UHPC Microstructure and Related Durability Performance
Laboratory Assessment and Field Experience Examples

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ABSTRACT

This paper reviews the main results obtained on durability performance of Ultra-High Performance Concretes (UHPC), as assessed over 9 years of accelerated tests. The origin of this ultra-high durability is presented and discussed, based on the chemical and microstructural characterization, using a complete set of modern analytical techniques. The UHPC resistance to aggressive media appears to result from three complimentary mechanisms: the high stability of the hydrates formed on curing, the very low connectivity of the pores in the nanometer range (which prevents the aggressive ions from diffusing in the matrix) and the self-sealing mechanism due to the residual clinker hydration.

The examples provided in this report provide feedback on UHPC behaviour during several years of full scale field exposure to aggressive environments.

Keywords: Ultra-High Performance Concrete, Durability, Microstructure.

INTRODUCTION

Ultra-High Performance Fiber Reinforced Concretes (UHPFRC) were developed in France since 1991, first with the Reactive Powder Concrete[1]. Several other UHPFRC were developed afterwards[2,3] and today these products have found many industrial applications[4 to 14]. One of them (Ductal®) is available as a premix and has been licensed in Japan, France, USA and Canada[3]. Their mechanical properties have been completely characterized, allowing calculation and design rules for civil engineering applications to be assessed and published[15 to 20]. The formulation techniques to obtain good flowing properties and adequate placing and curing techniques are also available[1, 4, 22]. First aimed at ultra-high mechanical performances and ductility[1], these materials also present remarkable durability performances, thanks to their particular microstructure[23 to 29]. Nine years of accelerated tests have shown that UHPFRC could also be called “Ultra-High-Durability Concretes” (UHDC). Very high service life applications are important criteria in the areas of nuclear and industrial waste management[7, 8, 9] and also in structural applications involving aggressive environments[7, 10, 11].

COMPOSITION RANGE OVERVIEW

UHPFRC’s present a high cement content, a high amount of ultra-fine components like silica fume and quartz flour which extend the particles size range and small sized aggregates or sand. A typical UHPFRC formulation[21] is presented in the following (Table 1):

Table 1 - Typical UHPFRC Composition

Components	Steel Fibers	Quartz Sand	HSR Cement	Quartz Flour	Silica Fume	S.P. Admix.	Total Water
Length (mm)	13						
Diameter (µm)	200.0	310.0	10.0	2.0	0.2		
Density	7.79	2.65	3.17	2.65	2.27	1.21	
Mass ratio /cement	0.216	1.430	1.000	0.300	0.325	0.012	0.200
Vol. Fraction	0.021	0.402	0.235	0.084	0.11	0.004	0.142
kg/m^3	161	1066	746	224	242	9	142

UHPFRC typically has a high content in superplasticizer (S.P.), a very low water amount, (typical water to cement ratio w/c=0.20, typical water to binder ratio w/b=0.15). It shows a self-levelling behaviour, but a high viscosity. This water amount corresponds approximately to half the stoichiometric value, required for complete clinker hydration. Therefore in UHPFRC, a large part of the clinker grains (typically 50%) remains unhydrated[23, 24, 25]. These remaining clinker particles can be considered as surface-reactive micro-aggregates of high elastic modulus, (approx. 120 GPa). These particles are strongly bonded by low C/S calcium silicate hydrate (CSH) and improve the mechanical performance of the material. The following data refers to UHPFRC, corresponding to the composition given in Table 1 and some analogues.

POROSIMETRY

A large part of the remarkable durability of UHPFRC is due to a large reduction in pore size and volume. The UHPFRC porosity was characterized using mercury intrusion, nitrogen absorption (BET) and Transmission Electron Microscopy (Table 2), as well as water desorption and proton nuclear relaxation techniques[26] (Table 3). All of these methods give results in good agreement and show a low content in those capillary pores typically found in ordinary concrete (OC) and high performance concrete (HPC). UHPFRC presents 1 to 3% entrapped air as spherical bubbles of millimeter size range.

Table 2 - Porometry Results

Curing Mode	20°C (28 days)	20°C (2days) + 90°C (2 days)
BET Nitrogen (m^2/g)	8.0	1.0
BET H_2O (m^2/g)	182	110
Equivalent Layer Thickness (nm)	2.4	3.8
MIP porosity. Histogram max. (nm)	2.7	2.4
Nitrogen porosity (%)	5.8	1.1
Mercury porosity <10µm (%)	2.6	1.3
Calculated final capillary porosity	2.5	1.4

Table 3 - Comparison of Porometry Techniques

Techniques	**Proton Relaxation**		**Water Desorption**		**Mercury Intrusion**	
Pore type	Pore diameter (nm)	Volume fraction (Vol.%)	Pore diameter (nm)	Volume fraction (Vol.%)	Pore diameter (nm)	Volume fraction (Vol.%)
Interlayer pore	1.8	52	2.0	60	< 3	50
Intercrystallite pore	5.8	28			3-10	25
2^{nd} type defect	16.8	15			10-20	12
Crystallite Lack	61.2	5			30-70	3
Capillary Pore					300-600	1

The main part of the porosity is found at the nanometer scale, within the hydrates nano-structure. These results can be interpreted from the nano-structure of the CSH formed during UHPFRC hydration, modelled from the nitrogen and H_2O BET surfaces, or observed using Nuclear Magnetic Resonance Proton Relaxation[26] and Transmission Electron Microscopy observations[23, 24].

The great reduction in porosity, compared to ordinary concrete and even high performance concrete, is well illustrated on the mercury porosity curves (Fig.1): we can observe a reduction of more than ten times the larger pores size, compared to HPC and a hundred times, compared to ordinary concrete.

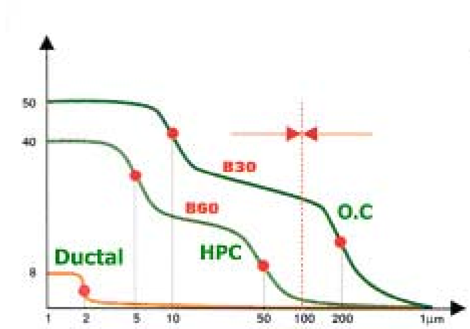

Fig. 1 - Comparison of the mercury porosities of different kinds of concretes
(vs pores size in micro-meters).

At the micrometer scale, the residual clinker grains and the small volume of capillary pores in this range of size is illustrated by the Scanning Electron Microscopy observations. Grey-level, coded back-scattered electron images can be post-treated by an image analysis software to obtain a set of colors, each of them corresponding to one of the components. Gradients of Ca/Si ratio within the hydrates appear as a scale of green levels; the lighter levels corresponding to the lime-rich zones (Fig. 2).

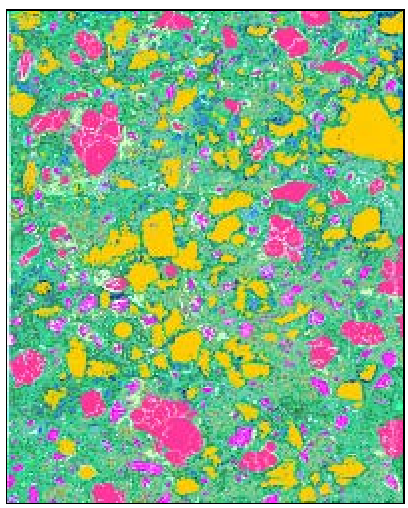

Fig. 2 - SEM view of the UHPC matrix
(Back-scattered electrons + image analysis)
Color code: Pink: clinker, Yellow: quartz, Green: silica fume (dark) and hydrates

High Resolution Transmission Electron Microscopy (HR-STEM) was used to observe the morphology of the pozzolanic silica fume particles partially reacted and the structure of the hydrates at the nanometer scale (Fig.3). The silica fume particles appear to be only surface-reacted. This is in agreement with ^{29}Si NMR measurements of the reaction degrees[25].

Fig.3 - HR-STEM view at 2 days of a surface-reacted silica fume particle

At the end of the curing time, the CSH particles compose a porous matrix with partly disconnected nano-pores, approx. 2 nanometers in size (Fig.4).

Fig. 4 – Sketch of the CSH connection after 28 days

The CSH structure, appears to be composed of small elements or “nano-crystallites” sizing approx. 6 x 17 x 60 nm and presenting a locally layered (but disordered at long distances) internal structure, composed of approx. 3 layers, 1.4 to 1.8 nm thick (Fig 4, Fig. 5).

At the nanometer scale, three defects are observed, depending on the packing mode of these elements:

(i) Intercrystallite pores, between non-parallel elements in contact,
(ii) Crystallite packing defect, due to a shift of parallel elements and corresponding to the thickness of the elements.
(iii) Crystallite lack, when a complete element is lacking in the packing. These defects give CSH an amorphous character, when observed at larger scales.

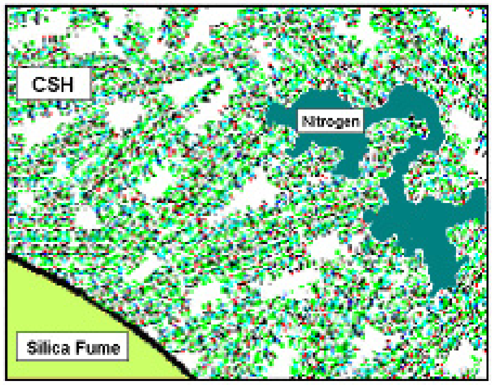

Fig. 5 – Sketch of the CSH crystallites and UHPC nanoporosity

Observed using HR-STEM at the nanometer scale, the molecular structure of CSH explains the transfer properties of this material (Fig.5, Fig. 6): Layers of calcium and silicate ions are separated by layers of water molecules. During the BET experiments, the nitrogen molecules can fill the opened nanopores but they cannot go through bottlenecks. On the contrary, water can fill all the nanopores (coloured in white in Fig.5), but has to pass through the CSH interlayers.

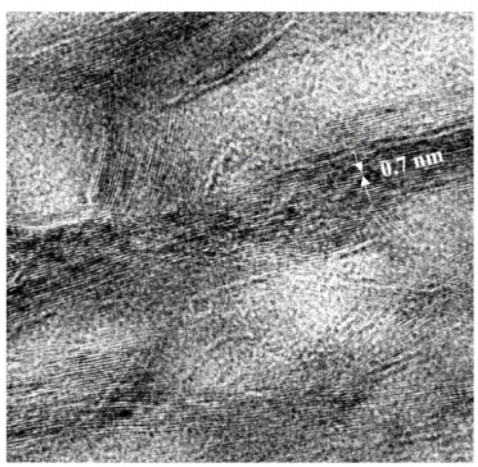

Fig. 6 - HR STEM of tobermorite-like CSH in Ductal

PERMEABILITY

Water porosity and permeability is also close to the detection limit, in relation with the absence of capillary porosity and to the disconnected nanopores shown in Fig 5. The only way of permeation is the interlayer structure of the hydrates, presenting a very high tortuosity. These performances are one order of magnitude better than HPC and two orders of magnitude better than ordinary concrete. It is well known that for all concretes, drying modifies the CSH structure and increases permeability. After severe drying at 105°C, UHPFRC reinforced with steel fibers show oxygen permeabilities lower than the detection limit of the AFPC-AFREM[30] and the CEMBUREAU method (Table 4).

Table 4 - Permeability of UHPC Compared to Other Concretes

Concrete type		UHPC	UHPC	HPC	OC
Curing mode		20 °C (28d)	20°C (2d) +90°C (2d)	20 °C (28d)	20 °C (28d)
w/c		0.2	0.2	0.35	0.5
Permeability (m^2)	N_2, O_2 (no drying)	$1.0\ 10^{-22}$	$1.0\ 10^{-22}$	$1.0\ 10^{-19}$	$2.0\ 10^{-18}$
	id. (severe drying)	$< 1\ 10^{-20}$	$< 1.0\ 10^{-20}$	$5.0\ 10^{-18}$	$3.5\ 10^{-17}$

IONIC DIFFUSIVITY

Thanks to the disconnected pores structure, the diffusivity of ions like chlorides or cesium and tritium is very low (Table 5). This is in agreement with its very low electric conductivity, which is of the order of magnitude of semi-conductors.

Table 5 - Ionic Diffusivity of UHPC Compared to Other Concretes

Concrete type		UHPC	HPC	OC
Diffusivity	Cl- , Cs+	$2.0\ 10^{-14}$	$1.5\ 10^{-12}$	$1.8\ 10^{-11}$
(m^2/s)	Tritiated water HTO	$< 2.0\ 10^{-14}$	$1.7\ 10^{-12}$	$2.0\ 10^{-11}$

Note:
The porosity, permeability and diffusivity results of UHPC are generally better than for granite rock.

The application of Fick's Law allows to estimate the diffusion time as a function of the thickness of UHPC walls (Fig.7):

According to this model, if three years are required for a tritium ion to pass through a 3 mm thick UHPC (experimental data), a duration of 800 years is estimated for an ion to pass through a 50 mm wall.

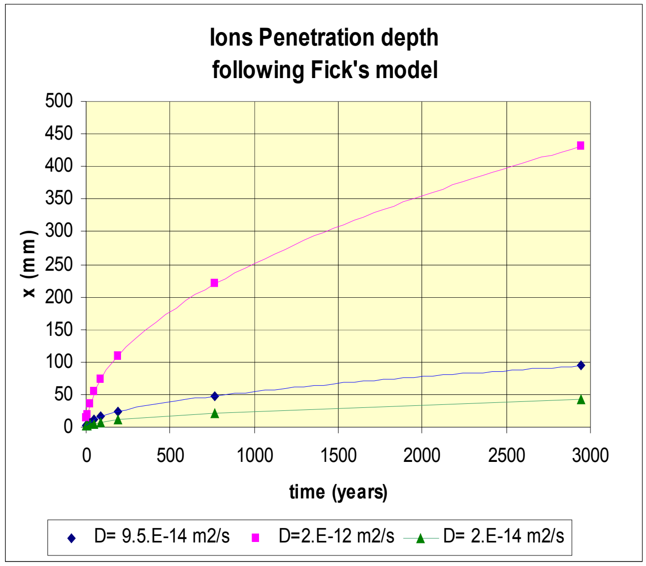

Fig.7 - Penetration depth of tritium ions as a function of time, following Fick's Law. Pink curve : HPC. Blue curve : UHPFRC 1 w/c = 0.25 Green curve UHPFRC 2 w/c = 0.19

PERFORMANCE ON FREEZING AND THAWING

The absence of capillary pores containing water able to freeze give to UHPFRC a remarkable resistance to freezing and thawing, even in presence of de-icing salts (scaling tests). After 1000 cycles (ASTM C 666), UHPC present a constant or slight increase in mechanical performance. The scaled-off mass loss is lower than 10 g/m^2 after 56 cycles (ASTM C 672), with a stabilization after about 40 cycles, showing that the scaling phenomenon is stopped. (Table 6).

RESISTANCE TO CARBONATION AND AGGRESSIVE MEDIA.

Table 6 – UHPFRC performance on freeze-thaw and carbonation accelerated tests

Concrete	Ductal	Ductal	High Performance Concrete	Ordinary Concrete
Curing step 1	20°C 28 days	20°C 2 days	20°C 28 days	20°C 28 days
Curing Step 2		90°C 2 days		
w/c	0.2	0.2	0.35	0.50
Freeze-thaw scaling (g/cm^2)	7	7	900	> 1000
Carbonation depth (mm)	0.05	0.04	2	10

All results of accelerated tests confirm the exceptional resistance of UHPFRC to chemical aggression; generally 20 to 100 times better than for HPC (Table 6).

Accelerated tests following the API specifications were done in France by the Institut Français du Pétrole (IFP). Up to 290 bar (4200 Psi) and 140°C, which are typical conditions in deep oilwells, Ductal samples show an increase in strength in contact with the standard API fluid (sea water 20%, gas oil 50%, CO_2 1%, CH_4 27%, H_2S 2%). (Fig. 8)

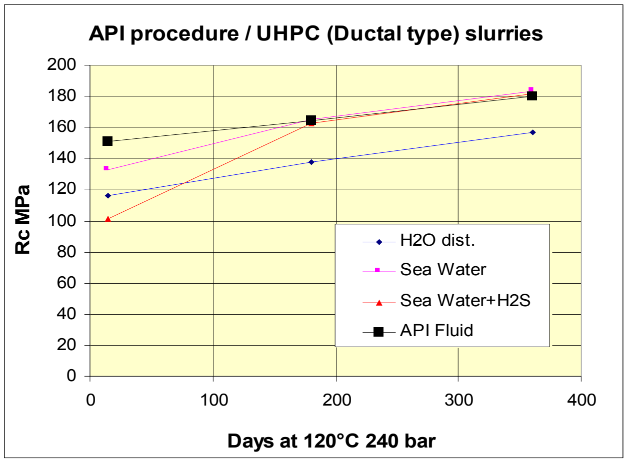

Fig. 8 - API accelerated tests in different fluids

CHEMICAL STABILITY

ALKAI-SILIA REACTION (ASR)

Thanks to its high content in silica fume, UHPFRC is not affected by ASR. As for HPC, correct dispersion of the silica fume is required, in order to prevent silica fume agglomerates from reacting. The alkalies and lime present in cement are then combined within the pozzolanic CSH hydrate.

DELAYED ETTRINGITE FORMATION (DEF)

DEF resistance of two UHPFRC was investigated in the French REACTIF program, using a severe accelerated test. The 4 x 4 x 16 cm samples were submitted to 50°C drying and water-soaking cycles during 150 days. No significant length variation was observed. Another set of samples were mechanically pre-cracked in bending mode These samples also showed no length variations after the drying-soaking tests.

RPC and Ductal type UHPFRC can either be cured at 20°C, or post-cured at 90°C after a period of maturation of 24 to 48 h at 20 to 40°C. This maturation period is a good precaution to protect these UHPC from DEF. (Fig.9). Ductal 90°C humid curing respects the main hydration reaction kinetics:

- limited heating during the first periods of AFT formation,
- slow cooling during period IV,
- humid curing at 90°C in period V, after the main hydration reaction.

- heating in the last period allows to develop the pozzolanic reaction without thermal shrinkage and is not disturbing for cement equilibria. Recent results [32] show that low C/S CSH, like CSH obtained from pozzolanic reactions, absorb only small amounts of sulphates, compared to cement paste CSH.

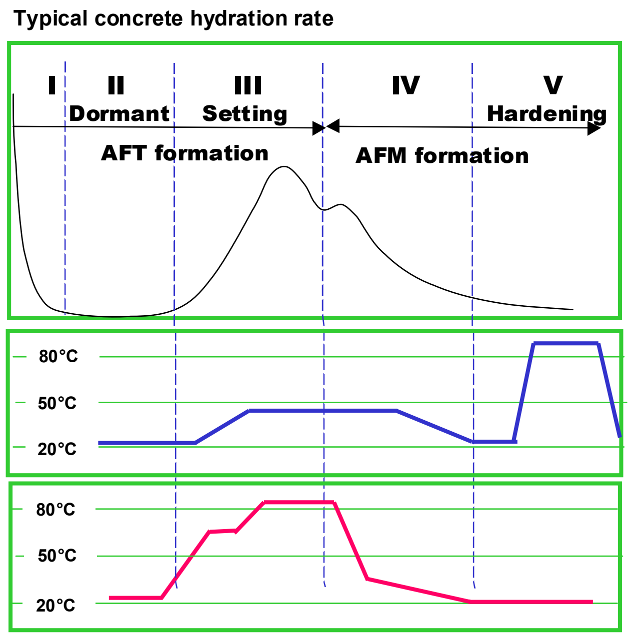

Fig. 9 – Principle of DEF prevention.
Black curve: reaction rate and periods, Blue curve: Ductal curing cycle,
Red curve: precast concrete typical curing cycle

RESISTANCE TO LEACHING

The high basic content of UHPFRC, due to its high residual clinker amount, combined to its very low permeability and diffusivity, give to this material a very high leaching resistance to water and acidic media. This behaviour was investigated in a recent BRITE European Research Program called "UNICORN"[32] and devoted to modelling the long term service life of UHPFRC for nuclear waste storage applications. After one year of leaching under a constant flow of granitic water, the calcium leached zone is approx. 40-100 µm thick.

Assuming a square root law (Fick's Law), the thickness of the degraded zone should be less than 10 mm after 100 years. When in contact with distilled water, the reacted zone is mechanically degraded, while in natural water, this zone remains cohesive, and behaves like a protecting barrier against acid attack. ^{29}Si and ^{27}Al high resolution NMR spectrometry shows the stability of the hydrates on leaching[33]. In HPC, aluminium is combined into ettringite and AFM phases. In Ductal, aluminium atoms are combined in stable phases: hydrogarnets and tobermorite-like CSH, which become slightly longer, but remain stable on leaching (Fig. 10 & 11).

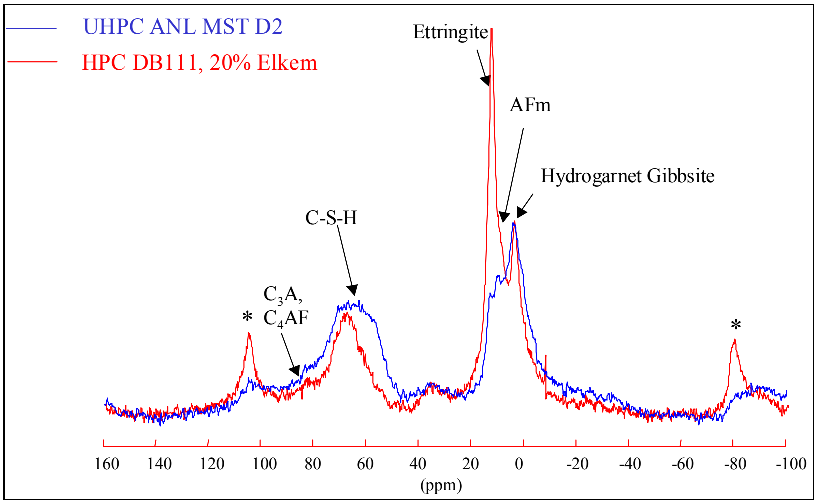

Fig. 10 – ^{27}Al HR NMR of UHPC compared to HPC
From C. Porteneuve[33]. The blue line is the Ductal curve.

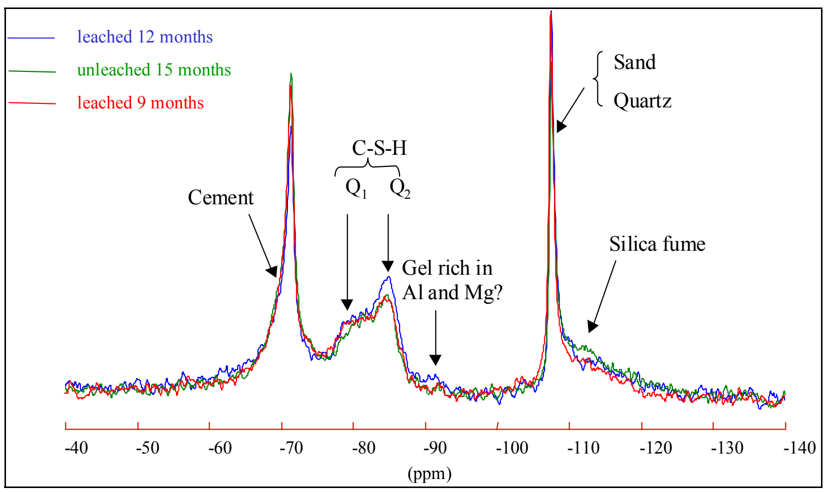

Fig.11 - ^{29}Si HR NMR spectrometry
From C. Porteneuve[33] . The hydrates structure is not modified by leaching.

RESISTANCE TO CORROSION

RPC resistance to corrosion was studied by the CSIC in Madrid (Spain). The observed electrochemical parameters of the steel fibers (Table 7) is indicative of a very high resistance to corrosion[27].

Table 7 - Compared Electrochemical Data and Corrosion Risk Assessment

(from CSIC Madrid, 1996)	Corrosion risk when :	Ordinary concrete 30 MPa	HPC 80 MPa	Ductal FM
Electrical Resistivity (kΩ-cm)		16	96	1130
Corrosion potential Ecorr (mV)	< -200	-0.82	0.28	0.90
Polarisation Resistance (kΩ-cm)	< 500	0.37	12	3022
High Frequency Capacity (pF/cm^2)		10.8	145	14
Corrosion Rate (µm/year)	> 1	1.2	0.25	< 0.01

These electrochemical data are well assessed by an other set of results, obtained in the REACTIF-ENS program funded by the French government in 2000-2001.

After one year of drying and wetting cycles, the metallic fibers in Ductal FM remain sound, even in a mechanically pre-cracked sample (Fig. 12).Only surface stains, approx. 0.1µm depth, are observed.

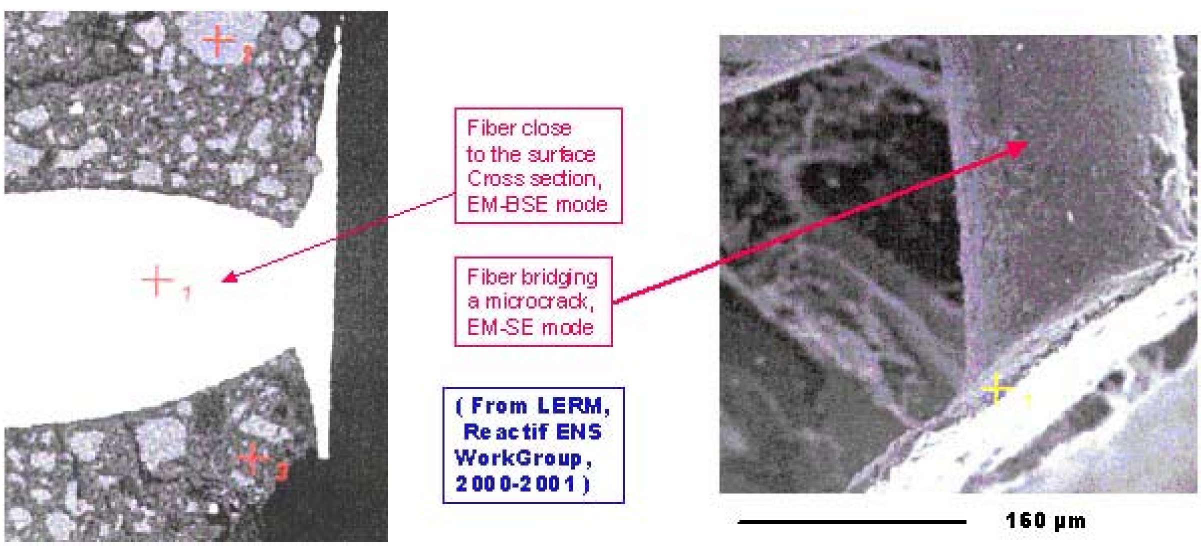

Fig. 12 – SEM observation of fibers in RPC samples submitted to accelerated corrosion tests.

SELF-SEALING

Mechanically pre-cracked samples, over the limit of elasticity (in the toughening regime), when submitted to water soaking, show a self-healing mechanism: micro-cracks of approx. 40 µm width are rapidly filled up with new hydrates formed from the residual clinker present in the matrix (Fig. 13). These hydrates are the same as in the initial hydration reaction mechanism, and composed of CSH with intermixed ettringite. A part of the mechanical resistance can be recovered by this healing mechanism. Further work is in progress to quantify the efficacy of recovery.

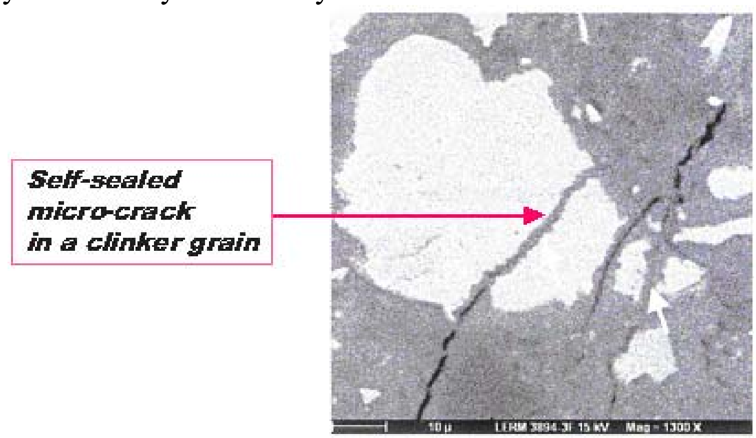

Fig. 13 – Self-sealing of microcracks by clinker hydration

FEEDBACK FROM FIELD EXPOSURE TO AGGRESSIVE ENVIRONMENTS

Several data on field performance in aggressive environments are available today, to illustrate the properties of UHPFRC.

EXISTING BUILDINGS AND ARTWORKS

The existing artworks provide a first assessment of their durability:

- The oldest, built in 1997, is the Sherbrooke Footbridge on the Magog River, Quebec, Canada (Fig 14).

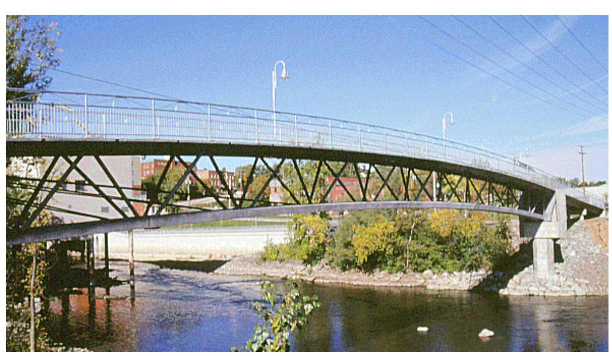

Fig.14 - The Sherbrooke Footbridge, made of Reactive Powder Concrete (RPC).

- The Cattenom (France) nuclear plant air-coolers were repaired in 1997-1998, using prestressed Ductal and BSI beams to replace corroded metallic structures. The environment is very aggressive, with a combination of leaching, freeze/thaw, salts and algae development. After 6 years, the beams present no sign of degradation.

- The Martel Tree is a copy of a cubist sculpture of the Martel brothers. Installed at Boulogne-Billancourt, near Paris (France), it is 8.5 m high and made of prestressed White Ductal (Fig.15). The aspect remains unchanged from 1999.

Fig. 15 - The Martel Tree at Boulogne-Billancourt (France)

- Decorative (architectural) panels used for the Rhodia headquarters building in Paris also provide an illustration of the very good surface aspect of White Ductal after several years of exposure to acid rain and town gasses (Fig. 16).

Fig. 16 - Rhodia Headquarters- Ductal Panels

MARINE ENVIRONMENT

Other applications of UHPFRC show very good resistance to marine environments:

- RPC blocks stored along the St. Laurent River in Montreal, Canada, exposed to freezing and sea water since 1994.

- Ductal Anchor plates on the seaside at La Réunion Island[34].

- Ductal samples in the Natural Weathering Exposure Station (WES) at Treat Island, Maine, USA (Fig.17).

Among 22 active field exposure durability studies and programs underway at this station, we can find the following: "Reactive Powder Concrete (RPC) in marine environment". Samples are located at Row 5, Section 55.

Three beam specimens (152 mm by 152 mm by 533 mm long), containing 13 mm diameter steel reinforcement were cast using an RPC wet mixture. The specimens were identified as "960015, 960016, and 960017" and had concrete cover depths of 25mm, 19mm, and 10mm, respectively. The specimens were cured in limewater for 28 days. In October 1996, specimens were installed by WES at Treat Island, Maine to study the effects of seawater on the corrosion of mild steel that was placed in RPC at different depths (Fig. 18). The performances of specimens are being evaluated via visual inspection and ultrasonic pulse velocity measurements (ASTM C597).

Fig. 17 - Natural Weathering Exposure Station, Treat Island, Maine USA

Fig. 18 – Specimens of Reinforced RPC beams

There is no significant variation of the recorded data since 1997, after 500 freeze/thaw cycles and 4500 wet/dry cycles in saturated sea water.

CONCLUSIONS

Delivery and formulation techniques, flowing and placing properties, curing mode, design codes for structures; all components of the future industrial development of UHPFRC are available today. We can be sure that this development will continue.

The exceptional durability performances of UHPFRC, joined to their high toughness and compressive strength, allow for new solutions to difficult problems of construction, like earthquake resistance and long term service life in civil engineering or nuclear applications.

But many other applications involving a smooth and durable surface aspect, or thin section panels and structural members, pipes, tunnels, will exploit the usage value of UHPFRC. The main feature of these new materials is their scientific origin: we have illustrated the close correspondence between the mechanisms leading to high durability performance, the microstructure observed at different scales, and the field performance.

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