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Chemical Strength of HPC Cured in a Sulphate Environment

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ABSTRACT

A large variety of sulphates, generally coming from underground water or sea waters, can come into contact with the concrete and react chemically with the hydrates, in particular with aluminates, and cause the cracking and the failure of the concrete. The durability of the concretes in a sulphate environment is normally ensured by a sufficient content of cement and the dense structure of the hydrated paste. The combination of natural pozzolans with portland cement makes possible the development of concretes having mechanical properties and a durability much higher than that of a concrete without addition.

In order to better determine the pozzolanic effect of the pozzolan addition in the concrete, the evolution of the crystalline phases have been analyzed using x-ray diffraction analysis examined using scanning electron microscopic techniques including the use of chemical analysis to confirm their chemical composition. In parallel with these tests, the evolution of the mechanical bending and compressive strengths have been observed using an automatic test machine. The present study confirms the pozzolanic reactivity of the natural pozzolans used.

INTRODUTION

Concrete is the most used material in the field of construction. Its use is still growing, thus creating a problem involved in the availability of suitable aggregates for use in concrete in some regions. The continuous extraction of aggregates in large quantities generates a certain number of disadvantages including disturbing the ecological balance. In this way, high performance concrete with elevated strength offer a material for construction that has improved better durability and possible cost savings in materials up to 40% [De Larrard 1988 and Hamrat 1996].

When concretes are produced that are well compacted and have a high cement content they are well-suited to be used in aggressive chemical environments. However, its main components, cement, sand or aggregates can all undergo degradation in a short term. When deterioration (which is due to chemical or mechanical mechanisms) occurs in the concrete the stability of the structure may be endangered. Chemical deteriorations are mainly due to attack by acids or bases, or exposure to salt solutions. These reactions almost always involve the dissolution of lime and most often, in association with this dissolution, formation of new compounds [Rendell et al, 2002].

The degradation of the concretes by sulphates is mainly due to expansion due to the crystallization of "secondary" ettringite. The formation of this ettringite is to be distinguished from that of primary ettringite, known to be formed at the first stages of the hydration of portland cement by reaction with gypsum, this primary ettringite is never expansive [Duval and Hornain 1992].

The action of sulphated groundwater offers the simplest case of an aggressive chemical reaction and the formation of expansive new compounds starting from the principal components of cement. The basic reaction is the formation of ettringite or Candlot's salt [$C_3A \cdot 3CaSO_4 \cdot 32H_2O$].

It should be noted that the normally formed ettringite at the time of the setting of cement, changes quickly, under the usual conditions of preservation, to monosulfoaluminate. Moreover, the gypsum added to the clinker reacts to form other compounds and is principally tied up and unavailable for further reaction in the hardened concrete.

It is possible to modify the microstructure of the concrete by incorporating mineral admixtures. These additions to the cementious mixture modify the microstructure of concrete in term of physical and chemical characteristics. It was proven that the introduction of large capillary pores offer a great number of sites of germination for the precipitation of the products of hydration which accelerate the hydration of cement and allow reduced dimensions of the lime crystals.

The pozzolanic mechanism of reaction of the cementing additions can be briefly described as a reaction of silica with the lime released by the hydration of cement, in the presence of water. HSC with poor Ca/Si ratio are obtained. Although this reaction is rapid and precocious, it is limited by the quantity of water in the HPC.

EXPERIMENTAL

Materials The cement

The cement used is a CPA CEM I 52.5 from the factory Saint Pierre Lacour, whose chemical composition is presented in table 1.

Table 1. Chemical composition of cement CEM I 52.5

Elements	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	RI
%	64.50	21.01	4.90	2.80	0.90	3.00	0.90	0.20	0.20
Elements	PAF	CaO_l							
%	1.10	0.45							

The mineralogical Composition of this cement obtained used Bogue's method is as follows : **C_3S** (65.94 %) - **C_2S** (10.47 %) - **C_3A** (8.24 %) - **C_4AF** (8.52 %). On the partial and cumulated grading curves of anhydrous cement (Figure1). obtained using a laser grading equipment (CILAS 1 180). functioning in multitasks under Windows. allowing to combine processing capability and simplification of use. it can be observed an average continuous grading between 0.3 and 60 µm.

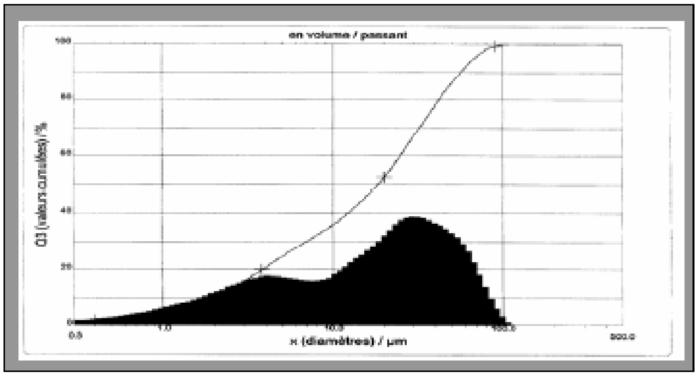

Fig. 1. Size distribution of cement CEM I 52.5

The rate of particles of diameter lower than 56 µm (90%), reflects well the high smoothness of cement, which increases the kinetics of hydration.

The pozzolans

Pozzolans used in this study is a natural pozzolan of volcanic origin, extracted from the quarry of Béni-saf (Algeria); table 2 presents its chemical composition.

Table 2. Chemical composition of pozzolan

Elements	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
%	14.59	44.95	16.91	09.47	3.70	0.20	1.35	1.34
Elements	RI	PAF						
%	0.56	4.30						

The grading of pozzolan is tighter compared to that of cement used, it is spread out between only 2 and 15 µm (Figure 2).

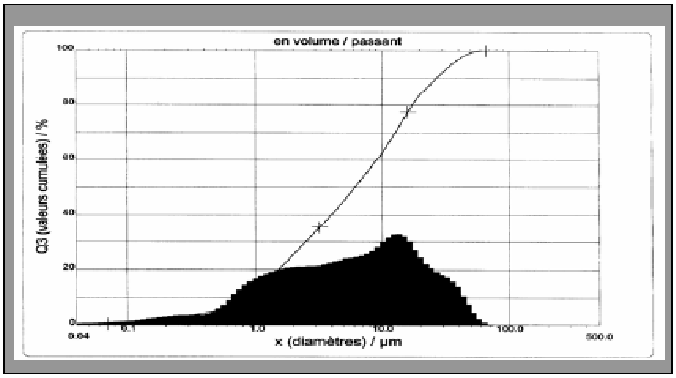

Fig. 2. Grain size distribution of pozzolan [Chaid et al. 2007]

The High-Range, Water-reducing admixture

The additive used. is a plasticizing water reducer for high performance concretes in conformity with standard *NF INTO 934-2* provided by company SIKA. The SIKAMET FF 86 allows the concrete making with a very low W/C ratio having very high mechanical strengths in particular at the early ages. The SIKAMET FF 86 allows to make fluid concretes particularly adapted to high performance concretes (characteristic strength > 50 MPa).

The Coarse and Fine aggregate

- The sand used was a quarry sand (04) recomposed in accordance with standard *NF P 18-540*. The calculated fineness modulus was 2.47, which corresponds to the sands used for the search of high strengths, but in general, it leads to a worse workability and risks of segregation. However, the content of the presumably argillaceous part of diameter lower than 0.14 mm is 7.3 %.
- The gravels used are crushed gravels of fractions (3/8 and 8/15).

Formulation

Obtaining the required concrete characteristics requires the definition of a composition which will obtain the optimal mixture of the various aggregates.

Former tests directed us towards the production of concretes in two phases. with a view to obtain a concrete approaching. as much as possible. a massive rock having the lowest porosity.

The first phase is constituted by the inert skeleton (gravel and sand) determined by the Dreux Gorisse method which is very practical and inspired from the theory of Caquot. It represents a synthesis of several methods which all are based on the preliminary knowledge of a grading curve of reference.

While the second phase presents the binding paste (cement, high-range water-reducing admixture, water and cementing additions). The latter was optimized by the method of grouts.

The final compositions of control concrete (CC) without addition and that of concrete with pozzolan (PC), after correction are presented on table 3.

The concrete specimens are preserved in their moulds in humid room (20°C. 95% HR) during 24 hours. They are then put in the bath of conservation (gypsum water). The times of conservation were fixed to 7 days. 28 days. 3 months and 1 year.

The durability of concretes is quantified by the evolution of the mechanical strength. The tests are carried out by means of a control hydraulic press (MOHR & FEDERHAFF Germany).

The evolution of the various crystalline phases present in the concrete or lately formed in the various mediums is followed by X-rays diffraction. The diffractometer used was a Philip PW3710, with a Copper target and a Ni filter. The X-ray diffraction analyses are carried out on powder. To avoid any segregation, the samples are completely crushed to powders passing to the sieve of 80 µm.

To confirm the results obtained by the X-ray diffraction analysis, we made observations with a Jeol (JSM 6400) scanning electron microscope intended for the observation of dry and conducting samples and for the analysis by a spectrometer of dispersion of energy OXFORD Link Isis and coupled to a microanalysis.

Table 3. Compositions of concretes with and without pozzolan

Components	Control Concrete (CC)	Pozzolan Concrete (PC)
Cement	500 kg/m^3	475 kg/m^3
Sand	573 kg/m^3	573 kg/m^3
Gravel 3/8	130 kg/m^3	130 kg/m^3
Gravel 8/15	915 kg/m^3	915 kg/m^3
Water	150 l/m^3	150 l/m^3
Plasticizer	8 l/m^3	8 l/m^3
Pozzolan	-	25 kg/m^3

RESULTANTS AND DISCUSSION

Density

Figure 3 shows the evolution of the density of the various concretes preserved in gypsum water. It can be noted a thickening (denseness) of the concrete with pozzolan addition.

Indeed, the high grinding of the pozzolan, combined with its reaction with the calcium hydroxide to form no soluble calcium hydrosilicates, support the increase in the compactness of the hardened concrete. This explains the increase in its density compared to the control concrete.

On the other hand, the older the concrete, the greater the propagation of sound velocity in the two compositions of concrete; this correlates with the evolution of compactness in time. A considerable variation is observed between the concrete with addition of pozzolan and that of control.

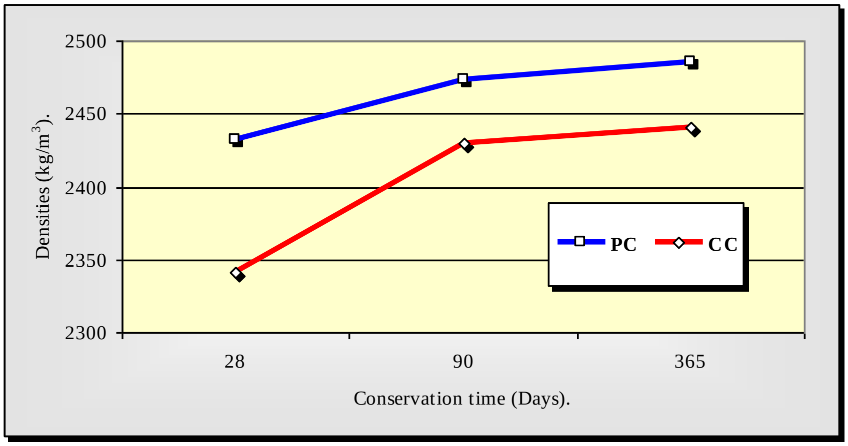

Fig. 3. Evolution of the densities of the concretes as a function of curing time

According to the results obtained (Figure 4), we notice that the concrete with pozzolan addition, shows higher velocities compared to those of the concrete without addition.
This increase can be related to the fact that the density of the concrete containing pozzolan is higher compared to that of the control concrete. This follows from the action of the pozzolan which acts by its large smoothness as a filler and by virtue of its pozzolanic activity.

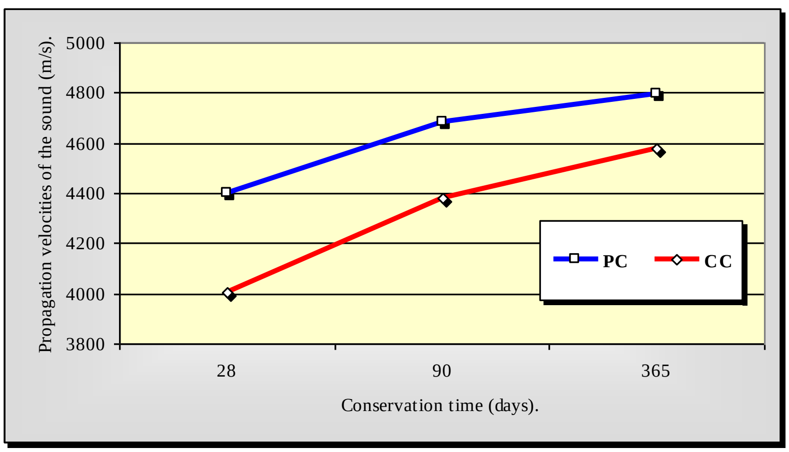

Fig. 4. Evolution of propagation of sound velocities through the concretes as a function of curing time

Internal structure

The observation using the scanning electron microscope enabled us to examine the microstructure of the hydrates formed within the concretes after 365 days of hardening (Figure 5). A microstructure relatively improved in concretes with pozzolan addition was noticed with interfaces relatively more densified and rich in CSH, representing the HPC characteristics.

The majority of authors consider pozzolan as a filler liable to rapidly combine chemically with the lime released by cement, in the presence of water.

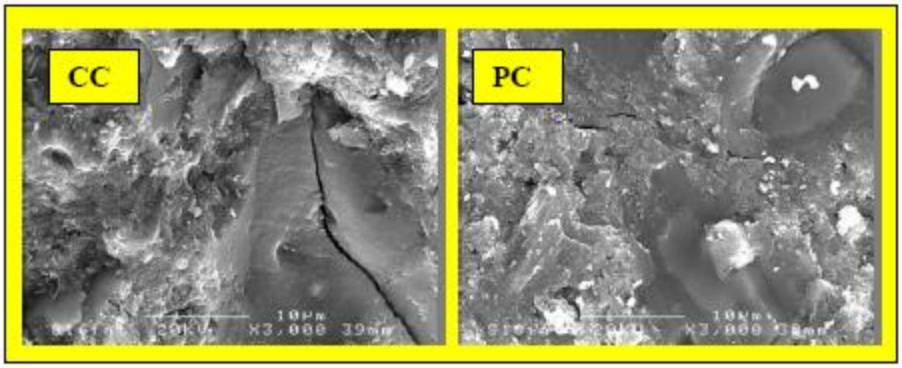

Fig. 5. SEM Observation of the internal structural of concrete specimens after 365 days of curing

The pozzolanic reactions are faster because of the very small size and thereby the increased surface area of the reactive particles. The newly formed products are initially more easily dispersed or better set in materials, on the other hand their composition is more favourable to the incorporation of alkaline cations into their crystalline structure [Kouame 1991].

The analysis by X-ray diffraction (Figure 6) illustrates the various crystalline phases which are identical for concretes with and without pozzolan. However, it is necessary to note, that for the pozzolan concrete, the hydration of their anhydrous compounds is slower when compared to that of the control. This is the consequence of the thickening of the matrix. The formation of this more compact microstructure consequentially leads to a much higher chemical resistances.

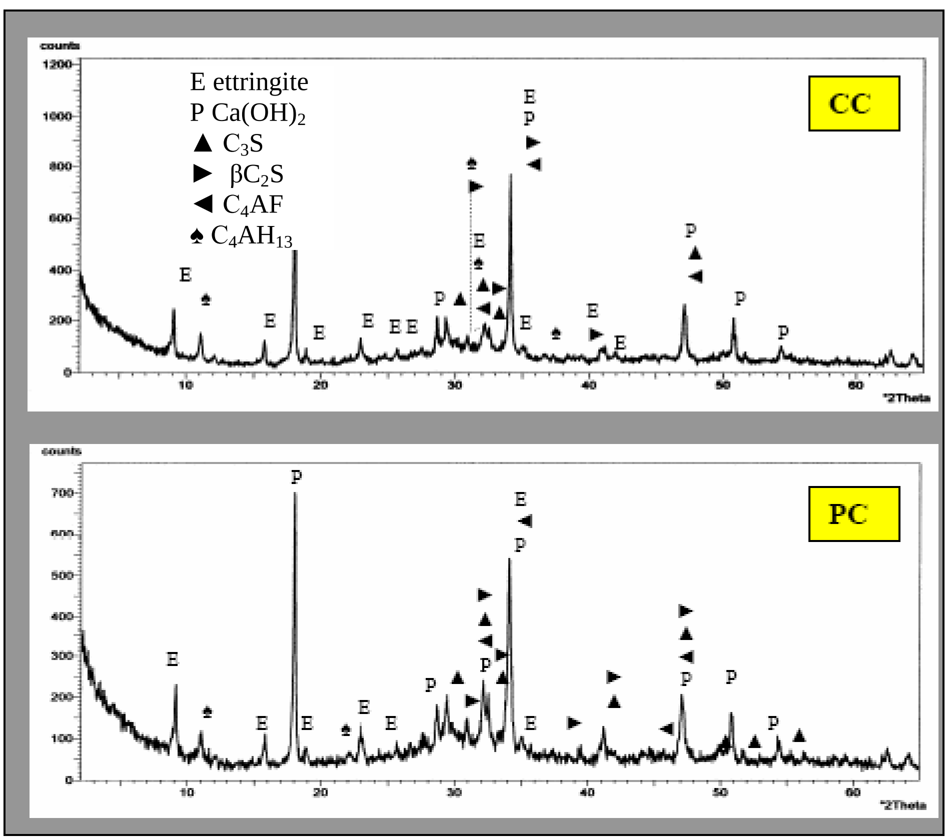

Fig. 6. X-ray diffraction patterns of control and pozzolan-enhanced concretes cured in gypsum water

The calcium silicate hydrates (CSH) are composed of very small crystallites and are not easily identifiable by X-rays diffraction analysis; only some lines appear but they are superposed on the lines of the other crystalline phases [Ollivier 1975].

The calcium hydroaluminates are crystallized in the form of C_4AH_{13} ($4CaO \cdot Al_2O_3 \cdot 13H_2O$) for the normal concretes, and are detected by certain lines of X-rays diffraction. It is noted there is an absence of lines of X-rays diffraction of the gypsum; this being completely consumed during the hydration and contributes to the formation of ettringite.

Mechanical strength

It can be noted that the compressive strengths of concrete with pozzolan addition are higher than that of concrete of control at the various stages. We thus have to deal with high performance concretes. This quality is not all affected by the chemically aggressive surrouding medium .

The high grinding of pozzolan has allowed the increase in the compactness of the concrete, which explains the increase in its density compared to the concrete of control. On the physic mechanical level, pozzolan reacts by its smoothness and its pozzolanic activity, thus generating a more coherent skeleton and consequently a more resistant and more durable concrete in gypsum water.

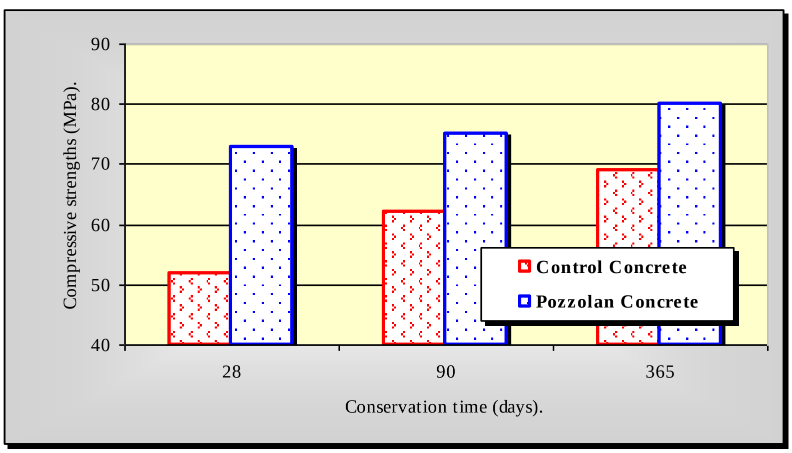

Fig.7. Evolution of the compressive strengths according to the curing time

The development of flexural strengths occurs at a faster rate than the compressive strengths for the same mixture. The density of the matrix and the evolution of the interface paste aggregate are at the origin of the improvement of flexural strength.

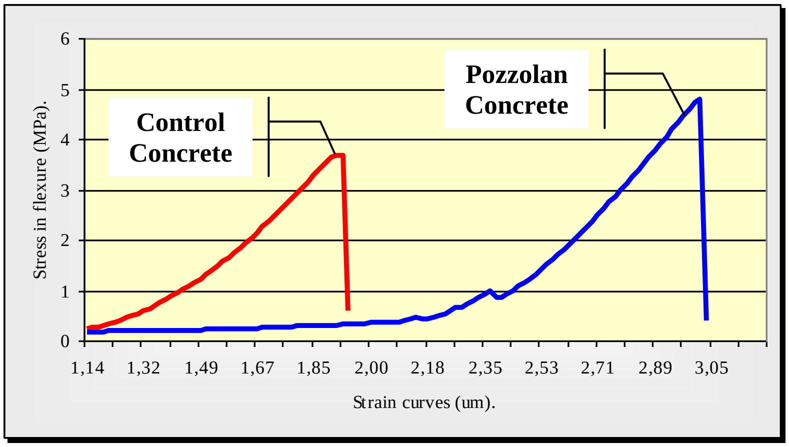

Fig. 8. Evolution stress/strain curves (in flexure) after 3 months of hardening

The flexural strength is thought to be related to the variations in the paste-aggregates bonding. We can thus by an indirect tensile test account for the differences in bond which involve the cementing additions.

Figure 8 shows bending stresses of the various concretes after 3 months of hardening, for prismatic specimens (7 x 7 x 28 cm^3) preserved in gypsum water. It can be noted that the bending stresses are more developed for concrete with pozzolan addition (4.8 MPa) that for the reference concrete (3.6 MPa).

Skin of concrete

The test-specimens preserved in the various mediums during one year, are then crushed and their surface in contact with the medium of curing is observed using SEM. The crystalline forms observed are subjected to the micro analysis and the crystalline phases are determined by x-ray diffraction.

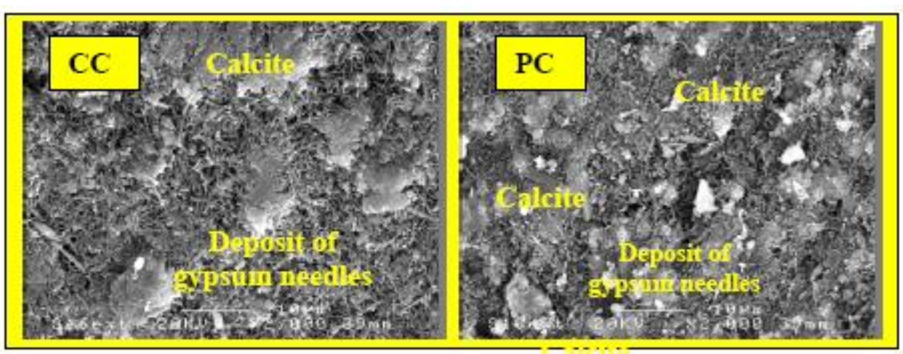

Fig. 9. SEM observation of the surface of concrete specimens cured in gypsum water

On the surface of the specimens, preserved in gypsum water, a large deposit of gypsum needles is observed (Figure 9), which covers practically all the surface of the concrete of control and partially that of the pozzolan concrete. On the contrary, the presence of calcite crystals on the surface of the pozzolan concrete is relatively marked compared to the concrete of control.

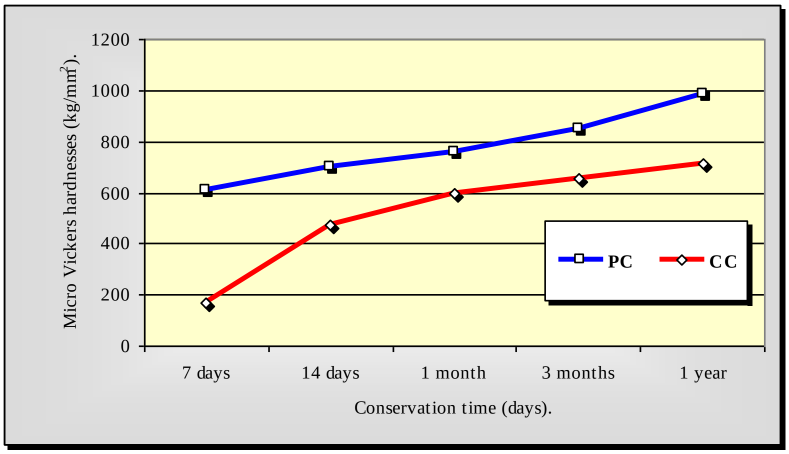

Fig. 10. Evolution of micro Vickers hardnesses after one year of conservation in gypsum water

Surface hardness was measured using Leitz Microduremetre. This consists of a diamond penetration device of the Vickers type, having a pyramidal shape with a square base and an interdependent mechanical device which enables diamond to come down to the contact with perfectly plane surface of the sample and while applying the loads tests on the penetrating diamond.

The micro Vickers pyramid hardness was used on the surface of the test-specimens in contact with the medium of conservation (gypsum water). Micro Vickers pyramid hardness enabled to quantify the surface deterioration of the different concretes cured during one year in gypsum water.
The results illustrated on Figure 10 shows that micro Vickers pyramid hardnesses are greater for the concrete with addition of pozzolan compared to the control concrete. In general, the calcite formation on the surface of the concretes specimens is at the origin of higher Vickers pyramid hardnesses.

A considerable deposit of the gypsum needles (observed on figure 10) for the control concrete reduce the permeability of the skin of the concrete and this results in a reduced chemical resistance.

CONCLUSION

The method of Dreux Gorisse combined with that of grouting, have led to satisfactory proportioning concrete mixtures, presenting increases in mechanical strength. The high grinding of the cementing additions allowed the increase in the compactness of the concretes, which explains the increase in their densities and propagation of wave sound velocities compared to the concrete of reference.

On the physico-mechanical level, pozzolan reacts by its smoothness and its pozzolanic activity, thus generating a more coherent skeleton, a concrete skin relatively more impermeable and consequently a more resistant and more durable concrete.

Lime being presented in the form of fragile crystals, its consumption by pozzolanic reaction in the presence of the active mineral additions and the disappearance of the interfacial transition zone induced a very great influence on the mechanical strengths of the concrete.

It appears that the smoothness of pozzolan is a significant factor when designing a high performance concrete [Chaid et al. 2004].

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