Contribution to the Study of the Corrosion of the Pouzzolana High Performance Concrete (HPC) in Sulfates

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SUMMARY

The natural pozzolan of volcanic origin has a marked influence on the physico - mechanical characteristics of the concretes. When it is coupled to a water reducing superplasticizer by a correct adjustment of the composition, it greatly improves the concrete properties. The analysis of the experimental results on pozzolan concrete at 5% content and fineness of 9565 cm^2/g, in a sulphated environment, showed that it contributes positively to the improvement of its mechanical characteristics, its durability with respect to water absorption, and to the permeability to the chlorine ions as well as to the resistance to the sulphates.

1. INTRODUCTION

The concrete changes, observed in presence of aggressive agents, whether they are mineral organic or biologic, are of chemical or physical order.
The physical changes can be:
In surface: abrasion, erosion, cavitation, scaling.
Internal (cracks): structural loading, gradients of humidity or temperature, pressure of crystallization, exhibition to the extreme temperatures.

The chemical changes are essentially due to acids, bases and to the saline solutions, they almost always drag the dissolution of the lime and the most often, in association with this dissolution the formation of the new compounds **[1]** whose consequences are of macroscopic order:
Mechanical: fall of resistance and rigidity, cracking and distortion of the material.
Physico-chemical: Weakening of the binding properties, modification of the porosity and the transfer properties (porosity, permeability, diffusivity).

2. SULPHATIC ATTACK

The sulphate action of internal source doesn't present any detrimental effects on the concrete because the formed hydrate is certainly expansive, but crystallizes in a paste of non enclosed cool cement, they evolve together to form a hardened concrete. On the other hand in the external attack, the crystallization of the hydrate makes itself in confined media such as the pores and its capillary expansion gives birth on the partitions of the porous network to pressures of traction causing expansion, cracking and finally bursting of the concrete **[2].**

3. MECHANISMS OF CONCRETE CHANGES

The sulphates can alter the concrete according to two physico-chemical mechanisms **[3]:**

- Expansion
- Loss of binding properties of the C-S-H

3.1 Chemical interactions

3.1.1. Secondary gypsum formation

a) Sulphate of sodium Na_2SO_4

Ionic substitution between the portlandite and the sulphates

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + 2NaOH$$

(Secondary gypsum, expansion)

3.1.2. Secondary ettringite formation

. from the residual anhydrous C_3A

$$C_3A + 3CaSO_4.2H_2O + 26H_2O \longrightarrow C_3A.3CaSO_4.32H_2O$$

(Ettringite, expansion)

from hydrated aluminates (Monosulfoaluminates)

$$C_3A.CaSO_4.18H_2O + 2Ca(OH)_2 + 2SO_4 + 12H_2O \longrightarrow C_3A.\ 3CaSO_4.32H_2O$$

(Ettringite, expansion)

b) Sulphate of magnesium $MgSO_4$

Double action: the formation of ettringite and the substitution of the ions Ca^{2+} in Mg^{2+}

3.1.3. Formation of expansive products

$$Ca(OH)_2 + MgSO_4 \longrightarrow CaSO_4 + Mg(OH)_2$$ (Brucite, weak solubility)

$$C_3A + 3CaSO_4.2H_2O + 26H_2O \longrightarrow C_3A.3CaSO_4.32H_2O$$ (Ettringite, expansive)

3.1.4. Substitution of the ions Ca^{2+} by the ions Mg^{2+} in the C-S-H

$$C\text{-}S\text{-}H + MgSO_4 \longrightarrow CaSO_4.2H_2O + (C, M)\text{-}S\text{-}H$$ (Weakly cohesive)

The silicate of hydrated magnesium (Mg-S-h) thus formed doesn't have any binding properties, and therefore the hydrated dough becomes soft and disjointed.
The attack of the sulphates generates two types of products therefore, secondary gypsum lightly expansive and the secondary ettringite which is the main cause of concrete changes in sulphated environment.

4. EXPERIMENTAL MODE

For this survey, we used:

- Portland cement of CPJ-CEMII/A 42.5 the cement factory of M'SILA (ACC)

Chemical composition											minéralogy Composition			
CaO	SiO_2	Al_2O_3	FeO_3	MgO	RI	SO_3	PAF	Na_2O	K_2O	CaOl	C_3S	$ßC_2S$	C_3A	C_4AF
60.88	24.35	5.56	3.83	1.08	3.30	0.27	2.37	0.23	0.48	0.71	59.83	16.94	6.56	11.64

Tab1: Chemical composition of the cement

- Sand rolled of river.
  Density = 2, 60 g/ cm^3

- Aggregates class 3/8 and 8/16 of silico - chalky origin (career).
  Density = 2, 50 g/ cm^3

- Natural pozzolan of volcanic origin.

Eléments	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	P.A.F	R.I
%	44,95	16,91	9,47	14,59	3,76	0,20	1,35	1,34	4,30	0,56

Tab2: Chemical composition of the pozzolan

- Reducing superplasticizer of water MEDAFLOW 30.

4.1. Physico-chemical properties of the pozzolan

Density = 2, 65 g/cm^3.
Specific surface = 9500 cm^2/g.
Pozzolanic activity = 110 mg CaO/g **[4].**

Dosage in pozzolan and in superplasticizer is adjusted respectively to 5% and 2% in relation to the mass of cement, dosage that allows getting a maximal compression strengh to 28 days accompanied by a good manageability **[5].**

4.2. Chemical amixture

The admixture" MEDAFLOW 30" used is a high reducing water superplasticizer of the 3rd generation derived from polycarboxylates, it allows:

• On cool concrete: to get a weak W/C, an improvement of fluidity, and to sustain a long.

• On hardened concrete: to increase the mechanical resistances to young age and long-term, to improve the durability.

Its normal use scale is fixed by the manufacturer's recommendation of 0, 5 to 2% of the cement weight.

4.3. Composition of the concretes

Sand	Gravel 3/8	Gravel 8/16	Cement (C)	Water (W)	W/C
763,5	137	837	425	212,5	0,5

Tab3: Composition of the ordinary concrete in Kg /m^3 **(B.O)**

Sand	Gravel 3/8	Gravel 8/16	C	W	W/C	MF30
763,5	137	837	425	107,66	0,3	26,48 l 28,33 Kg

Tab4: Composition of the HPC in Kg /m^3 **(HPC)**

Sand	Gravel 3/8	Gravel 8/16	PZ 5%	C	W	W/C	MF30
763,5	137	837	21,25	403,75	107,66	0,3	26,48 (l) 28,33 (Kg)

Tab5: Composition of the HPC with addition of pozzolan in Kg /m^3 **(HPCZ)**

The different prismatic specimen 7×7×28 cm and cylindrical 16×32 cm thus prepared are kept in humid room (20°C, 95% HR) during 28 days. They are then put in conservation baths containing 5% of the ammonium NH_4 SO_4 sulphate. The duration of conservation has been fixed to 7 days, 28 days, 3 months and 1 year.

5. EXPERIMENTAL RESULTS AND INTERPRETATION

5.1. Evolution of the mechanical resistances

The evolution of the mechanical resistances of the specimen kept in the sulphated environment and the drinking water followed during one year is represented on the figures (1, 2, 3, 4).

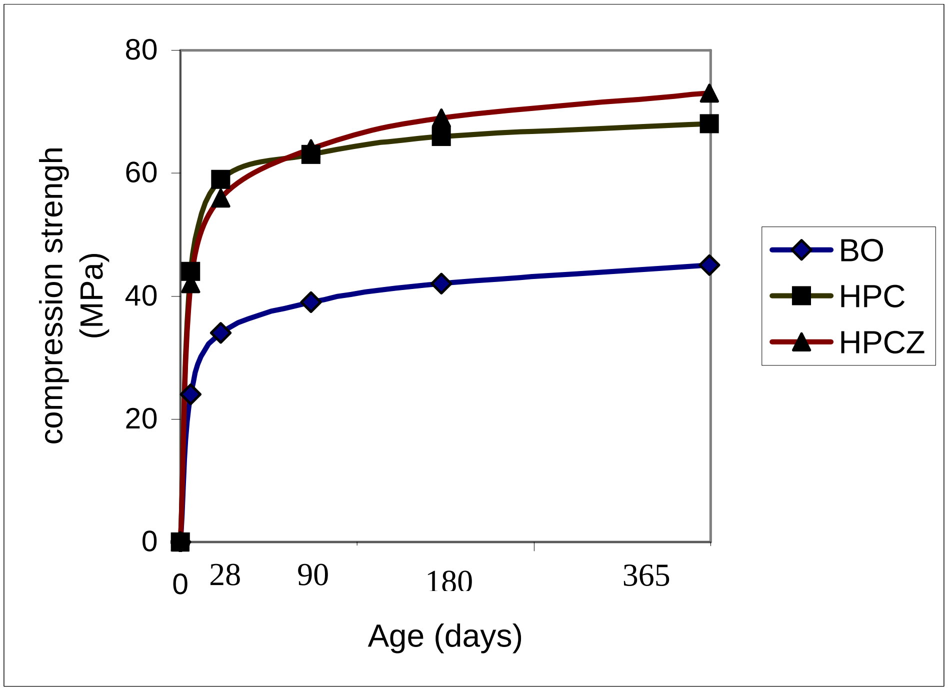

Fig 1: Evolution of the compressive strength of the concrete specimens kept in drinking water

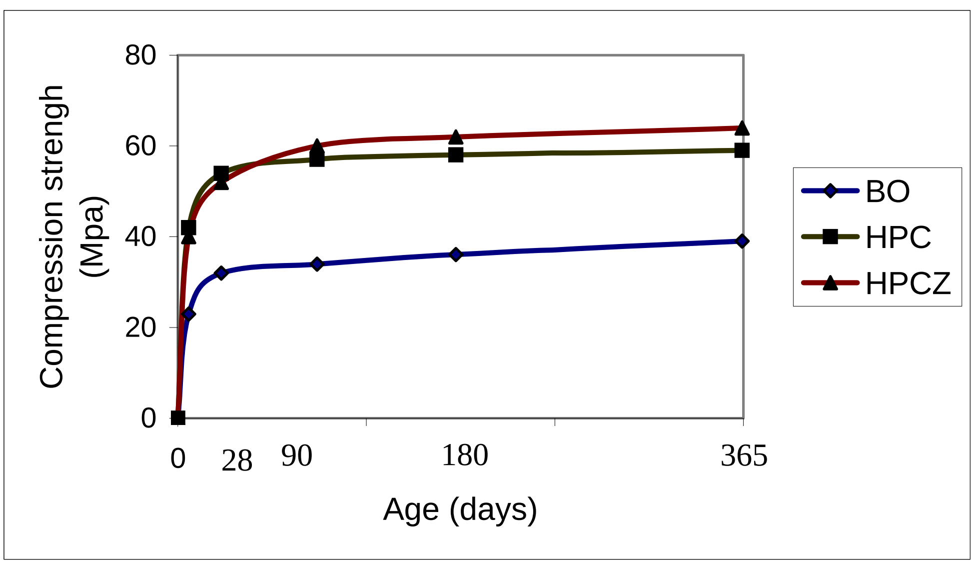

Fig 2: Evolution of the compressive strength of the concrete specimens kept in the sulphated environment.

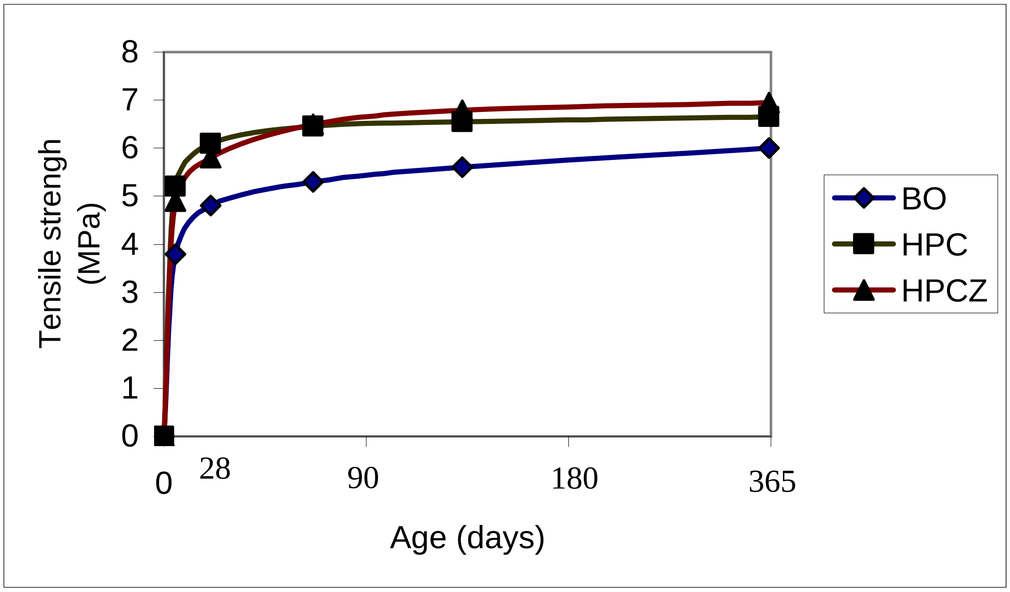

Fig 3: Evolution of the tensile strengh of the concrete specimens kept in drinking water.

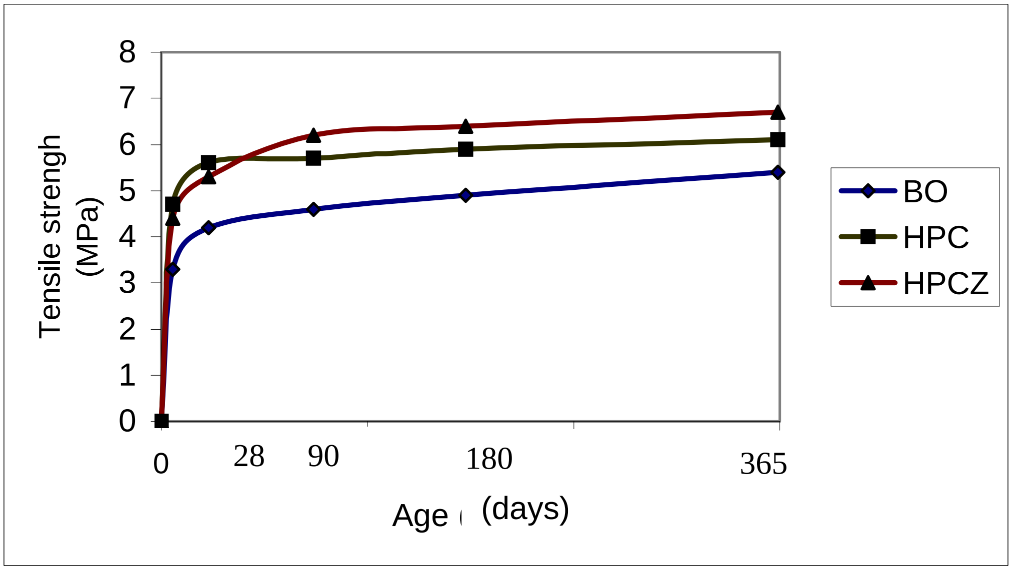

Fig 4: Evolution of the tensile strengh of the concrete specimens kept in the sulphated environment.

5.2. Permeability to the chlorine ions

The ASTM procedure C1202 is one of the trial procedures the more used to estimate the capacity of the concrete to resist the penetration of the chlorine ions.
The resistance to the penetration of the chlorine ions is estimated while measuring the

total load (in coulomb) that passes through haggard concrete specimens 100×50 mm maintained under an electric tension of 60V during 6 hours by means of electrodes made of rustproof steel between the two cells of the two compartments. One of the faces of the specimen is in contact of a 30g/l NaCl solution (cathode), and the other face is in contact of a 0,3N solution of NaOH (anode).

The cylindrical surface of the specimen is impregnated with a layer of epoxydic resin.

This simple and fast procedure, only give an evaluation of the resistance to the penetration of the chlorine ions while using a measure mainly based on the conductivity of the concrete.

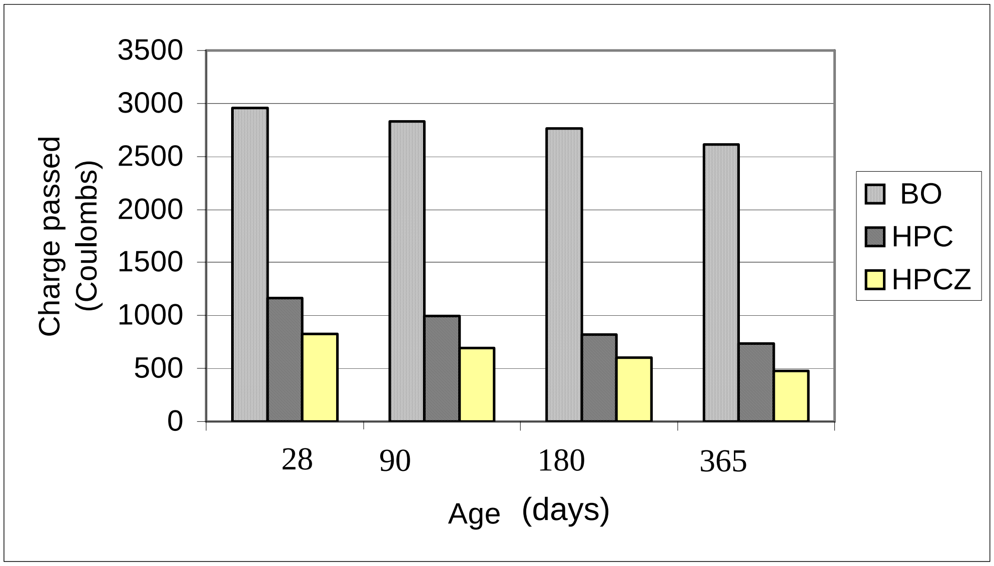

Fig 5: Charge passed in the concrete specimen kept in the drinkable environment.

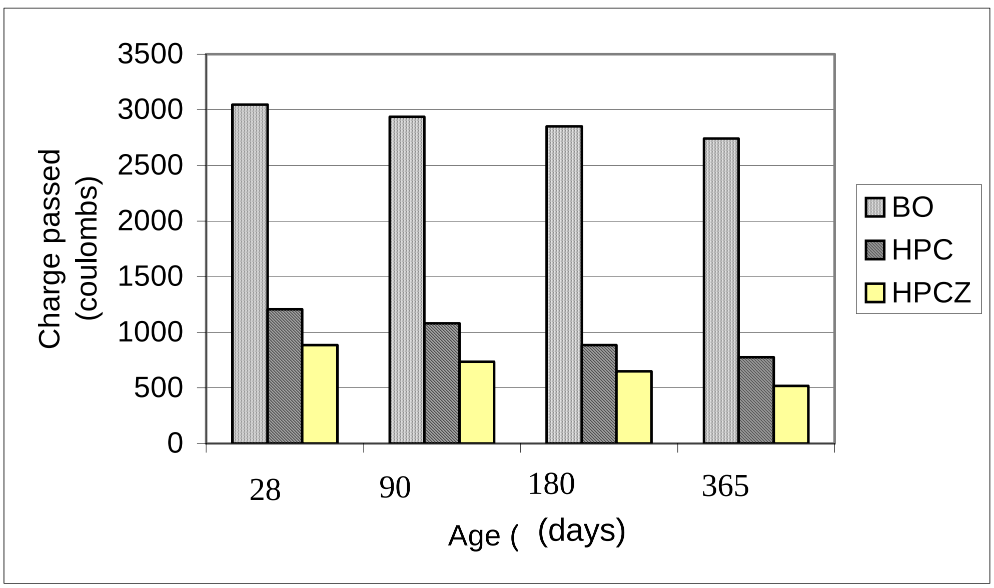

Fig 6: Charge passed in the concrete specimen kept in the sulphated environment

One can note that the compressive strengh and traction strengh of the concretes with additions of pozzolan are all superior to the ordinary concretes and high performance concretes without addition and some either the fashion of conservation. On the other hand, the permeability to the ions chlorine of the concretes with addition of pozzolan is lower to the ordinary concretes and high performance concretes without addition.

5.3. Expansion

The results of the tests of expansion of the concrete specimens immersed in the solution of ammonium NH_4 SO_4 are presented on the (figure 7).

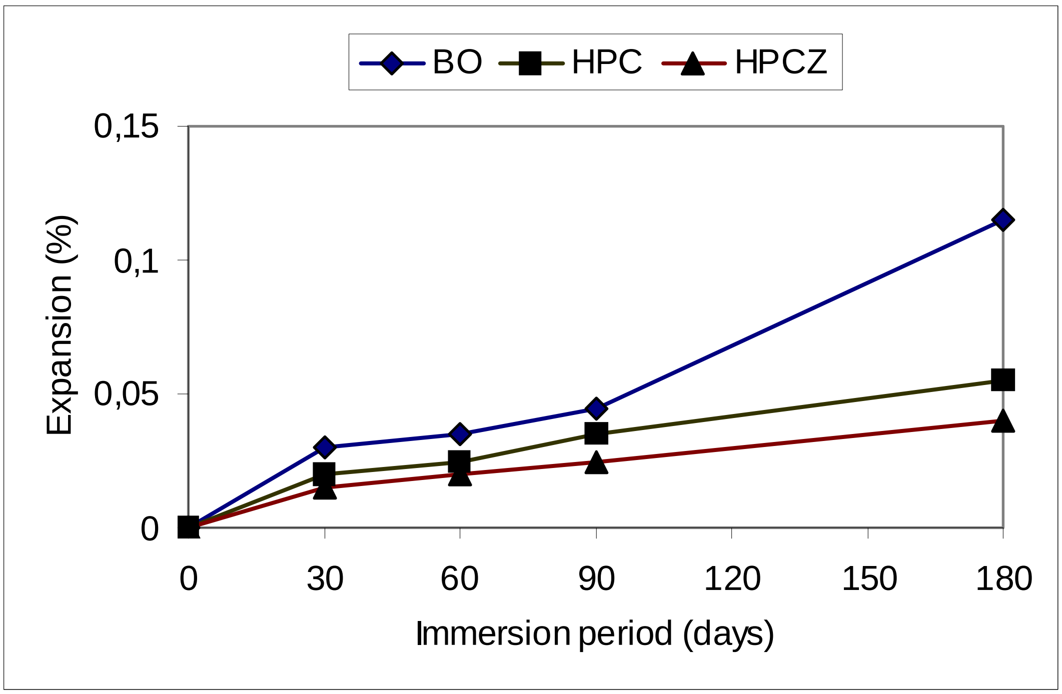

Fig 7: Expansion of the concrete specimens immersed in the solution containing 5% NH_4SO_4 ammonium sulphate

The results show that the concretes undergo an expansion, nevertheless the one of the ordinary concrete is accentuated more that the one of the concretes with or without addition of pozzolan.

The ordinary concrete with a W/C report = 0, 5, present a matrix very porous that facilitates the penetration of the solution charged of ions sulphate in its interior. These, in presence of aluminate anhydrous tricalcique of hydrates or of aluminized them hydrated react to form the secondary, chatty ettringite the expansion.

5.4 Skrinkage

The tests of autogenous skrinkage and drying done on prismatic specimen 7×7×28 cm, kept to the free air and the ambient temperature of the laboratory 20 ± 2°C, provided the illustrated results:

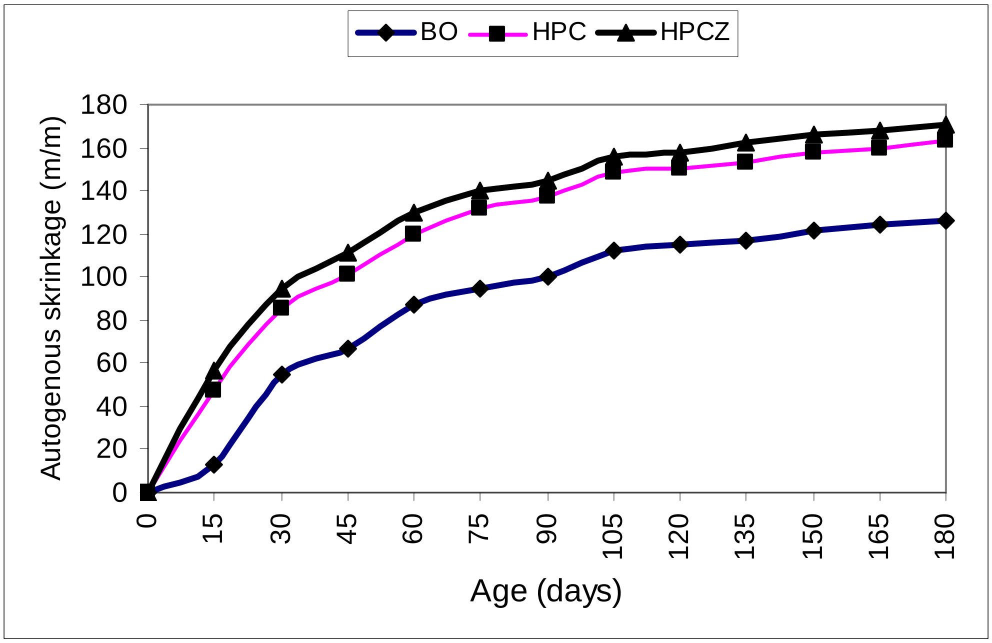

Fig 8: Autogenous skrinkage of different kinds of concrete.

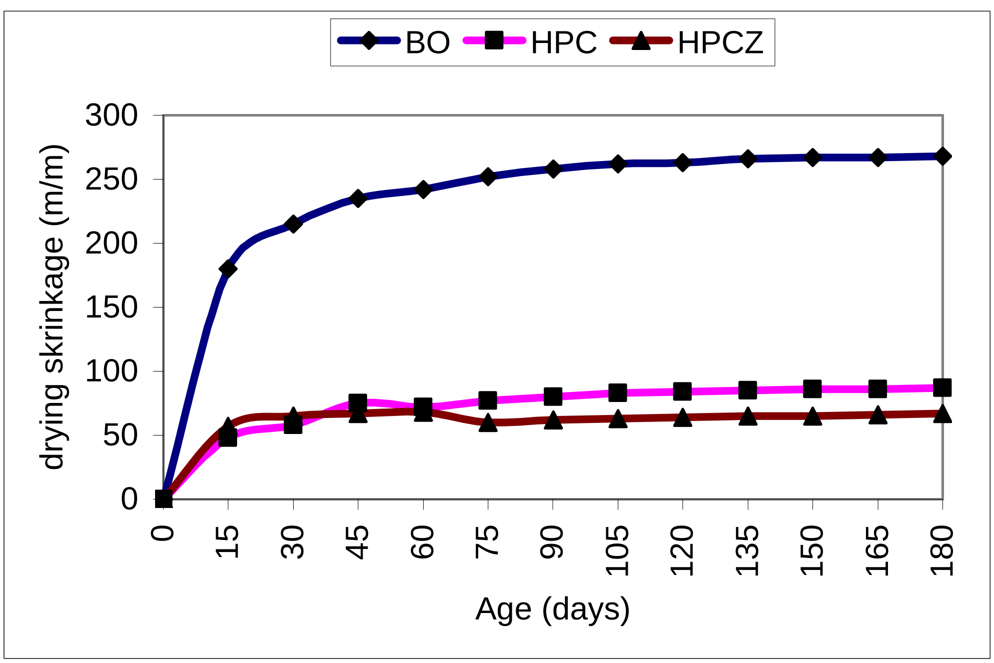

Fig 9: Drying skrinkage of different kinds of concrete.

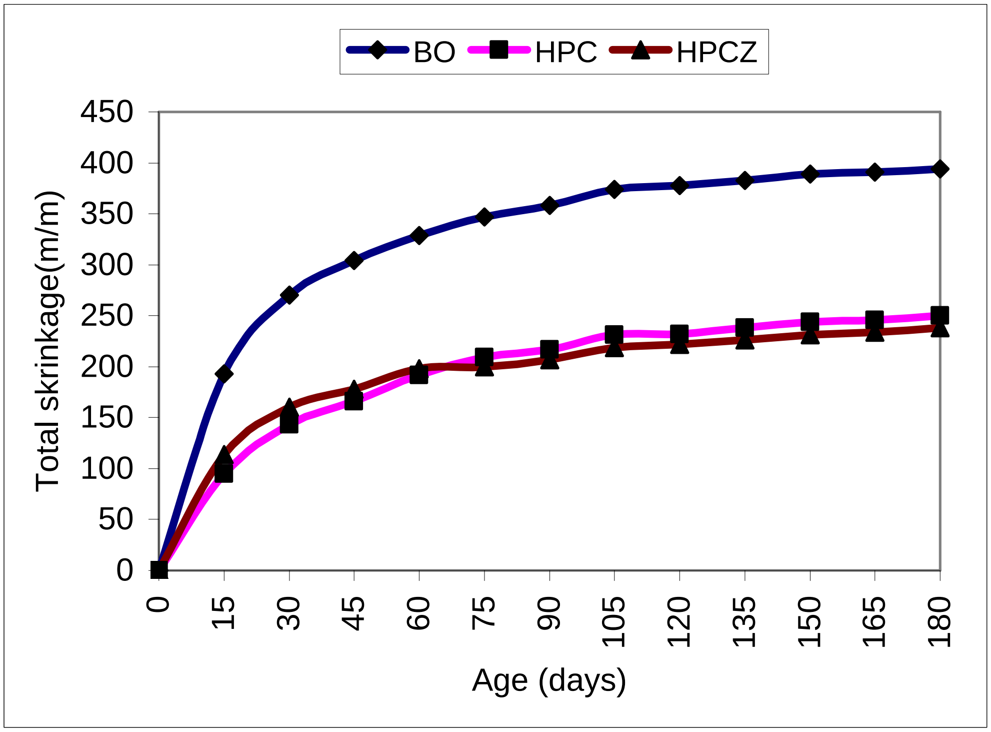

Fig 10: Total skrinkage of different kinds of concrete.

Several parameters can influence the skrinkage concretes, among the most important are: the fineness and the composition of the cement used, the temperature, the ambient humidity, the heat of hydration and the W/C report.

The skrinkage is especially small that the W/C report is also, the skrinkage high performance concretes that they are with or without addition and having an W/C report = 0,3 are weaker than the one of the ordinary concrete prepared with an W/C report = 0,5.

The natural pozzolan used for the confection the high performances concrete with addition (HPCZ) acts by its very advanced fineness, its latent property and by its heat of hydration. The effect combined of these three parameters generates a sensitive increase of the skrinkage to the first ages. To means term, the supplementary CSH descended of the reaction pouzzolanique generate a reduction of the distortion due to the skrinkage. Indeed, the dense structure of the concretes due to the reduction of the measurements and percentage of the pores prevents the migration of the water.

6. CONCLUSION

Thanks to the addition of pozzolan, to the use of superplasticizer and in return for a correctly adjusted composition, we got mechanical resistance concretes on 28 days superior in 70 MPa. Compared to the ordinary concretes, these possess a better durability due to their very elevated compactness that represents a brake to the chemical agents penetration.

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