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Durability performance of uncracked and cracked nanoadditioned UHPFRCs in a dynamic leaching system.

M. Criado, M. Gimenez, E. Menéndez, M.C. Alonso

Instituto de Ciencias de Construcción Eduardo Torroja-CSIC, Calle Serrano Galvache 4, 28033 Madrid, Spain – maria.criado@ietcc.csic.es, mercedes.gimenez@ietcc.csic.es, emm@ietcc.csic.es, mcalonso@ietcc.csic.es

Abstract

This work aims to analyze the aggressiveness induced by waters rich in sulfate and chloride simulating the water from geothermal power plants with an ultra high performance fiber reinforced concrete (UHPFRC) in cracked and un-cracked states. A dynamic water interaction has been reproduced by a test in which water impacts on the surface of the concrete. The chemical composition of the water leads to a leaching and interaction with the concrete surface, and the movement of the water provokes a mechanical erosion. Ionic composition and pH of the leachates have been evaluated together with mass losses. The self-healing ability of the cracked UHPFRC is evaluated with Non-Destructive Techniques (NDT) and visual inspection.

The plain UHPFRCs exhibit a good response during one year of exposure. No sealing of the crack surface has been observed neither mass losses are detected. The pH of the leachates varies during tests in the range from the initial pH=3 to near-neutral conditions. The ionic data indicate that alkalis (K and Ca) are the main elements released from the concretes. Chloride ions remain in the leachate indicating no entrance in the concrete matrix, while sulfate and sodium ions decrease probably due to the reaction and solid phases precipitation on the concrete surface.

Keywords: UHPFRC; crystalline admixture, chemical attack; leaching and erosion; crack; self-healing.

1. Introduction

The mechanisms of interaction of the aggressive environment with concrete are responsible of the durability of a structure. The source governing the performance can have its origin from different phenomena: physical-mechanical or chemical causes. Specific physical-mechanical sources are abrasion or freeze and thaw. In the case of the chemical ones, they are due to chloride penetration, carbonation allowing corrosion of reinforcement, or expansive reactions occurring in the concrete bulk due to sulfate attack or alkali-silica reaction with aggregates [1,2]. Even a combination of actions can occur increasing the consequences of damages.

The concrete structures under chemical aggressive environments, denoted as XA in the standards and provoked by natural soils and groundwater, industrial activities as well as rain in a polluted environment, follows a chemical attack. Concrete exposed to such environments very often present pathologies such as cracking produced by expansion in the case of sulfate attack, cement paste dissolution, or efflorescence, in the case of acid attacks depending on the aggressiveness of the environment chemical composition or the concrete characteristics [2,3] that seriously compromise the service life of the structure [4].

To ensure the safety of the concrete structures throughout a longer service life span of them and reduce maintenance operations and related costs, a continuous increase in the durability requirements is demanded when they are exposed to aggressive environments. Because of this, advanced concrete solutions, e.g. employing ultra high-performance fibre-reinforced concretes (UHPFRCs) are undergoing continuous progress and development [5]. Although the characteristics of UHPFRC could vary depending on the curing process and its composition, UHPFRC are characterized by low water to binder ratio for getting a very dense material, jointly with the inclusion of fibres for enhancing the mechanical properties [6]. Owing to these, this type of concrete is capable of containing single cracks and leads to a multi cracked surface, being able to show a tensile strain-hardening behavior depending on the type of fiber, dosage, efficiency and matrix characteristics [5, 7]. Besides, due to the compactness, UHPFRC is nearly impermeable to chlorides, carbon dioxide, and sulfates, i.e. they present excellent durability due to a dense microstructure, ultra-low porosity, an enhancement inhomogeneity, and an increase in toughness [5, 8, 9]. Despite these qualities, not only the bulk of the concrete but also the fibres are under risks because they are also affected by environmental actions.

Durability requirements on concrete structures have also led to investigate, design, and improve the self-healing capability of cementitious materials that allow an autonomous way of sealing of cracks, which provide an entrance for the aggressive substances. There are two types of self-healing, autogenous or autonomous/engineered healing. Autogenous healing consists of the healing of the small cracks mainly by further hydration of cement and/or precipitation of calcium carbonate 8[10]. In the second one, the healing is caused by the specifically engineered additions designed to promote it and purposely added to the concrete mix-design [11]. One of these engineered additions, employed in this work, is the crystalline admixture, which is a porosity reducer, an additive for reducing the penetration of water under pressure, an anti-shrinkage agent, and a promoter of self-healing with long-term efficacy in a humid environment [12, 13].

This work aims to study the durability performance of ultra high-performance fiber-reinforced concretes (UHPFRCs) containing a crystalline admixture addition exposed to the chemical environment (XA) through a dynamic leaching sulfate and chloride rich-water test combined with erosion. The specific XA environment simulates the conditions under the material is subjected in the basins of water-cooling towers from a geothermal power plant. The durability performance of the mix is evaluated in the un-cracked state based on the interaction between the concrete and the water during the time, while the performance due to the fibre addition and the capability of sealing because of the crystalline admixture addition is analyzed in cracked samples using NDT.

2. Materials and methods

A specific ultra-high performance concrete (UHPFRC) mixture was designed by the Polytechnic University of Milan, which was a blend of 50% cement Portland and 50% blast furnace slag, it was referred as XA-CA in the manuscript. In addition, this concrete incorporated crystalline admixture (supplied by Penetron Italia), and its formulation was reported in reference [14]:

Crack generation:

The UHPFRC specimens were cured in a moist room at 20ºC and 95%RH for 2 months. Six cylinders Ø100x50mm un-cracked and cracked specimens were employed in this test, obtained from samples of Ø100x300mm. The method employed to produce the crack was preceded by the creation of notches specimens. These samples had 5mm deep notches on one of the plain surfaces to favor and induce the crack propagation in the center of the sample. For a crack generation, an increasing load according to Brazilian splitting tension test with a constant load rate of 0.5µm/s was applied controlling the crack mouth opening displacement (CMOD) with an extensometer placed between two steel plates stuck on both sides of the notch. The test stopped once the CMOD reaches a value of 1000µm (see Figure 1). Three identical samples of each type, crack and un-cracked state, were evaluated.

After the test, the samples were evaluated in order to register the range of the real width and determine that crack had reached the bottom of the sample. The obtained cracks are heterogeneous along all the diameter, as it was expected [15], leading to different crack widths lightly higher than 1mm in the center of the sample to few µm in the edges of the sample. This allows studying the evolution of different widths depending on the part of the sample under inspection.

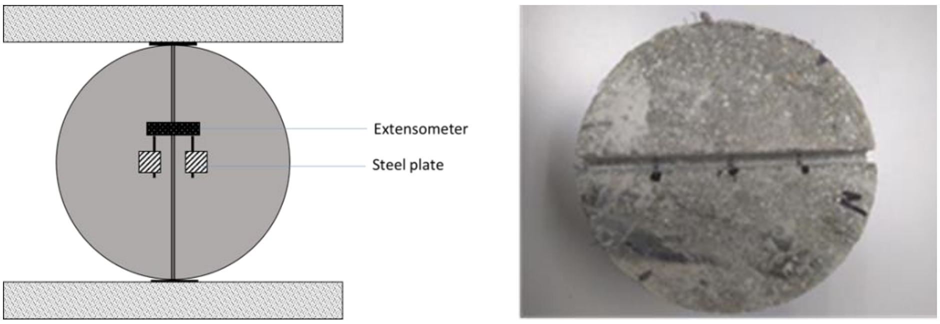

Figure 1. Cracking equipment scheme and cracked specimen.

Dynamic leaching test:

A dynamic test with water impact was designed to simulate the leaching and erosion phenomena simulating the operation conditions of water in the cooling towers in geothermal plants. The specimen was not pres-saturated so as not to interfere with crack self-healing. It was placed over a rigid plastic mesh to avoid direct contact with the water located into a plastic container, as shown in Figure 2. The water movement was generated by a pump, the flow rate was 70 ml/s, where a water flow fell in the notched surface to guarantee the impact on the crack from a height of 20cm, see Figure 2 left and middle. The water was continuously recirculated through the pump, and the evaporated water was filled every month with the test solution to maintain a constant final volume in the plastic container, without stops during all the period of testing. The leaching medium employed simulated the water of a cooling tower from a geothermal power plant [16]. The simulated geothermal water contained both sulfate and chloride ions (SO_4^{2-} = 2300 ppm and Cl^- = 300 ppm) and its pH was 3, the full chemical composition is included in Table 1.

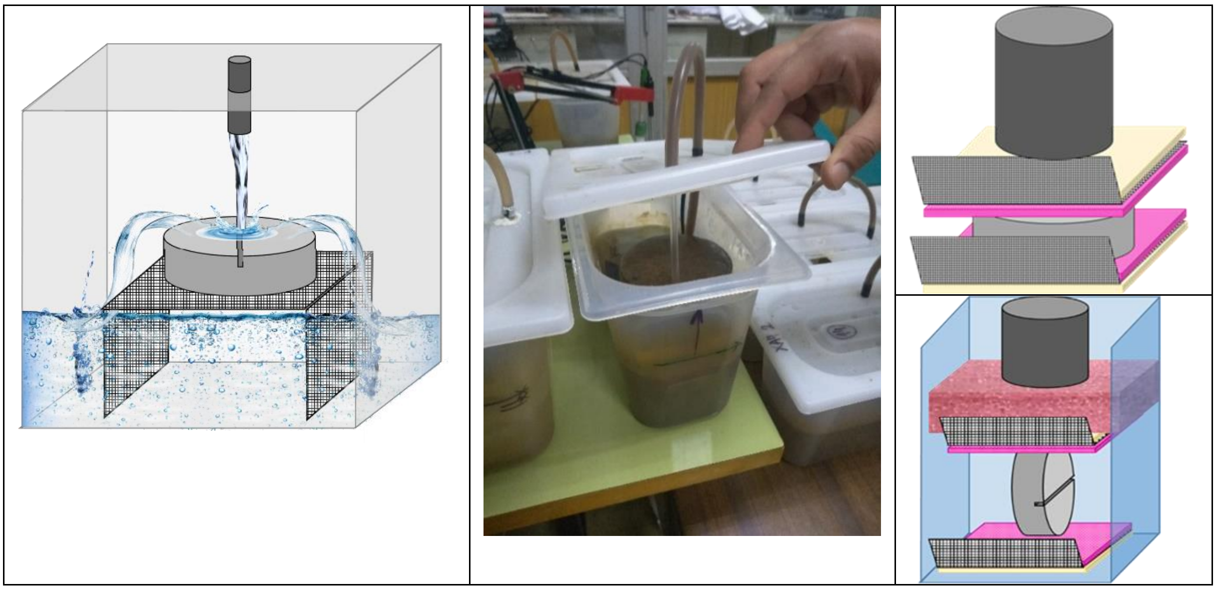

Figure 2. Left and middle: Water interaction for erosion and leaching set up.Right: Resistivity/resistance measurement towards (up) and against (down) the crack.

Table 1. Chemical composition of the geothermal water simulating that used in the cooling tower.

Ions	Cl^-	SO_4^{2-}	Ca^{2+}	K^+	Na^+	Mg^{2+}
Concentration (ppm)	300	2300	4.01	19.8	1279.9	0.3

The erosion damage was evaluated through mass changes and concrete corrosion depth. First measurements of both parameters were performed after 7 days of exposure when the specimen was fully saturated. For the mass changes, four measurements of the height of the sample in the center where water impact occurs were made using a caliper with a sensitivity of ±0.01mm.

The chemical composition of an aliquot of the leaching solution was periodically analyzed by ICP and these values at different ages were expressed regarding the initial concentration value of each ion. Other parameters such as pH, temperature, and electrical conductivity were also evaluated. The temperature was influenced by the environmental conditions and it was decided to place a conditioned air in the room to control the temperature and stabilize between 25ºC and 27ºC.

Cracked performance (self-healing):

The self-healing capability was studied by non-destructive techniques (NDT). Crack sealing and crack size changes were analyzed using an electronic microscope. The objective of the visual inspection was to distinguish if there were precipitates in the edges of the cracks (sealing) or differences in its morphology due to the impact and erosion of water. The visual inspection has been performed in both sides of the sample (top and bottom) along all the crack and comparisons between both sides, between the different widths along the crack and during time has been carried out. Electrical resistivity (ER) was employed for the evaluation of the internal evolution of the cracks sealing using two configurations: towards the crack (configuration 1) and against the crack (configuration 2), see Figure 2 right. Due to the geometry of the samples, the resistivity could not be determined; however, the resistance (R) of the concrete could be considered proportional to the resistivity as long as the contact area and the distance between meshes was maintained. For each configuration, the uniform electrical current flow generated by two electrodes connected to parallel sides of the specimen was measured. The measurements were performed with an AUTOLAB 84750 potentiostat/galvanostat, using a pure sine wave AC voltage of 32 mV RMS at a frequency of 10kHz.

3. Results and discussion

3.1. The effect of water erosion on HPFRC

Concrete mass and height changes are measured for the erosion evaluation. Figure 3 shows the mass and sample thickness changes during approximately one year of water impact for XA-CA concrete. When a water flow hits the concrete surface, it could be thought that mass and volume losses can occur due to erosion of the surface. However, in this case, the concretes gain mass over time. they slowly absorb the simulated geothermal water until reaching a mass practically stabilized. Therefore, the absorption of water is detected, but no damage is observed. The height changes for the XA-CA concrete in the un-cracked state with exposure time are reported in Figure 3 Right. The heights of the specimens remain constant throughout the test (between 1% and -1%), remaining as initial after 300 days of water impact, without volume loss. Therefore, the un-cracked XA-CA concrete presents good behavior against the erosion process in the salted water.

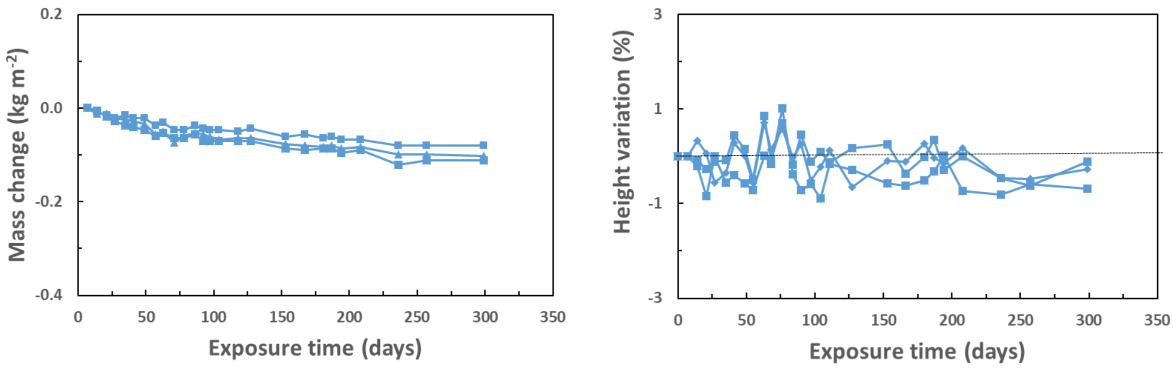

Figure 3. Left: Mass changes and Right: Height changes for the un-cracked XA-CA samples over exposure time.

3.2. The effect of leaching of UHPRC in geothermal simulated water

Ionic data of the aliquots of the water extracted at different ages are shown in Figure 4.The ionic analysis represents the relative variation between the content of the ions at a given age (ion_t) and the initial content (ion_0). If the ion_t/ion_0 ratio is equal to 1 indicates that the ion concentration does not vary over time, if the ratio is greater than 1, there is a greater amount of ion in the medium and if the ratio is less than 1, there is a consumption of it due to interaction with concrete components.

The ionic data indicate that K and Ca are far (ion_t/ion_0 ratio greater than 1), indicating a dissolution from the cement paste, characteristic of the concrete leaching process. However, their tendencies are different, Ca concentration decreases over exposure time, while K ions remain constant. The retention of Ca ions could be associated with secondary hydration processes or the formation of carbonated phases, as was also previously observed by J. L. García Calvo et al. [17]. Cl^- ions in the solution remain practically unaltered during approximately the first year in the leachate indicating no entrance in the concrete matrix. On the contrary, sulfates and sodium ions are clearly below the initial concentration indicating interaction with the concrete. This interaction is preferential with sulfates since they could form more insoluble compounds and therefore the chlorides remain free in the system. However, their transport in the very dense matrix is limited, since the UHPFRC has very low porosity, as previously the authors observed through MIP, with a porosity of 4.5% [14].

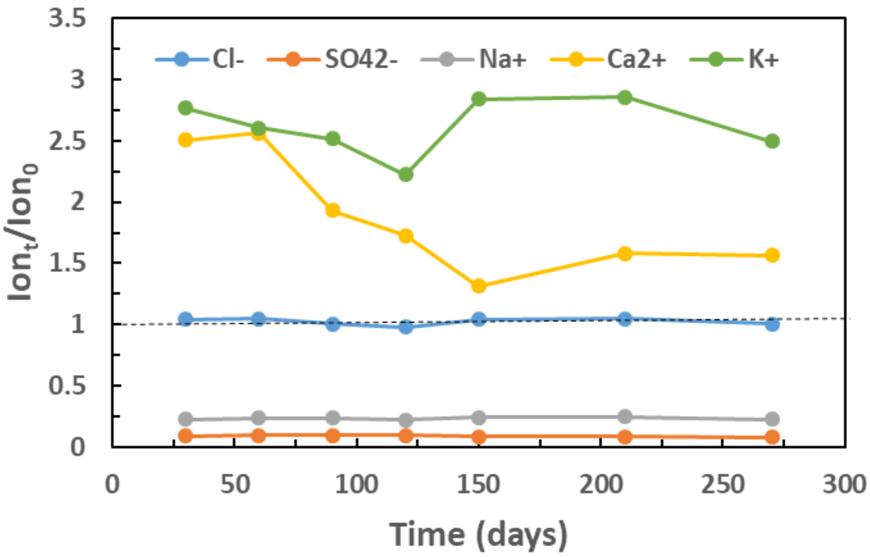

Figure 4. Leaching analysis from the geothermal water over time.

Figure 5 shows the pH and electrical conductivity from the leaching water over time. An initial pH of the geothermal water simulating that used in the cooling tower is 3, but this value increases quickly up to 8.3 after 1 day of the test. It is due to the interaction between the water with the concrete, where alkali ions (Ca^{2+} and K^+) are released. The pH values are kept constant over time, with slight variations, between 8.5 and 8.9.

During the first 30 days, the electrical conductivity (EC) values of the geothermal water are around 2000-3000 µS/cm, see Figure 5 Right. An increased tendency of this parameter is observed over time, indicating the advance of the interaction water-concrete occurring during the leaching process. Localized jumps in the evolution of EC are related to the filling of geothermal water.

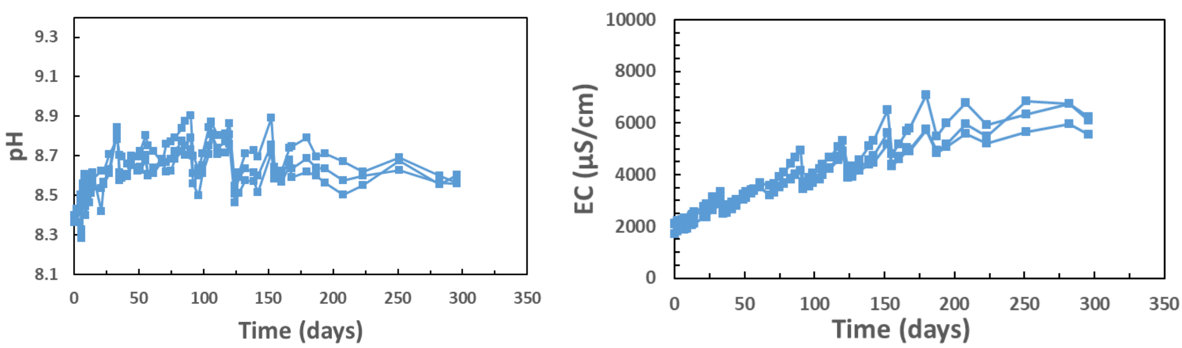

Figure 5. Left: pH and Right: Electrical conductivity from the leaching water over time.

3.2. Efficiency of crack sealing of UHPFRC under dynamic water impact

The electrical resistivity indicates the electrical conductivity of the material. A low electrical resistivity corresponds to the high conductivity of the material.

The location of the sensors and the geometry of the samples not always made possible de determination of the electrical resistivity. However, the proportionally between electrical resistivity and electrical resistance has been checked in order to be able to use resistance values for the analysis. Measurements are obtained following two configurations: following the crack direction, towards the crack (method 1) and perpendicularly to the crack, against the crack (method 2), see Figure 2 Right.

In general, when the distance between electrodes increases, an insulating effect is expected, which means higher resistivity values. However, due to the different geometry of the samples regarding the measurement procedure (configuration), the absolute value of the resistance cannot be compared because of the differences between contact area and distances.

Since the higher resistance is related with the lower conductivity, when the same material is studied, the higher resistance would be in relation to the material with more defects such as cracks, pores, or other internal defects. On the other hand, when the results of both configurations are compared, the isolation effect that could be expected do not occur probably due to the configuration arrangement, in which neither surface contact, nor distance between electrodes is not the same. Despite this, though the results from both configurations are not directly comparable, a relative comparison of tendencies and variations due to the cracked state can be done.

Figure 6 shows the electrical resistance measurement towards and against the crack analyzed throughout the time in un-cracked and cracked samples. Slight differences can be observed between un-cracked and cracked values (dash and bold lines), being the un-cracked values lower as expected. When both configurations are compared, the electrical resistance corresponding to the measurement towards the crack (configuration 1) is higher than the obtained measuring against the crack (configuration 2). This could be explained by the different position and geometry in both configurations.

In both cases, there is scatter between measurements and no clear differences have been detected. The results of the electrical resistance in time are slightly constants, showing no increase or decrease tendencies, which agrees with the stability of the physical properties of the samples.

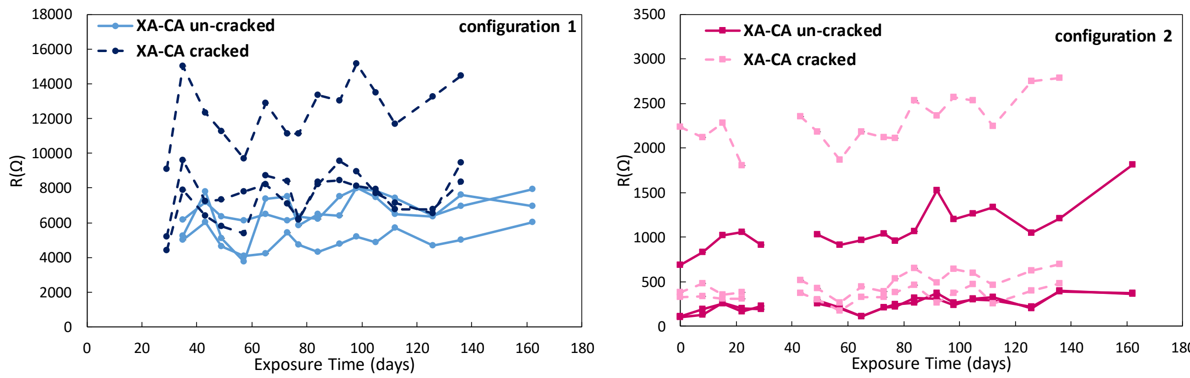

Figure 6. Evolution of electrical resistance for un-cracked and cracked XA-CA using configuration 1 (left) and configuration 2 (right)

A visual inspection to evaluate if the surface sealing of the initial crack is taking place has been performed using an optical microscope (Figure 7). Two visual characterizations have been performed: one initial and one after 7 months.

After 7 months of exposure, the crack width is compared, but also the surface evolution is analyzed. Figure 7 shows a general and a detailed image of an un-cracked and cracked samples. In both samples, steel fibers are affected by corrosion, and a white product can be observed gathered throughout the surface of the sample regardless of the presence of cracks or the water impact, probably as a consequence of the interaction of the aggressive medium with the concrete responsible for the chemical changes observed in figure 4. More detailed analyses by SEM-EDX is needed to confirm the type of product and determine why it is mostly present in the bottom of the samples.

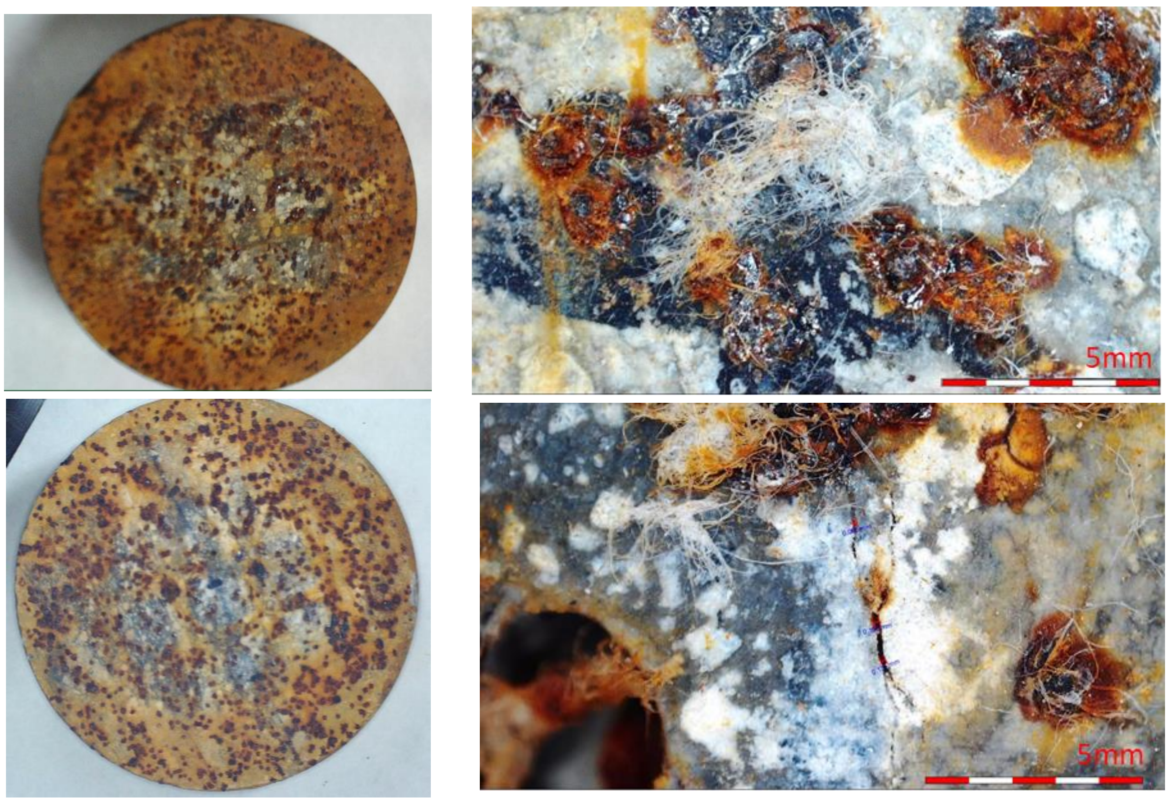

Figure 7. Un-cracked (up) and cracked (down) samples after 7 months of exposure

Different sizes of cracks corresponding to the different parts of single cracks are analyzed in both faces of the samples: the top, in which the impact of water is taking place, and the bottom in which there is no impact but water movement. Figure 8 shows the maximum crack width recorded for one of the samples of XA-CA on the top (870µm) and the different of width in comparison to the bottom of the same sample (310µm), in these pictures it should be highlighted the morphology of the cracks, which allows comparing different widths from the tip of propagation to the center of the crack. However, even with small crack widths, no surface sealing of the crack has been observed yet and the edges of the cracks are clean without precipitated substances neither in the top nor the bottom of the sample. Cuenca et al. [18] observed that crack healing depends mainly on exposure condition and initial crack opening, being tank water immersion the most efficient exposure condition for the sealing of the cracks compare to wet/dry cycles or open-air exposure. In this test, in which self-healing is not induced and the water is in continuous movement and impact with the concrete surface and they could interfere in the crack closure.

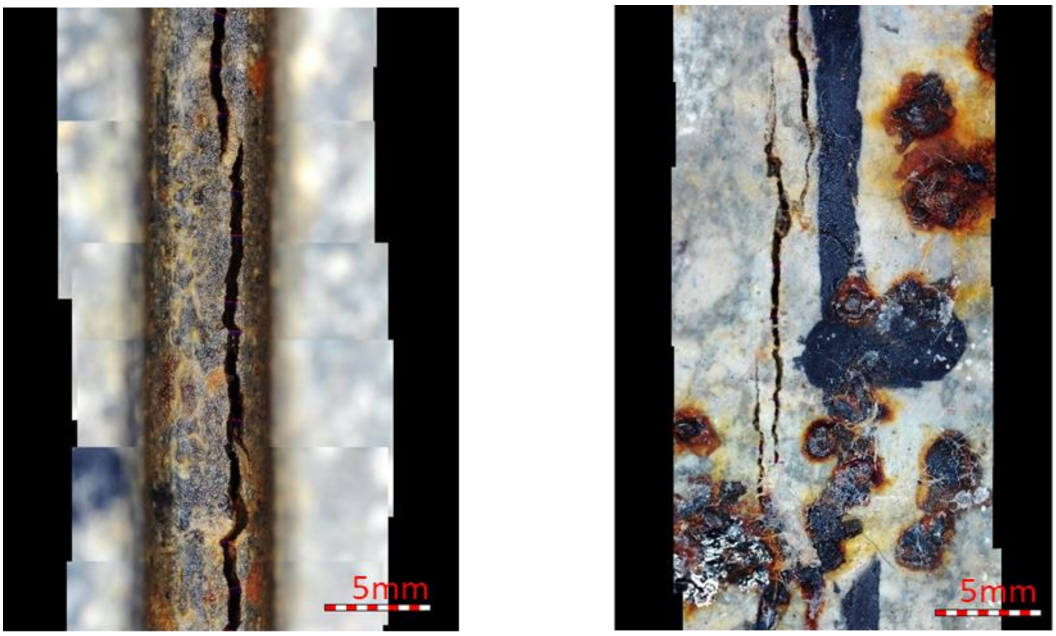

Figure 8. Left) Crack appearance after 7 months of geothermal water impact (top of the sample). Right) Crack appearance after 7 months of geothermal water exposure (bottom of the sample)

4. Conclusions

From the dynamic erosion and leaching test results obtained in this study, the following conclusions can be drawn:

- The un-cracked XA-CA concretes present a good response of the erosion of the UHPFRC surface, no mass loss and height changes are observed after 12 months exposure.
- The chemical composition of the leaching solutions shows Cl^- ions remain practically unaltered, while SO_4^{2-} ions decrease as a consequence of the interaction with the concrete surface.

From the NDT results obtained in this study, the following conclusions regarding crack self-healing can be drawn:

- Differences between cracked and un-cracked samples cannot be detected using electrical resistivity.
- After 7 months of exposure, self-healing is detected neither in the impact surface nor on the bottom surface.

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