American Journal of Civil Engineering and Architecture, 2016, Vol. 4, No. 4, 133-141
Available online at http://pubs.sciepub.com/ajcea/4/4/4

DOI:10.12691/ajcea-4-4-4

Physical, Mechanical and Microstructural Properties of Limestone High Performance Concrete

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Abstract The production of a high performance concrete (HPC) has expanded the scope use of concrete exposed to aggressive environments, thanks to the limited porosity, the durability, the rheological, physical and mechanical properties with the respect remarkable to a conventional concrete. The objective of this study is to develop a HPC incorporating finely ground limestone. The results show that the substitution of one part of cement by limestone contributes more to the improvement of physical, mechanical and microstructural properties of concrete. The couple cement/limestone contributes significantly to a densification of the matrix unlike when the cement is not substituted by addition. The survey also shows that the limestone does not fall into any chemical reaction. However, the development of resistance (physical phenomenon), obviously depends on the quality of hydrates supplied by the hydration, but also how these hydrates are assembled, their arrangement in space and their connections.

Keywords: *limestone, HPC, microstructure, creep, shrinkage*

Cite This Article: R. Chaid, A. Bali, A. PERROT, and M. Mansour, “Physical, Mechanical and Microstructural Properties of Limestone High Performance Concrete.” *American Journal of Civil Engineering and Architecture*, vol. 4, no. 4 (2016): 133-141. doi: 10.12691/ajcea-4-4-4.

1. Introduction

In the perspective of developing high performance concretes "HPC" based on local raw materials, so we proceeded with the introduction of limestone mineral addition can meet some of the same performance than those conferred by imported products such as: silica fume and others.

In previous studies, the durability of these concretes preserved in various aggressive environments was investigated. On the microstructural, it had been shown that the limestone was an inert cementitious addition playing a dual role: it had the effect of filler characterized by a high grinding which facilitated the penetration between cement grains. Then, a physical effect called "heterogeneous nucleation" or the germination of calcium silicate hydrate occurred more easily in contact with calcite crystals. Some authors even talk of epitaxially germination on calcite [1,2].

Upon limestone addition, hydration products of cement were accumulated around limestone particles [3]. The limestone powder prevents the transformation of ettringite to sulphoaluminates (monosulphate, hemisulphate and solid solutions) [4].

Structures are designed according to the load combinations (dead loads, imposed loads and wind loads). In addition, in the case of viscoelastic concrete elements, they undergo deformations induced by the application of constant maintained load (creep phenomenon) and gradual drying of concrete (shrinkage).

These long term deformations and their consequences, when taken into account, may be considered as a basic loading design phase.

For this purpose, the study of the characterization of these concretes has been carried out. It has consisted of following the evolution of mechanical strengths and damage as well as instantaneous and deferred deformations. To better identify the effect of limestone in elaborated concrete, the hydration of concrete mixtures have been analyzed by X-ray diffraction. A scanning electron microscope microanalysis of the minerals has confirmed their chemical composition.

2. Materials Used

2.1. Cement

The used Portland cement was CEM I 52.5 of the Saint Pierre Lacour factory whose X-ray diffraction diagram (Figure 1), performed on the anhydrous cement shows the presence of the different crystalline phases: the four essential minerals (C_3S, βC_2S, C_3A and C_4AF) responsible for the setting and hardening of cement and gypsum ($CaSO_4.2H_2O$) considered as setting regulator.

The particle size analysis was performed using a laser granulometer (Cilas 1180), working in multitask under Windows, allowing combining power processing and simplification of use.

On partial and cumulative anhydrous cement grading curves (Figure 2), it can be observed a continuous graded average particle size of between 0.3 and 60 microns.

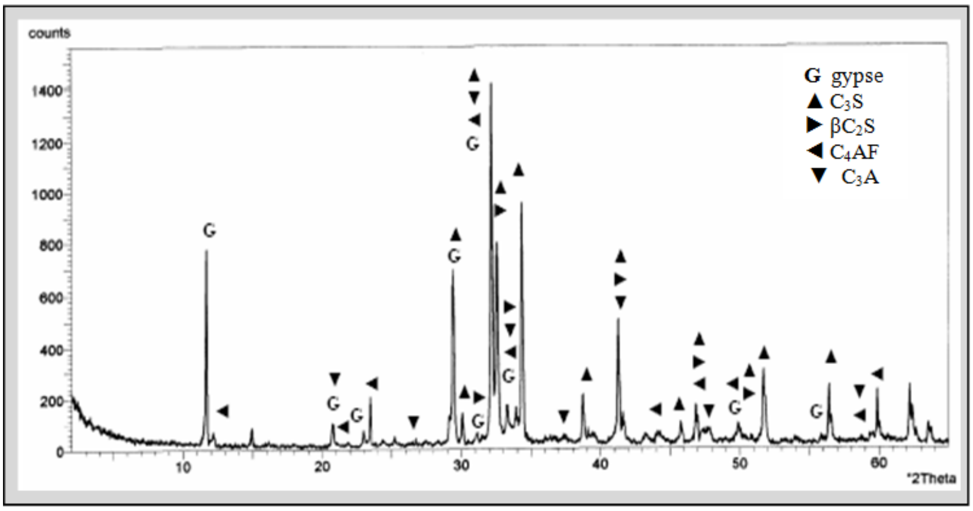

Figure 1. X-ray diffraction analysis of anhydrous cement CEM I 52,5 (λCu k_α filtre Ni)

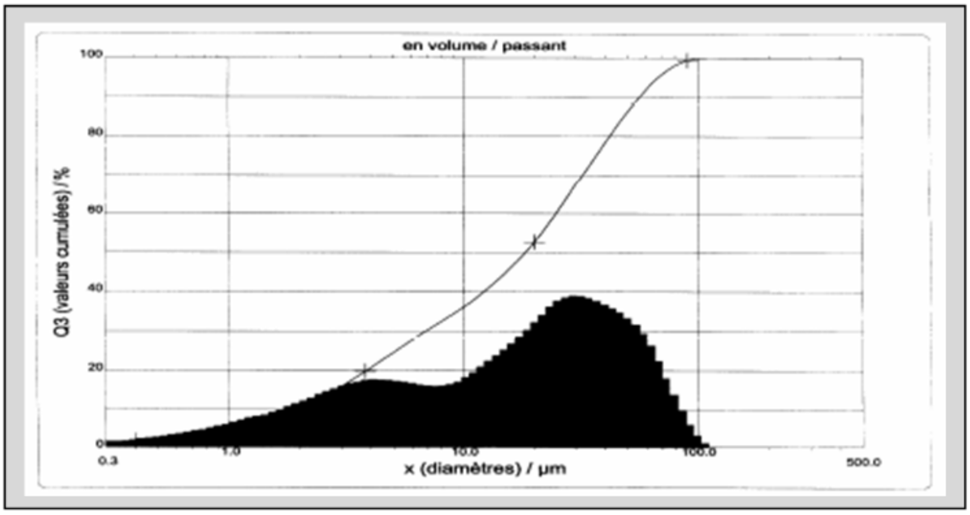

Figure 2. Grading distribution of anhydrous cement CEM I 52.5

Table 1. Strength evolution of normal mortar (CEM I 52.5)

Age - days	02	07	28
Flexural strength (MPa)	4.8	6.8	7.7
Compressive strength (MPa)	30	45	61

To select the concrete mix design proportions, it is necessary to determine the true strength of the used cement (CEM I 52.5). Normal mortar tested is designed according to NF P 15-403 with a water/cement ratio (W/C) of 0.5. The mortar specimens (4 x 4 x 16 cm^3) are cured in humid room (20°C, 95% RH) for 7days, and then stored in air-conditioned room (20 °C, 50% RH) until the age of testing. The test results of specimens subjected to bending and compressive loading are given in Table 1.

2.2. Limestone

The limestone used is from Meftah quarry (Algeria): Title 95.80 and a Blaine specific surface of 16 600 cm^2/g. According to the XRD analysis (Figure 3), limestone is composed of calcite ($CaCO_3$).

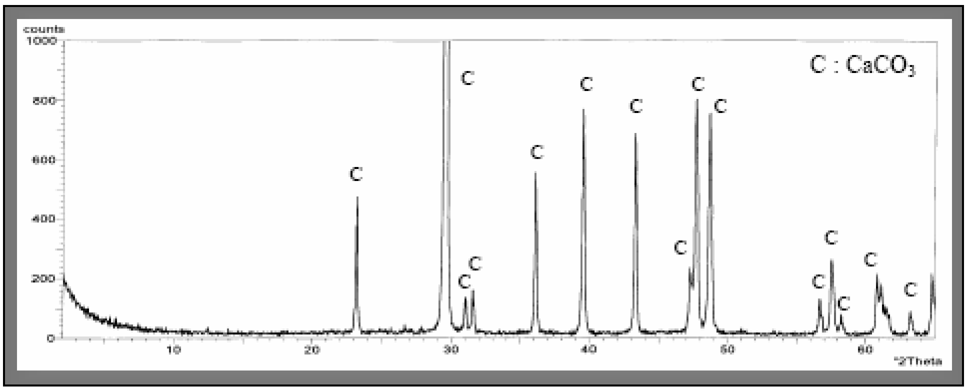

Figure 3. X-ray diffraction analysis of limestone (Cu Kα filtered)

A scanning electron micrograph of limestone (Figure 4): a) x 5000 and b) x 20000 shows that particles are in the form of rosettes, consisting of several interlocking plates. An overall microanalysis spread over a range (x 2000) and various points confirms the chemical composition of calcite ($CaCO_3$).

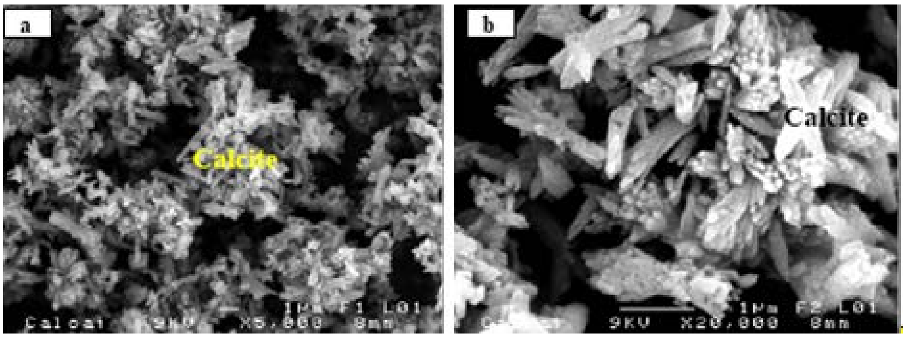

Figure 4. Scanning electron micrograph of ground limestone

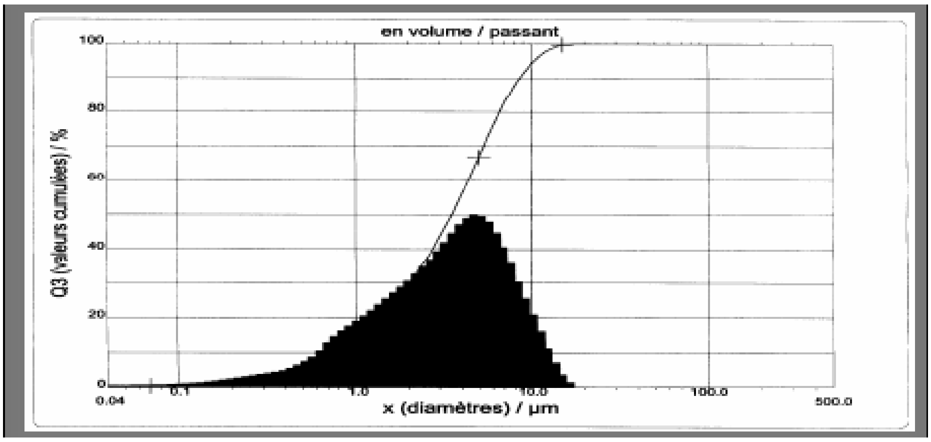

Figure 5. Grading distribution of limestone

The particle size of the used limestone is thinner than that of the cement (Figure 2). The dimensions of its particles hardly exceed 16 microns (Figure 5).

2.3. Aggregates

The required characteristics for concrete necessarily involve the selecting of optimal compositions of different aggregates.

These aggregates are largely rounded: quaternary deposit of the Vilaine River (Ille et Vilaine, French), which are mainly siliceous under the form of quartz and for a small part, crushed: corneal and meta-quartzite. In this work, after preliminary tests on both the rheology of concrete mixes and its crushing as hardened material, the choice was made on the aggregate Classes of 3/8 and 8/15.

A normal river whose fineness modulus is 2.47 has been used for the purpose of this investigation.

2.4. Admixture

The admixture used is a water-reducing plasticizer for high performance concretes in accordance with the NF EN 934-2 provided by SIKA industry.

The FF Sikament 86 admixture allows making concrete with a very low W/C ratio leading to very high mechanical strengths in particular at early ages.

3. Experimental Program

The concrete physical, mechanical and microstructural characteristics with and without limestone addition are studied and the results are compared.

The mixing procedure for making concrete specimens is:

1 - Aggregates and binder (cement + lime) are dry mixed for one minute.

2 - The mixing water is added together with a third of the volume of superplasticizer and mixing is continued for 2.5 minutes.

3 - The remaining superplasticizer is added and the final mixing lasts one minute.

The concrete specimens are preserved in their mold in a wet room (θ = 20 ± 1 °C, RH = 90 ± 10%) for 24 hours. They then undergo an appropriate curing depending on the type of test:

- For mechanical testing and speed of sound, they are immersed in ordinary water at 20°C until the testing time.

- For creep and shrinkage tests, they are placed unprotected in an air conditioned room (θ = 20 ± 1°C, RH = 50 ± 10%).

Table 2. Mix proportions for the elaborated concretes

Material		Mix proportioning	
		RC	LC
Cement	kg/m^3	475	427.5
Sand	kg/m^3	573	573
Gravel (3/8)	kg/m^3	130	130
Gravel (8/15)	kg/m^3	915	915
Water	l/m^3	150	150
Plasticiser	l/m^3	8	8
Limestone	kg/m^3	-	47.5

The mix proportions of high performance concretes with limestone fines and without any cementitious addition, after optimization, are shown in Table 2. The water / binder ratio for both types of concrete is 0.32.

The following legend has been adopted throughout the paper:

- **LC**: Concrete with limestone fines.
- **RC**: Reference Concrete (without addition).

4. Results and Analysis

4.1. Mechanical Strength

According to the graphs showing the evolution of the mechanical strength of the two tested concretes, it can be noticed a significant improvement as well in compressive strength (Figure 6) as in tensile strength (Figure 7) of limestone concrete with respect to concrete reference.

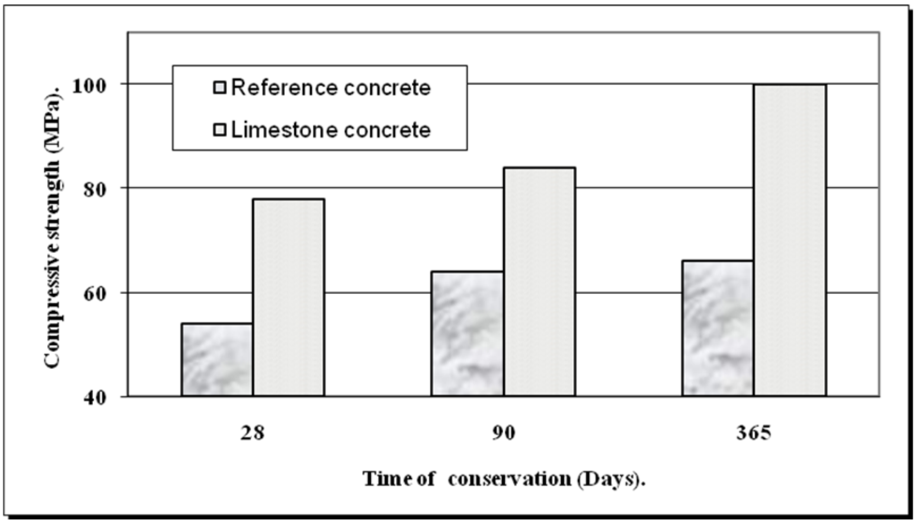

Figure 6. Influence of curing time on the specimen compressive strength

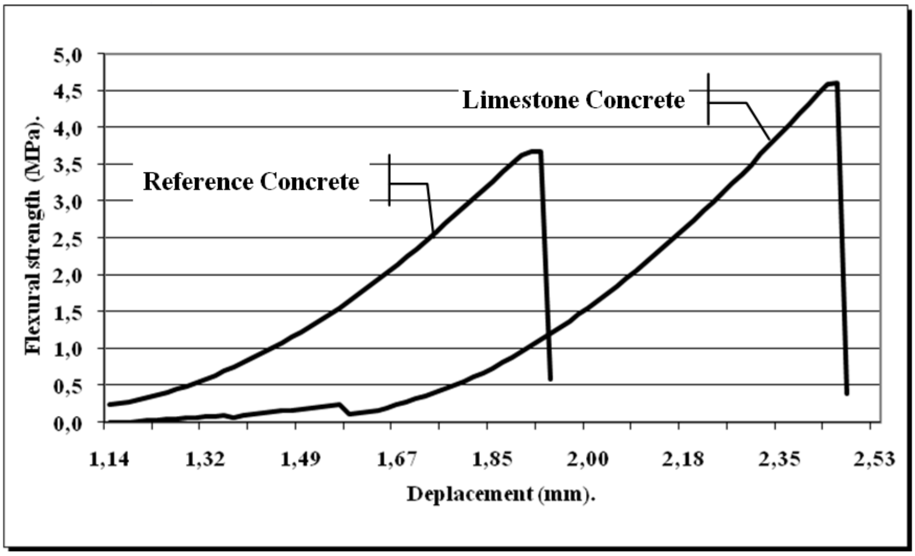

Figure 7. Flexural stress – displacement curves evolution after 3 months hardening

After 365day curing, an increase in compressive strength of about 51% has been recorded whereas tensile strength increased by 25% after three month curing. This was expected due to the beneficial role of the simultaneous use of limestone and a water reducer superplasticizer [5].

This improvement is attributed to the good quality of the materials mainly coarse aggregates and cement. It should be noted that, even for the reference concrete, the reached mechanical strengths have been very satisfactory. On the other hand, the incorporation of limestone leads to a significant increase in strength. This is obviously due to its dual role [6, 7]:

- The densification of the matrix by filler effect, thanks to its ultrafine particles which are inserted into the pores created by hydration of the cement and paste - aggregate interface transition zone.

- The addition of $CaCO_3$ accelerates the hydration of the C_3S at the early age by modifying the surface of the latter and by its nucleating effect [8].

4.2. Densities and Propagation Velocity of Sound Waves

The evolution of the densities of the different tested concretes is presented in Figure 8. The density of limestone concrete is systematically higher than that of the reference concrete: it is thus confirmed that the high fineness of limestone contributes to the increase in the compactness of the cement matrix.

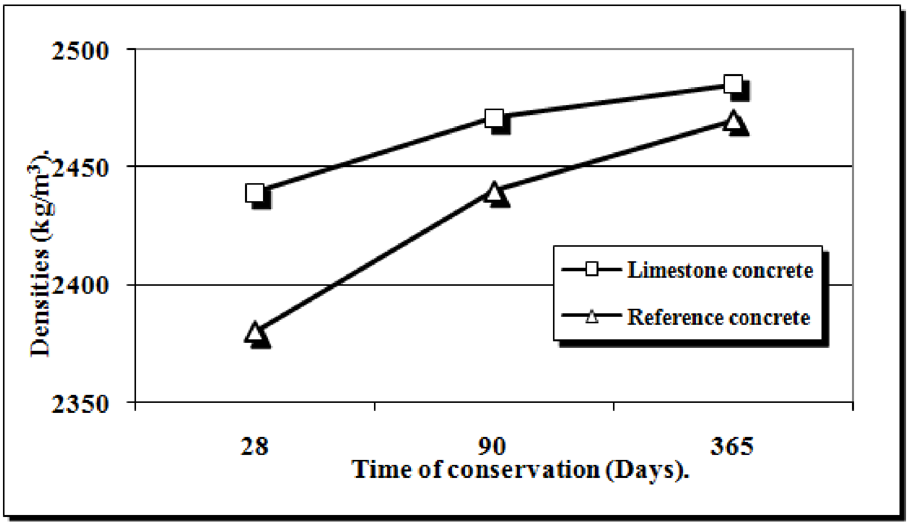

Figure 8. Influence of curing time on concrete density

Indeed, the incorporation of limestone with fineness greater than that of the used cement is inserted into the capillary pores and voids. This leads to the densification of the concrete skeleton. Non-destructive ultrasonic pulse velocity test is one of the most appropriate methods to assess the mechanical properties of a material.

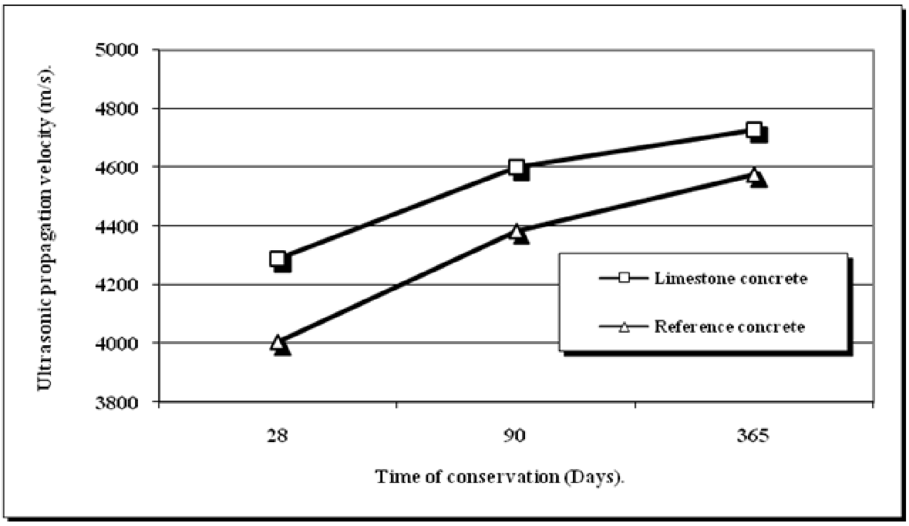

Figure 9. Influence of curing time on sound wave velocity through the elaborated concretes

It should be noted, from the results obtained (Figure 9), that the older the concrete, the greater is the velocity of sound for both concrete compositions, which is coherent with the evolution of compactness over time. A significant difference has been observed between the reference concrete and limestone concrete. The velocity is greater at all maturity ages, which is a result of the densification of the structure.

4.3. Shrinkage and Creep

Any concrete which is not stored in water undergoes the endogenous shrinkage which is a consequence of chemical contraction developed during the hydration of Portland cement. The absolute volume of hydrates formed is less than the absolute sum of the volume of cement and the initial water. The shrinkage is also a phenomenon that significantly influences cracking of concrete and, on the other hand, certainly influences too tensile strength.

In concrete with very low w/c ratio, when the cement starts to hydrate, fine capillaries begin to dry quickly creating high tensile stresses [9]. These tensile stresses develop at a time when the strength of the hydrated cement paste is low, which can cause a concrete cracking. Jensen et al. [10] have shown that the cement paste with a w/c ratio of 0.36 which hydrates in the presence of an external source of water undergoes small shrinkage and once all the grains of cement have hydrated does not show any porosity.

The total shrinkage of concrete containing limestone addition, measured on 28 x 7 x 7 cm^3 test specimens is less than that measured on the reference concrete (Figure 10). The initial shrinkage of limestone HPC is directly proportional to the amount of cement, which here is lower than that of reference HPC, it will thus be reduced.

Deferred behaviour is mainly controlled by the gradual moisture movements in the hydrated cement paste which are influenced by various factors. The first parameter is the hydration process which is considered as a consumer of the water introduced during the preparation of concrete. Next, environmental conditions introduce a water gradient within the heart of the material. Finally, there is also in the case of creep, the influence of the load, its intensity and the age of concrete at loading, the materials and mix-proportions, temperature as well as the time and humidity.

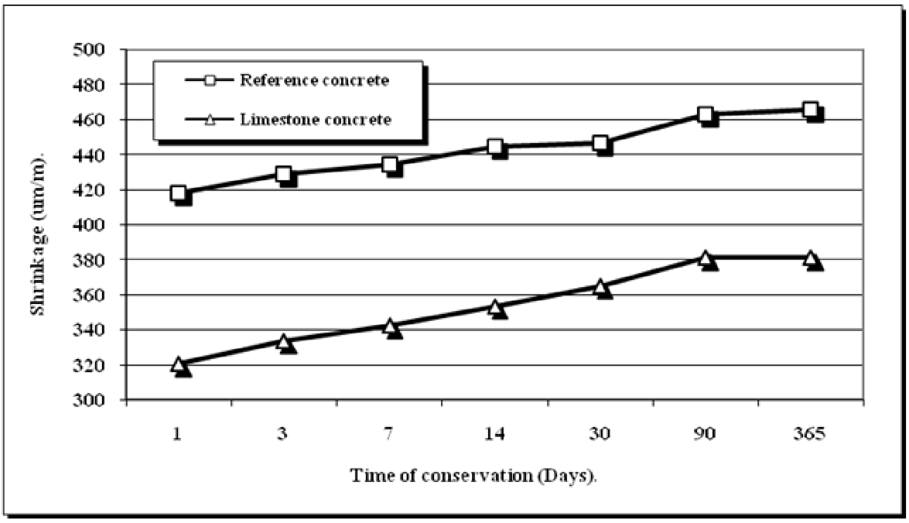

Figure 10. Influence of curing time on shrinkage of the different concretes

Mechanisms of shrinkage (spontaneous strain) and creep (time-dependant strain under steady load) are similar to the point that shrinkage can be referred to as creep under water loading.

The three phases of creep phenomenon can be explained by the following mechanisms:

Phase 1: It is associated with a short-term deformation. The reversible nature of this part of deformation was highlighted by Jensen et al. [10]. This phase is probably due to a redistribution of water to areas of lower pressure by microdiffusion.

Phase 2: This illustrates the linearity between shrinkage and creep. This puts forward the idea that shrinkage is similar to water flow behaviour under load. This phase is irreversible and can be attributed to micro shear stresses in hydrated gel, and thus to a release of stored energy. In the case of shrinkage only the potential energy may not be sufficient. On the opposite, it should be noted that creep specimens have sufficient energy to dislocate the C-S-H layers.

Phase 3: In this particular case, the energy level is higher and can potentially increase the number of sites likely to be affected by micro shear stresses. The possible existence of this phase reflects the existence of a threshold below which there is no possible movement within the microstructure. It could be assumed that the energy dissipation is such that no other failure can occur. It should be noted that this third phase is not assimilated to tertiary creep leading to the ruin of the material [11].

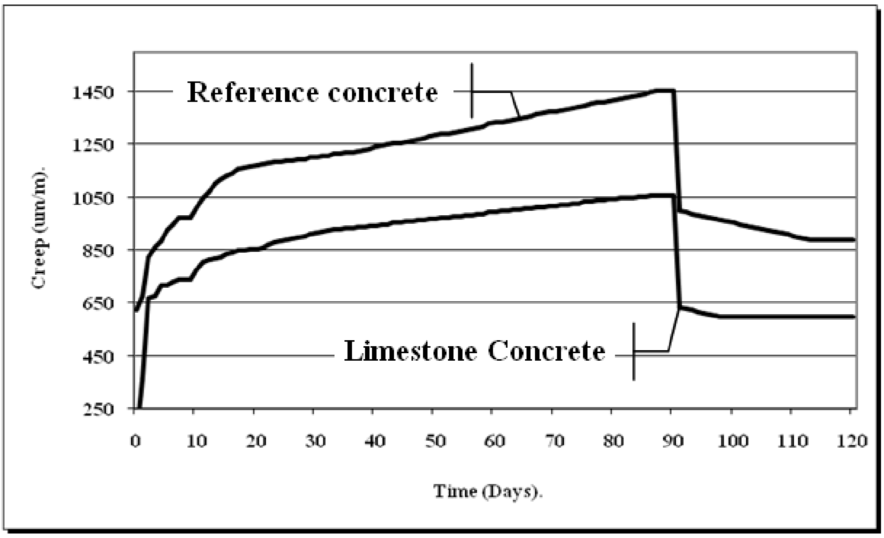

Figure 11. Creep evolution of the different concretes

A low total creep deformation of high-performance limestone concrete results from low W/B. The water movement between the layers of hydrates is leading to the activation of concrete creep. The substitution of 10% cement by limestone with finesse, greater than that of cement, should lead to a higher densification. Thus, if creep was mainly due to the moisture movement between the layers of C-S-H, its amplitude should be thus reduced.

Fine limestone particles, owing to their higher surface area on the order of 16 600 cm^2/g, agglomerate around anhydrous cement grains and prevent hydration at the early ages after manufacture. The barrier they form, leads to an expansion under load (dilatancy) limiting creep which, at long term, is lower than that of reference concrete (Figure 11).

4.4. Microstructure

4.4.1. Internal Microstructure

The cement is one of the most complex systems to describe in terms of chemical composition, crystalline structure or morphology of the solid phases resulting from hydration. The morphology of C-S-H has been widely studied by Transmission Electron Microscopy. Viehland et al. [12,13] have shown the existence of two morphological profiles in the tobermorite, described as an amorphous region and a nanocrystalline isotropic region.

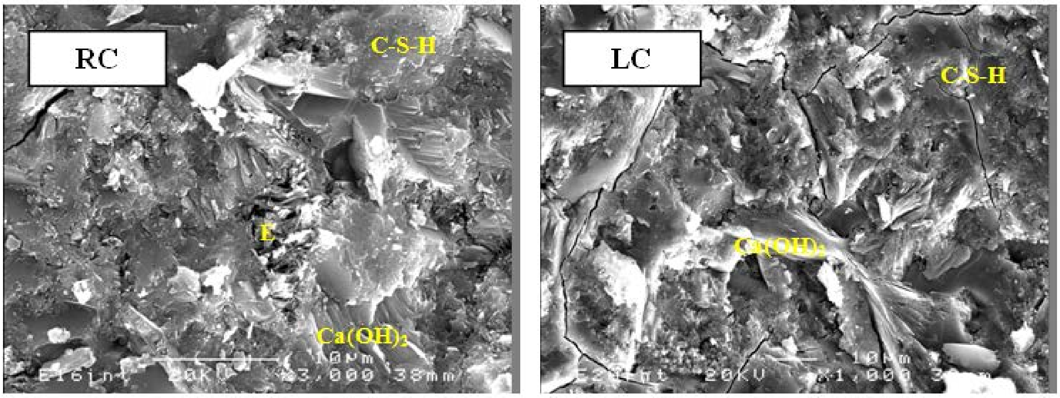

Figure 12. Scanning electron micrograph of different concrete specimen microstructure

High magnification electron micrographs on concrete after 365 days of curing (Figure 12) have been performed to highlight the morphological aspects. It should be noted that the microstructure of limestone concrete has been slightly improved with relatively denser interfaces and containing more C-S-H, which characterize HPC incorporating cementitious materials. The calcium silicate hydrate (C-S-H) appears to be in a cellular form (honeycomb) and more particularly showing dense morphology [14].

These observations confirm the measurement results of ultrasonic wave velocity from which the densification of the cement matrix with the introduction of limestone is shown evident. This explains the high mechanical strength and the higher densities previously noticed [15].

However, in reference concrete at an age of 365 days, an important presence of lime in the form of Ca $(OH)_2$ crystallized in piled hexagonal layers has been noticed.

4.4.2. Interfacial Transition Zone

The study of aggregates - cement paste bond has been the subject of a lot of work and all authors agree that these bonds account for the acquisition of the mechanical properties of concrete.

In the interfacial transition zone that forms between the cement paste and the aggregate in concrete, the hydrate crystallization is different from the bulk hydrated cement paste. This interfacial transition zone is generally the weakest point of concrete because it is considered as a zone of reduced cohesion in which cracks propagate and the strength is considerably limited. Several authors have reported that in this area the portlandite (CH) is formed in large quantities at the expense of the rest of the cement paste [16].

On the behaviour of concretes submitted to indirect tensile tests, rupture occurs along the aggregate, this interfacial area called interfacial transition zone which seems to be the most stressed and the most susceptible to failure in a concrete under a tensile loading.

The rupture maps cross differently the aggregates and the paste- aggregate bond. This leads to think that the applied force is distributed over the interfacial transition zone and aggregates. When the failure occurs at the transition zone, this may happen as a result of the good strength of aggregates whereas the interfacial transition zone is considered as mechanically weak. When the fracture is intergranular, this means that aggregates are not strong enough [17].

The examinations of the interfacial transition zone in reference concrete (Figure 13) show that this area is more crystalline, more porous and softer than the bulk cement paste due to excessive ettringite. Cracks bypass the aggregates then spread into the matrix, while in the case of calcareous concrete the interfacial transition zone is denser and more compact because of the incorporation of limestone [1].

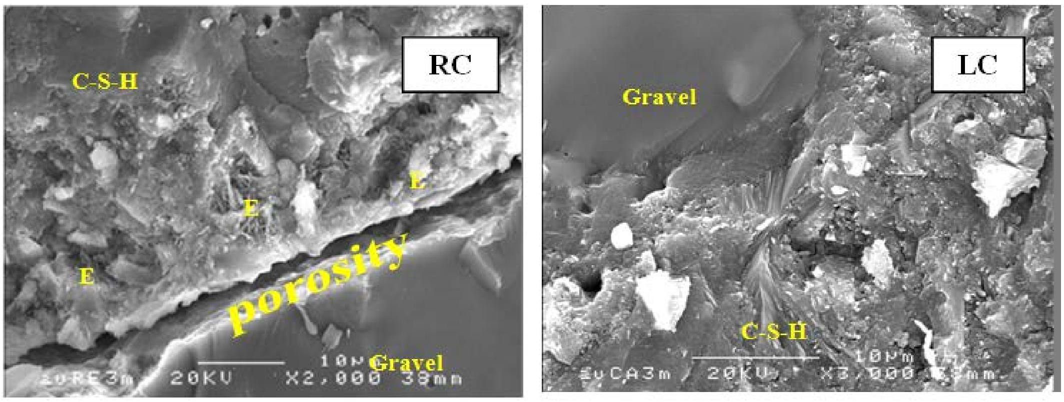

Figure 13. Scanning electron micrograph of the interfacial transition zone of different concrete specimens

4.4.3. Analysis by X-ray Diffraction.

Figure 14 illustrates the influence of the addition of limestone on the different mineral formations. Crystalline phases of both reference and limestone concretes are identical in nature but of very different amounts. The calcium silicate hydrates of general formula $xCaO.ySiO_2.zH_2O$ have a nanometric local structural order that makes them difficult to identify by X-ray diffraction [18].

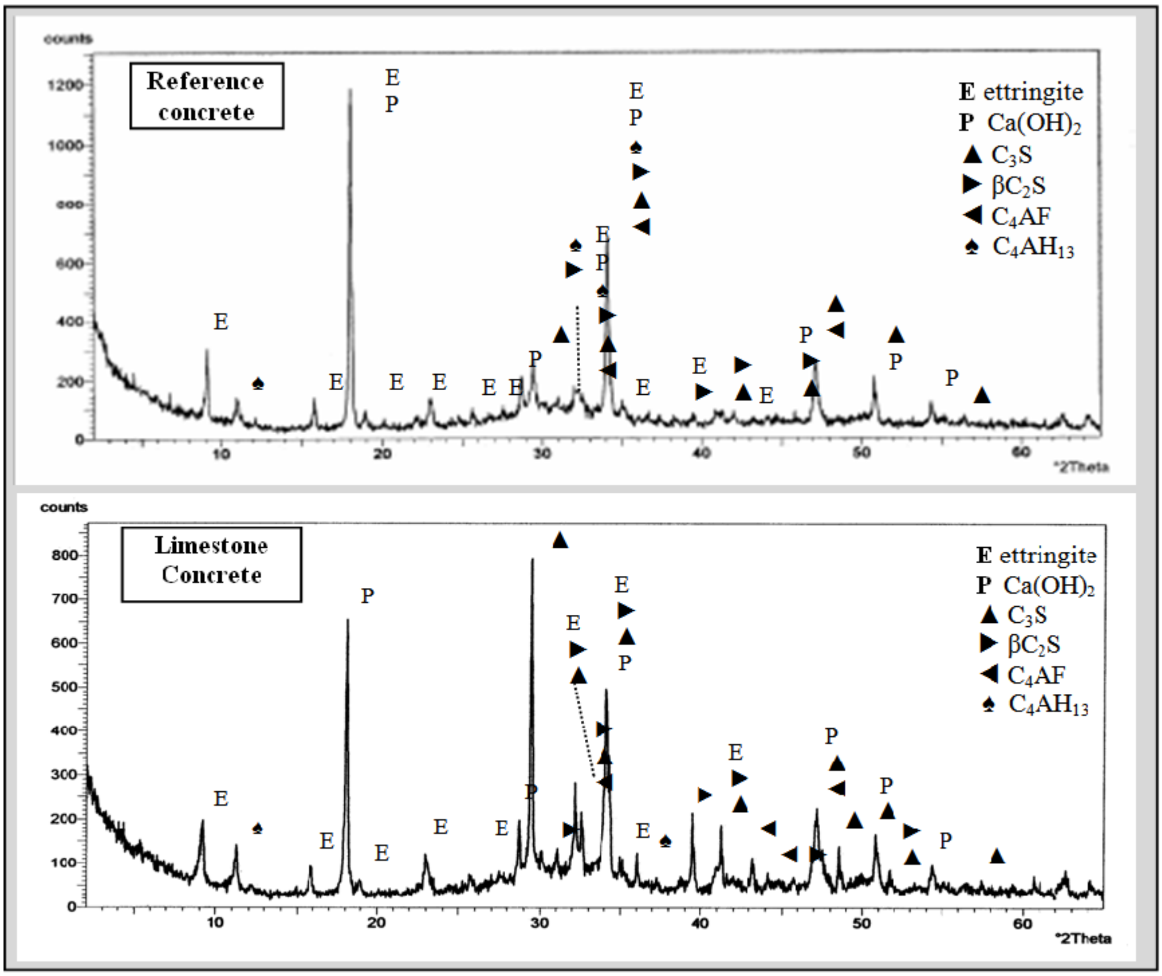

Figure 14. X-ray diffraction analysis of concrete specimens after 365 days of hardening

For a given cement, the amount of formed C-S-H and Ca $(OH)_2$ mainly depends on the water / cement ratio and reaction time. In a completely hydrated cement paste, the calcium silicate hydrates occupy 50 to 65% by volume of solids, whereas the calcium hydroxide (Ca $(OH)_2$) constitutes 25 to 27% of the latter volume. The C-S-H phase is therefore the predominant phase on which depend the evolution of physical characteristics, particularly the mechanical properties of the material. The structure of C-S-H is not well defined, but all observations indicate that it forms a pseudo gel poorly crystallized [19].

Ettringite crystallizes in the form of needles (with hexagonal base), often radiating around anhydrous cement grains (not expansive). The shape and size of the ettringite depend directly on the nature of the ions in the interstitial phase, the concentration of Ca $(OH)_2$ and ambient temperature [17,20]. It should be noted that in the limestone concrete, the presence of ettringite is lower compared to reference concrete.

5. Conclusion

The results of this investigation show that the addition of limestone contributes to improve the physical, mechanical and microstructural properties of elaborated high performance concretes.

At 365 days of conservation, an increase in the compressive strength of about 51% and in tensile strength by 25% has been noted. This was expected due to the beneficial role of the simultaneous use of limestone and water reducer superplasticizer.

Indeed, the limestone addition with a higher fineness than that of the used cement is inserted into voids and capillary pores and leads to the densification of the concrete skeleton. The ultrasonic propagation velocity which is high enough in limestone concrete confirms this result.

The total shrinkage of concrete with addition of limestone is lower than that measured on the reference concrete. This occurs as a result of cement amount reduction and the sufficiently rigid cementitious skeleton that opposes deformations caused by the removal of adsorbed water. It is assumed that creep is mainly due to the moisture movement between the C-S-H layers. The amplitude is here reduced, probably because of the new hydrated compounds which create a barrier to the latter movement.

It has been shown that the finely ground limestone improves the microstructure with significantly denser morphologies and high C-S-H content, but less portlandite is produced. Therefore, the densification of the matrix induces a significant increase in both tensile and compressive strengths.

The interfacial transition zone is the link of the chain the most sensitive to rupture in a conventional concrete especially in tension, which is not, however, the case of concrete with limestone addition in which this transition zone is denser and more compact.

For limestone HPC, the tensile strength is significantly improved compared to the reference concrete. However, it should be noted that a failure occurs suddenly and this is may explain the increase in strength which is often associated with greater brittleness.

Acknowledgments

The study was performed with the financial support of the French-Algerian research collaboration (CMEP-Tassili) between the laboratory of materials, procedures and environments of the University of Boumerdes and the civil and mechanical engineering laboratory of INSA-Rennes in France. The authors would like to thank EGIDE and the laboratory of chemical science and inorganic materials for their support.

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