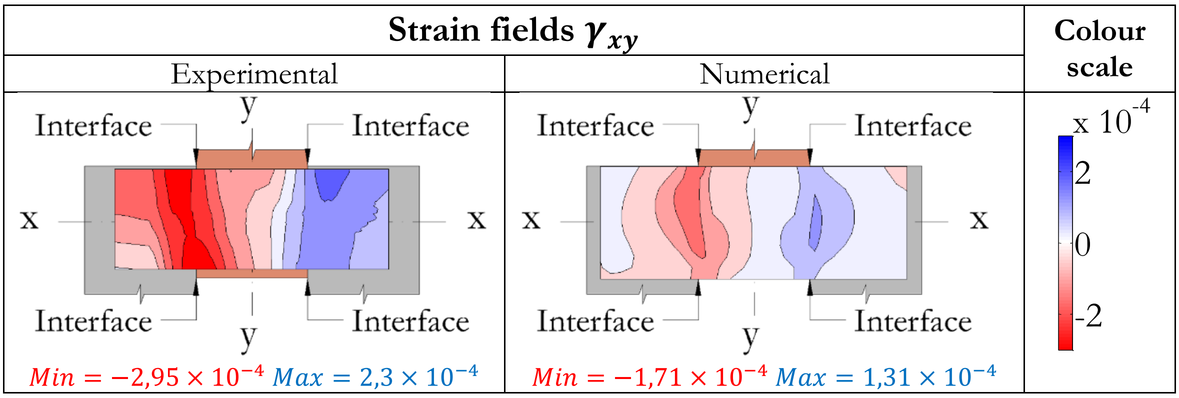

Figure 9 Comparison between shear strain field of real reversed composite (experimental) and numerically modelled (perfect bond) for similar boundary conditions

The analysis of the results obtained on the reversed Y-shaped samples also allowed a comparison of the results obtained for the other tests, in order to verify their reliability. The average values of the moduli of elasticities obtained following the various tests are consistent, despite a certain dispersion of the values linked to the specific conditions generated by the reduced observation scale. This assertion is supported by the similarity of the experimental loading forces with those resulting from a simulation of the elastic behavior of the samples in paste in the form of reversed Y, where the modulus of elasticity was considered equal to that measured following the tensile tests. In addition, the softening effect of ITZ is confirmed by the same kind of simulation on composite samples, as numerical model wich consider perfect cement paste/aggregate bond present lower strains than the real one, for similar boundary conditions (Figure 9).

Over all tensile and shear tests, a visible difference was noted between vertically cast composites and horizontally cast composites in terms of tensile stress and modulus of elasticity. Vertically cast composites have been shown to be stronger and more rigid. Bearing in mind this remark, the possibility of studying the effect of casting orientation of sample on the mechanical properties of the interface by adjusting the orientation of the pour direction was mentioned. Through the mechanical tests carried out on sound samples, the vulnerability of the material to tensile stress for the mechanical behavior of the samples has led us to choose this type of test for the study of degraded samples.

6.3. Influence of leaching on mechanical properties of concrete at local scale

In this subsection, the effect of leaching on the mechanical properties of cement paste and cement paste / aggregate composites was investigated in support of tensile testing. The effect of chemical degradation on the stiffness and strength of the samples will be evaluated through stress / strain curves. This analysis will be supplemented by a discussion of the influence of the cracking which is observed on these degraded samples. In this sense, for each degradation rate associated with the 5 degradation times, 10 cement paste samples and 10 composites were analyzed. It is mentioned that the vertically casted composite samples were used for testing due to a stronger paste /

aggregate bond than in the case of horizontally casted composites. The choice of this type of composite made it possible to preserve sufficient adhesion between paste and aggregate for high degradation rates, in order to be able to observe the loss of adhesion at the interface over a sufficiently large area.

As for sound samples, mechanical properties of degraded ones were obtained through stress/strain curves (Figure 10). However, unlike sound samples, stress/strain curves of degraded samples are no mere linear and were approximated by polynomial curves.

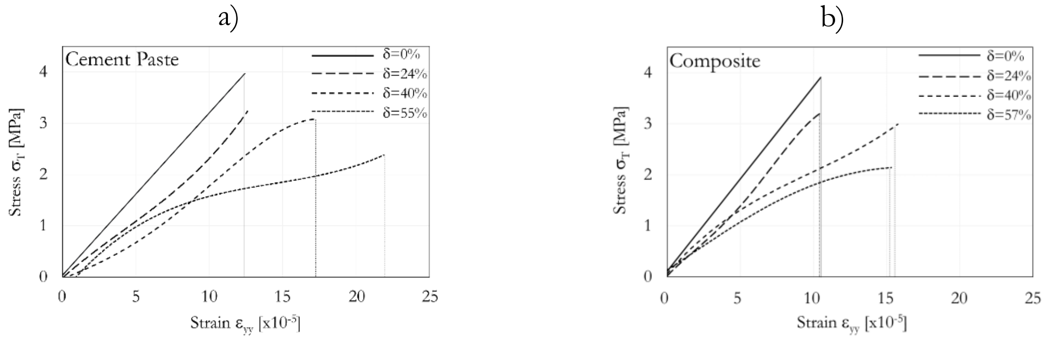

Figure 10 Stress/strain curves of sound and degraded cement paste (a) and cement paste/aggregate composite of cement paste and cement paste aggregate (b)

Non linearity is a consequence of cracking on the observed face. It can be observed also that nonlinear part of curves increases with chemical degradation rate, as crack onset for increasingly lower stresses. Actually, for chemical degradation rate higher than 60%, stress/strain curves were no more processed, as the samples became precracked.

So, tensile tests coupled with DIC for strain measurement and crack visualization allowed overall observation of mechanical behaviour of cement paste/aggregate bond. This global observation can be summarized by a graph which illustrates evolution as a function of chemical degradation rate of three characteristic quantities for the mechanical behaviour of the cement paste aggregate bond. These are the ratio between stresses et rupture (σ_{Tr}) of composite and cement paste, ratio between Young Moduli, E, of real and ideal composite, and percentage of composite that present ruptures at interfaces (Figure 11). For chemical degradation rates lower than about 25%, the adhesion between cement paste and aggregate can be qualified as good, since decrease of Young modulus is low and composites present ruptures in cement paste for stresses similar to those of cement paste. The next phase, up to 60% is can be distinguished by a decrease of adhesion, since Young modulus decreases faster, and more samples begin to present ruptures at interface. However, average stress at rupture remains close to that of cement paste. But for chemical degradation rates higher than 60%, samples become pre cracked, composites present ruptures at interfaces, for stresses that reach almost zero when interface is degraded in its integrality, indicating complete loss of adhesion.

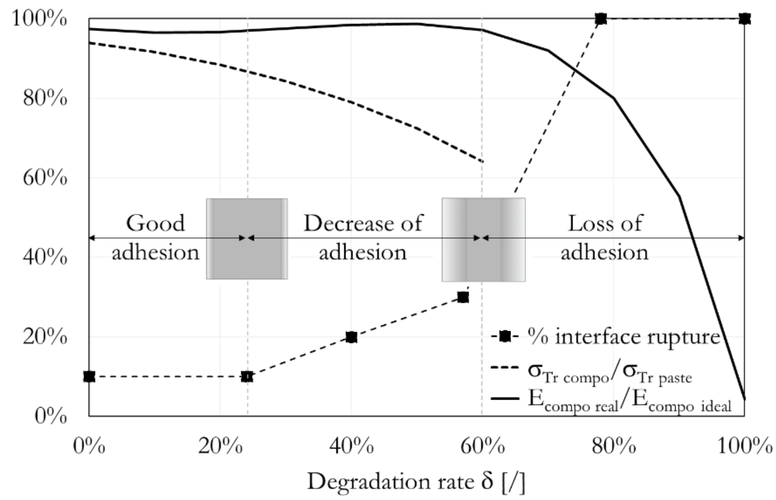

Figure 11 Loss of adhesion progression of cement paste/aggregate bond as a function of chemical degradation rate

Following these observations, within this section, the nature of the effect of chemical degradation by leaching on the mechanical properties of cement paste and paste / aggregate composites at local scale was highlighted. Differences that were noticed between the chemical degradation of cement paste and that of ITZ were reflected in the mechanical behavior of the cement paste samples and composites. The chemical degradation of ITZ was more pronounced than that of the bulk cement paste due to important chemical dissolution of portlandite which is found in excess in sound ITZ. The strong dissolution at ITZ resulted in a porosity increase which had generated a slight acceleration of the degradation kinetics. Regarding the mechanical behavior, the leaching generates a significant decrease in the Young's modulus and the tensile stress of composites. Among other aspects, this is mainly a consequence of the significant chemical dissolution that occurs in the ITZ. The decrease in the mechanical properties of the composite is greater than that of the cement paste and culminates with a complete loss of adhesion of the interface in the degraded zone.

6.4. Discussion on experimental results

Microstructure-scale analyzes and local-scale mechanical tests were used to interpret the mechanical behavior of the paste and the paste / aggregate bond. The strategy adopted was to evaluate the effect of ITZ on the mechanical behavior of the cement paste / aggregate bond in a sond and degraded state, taking the cement paste as a reference.

In this sense, the basic configuration is represented by the parallelepipedal samples in paste and vertically casted composites. The rest of the samples were used only for mechanical tests in a sound state, in order to verify certain aspects observed on the basic configuration or to add additional information useful in the interpretation of the general problem. The first aspect addressed was the degradation kinetics of the cement paste and ITZ, due to the measurement of degraded depth by image analysis for several degradation times. This allowed the calculation of chemical degradation rates, used as a characteristic variable for the chemical degradation state. Due to the diffusive nature of the propagation of chemical degradation, the cement paste degradation kinetics are proportional to the square root of time. In contrast, that of the ITZ initially coincides with that of the paste, but accelerates slightly after a critical threshold to reach a maximum relative difference of 10%. The acceleration of the degradation kinetics of ITZ relatively to cement paste is probably a consequence of the increased diffusivity generated by the large porosity that formed as a result of the chemical dissolution of portlandite.

In order to fullfill the characterization of the chemical degradation, the determination of the degradation kinetics was accompanied by an analysis of the chemical dissolution, through measurements carried out by EDS. Chemical dissolution was assessed through the spatial distribution of Ca / Si molar ratios in the cement paste microstructure and ITZ on composite samples for a single degradation time. Therefore, by observing the spatial distribution of the Ca / Si ratios in sound and degraded areas, the degraded depth values measured by image analysis were confirmed. Apart from this, through the same spatial distribution of the Ca / Si ratios, in the degraded zone of the cement paste and ITZ, the existence of an intermediate zone and a strongly degraded zone were revealed. Regarding the extent of chemical dissolution, the pronounced decalcification in the degraded zone of ITZ was found to be the consequence of extensive dissolution of portlandite.

After characterization of the chemical degradation, still at the microstructure scale, micro indentation was used to investigate the effect of leaching on the Young's modulus in the degraded zone of the cement paste. The results show a clear correlation between the gray level measured by image analysis, the Ca / Si ratio and the Young's modulus. So, by analogy from the gray levels, it is considered that the degraded zone of ITZ and of the cement paste is formed by an intermediate zone with decreasing average stiffness and a strongly degraded zone with reduced stiffness.

At local scale, tensile and shear tests were carried out to assess the effect of ITZ on the mechanical behavior of the cement paste / aggregate bond, through stress / strain curves. This effect of ITZ manifests by the existence of the less rigid and less resistant bonds compared to cement paste. This assertion is rather qualitative in nature, and not quantifiable presently, as in some cases additional measurements are required to access the moduli of elasticity and tensile stress of the cement paste and ITZ. In this context, taking into account the difficulty of measuring very small strains, the question of the reliability of the results arose. Despite a fairly large dispersion, the reliability of the mean values of the elastic moduli was confirmed on the parallelepipedal samples subjected to shear and through tests on reversed Y samples. Additional information is represented by the visible difference between the quality of the bond for composites casted vertically and for those casted horizontally.

As regards the degraded samples, only tensile tests on vertically casted paste and composite samples were carried out. The evolution of the mechanical behavior of the samples was analyzed as a function of the chemical degradation rate. This chemical degradation rate is the ratio of the area of the degraded zone to the total area of the cross section. In terms of rigidity, the influence of ITZ materialized by the softening of the cement paste / aggregate bond which becomes more pronounced following chemical degradation. This aspect is revealed by the evolution of the Young's modulus of the composite as a function of the chemical degradation rate, which undergoes a greater decrease than that of the cement paste because of the significant dissolution within ITZ. Apart from that, taking into account that the Young's modulus was measured by micro indentation and mechanical tests, a comparison was made between the values obtained by the two methods. Despite the fact that the average values obtained by the two types of tests are close together, the greater dispersion of the values obtained by the tensile test indicate an overestimation generated by the uncertainties associated with the installation. With regard to the stresses at rupture, it has been observed that those of the composites decrease more rapidly as a function of the chemical degradation rate than those of the cement paste. For the cement paste samples, the evolution of the tensile stress shows an almost linear dependence on the chemical degradation rate, which is probably favored by shallow cracking. In contrast, for composite samples, the average stress at rupture is close to that of the cement paste up to a certain critical degradation rate. This critical chemical degradation rate corresponds to the onset of pre-cracking and the localization of ruptures at the paste / aggregate interface. After this critical chemical degradation rate, the loss of tensile stress in composites accelerates more than that of the cement paste, possibly due to a greater depth of cracking. Finally, the loss of paste / aggregate adhesion is complete when the ITZ is completely degraded.

7. General conclusions

Leaching of concrete, like other chemical phenomena, produces changes in the microstructure and gives rise to a pathology that reduces the durability of structures. In concrete, especially degraded one, the ITZ which forms between the cement paste and the aggregate is an area which affects the mechanical properties of the cement paste / aggregate bond. However, due to the difficulty of focusing on this area, the mechanical behavior of concrete at the local scale of the paste / aggregate bond remains insufficiently explored.

A better knowledge of the mechanical behavior of concrete structures therefore requires a better understanding of the phenomena that occur at the local scale of the cement paste / aggregate bond. In this context, this thesis aimed to explore the effect of leaching on the mechanical behavior of concrete at the local scale, also analyzing the experimental investigation methods used.

This research problem is not, however, completely unexplored, as the basic characteristics of the leaching scenario have already been highlighted, mainly through observations at the macroscopic scale. In fact, leaching involves partial dissolution of the cementitious matrix. The consequences of this degradation are amplified by ITZ which promotes the acceleration of the degradation kinetics and significant chemical dissolution.

Despite the fact that this general phenomenology is known, a focused investigation on the cement paste / aggregate bond is necessary in order to take a more local look at the extent of these effects on the mechanical properties. An experimental protocol has been set up to allow the characterization of the chemical degradation and the mechanical behavior of the material. This experimental protocol was implemented while Jebli's thesis (Jebli, 2016). In the present study, this protocol has evolved to extend the field of investigation to the relationships that exist between the progress of chemical degradation and the decrease of mechanical properties of the cement paste / aggregate bond and of the paste.

This objective was facilitated by the use of samples with a specific geometry to allow the measurement of the area of the degraded zone, as well as average mechanical stress on the cross section. These are cement paste and cement paste / aggregate composite samples with a square cross section of 10x10 mm^2, in two different shapes: parallelepiped samples and inverted Y-shaped samples. The parallelepipedal composite samples were manufactured with two different orientations relative to the direction of casting: composites casted in a vertical position and in a horizontal position. The second orientation was used to simulate bleeding in real concrete. Chemical degradation was achieved by using ammonium nitrate as an aggressive solution to allow degradation acceleration compared to the real scenario, but also similar spread. This degradation was unidirectional applied, for the parallelepiped configuration only, to the cement paste and composite samples casted in a vertical position.

In the general framework of the exploration of the chemical and mechanical behavior of concrete at the local scale, the first aspect addressed was the degradation kinetics of the paste and the ITZ. The determination of the degradation kinetics was made possible by measuring the degraded depths on cross sections for several degradation times. This was done due to the contrast between the gray levels observed between the sound zone and the degraded one, which allowed the measurement of the degraded depths for several degradation times following the analysis of the digital images of the cross sections. This type of analysis was supplemented by the analysis of chemical concentrations, carried out by SEM EDS and which allowed the confirmation of the degraded depths obtained by image analysis, as well as the evaluation of the dissolution of Calcium in ITZ and in bulk cement dough. Then, in order to highlight the effect of chemical degradation on a mechanical property of the cement paste, micro-indentation was used to determine the evolution of Young's modulus in the degraded zone.

The analysis of the micro-indentation tests is also useful in the perspective of the multiscale aspect because it allows the calculation of a quantity, the Young's modulus, also obtained following the treatment of the mechanical tests at the local scale.

These tensile and shear tests at local scale were carried out on cement paste and composite samples and coupled with the Digital Image Correlation (DIC) to compute displacement and strain fields. The displacement and strain measurements by DIC was carried out using a high-resolution camera, in order to obtain sufficient precision in the measurement of local strains. Particular attention has been paid to tensile testing in order to reduce the dispersion of results, using additional accessories to decrease geometric defects and minimize their impact on experimental results.

The shear tests on parallelepipedal samples and the shear tests on reversed Y-shaped samples were carried out mainly to compare their results with those obtained by tensile tests. The results obtained following the analyzes mentioned above were interpreted mainly by comparing the properties of the cement paste and of the cement paste / aggregate bond.

As concerns the experimental results, the first aspect addressed was the degradation kinetics. With regard to cement paste, the degraded depth follows an evolution proportional to the square root of time; the proportionality factor being consistent with the values indicated in the literature. As for ITZ, the degraded depth initially shows a similar evolution as that of cement paste, but which accelerates after a critical thresshold. The maximum relative difference between the degraded depth of cement paste and that of the ITZ is approximately 10% when the ITZ is fully degraded. This acceleration of the degradation kinetics of ITZ is probably an effect of the increased diffusivity generated by the high porosity created as a result of important dissolution.

Chemical dissolution analysis was performed to compare the extent and distribution of calcium dissolution in the degraded area of ITZ and bulk cement paste. This analysis was performed on composite samples casted vertically for a single degradation time, the first one for which differences were observed between the degraded depths of the paste and that of the ITZ. The indicator chosen to illustrate the state of chemical degradation was the Ca / Si molar ratio, the distribution of which along the linear profiles was obtained. In principle, it has been observed that the degraded areas of ITZ and paste are formed by a highly degraded area and an intermediate degraded area. In the highly degraded zone, the Ca / Si ratios are reduced, while in the intermediate zone, the Ca / Si ratios show a pronounced variation between the reduced values encountered in the highly degraded zone and the high values encountered in the sound zone.

Using this information, firstly, the delineation of the three degradation zones allowed confirmation of degraded depth measured by image analysis. Secondly, the distribution of local Ca / Si ratio values indicated a higher dissolution of portlandite at ITZ compared to cement paste. Subsequently, a first illustration of the effect of chemical degradation on the mechanical properties of the paste was obtained by comparing the evolution of gray levels, of the Ca / Si ratio and of the Young's modulus obtained by micro indentation. By comparing the evolutions of these three quantities, an obvious correlation between them was noticed. These changes are manifested by similar trends in the highly degraded zone and in the intermediate degraded zone. Indeed, due to the correlation between gray level and Young's modulus, image analysis indicates for all samples, both in the paste and in the ITZ, the existence of highly degraded and intermediate degraded areas. However, the decrease in Young's modulus of ITZ is probably greater than that of cement paste, because of the greater chemical dissolution. This aspect can be verified following local mechanical tests on paste and composite samples. Regarding the mechanical tests, they were first carried out in a sound state in all configurations to globally investigate the peculiarities of the mechanical behavior of the cement paste / aggregate bond and of the cement paste. The determination of the elastic moduli and the stress at rupture of the samples was carried out from the stress / strain curves obtained in the areas of interest stressed in tension or shear. As a general rule, the effect of ITZ manifests itself at the paste / aggregate interfaces by lower moduli (Young and shear) and lower stresses at rupture than the paste. The effect of casting orientation is visible because the paste / aggregate bond of horizontally casted composites is less rigid and less resistant than that of vertically cast composites. These observations were supplemented by the analysis of the strain state over the entire analyzed face of the sample. These strain fields indicated the presence of the expected strains in the areas of interest, but also significant strains in the loading areas which, in some cases, accelerate failure.

For shear tests on reversed Y-shaped samples, their results were used to confirm those obtained by other types of tests. The shear moduli measured on the reversed Y-shaped paste and composite samples are consistent with those measured on other types of tests, initially confirming the values obtained using the DIC. In addition, on the reversed Y-shaped samples, the average value of the Young's modulus of the cement paste obtained in tension as well as the softening effect of ITZ on the cement paste / aggregate bond were confirmed through a simulation in the elastic domain.

Subsequently, the effect of leaching on the mechanical behavior of the cement paste and of the paste / aggregate bond was analyzed following tensile tests on parallelepipedal samples of cement paste and composites casted vertically. This configuration was chosen in order to apply the most aggressive mechanical stress to the material (tension). As for the vertically casted composite, they were in order to be able to preserve the adhesion between paste and aggregate for high degradation states. The evolution of mechanical properties was analyzed as a function of the progress of chemical degradation for several degradation times. The quantity chosen to characterize the progress of degradation is the chemical degradation rate. This quantity is equal to the ratio between the area of the degraded zone and the total area of the cross section. Its determination was possible due to the knowledge of the degraded depth. For the composite sample, the corresponding chemical degradation rate was calculated at the interface, and considered representative for ITZ. Thus, evolution of Young's moduli and stresses at rupture of cement paste and composite samples were obtained as a function of chemical degradation rate. The decrease of Young's modulus of composite as a function of the chemical degradation rate is greater than that of the cement paste, due to the significant chemical dissolution within ITZ. A comparison between the Young's moduli of sound and degraded paste obtained by micro indentation and tensile tests confirms the average values obtained, which are close (less than 10% difference). On the other hand, the dispersion of the Young's modulus obtained by tensile tests is amplified by the influence of the uncertainty on the installation conditions.

As regards stresses at rupture of the cement paste and of the composites, their changes as a function of the chemical degradation rate were analyzed with reference to cracking, which is observed on the displacement fields. On cement paste samples, the stress at the time of crack initiation shows an accentuated decrease as a function of the chemical degradation rate which even reaches zero after the moment when samples become pre-cracked before loading. However, the fact that the evolution of the stress at rupture of the cement paste shows a less pronounced and quasi-linear decrease suggests that the cracking is limited to a superficial zone. In the case of composites, the stresses at rupture initially follow a similar trend to that of the cement paste, when the failure occur especially in cement paste, but which changes when the pre-cracking appears at the interface. After the chemical degradation rate that corresponds to the onset of pre-cracking, failure occur at the interface for stresses that decrease significantly to zero for a chemical degradation rate of 100%. At this stage, the decohesion of the paste / aggregate bond in the degraded zone is complete. An overall observation of the mechanical behavior of the samples indicates that the loss of adhesion between paste and composite occurs in a gradual, but accelerated manner. This is promoted initially by the significant chemical dissolution in the ITZ and then by the cracking of the paste / aggregate interfaces.

Overall, the main conclusion concerns the mechanism by which the ITZ influences the behavior of the degraded cement paste / aggregate interface after leaching. First, an acceleration of the degradation kinetics of ITZ relative to the cement paste occurs due to increase of porosity generated by the dissolution of portlandite. However, the relative difference remains small. In contrast, the more pronounced chemical degradation of ITZ results in a much greater decrease of the mechanical properties of the paste / aggregate bond compared to cement paste. This corroborates the loss of adhesion between cement paste and aggregate in the degraded area.

A second part of the study concerned the adaptation of methods for investigating the parameters of chemical and mechanical origin of concrete at the local scale of the paste / aggregate bond. The coupling between digital image analysis and EDS was used to determine the degraded depth and the distribution of the Calcium dissolution in the degraded zone. Still at the microstructure scale, the micro indentation allowed to underline a similar evolution of the Young's modulus of the cement paste with that of the quantities measured by image analysis and EDS. At local scale, a new way to simulate the effect of concrete bleeding on the paste / aggregate bond has been proposed by varying the orientation of the sample during manufacture. In addition, the analysis of the displacement fields highlighted the appearance of cracking during mechanical testing and the level of stress at which it occurs. The perspectives, related to the identification of mechanical parameters at the local scale to feed numerical models at the macroscopic scale will be discussed in the following paragraph.

8. Perspectives

In perspective, the adaptation of the experimental protocol is envisaged to determine the constitutive relations of concrete at the local scale (paste, aggregate, paste / aggregate bond) under different scenarios (different formulations and different pathologies). This is necessary in order to allow the implementation of these constitutive relations in numerical models, once the mechanical parameters have been characterized.

Besides that, using optical observation techniques to estimate changes in the mechanical properties of cement paste and ITZ may help to simplify the experimental procedure, but it requires validation by additional analyzes. This perspective is based on the observation, made in this study, that the evolution of the gray level in the degraded zone of the cement paste is similar to that of the Young's modulus. The advantage of this approach would be the possibility of using a simple technical measurement, optical observation, to estimate quantities whose measurement usually involves significantly more constraints. Validation on representative batches of samples could allow the extrapolation of the results to a wider range of cases.

At the local level, the determination of the constitutive relations of the cement paste and of the paste / aggregate bond in tension and in shear is envisaged in the medium term. In this context, a challenge would be to obtain ruptures by simple stress states (tension or shear). Such a configuration would allow the determination of the mechanical strengths of the cement paste and of the cement paste / aggregate bond. As part of the current research program, other types of tests that involve complex stress are underway. The objective of these tests is to determine the failure criterion of the cement paste and the cement paste / aggregate bond, as well as the cracking energy. During this study, it was noticed that the difficulty of performing reliable mechanical tests lies above all in the control of the experimental boundary conditions. In this context, in order to facilitate the performance of mechanical tests, a new test device has been designed. The device designed to meet the demands mentioned is a modular testing frame.

The principle of this device consists in the possibility of carrying out several types of tests on the same basic frame by adapting the support and the loading system. The advantages of this device are the control of the boundary conditions (loading and supports), and the observation of the sample as a whole. Apart from the active vertical loading along the yy axis, passive horizontal confinement along the xx axis is possible. This device enables bending, shearing and compression tests to be carried out and cracking monitoring in different geometric configurations. This device is currently used for bending tests in variable position to study the cracking and failure of samples in mixed mode of tension and shear (Figure 117).

Regarding the implementation of the behavior laws obtained experimentally in the model which simulates the behavior of concrete at larger scales, it also depends on the quality of the model material and its good representation of the real material. In order to compare the two cases, analyzes at the microstructure scale can be performed.

Another way to reduce the gap between the properties of samples used for the experimental study and those of actual concrete is to make samples in mortar and mortar / aggregate composites. This type of samples would make it possible to obtain a spatial arrangement of the cement paste and the aggregate closer to that of the concrete, useful to validate the observations made in the simpler case of the cement paste and composite cement paste / aggregate samples.

Another perspective considered is represented by the enhancement and adaptation of digital image correlation techniques to determine the elastic parameters of the paste / aggregate bond. This aspect is problematic in the case of high performance concretes which have reduced ITZ thicknesses and therefore, gradients in mechanical properties that are difficult to characterize. Reverse analysis techniques based on the interpretation of displacement and strain fields can be used to identify these parameters. Indeed, a short simulation of the mechanical behavior in the elastic domain of samples in the form of reversed Y, represents a handling of the problem which is oriented in this direction. The presented approach can also be useful for measuring shrinkage, which is an essential aspect in the mechanical behavior of the paste / aggregate bond, but also in that of the paste.

Finally, through the perspectives envisaged, the medium-term objective is to validate models of concrete behavior at the macroscopic scale. It is also aimed to integrate into these models the mechanical parameters identified at the local scale. In this perspective, a first intermediate validation of numerical models is planned at the mesoscopic scale.

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