Durable Concrete for Infrastructure under Severe Conditions

Smart Admixtures, Self-responsiveness and Nano-additions

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Concept of Ultra High Durability Concrete for improved durability in chemical environments: Preliminary results

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Abstract
The aim of this work is to analyze the enhanced durability performance of an Ultra High Durability Concrete (UHDC) exposed to chemical attack (XA exposure conditions), with reference to an intended application into infrastructures serving geothermal plants. This study is based on a reference Ultra High Performance Concrete (UHPC) with steel fibers and crystalline admixtures (reference mix) and other two mixes that modify in some aspect the reference one: addition of alumina nanofibers (ANF) and addition of cellulose nanocrystals (CNC). Accelerated and short-term tests, complemented with mineralogical and microstructural characterization, have been employed to measure critical durability indicators according to an XA environment. Based on the monitoring and damage evolution of the UHPC under the intended exposure conditions, a criterion for durability performance assessment is being defined in order to understand the differences due to the incorporation of nanoadditions.

Keywords: Ultra High Durability Concrete, crystalline admixture, alumina nanofibers, cellulose nano-crystals, self-healing.

1. Introduction
The interest in guaranteeing and improving the durability of concrete structures is continuously growing. Though design codes recommend advanced concrete solutions in extremely aggressive exposures, they are not taking into account neither Ultra High Performance (Fiber Reinforced) Concrete nor new nanoadditions especially designed to improve durability performance. The development of advanced materials and novel structure concept able to convey superior durability in extremely aggressive environments has become a priority for the EC. Besides the high share of the annual budget of construction industry which is spent in repair and retrofitting of existing damages structures, it has been furthermore shown that 50% of the repaired concrete structures are likely to fail once again, 25% of which in the first 5 years, 75% within 10 years and 95% within 25 years [1]. This paper presents a preliminary research on the framework of the H2020 ReSHEALience project whose main objective is to develop an Ultra High Durability Concrete (UHDC) combining self-healing promoters (crystalline admixtures) and nanoadditions (alumina nanofibers and cellulose nanocrystals) to improve durability under extremely aggressive exposures such as chloride-induced corrosion and chemical attack. This work is focused on chemical attack exposure (XA) to simulate the conditions in which the concrete will be employed,

in this case the scenario in the mud-settling tanks and basins of water cooling towers, both serving geothermal power plants. The ReSHEALience project will provide its own solution in the aforementioned framework which is based on the concept of Ultra High Durability Concrete (UHDC). This will upgrade the well-known concept of UHPC in the framework of a metamaterial approach, which will exploit the incorporation of tailored nano- and micro-scale constituents, aimed at achieving fit-for-the-purpose properties. These will include optimized “in-structure” mechanical performance, thanks to the alignment of fibers due to the casting flow, [2] and superior durability not only in the un-cracked state due to the highly compact microstructure, [3] but also in the cracked state through the nano-addition synergy effects which may favor the autogenous self-healing capacity [4].

2. Materials and methods

Three UHDCs have been investigated in this paper (Table 1):
1) the reference mix for this scenario, which incorporates crystalline admixture (ref.);
2) the mix incorporating both crystalline admixture and alumina nanofibers (ANF)
3) the mix incorporating both crystalline admixture and cellulose nanocrystals (CNC).

Table 1: Dosage of the UHDCs exposed to chemical attack exposure (XA).

Constituents	Ref.	ANF	CNC
Cement CEM I 52.5 [kg/m^3]		600	
Slag [kg/m^3]		500	
Water [kg/m^3]		200	
Steel fibre [kg/m^3]		120	
Sand (0-2 mm) [kg/m^3]		982	
Superplasticizer [kg/m^3]		33	
Crystalline admixture [kg/m^3]		3	
Alumina nanofibers [% by cement mass]		0.25	
Cellulose nanocrystals [% by cement mass]			0.15

The different types of samples have been produced with each of the mixes detailed above: 40x40x160mm prisms for water sorptivity, flexural and compressive strength tests, and expansion tests; 100 mm side cubes for compressive strength tests and Ø100x50mm high cylinders for chloride transport, microstructural and water capillary suction tests. The UHDC specimens, after demolding, have been cured in a moist room (T=20ºC, RH=95%) up to the age of testing, if not specified otherwise.
A series of accelerated and short-term tests are being carried out for the preliminary evaluation of durability performance. The main parameters considered in the standards are analyzed according to the XA scenario (chemical attack) and classified into indirect and direct durability indicators. The indirect durability parameters considered for this scenario include the pore structure and pore size distribution as well as the microstructure composition, carried out by CSIC. For the evaluation of direct durability indicators: capillary suction tests and sorptivity tests have been performed performed, respectively by CSIC according to UNE 83982 and by Politecnico di Milano (PoliMi) as per EN 13057. Moreover, the evolution of the compressive and flexural strength has been monitored under both reference curing conditions (T = 20°C and RH = 95%) as well as under conditions replicating the service scenario, i.e. immersion in the same water as from the geothermal power plant where the pilot structures will be built employing the investigated materials. This water contains both sulfate and chloride ions (SO_4^{2-} = 2678 ppm and Cl^- = 441 ppm). Autogenous shrinkage tests have been

also performed at PoliMi to further assess the effects of the nanoadditions.

3. Results and discussion

3.1. Indirect durability indicators

The morphology and composition of the three different mixes have been studied by means of BSE/EDX (scanning electronic microscope in back-scattered electron with energy dispersive X-ray analyzer). Fig. 1 shows the micrographs for ref., ANF, and CNC mixes after 60 days of curing. These micrographs presented distinctive regions, identified with different greyscale intensities. The large angular particles (light grey region) corresponding to unreacted slag grains (S). The unreacted (or partially reacted) clinker (C) and slag particles are surrounded by a dense and compact matrix (average grey area) corresponding to the main binding phases, consisting mainly of Al-rich calcium silicate hydrate gel (C-(N)-A-S-H gel). All mixes feature a highly compact microstructure, with no microcracks observed in the ANF and CNC mixes; whereas some are present in the reference mix probably due to autogenous shrinkage, which has been mitigated by the nanoadditions (Figure 2a). Figure 2(b) shows the pore size distribution from Mercury Intrusion Porosimetry (MIP) test. Changes on the pore distribution are appreciated in the mixes with nanoadditions. An evolution to smaller capillary pores is detected in ANF and CNC mixes, >0.02μm, respect to the ref. mix that shows a unimodal peak pore distribution between 0.1 and 0.01μm. The more refined concrete pore structure in the presence of nanoadditions is reflected in the decreased of the total porosity of these concretes: 4.46% for ref. mix, 2.98% for ANF mix and 2.84% for CNC mix.

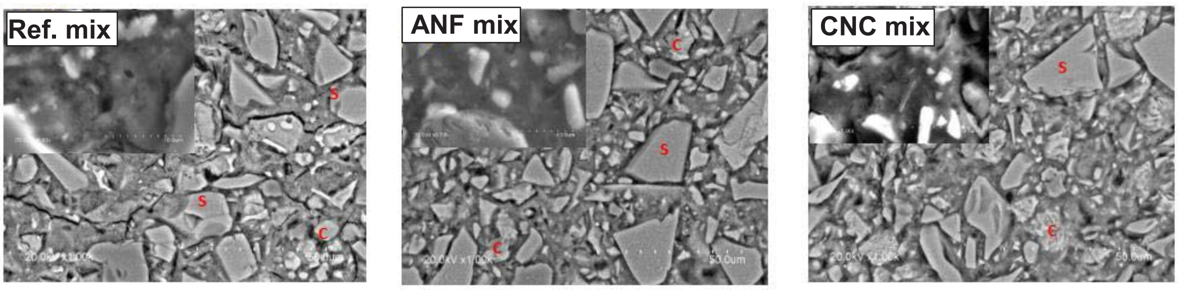

Figure 1: BSE images (1000x) for Ref., ANF, and CNC mixes.

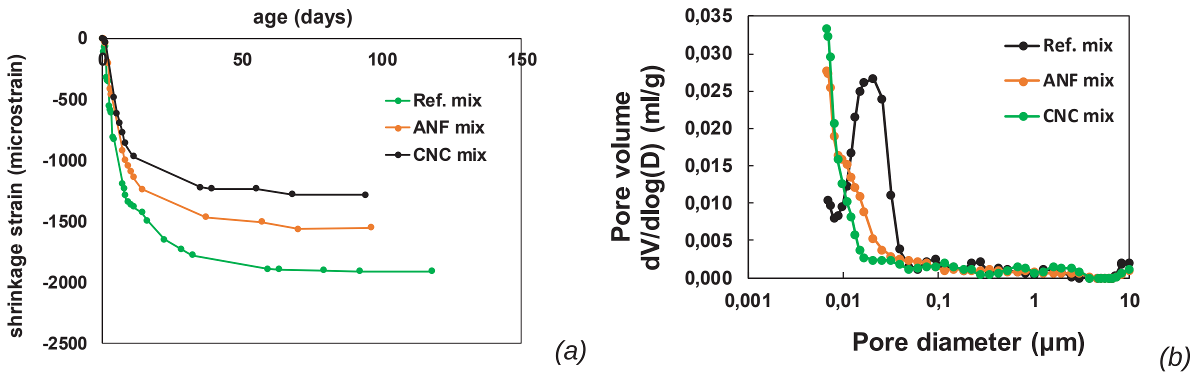

Figure 2: (a) Autogenous shrinkage for Ref. , ANF, and CNC mixes (b) Differential pore volume for Ref., ANF, and CNC mixes.

3.2. Direct durability indicators

From capillary suction tests performed by CSIC and sorptivity tests performed by PoliMi up to 24 hours, the values of capillary suction coefficient k (g/cm^{2}min$^{0.5}$) were evaluated. Same order of magnitude values have been obtained, with acceptable variations considering the methodology and the test conditions are different, respectively equal to 0.0032 (Ref. mix), 0.0029 (ANF mix), 0.0030 (CNC mix) from tests performed at CSIC and 0.0020 (Ref. mix), 0.0037 (ANF mix), 0.0036 (CNC mix) from tests performed at PoliMi. All these values do anyway correspond to concretes featuring very high durability.

3.3 Mechanical properties evolution

Data in Table 2 show the positive effect of nanoadditions in guaranteeing the material mechanical performance even when aging under extremely aggressive conditions. The effects are most relevant for flexural strength, where the toughening effects of nanoadditions can be better appreciated in interacting even with the smallest scale defects at their very onset. The phenomenon is currently under investigation.

Table 2: Influence of curing environment on compressive/flexural strength.

Mix	*Curing environment*	*Compressive strength [MPa]*			*Flexural strength [MPa]*		
		28 d	**56 d**	**84 d**	**28 d**	**56 d**	**84 d**
Ref.	Moist room	132.0	142.9	166.3	24.00	28.88	29.03
ANF		145.0	158.9	166.5	23.53	25.77	31.73
CNC		147.6	157.0	169.2	27.35	29.34	30.30
Ref.	Geothermal water immersion	140.4	152.8	161.4	23.50	25.00	27.48
ANF		123.8	155.0	174.2	29.42	30.44	32.43
CNC		149.0	154.0	169.2	30.40	30.93	34.90

4. Conclusions

According to the results on the durability tests of the three studied UHDC mixes exposed to XA scenario an excellent performance has been achieved. The inclusion of alumina nanofibers (ANF) and cellulose nanocrystals (CNC), besides slightly decreasing the total porosity and the capillary suction coefficient values, is also likely to enhance the material performance when curing and aging under the intended service scenario.

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