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Durability of ultra-high performance fibered concretes made from local raw materials in two aggressive media of hydrochloric acid and barium sulphates

Durabilitatea betoanelor fibrate de înaltă performanță obținute din materii prime locale în două medii agresive de acid clorhidric și sulfați de bariu

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Abstract. *The durability of ultra high performance fiber-reinforced concrete (UHPFC) made from local raw materials has been studied in this manuscript. An experimental study was carried out on the best variants of UHPFC using finely ground dune sand as ultrafine. The UHPFCs studied were developed from Portland cement (PC), dune sand (DS), fine sand (FS), metal fibers (MF) and superplasticizer additive (SP). The results show that it is possible to manufacture a more ductile and durable fiber concrete of 41.96 and 35.28 MPa for flexural tensile and 95.5 and 85.36 MPa for compressive strength for UHPFCs made from dune sand and immersed respectively in two chemical solutions concentrated at 5M hydrochloric acid and barium sulfate for one year. The manufacture of a concrete based on local raw materials with good mechanical properties and durability can reduce the consumption of cement.*

Key words: Dune sand, ultra fine, ultra high performance fiber-reinforced concrete (UHPFC), durability, mechanical properties.

1. Introduction

The durability of concrete structures is a very important feature, as it guarantees increased safety and service life of these structures [1]. This durability also guarantees considerable savings in the long term, as such structures will require little or no repair, resulting in cost savings from repairs, which can be very high and may even exceed initial construction costs [2]. The development of such works must necessarily involve mastering and understanding the factors affecting their sustainability [3].

Free water can penetrate the network of pores and capillaries in concrete and bring with it aggressive ions that can react with the hydrates and change their structure. A durable concrete is a concrete that resists the penetration of aggressive agents and allows a significant life span for concrete structures [4].

External aggressions such as chlorides, CO_2 and chemical attacks can degrade the physical and mechanical properties of concrete and its durability over time. Among chemical attacks, acids that can come from both industrial areas and urban activity most severely degrade concrete [5].

2. Content of the paper

2. Materials and experimental method

2.1. Used materials

Cement (CP): the cement used is of the CEMI 52.5 type, with a density of 3160 kg/m3 and a Blaine surface area of 4800 cm2/g. The physical, chemical and mineralogical characteristics are given in Table 1, and are in accordance with standard NF EN 197-1 standard [6-7].

Sand of dune (SD): in this work, finely ground dune sand up to a fineness of 4000 cm2/g is used as a substitute in cement on the one hand and as fines added in the concrete formulation on the other.

Fine sand (FS): For the sand, it was opted for quarry sand from the Bouzegza region sieved on a 2 mm screen and 76% sand equivalent, and sand expansion of 23.3%.

Superplasticizer (SP): In order to reduce the E/L ratio and increase the fluidity of the concretes for ease of application while maintaining a level of performance, a Tempo 12 high water-reducing superplasticizer from sika was used in accordance with EN 934-2 [7].

Metal fibers (MF): The metal fibers are then added to provide better strength and ductile behavior in concrete.

Table 1

Characteristics of cementitious materials

Minerals	CEM I 52.5 (PC)	Sand of dune (SD)
% SiO_2	20.03	94.40
% Al_2O_3	5.07	2.23
% Fe_2O_3	3.43	0.33
% CaO	62.43	0.45
% MgO	1.64	0.06
% SO_3	2.57	0.17
% K_2O	0.59	1.13
% Na_2O	0.04	0.36
%P_2O_5	0.15	0.01
%TiO_2	0.21	0.04
% P.A.F	3.81	0.82
% C_3S	62.89	-
% C_2S	10.33	-
% C_3A	7.64	-
% C_4AF	10.43	-
Specific mass (g/cm^3)	2.93	2.95
Specific surface (cm^2/g)	4800	4000

Table 2

Characteristics of the adjuvant

Characteristics	The adjuvant of SIKA
Aspect	Light brown liquid
Na_2O content Eq	≤ 1%
PH	6 ± 1
Density	1.06 ± 0.01
Dry extract	30.2± 1.3 %
Conditioning	230 Kg drums CP of 1000 L bulk

2.2 Working methodology

This study was carried out in three parts. First of all, the work consists in studying the effect of the sand of finely ground dunes (5, 10, 15 and 20% by mass) by replacing cement on the rheological behavior of the cement pastes used for the different concretes studied. In this case, the amount of superplasticizer has been optimized to ensure adequate fluidity and avoid segregation. The second part was carried out on ultra high performance concretes with an optimal percentage of dune sand substituted in the cement by measuring the mechanical strength at 2, 7 and 28 days. Then, the optimization of the BFUHP with 2, 3.5 and 5% metal fibers of the two variants BUHP1 and BUHP2 by measuring the mechanical resistance also at 2, 7 and 28 days.

Afterwards, the optimization of the substitution percentage and the fiber percentage optimization, the best variant was determined with the best mechanical properties at 28 days. Finally, the third part was devoted to studying the durability of the best variant specimens in two chemical media of 5M concentration for a period of one year.

2.3 Test methods

Rheological tests: Using a VT550 type viscometer with coaxial cylindrical geometry, rheological tests were carried out. The measurements were carried out according to the following protocol (first of all: Pre-shear and ramp the shear rate to 350 s^{-1} for 60s. Second step: maintain a constant shear rate at 350 s^{-1} for 300 seconds). All of the cementitious pastes tested were prepared with a fixed dosage of superplasticizer and a ratio of W/C=0.29 kept constant [8].

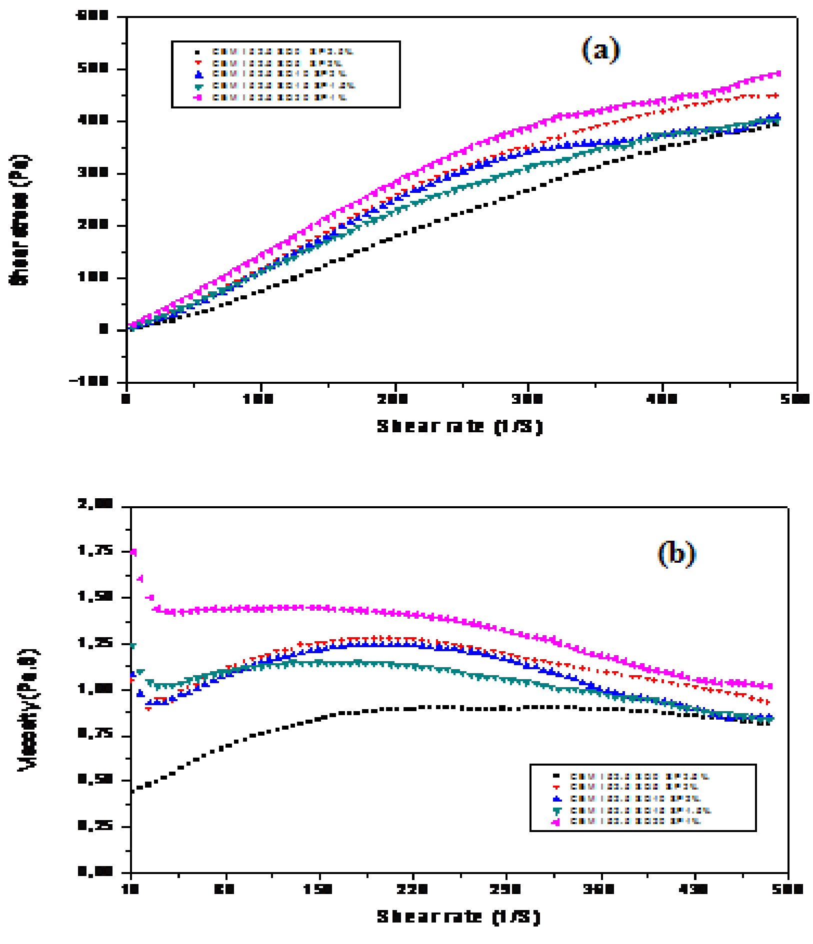

Fig. 1. Variation of shear stress (a) and plastic viscosity (b) as a function of shear rate

Mechanical tests: The specimens were made according to standard NF EN 196-1[9], cast in prismatic moulds (4x4x16 cm3) then unmoulded after 24 hours and stored in a water bath until the days of mechanical crushing. The compressive and bending strengths of the specimens were tested at 2, 7 and 28 days using a 200KN computer-controlled "IBERTEST" type apparatus. The three-point bending tests were performed on prismatic samples according to ASTM C348 [10]. The half-samples were subjected to compressive stress in accordance with ASTM C349 [11].

3. Results and discussion

3.1 Rheological study

Figures 1a and 1b show the variation in shear stress and viscosity of cement paste at different substitution rates by finely ground dune sand as a function of shear rate. It is clearly observed that the higher the doses of superplasticizer, the more fluid the cementitious pastes become [12-14]. This fluidity facilitates the formulation of ultra-high performance concretes, particularly in the presence of fibers [15].

Analysis of the experimental curves shows that the appearance of the curves remains broadly identical for all sand concentrations in the dunes. There is an increase in viscosity as the sand concentration of the dunes increases.

3.2 Effect of dune sand on the mechanical performance of UHPCs

Ultra high performance concretes (UHPC) with different percentages of finely ground dune sand (SDS) as a substitute in cement have been developed. Table 3 illustrates the different concrete compositions studied. Then, and in order to determine an optimal percentage of SD, the mechanical resistances were measured at 2, 7 and 28 days and the results obtained are given in Table 4.

Table 3

Different compositions of ultra high performance concretes (UHPC)

Components	UHPC0	UHPC1	UHPC2	UHPC3	UHPC4
PC [Kg]	1000	950	900	850	800
SD [Kg]	148.8	148.8	148.8	148.8	148.8
SDS [Kg]	0	50	100	150	200
FS [Kg]	958	958	958	958	958
SP [Kg]	24.8	20.3	20.3	15	10
Water [Kg]	246.7	250.9	251.6	255.3	258.6
W/B	0.23	0.23	0.23	0.23	0.23

Table 4

Mechanical Resistance of UHPC with SD Rate

	Flexural strength (MPa)			Compressive strength (MPa)		
	02D	07D	28D	02D	07D	28D
UHPC0	8.02	10.14	11.23	39.07	54.20	70.66
UHPC1	13.27	14.31	15.62	71.76	93.64	103
UHPC2	12.07	13.5	14.59	70.21	90.55	99.6
UHPC3	13.53	14.78	15.11	68.94	89.2	96.32
UHPC4	12.93	14.47	14.9	68.87	87.73	96.98

According to Table 4, dune sand has a beneficial effect on mechanical performance and shows a significant improvement in the bending and compressive strength of the concretes studied compared to the UHPC0 control concrete. This is because the addition of finely ground dune sand affects the hydration reactions by pozzolanic reaction of well-dispersed cement grains with portlandite ($(Ca(OH)_2)$, thus modifying their growth rate and morphology [16-20].

Due to their manoeuvrability, fibers are only added to the first two variants UHPC1 and UHPC2; UHPC3 and UHPC4 cannot accept the fibers they are firm.

3.3 Effect of dune sand on the mechanical performance of UHPFCs

In this section, and in order to assess the influence of dune sand as a mineral addition, concrete formulations were drawn from the previous section of the study. Metal fibers were selected and used at different contents in the binder mass fraction (2, 3.5 and 5%) as reinforcing fibers. Metal fibers were therefore added to ultra-high performance dune sand concrete to improve the ductility of the material, both in tension and compression [20-24]. The formulation of the UHPCs is given in Table 5.

Table 5

Formulation of BFUHP Ultra High Performance Fiber Concrete in 1m^3

Components		UHPFC1	UHPFC2
PC [Kg]		950	900
SD [Kg]		148.8	148.8
SDS [Kg]		50	100
FS [Kg]		958	958
MF [Kg]	2%	20	20
	3.5%	35	35
	5%	50	50
SP [Kg]		20.3	20.3
Water [Kg]		250.9	251.6
W/B		0.23	0.23

Mechanical performance was assessed by measuring compressive and bending strength at different ages (2, 7 and 28 days) and the results obtained are shown in Table 6.

Table 6

Mechanical Resistance of BFUHP with Fiber Rate

	MF(%)	Flexural strength (MPa)			Compressive strength (MPa)		
		02 D	07 D	28 D	02 D	07 D	28 D
UPFC1	2	14.12	20.63	22.23	75.15	97.18	113.63
	3.5	13.88	25.66	30.27	77.23	105.38	125.15
	5	15.47	26.63	33.9	77.54	103.32	134.43
UPFC2	2	14.83	23.16	30.1	78.2	95.65	120.55
	3.5	14.80	25.68	32.53	77.21	99.75	126.23
	5	16.48	30.2	34.08	85.25	102.97	135.33

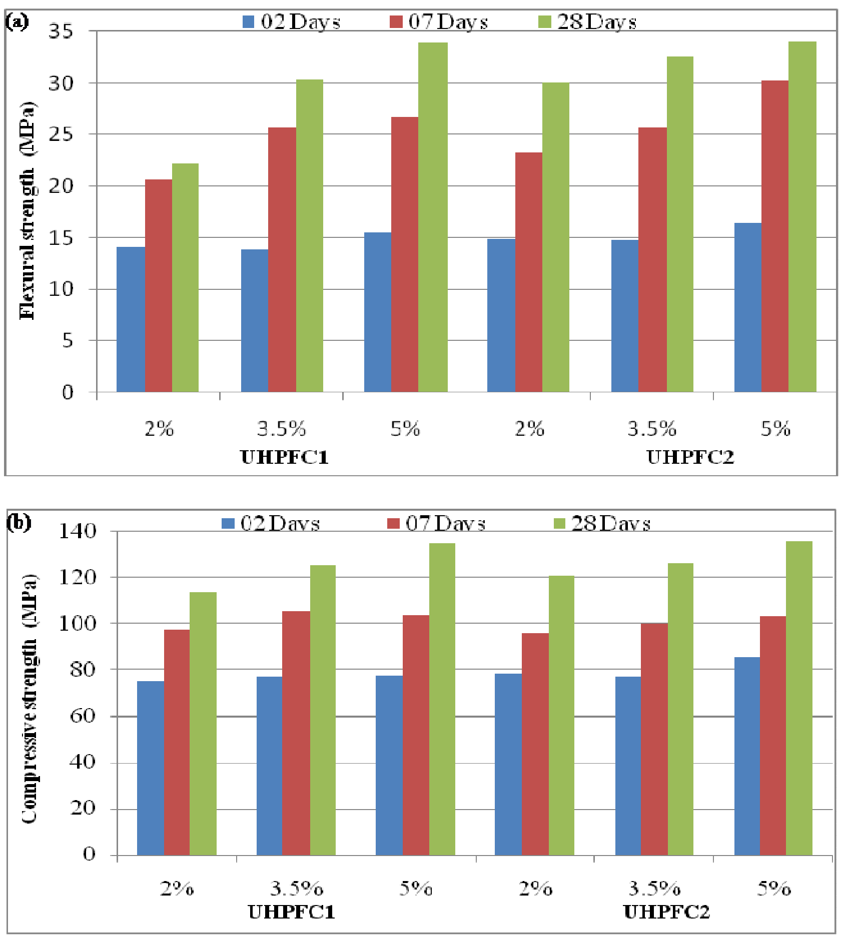

Fig. 2. Evolution of flexural (a) and compressive (b) strengths of UHPFC1 and UHPFC2 with fiber content and age

Figures 2a and 2b show the evolution of mechanical strength with age and fiber content. Resistance increases from 02 to 07 up to 28 days for each of the two variants BFUHP1 and BFUHP2, and the latter has higher values than UHPFC1 at 28 days for a percentage of 5% fiber. So the best variant is the one that substitutes 10% of the cement for the sand of the finely ground dunes with a 5% fiber content called BFUHP2 with 5% fibers.

3.4. Durability of UHPFC specimens

All specimens were made according to the same procedure followed in the previous section and were stored in a water bath at 20°C±2°C. After maturation, the specimens were removed from the water bath, air-dried and steamed at 105°C for 24 hours to constant masses. Two 5M solutions of hydrochloric acid (HCl) and barium sulphates (BaSO4) were prepared at PHs of 01 and 05 respectively. Then three specimens were immersed in each solution, and three others were left out in the open as a control. The chemical attack was followed in both media for one year and the solutions were repeated at the same PH after six months.

3.4.1. The loss of mass

The chemical resistance was evaluated according to ASTM C 267-96 [25] by measuring the mass loss of the specimen calculated by the following formula:

$$Mass\ variation\ (\%) = \frac{M_1 - M_2}{M_1} \times 100 \qquad (1)$$

With M_1, M_2 the masses of the specimens before and after immersion, respectively. This operation was performed after 6 and 12 months of immersion.

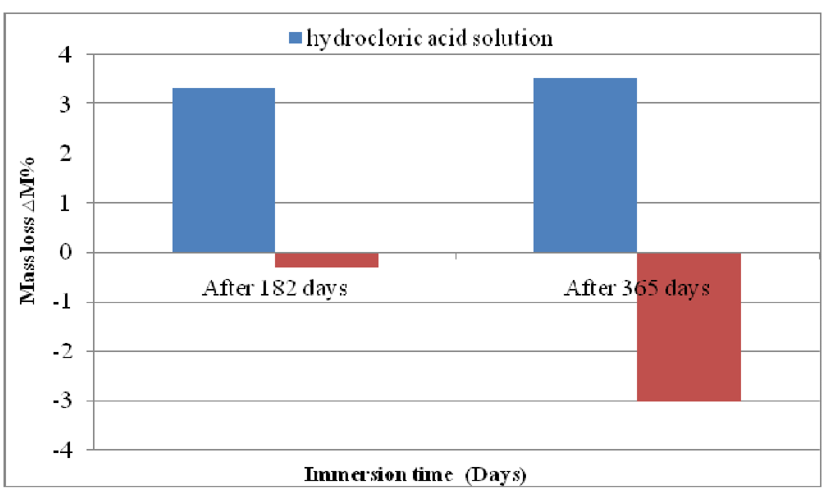

Fig.3.The loss of mass of the UHPFC as a function of the age of immersion in HCl and $BaSO_4$

UHPFCs show mass losses of 3.52% in hydrochloric acid solution and mass gains of 3.029% in the brium sulphates respectively after one year of chemical treatment:

- The loss of mass is due to the fact that the cement, after hydration, releases a considerable part of free calcium hydroxide ($Ca(OH)_2$) which can be leached out when it is subjected to attack by hydrochloric acid (HCl) by giving calcium hydroxide, according to the following chemical reaction[26]:

  $Ca\,(OH)_2 + 2HCl \rightarrow CaCl_2 + 2\,H_2O$ (2)

Hydrochloric acid, a strong acid which, by reaction with cement lime, gives rise to calcium chloride, a highly soluble salt that is very aggressive towards Portland cements [27, 28].

- The weight gain observed for BFUP immersed in the barium sulphates solution is surely due to the substitution of Ca^{2+} ions by Ba^{2+} [29] by giving gypsum, according to the following reaction:

  $Ca\,(OH)_2 + BaSO_4 \rightarrow CaSO_4 + Ba\,(OH)_2$ (3)

3.4.2. The density

The evolution of the density of UHPFC with immersion time is shown in Figure 3, which shows a decrease in acid and an increase in sulphates.

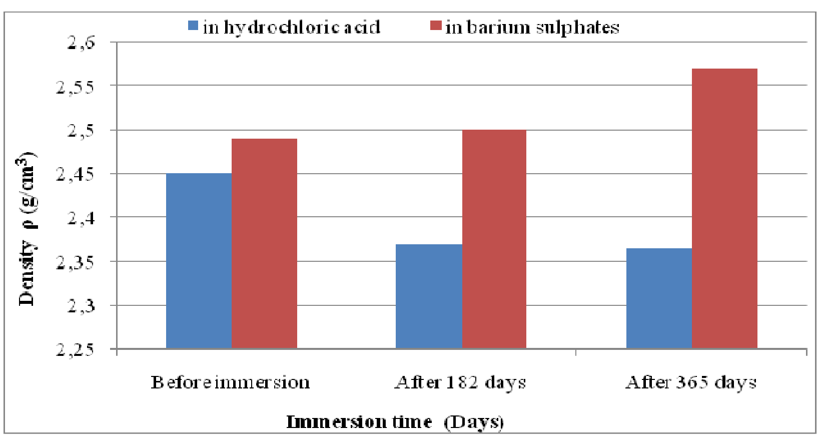

Fig. 4. The density of BFUHPs as a function of the age of immersion in HCl and $BaSO_4$

3.4.3. The mechanical performance of BFUPs

In order to evaluate the mechanical performance of the UHPCs left in the air as well as those immersed in the two aggressive solutions for one year, mechanical crushing was performed to measure the mechanical resistance.

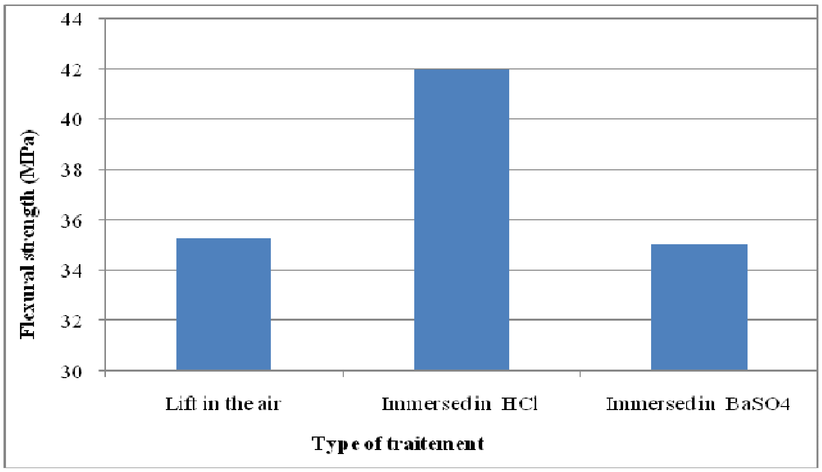

Fig.5. Evolution of flexural strengths with the type of treatment

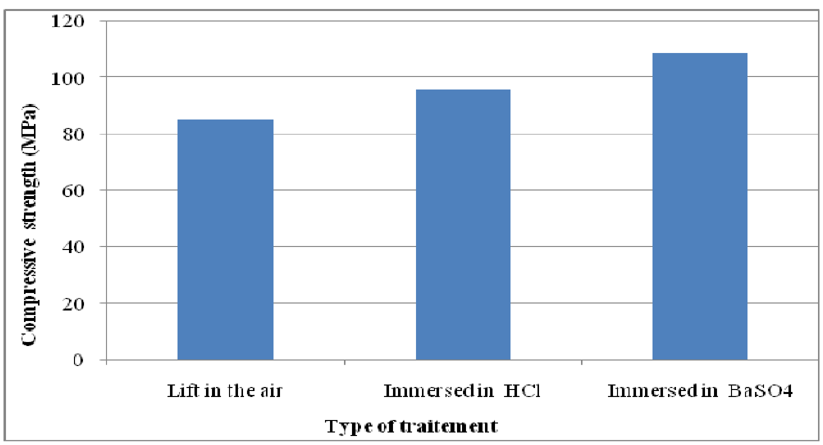

Fig.6. Evolution of compressive strengths with the type of treatment

From the results of the mechanical crashes we can see that:

- The bending tensile strength of UHPFCs immersed in five-fold molar hydrochloric acid solution is better than that of UHPFCs left in the air or immersed in barium sulfate solution for a period of one year.

- In compression, UHPFCs immersed in HCl are more resistant than those immersed in BaSO4 and less resistant when compared to those left in the air.

The results of the macroscopic study, including mass loss, density and mechanical crushing, show that the UHPFC submerged in the two aggressive five-fold molar solutions resist chemical aggression compared to those left in the air for one year.

The introduction of dune sands in the manufacture of high-performance, chemically resistant fibrated concrete is doubly beneficial in terms of strength and economy.

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4. Conclusions

The use of dune sand in the production of high-performance and resistant fiber-reinforced concrete for aggressive environments is beneficial.

In order to better understand the behavior of our UHPFCs regarding the chemical reactions responsible for slowing down degradation in their cementitious matrices in response to chemical attacks, microscopic analysis by X-ray diffraction (XRD) and scanning electron microscopy (SEM)on powders from UHPFC samples is necessary and will be the subject of the next study.

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