Ecological and economical mortars made with dune sand and cements in combination with local mineral additions

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ABSTRACT

The aim of this study is to formulate and characterize, with different methods, mortars prepared with dune sand and Algerian clinker in combination with several admixtures, natural additions or industrial by-products as pozzolan, granulated blast furnace slag and marble powder.
Mineralogical and chemical compositions of the initial products are studied with X-ray diffraction (XRD), SEM, EDX and X fluorescence (XRF). Grain size distribution of anhydrous cements and additions (absolute density, Blaine specific surface (SSB) and laser granulometry) were carried out.
Mortar strengths are acceptable at 28 days: between 5 and 6MPa in bending test and between 28 and 41MPa in compressive test. These resistances improve clearly to reach high performances after 1 year: between 7 and 9MPa in flexural test and between 43 and 61MPa in compressive test.
The microstructure was studied using SEM coupled with microanalysis EDX; these observations explain the increase mechanical strength.
Results show that it is possible to obtain mortars with high mechanical performances in long-term and, ecological and especially economic advantages with a good formulation of those mortars containing dune sand and additive cements (binary, ternary or quaternary) with super plasticizer adjuvant.
Keywords: mix design, characterization, pozzolan, slag, marble, dune sand Algeria.

1. INTRODUCTION

The Algerian South consists of an inexhaustible dune sand reserve, it is very important to investigate possibilities to insert this local material in mortars. In the last decades, the studies were multiplying on the physico-chemical characteristics of this sand characterized by its smoothness due to wind carriage and his very thin granular extend (Bédérina *et al.*, 2005).
On the other hand, most cement plants consume a lot of fossil energy and produce a large amount of undesirable products, which affect the environment. In order, to reduce energy consumption and CO_2 emission and increase production, cement manufacturers are blending or intergrinding mineral additions such as slag, natural pozzolan, sand and limestone (Kenai *et al.*, 2004). The valorization of waste and industrial by-products in civil engineering can give encouraging results as well in terms of economy, ecology and behavior (Marchal, 2002).
The additions of the blast furnace slag to cement present an economical interest in cement industry and a technical interest in the field of construction (Samet *et al.*, 2004 ; Pal *et al.*, 2003). The energy cost of this by-product is practically zero; nevertheless it requires more energy for crushing than the clinker (Dubosc, 1998).

The increase of the specific surface (3500 cm^2/g to 4200 cm^2/g) clearly improves the mechanical resistances for the concrete containing up to 30% of slag (comparable resistances to those of concrete without slag) (Naceri *et al.*, 2006).

The substitute of ordinary cement by the pozzolan of Beni-Saf (Algeria), available in considerable quantities, makes it possible to improve mechanical strengths of concrete at medium and later ages. Former American studies on the use of pozzolan indicate that cements mixed with pozzolan have damp-proof qualities (San Francisco Golden Gate). Algerian pozzolan (Beni Saf) was previously studied (Mebrouki *et al.*, 2004 ; Kaid *et al.*, 2009).

Chaid (Chaid *et al.*, 2004) studied the addition of ultrafine pozzolan in the aim to obtain high performances concretes. He obtained at 28 days compressive strength of concretes higher than 50MPa with the help of super plasticizer and correctly adjusted composition.

Recently, the use of the marble powder as material of replacement was studied. Agarwal and Gulati (2006) showed that the presence of marble powder in the matrix improves the compressive strength at the young age. Topçu *et al.* (2009) point out the filler effect of marble powder: the workability of self compacting concretes was not affected but mechanical decrease for high marble powder content (200 kg/m^3). According to other authors (Kavas and Olgun, 2008), short and long-term strength of mortars can be improved by incorporation of slag and fly-ashes in the matrix.

Combination of several cementing additions (2 or 3) with clinker and gypsum allows the development of new types of hydraulic binders (ternary or quaternary cements) having higher mechanical properties and better durability than Portland cement CEM I (clinker alone) (Laldji *et al.*, 2004).

In this experimental work, we studied the influence of cements in combination with several admixtures, natural additions or industrial by-products on the mechanical performances of the mortars containing dune sand.

2. PRODUCTS USED

2.1 Clinker

In our study, clinker (CLK) of the cement factory of Ain-El-Kébira (Sétif- Algeria) is used as activator, especially for blast furnace slag and natural volcanic pouzzolan ash. Its mineralogical composition (Bogue composition) is presented in Table 1. The natural gypsum (G) is used as regulator of setting time. In comparison with classical clinker, this one is rich in C_2S and C_4AF.

Table 1. Clinker Bogue composition (%, by weight).

C_3S	βC_2S	C_3A	C_4AF
61.23	17.13	3.57	15.60

2.2 Granulated slag

The granulated blast furnace slag (GBFS) used in this study is an industrial by-product from iron and steel industry obtained from the metallurgic unit of EL-Hadjar (Annaba- Algeria). This slag was studied by Achoura (2005) as sand and as filler.

2.3 Pozzolan

Natural pozzolan (PZ) extracted from Beni-Saf quarry, in west of Algeria, has the appearance of crushed pumice stone and slag. This material is described by Belas Belaribi *et al.* (2003). Durability of mortar with Beni Saf pozzolan was studied by Kaid *et al.* (2009) and performance characteristics of lightweight aggregate concrete containing this pozzolan by Mouli *et al.* (2008) and Ghrici *et al.* (2006).

2.4 Marble powder

The marble powder used (MP) is a waste of flooring tile from industry (Bordj Bou Arréridj, Algeria).

2.5 Chemical admixture

A super plasticizer (SP) provided by the company GRANITEX (Algiers, Algeria) was used. This super plasticizer, MEDAFLUID SFR122, contains combined polymers. It is recommended for the production of the rheoplastic concretes with a very low E/C ratio. It allows the increase of the mechanical resistances in the long term. It is applicable to any type of cements which is conforming to the standard EN 934-2. The interval of recommended use is between 0.8 and 2.5% of the weight of the binder. The set of concrete is obtained in a good delay with 1% of additive. Its physical and chemical characteristics are presented in Table 2.

Table 2. Physical and chemical characteristics of the additive.

Nature	Apparent density	pH (1% in water)	Cl^- content	Dry extract
Liquid	1,20± 0,02	6,6 ± 0,1	< 1g/L	40%

3. MINERAL AND CHEMICAL ANALYSIS

3.1 X-ray diffraction analysis

The mineralogical composition is determined by X-ray diffraction. The XRD data were collected with Philips PW 3710 X-ray diffractometer with Bragg–Brentano geometry using Ni-filtered Cu Kα radiation, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–60° (2θ) in steps of 2θ = 0.02°.

The results of Figs. 1, 2, 3, 4 and 5 highlight:

- for the CLK: prevalence of alite (C_3S) and the absence of alkali,
- for G: composed quasi entirely of gypsum ($CaSO_4.2H_2O$) with quartz traces (SiO_2),
- for the GBFS: amorphous material (vitrified),
- for the PZ: prevalence of cordierite ($2MgO.2Al_2O_3.5SiO_2$) and analcime ($Al_2O_3.Na_2O.4SiO_2.2H_2O$), small quantities of hematite (Fe_2O_3) and cristobalite (SiO_2).
- and for the MP: composed only of calcite ($CaCO_3$).

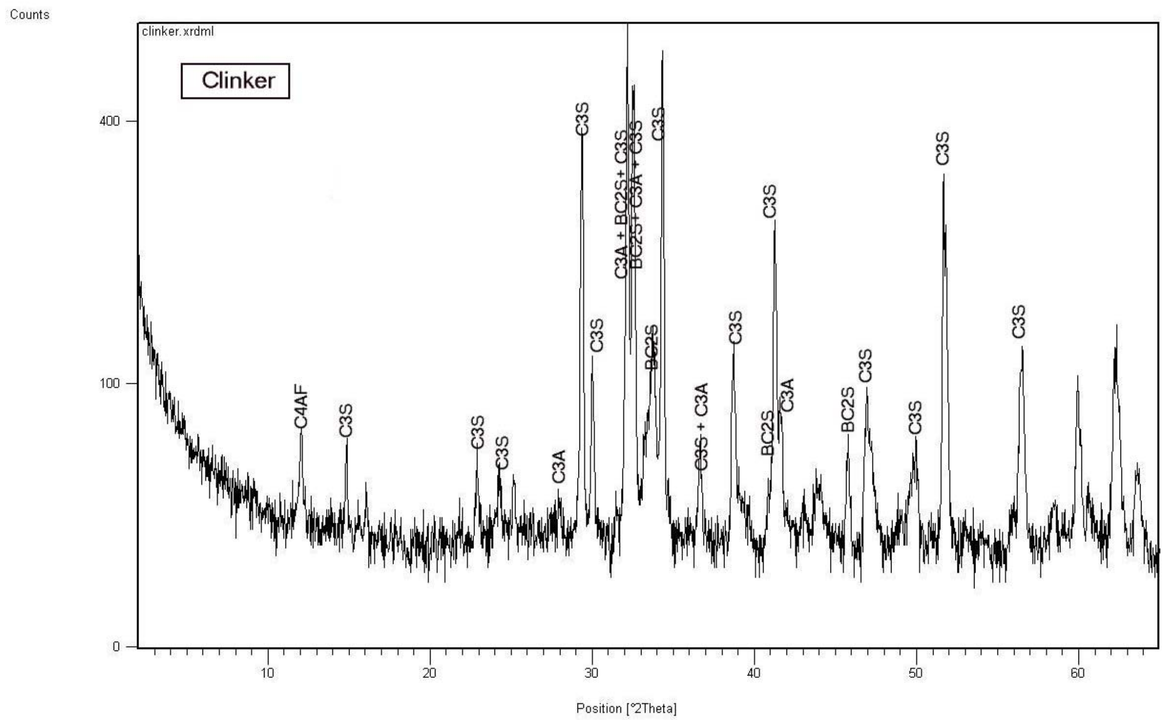

Figure 1. X-ray diffraction of the clinker (Cu Kα radiation, Ni filtered).

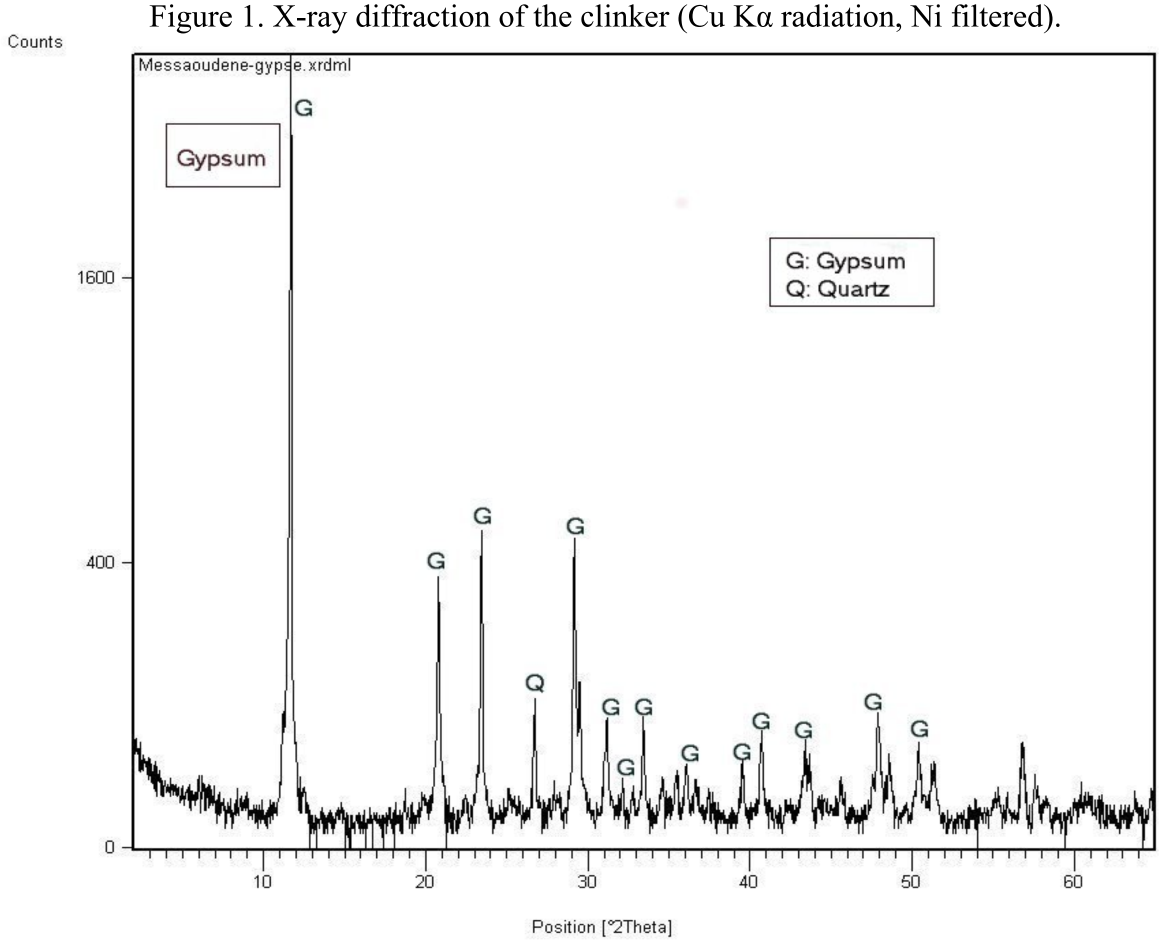

Figure 2. X-ray diffraction of the gypsum (Cu Kα radiation, Ni filtered).

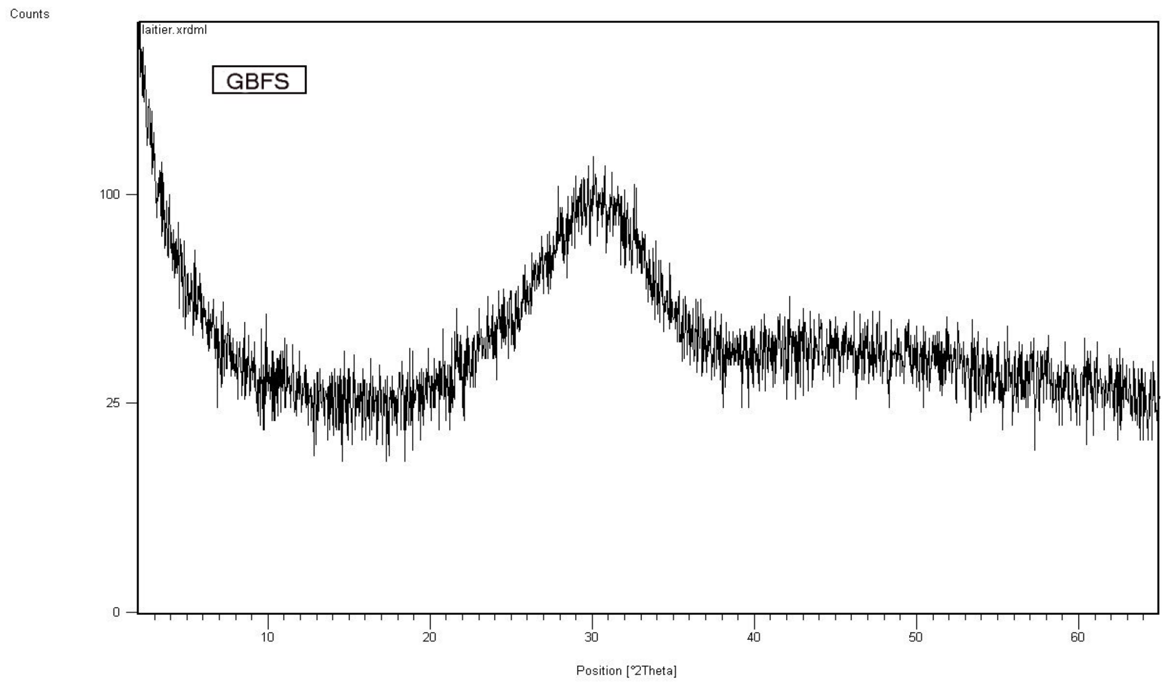

Figure 3. X-ray diffraction of the GBFS (Cu Kα radiation, Ni filtered).

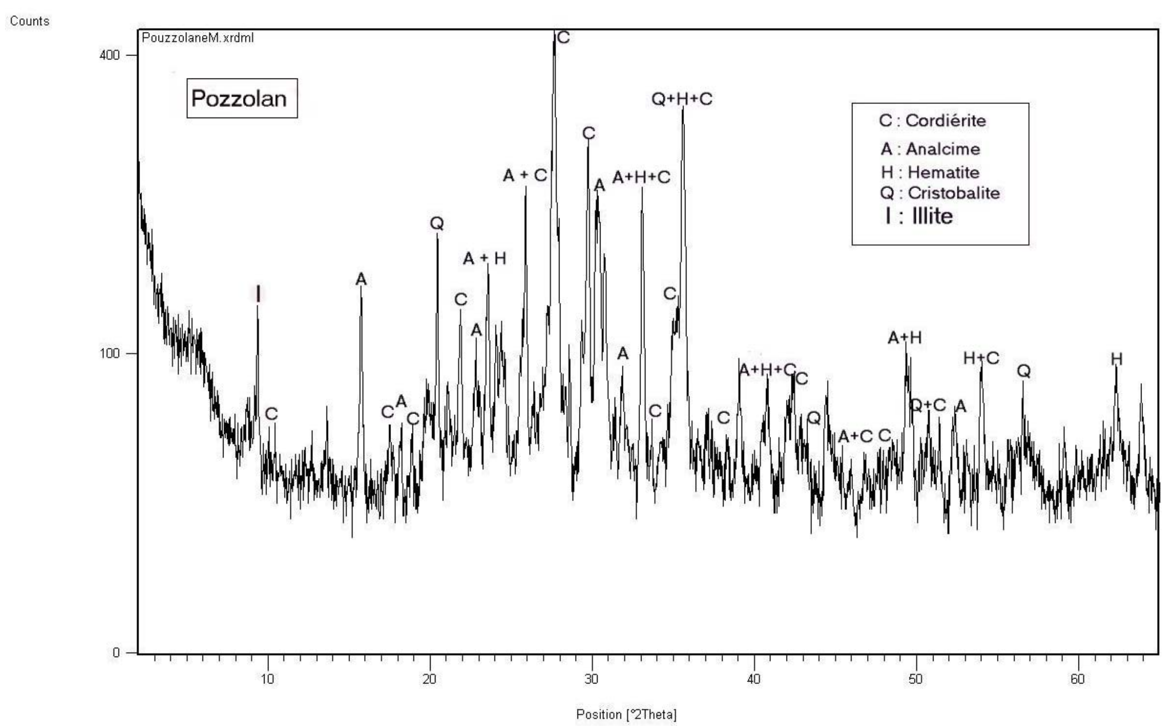

Figure 4. X-ray diffraction of the pozzolan (Cu Kα radiation, Ni filtered).

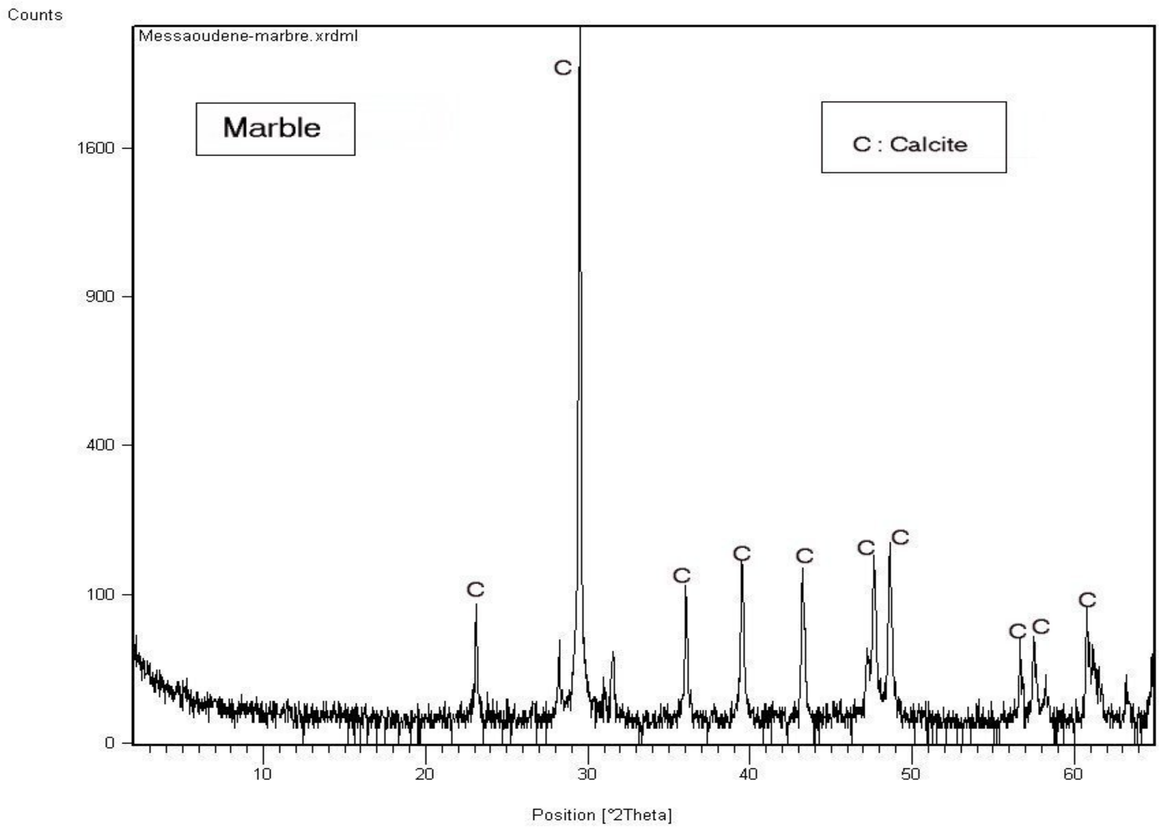

Figure 5. X-ray diffraction of the marble (Cu Kα radiation, Ni filtered).

3.2 SEM observations

SEM observations were conducted on a SEM FED (JEOL-JSM-6301F) using an accelerating voltage of 7 kV and a working distance of 15 mm. All the initial products are observed before crushing (Fig. 6).

Micro analysis data were collected using conventional JEOL-JSM-6400 Scanning microscope. Micro analysis of the samples was performed using an accelerating voltage of 20 kV and a working distance of 39 mm (Table 3).

These photos indicate:

1. for the CLK: particles of a few tens of micron, adherent ones with the others with a great porosity coming from hardening,
2. for G: its saccharoid form,
3. the PZ is presented in the form of ash and slag,
4. for the GBFS: a granulated form soaked with a closed porosity and finally for
5. the marble: poly crystalline with well formed crystals tangled up one in another.

The microanalysis by EDX confirms the observations of the analysis by diffraction.

Elementary proportioning of the CLK, the PZ and the GBFS are carried back in Table 3.

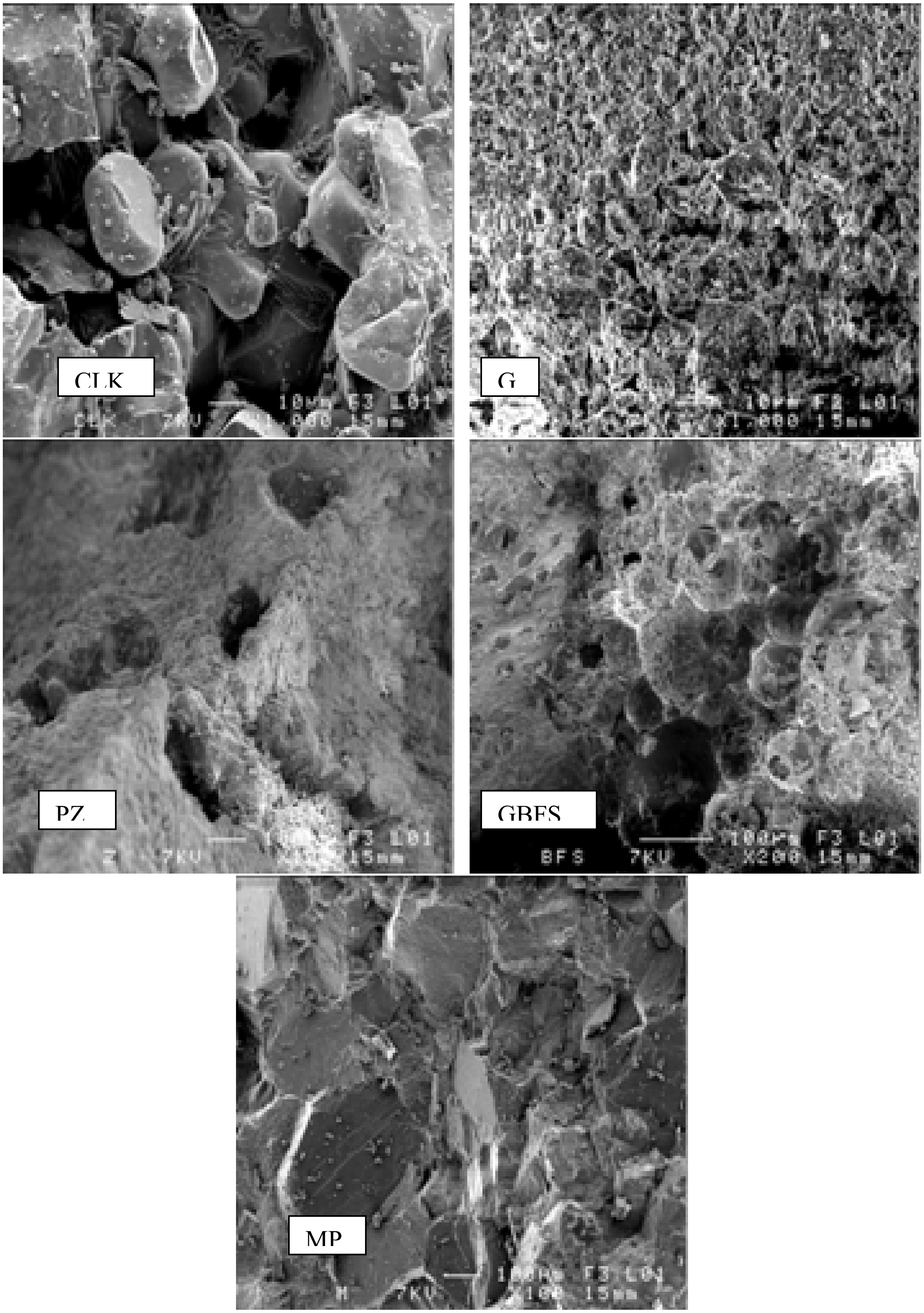

Figure 6. SEM observation of materials.

Table 3. Chemical composition of the clinker, pozzolan and slag

	Clinker		Pozzolan		Blast furnace slag	
	% mass	% atom	% mass	% atom	% mass	% atom
O	35.57	56.53	54.16	70.11	47.39	65.38
Mg	0.80	0.83	1.75	1.49	2.65	2.40
Al	0.92	0.87	7.78	5.97	3.76	3.07
Si	8.97	8.12	19.00	14.01	16.91	13.29
K	0.65	0.42	0.87	0.46	0.73	0.41
Ca	50.50	32.04	8.66	4.47	25.19	13.87
Fe	2.59	1.18	5.76	2.14		
Ti			1.01	0.44		
Na			1.01	0.91		
Mn					2.61	1.05
S					0.76	0.52

From these analyses, in one hand, we can observe that the most calcareous is the clinker. The slag contains half less Ca than clinker and the pozzolan 1/6th. In the other hand, the Si content increase as the Ca content decrease. During hydration process, the clinker will release lime. This lime would be consume by the slag and the pozzolan.

4. EXPERIMENTAL PROCEDURES

4.1 Preparation of mixtures

The products were crushed to obtain a granulometry lower than 1mm before being carefully mixed, then quads and prepared according to the proportions given in Table 4. Following the NF EN 197-1 standard, the binary cement (BC) is similar to a CEM I/B-S, and the four ternary cement (TC) and the quaternary cement (QC) are similar to CEMII/B-M. The grinding of the six types of cements were performed in vibratory mills. The chemical composition of cements thus prepared was determined by X-ray fluorescence, Table 5.

Table 4. Mixes composition of binders (%mass)

Binders	Clinker	Gypsum	Slag	Pozzolan	Marble	
BC	65	5	30	0	0	Binary cement
TC1	65	5	25	0	5	Ternary cement 1
TC2	65	5	20	0	10	Ternary cement 2
TC3	65	5	15	0	15	Ternary cement 3
TC4	65	5	0	22	8	Ternary cement 4
QC	65	5	11	11	8	Quaternary cement

Table 5. Chemical composition by X fluorescence (%mass)

Binders	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl^-
BC	24.87	5.33	4.77	58.81	2.36	2.20	0.36	0.06	0.00
TC1	23.03	4.85	3.93	58.16	2.22	2.79	0.40	0.13	0.02
TC2	20.75	4.38	3.69	57.30	2.35	2.29	0.37	0.10	0.04
TC3	18.95	4.00	3.55	58.28	2.25	2.57	0.33	0.14	0.06
TC4	23.64	6.39	5.38	52.01	2.31	2.48	0.53	0.21	0.04
QC	22.48	5.45	4.96	57.59	2.30	1.49	0.34	0.13	0.03

The absolute density of cements and Blaine specific surface (BSS) are carried back on Table 6. We can observe that for BC, TC1, TC2, TC3, more the addition of marble powder increases (or more the addition of slag decrease), more the density of cements decreases. It can be due to high density of slag and lower density of marble. On the contrary the densities of binary and quaternary cements are practically identical.

Table 6. Absolute density and specific surface Blaine

Binders	BC	TC1	TC2	TC3	TC4	QC
Absolute density	3,14	3,11	3,09	3,04	3,01	3,13
BSS (cm^2/g)	4170	4581	4770	4532	4438	4392

Granulometric analysis data given by a laser particle-measurement instrument were collected with CILAS 2 equipment.
The granulometry of the binders (Fig. 7) are practically the same for all types of cement. It is lower than 70 µm, with a maximum frequency around 11µm.

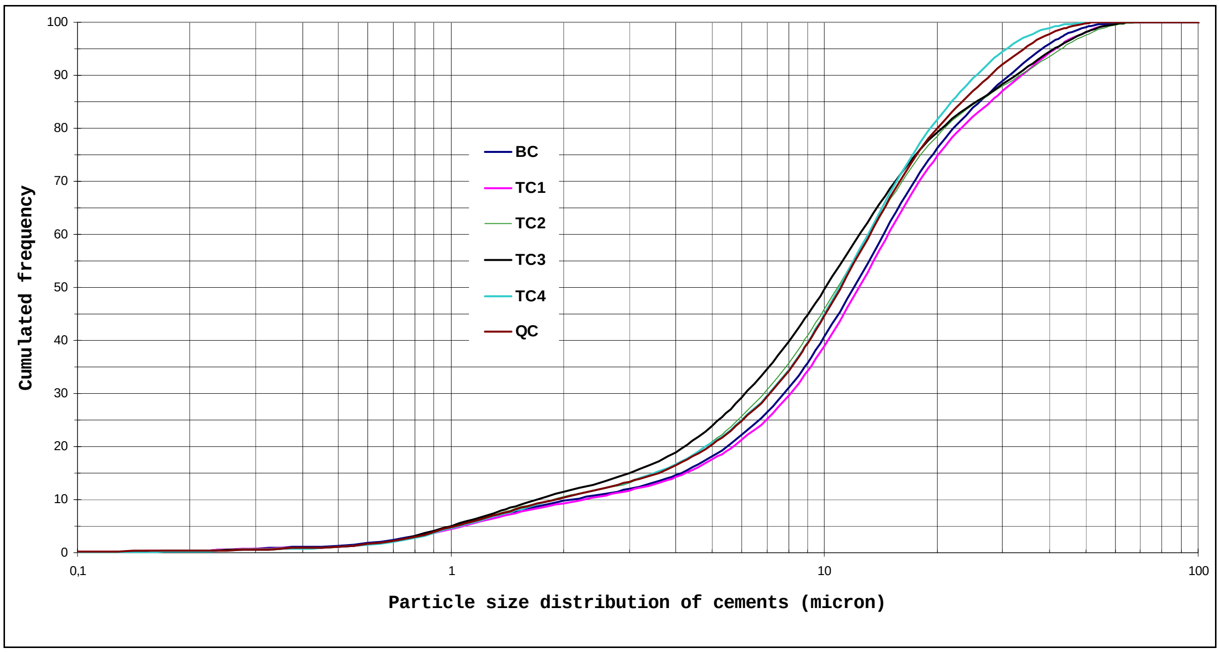

Figure 7. Granulometry of the binders.

4.2 Characterization of the dune sand

The dune sand (DS) was taken from "Maîter wadi", located between the hills of Boussaâda. This fine grained sand is carried by southerly winds. According to standard NF P18-304, the granulometric study is carried out after washing in a sieve of 80 µm and stored in the drying oven during 24h.
Figure 8 shows that 73% of the grains have a diameter lower than 0.63 mm. The fineness modulus is worth 2.39 (NF P 18-560). The visual sand equivalent is about 95% and 75% by piston; the methylene blue value is about 0.1. Therefore, we can conclude that it is clean sand. Its measured specific gravity is about 2.6.
The mineralogical composition (Fig. 9) determined by X-rays diffraction shows that this sand is siliceous, more than 95% of quartz and some traces of calcite.

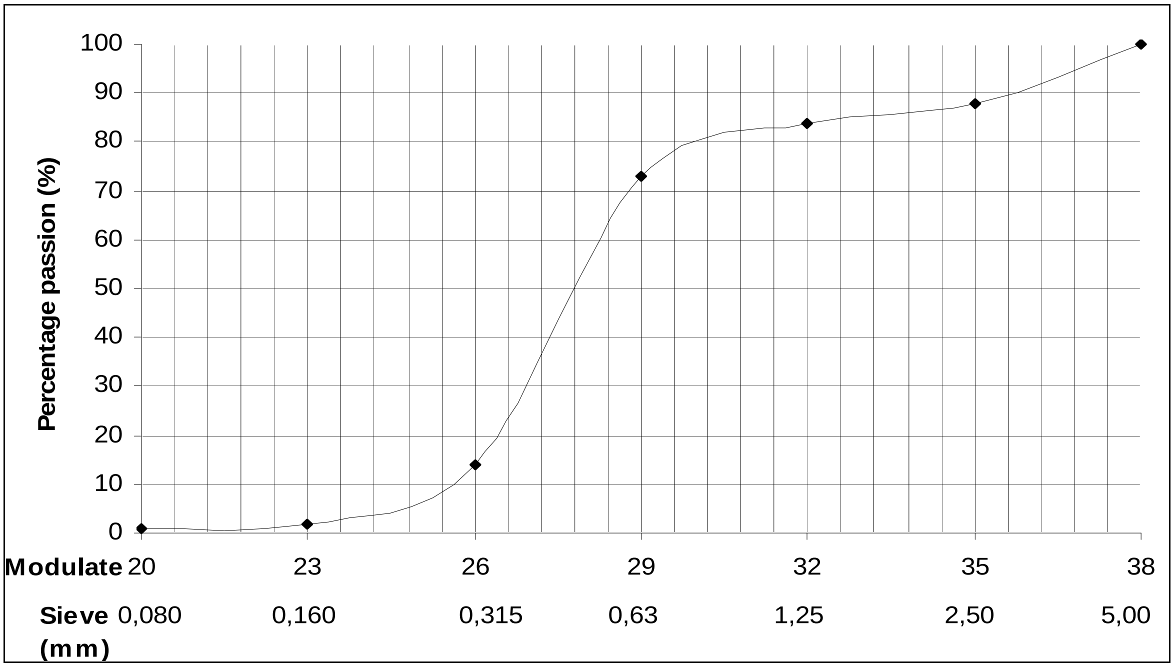

Figure 8. Granulometry of the dune sand.

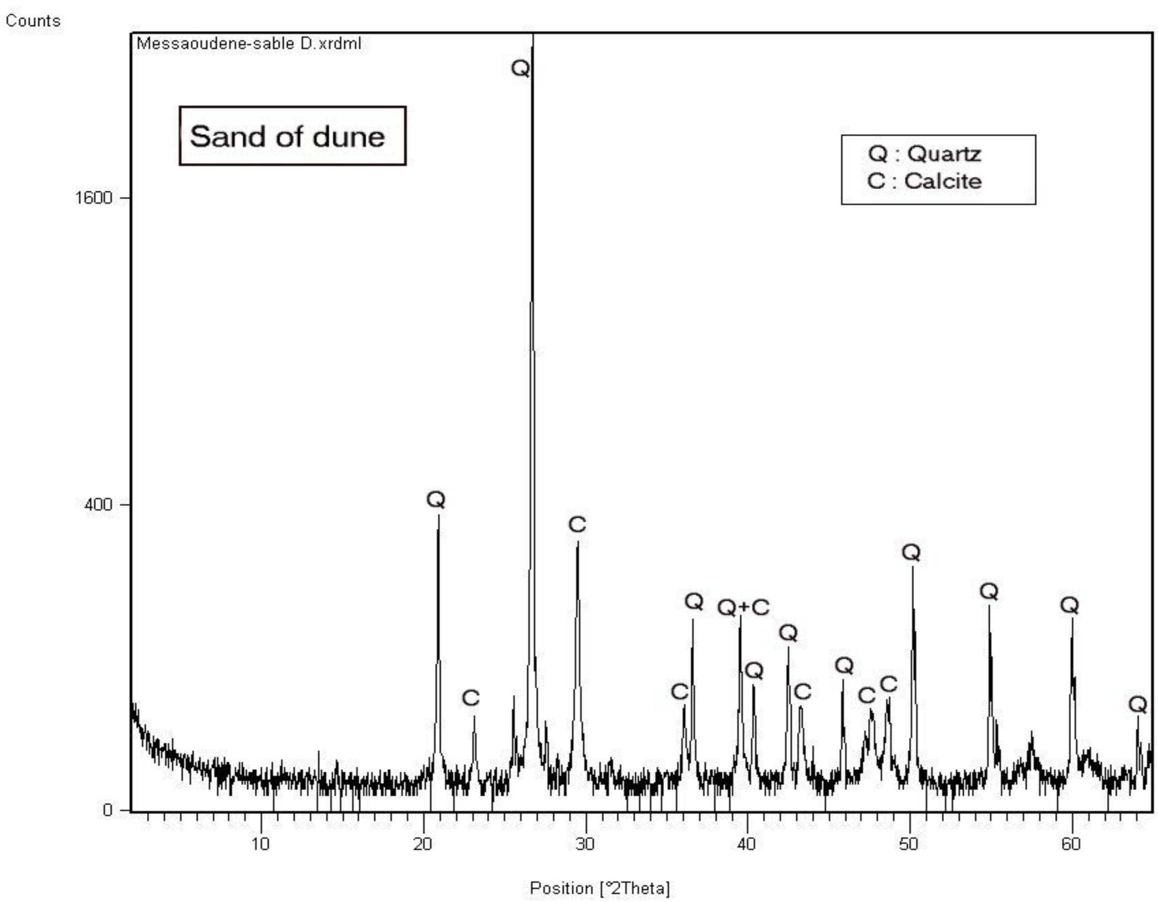

Figure 9. X-ray diffraction of the dune sand (Cu Kα radiation, Ni filtered).

4.3 Formulation of the mortars and mechanical characterization

Dune sand, cement and the chemical admixture are mixed with water according to the proportions presented in Table 7, with a water/binder ratio = 0.45. After production of mortars, the moulded specimens were covered with plastics sheets at 20 ± 1°C for 24 ± 1h in accordance with the standard EN 196 1. The samples were transferred and stored in water until the time of testing. For each mix, prisms of size 4 x 4 x 16 cm^3 were tested to determine flexural and compressive strengths, respectively, at 7, 28 days and 1 year. The results are presented on figures 10 and 11.

Table 7. Composition of the mortar

Binder (g)	DS (g)	Water (g)	SP 1% (ml)
450	1350	202,5	4

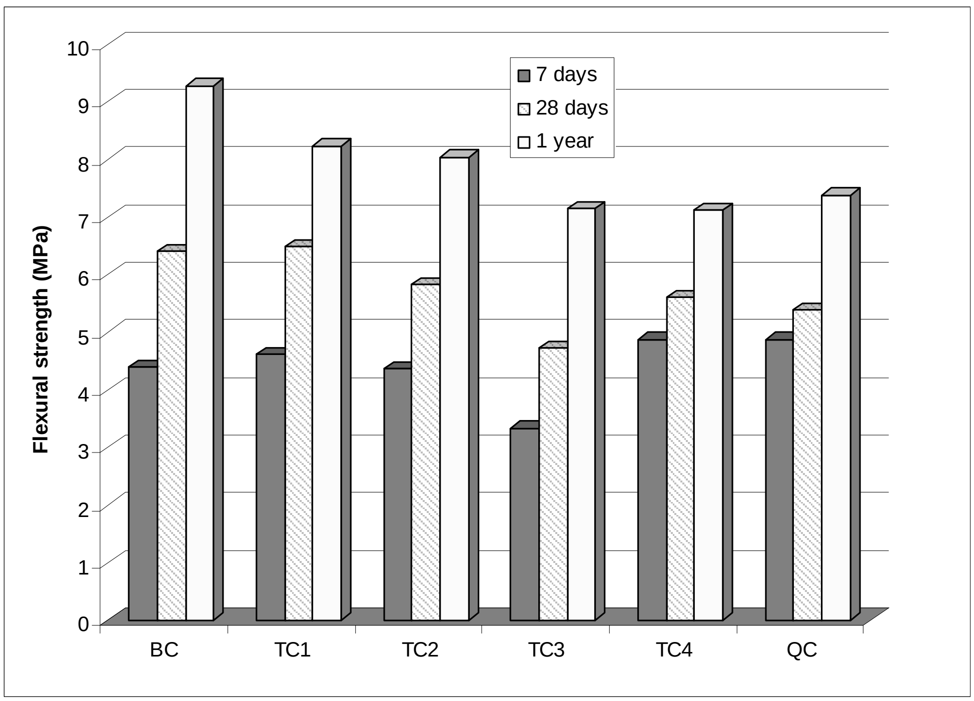

Figure 10. Evolution of flexural strengths.

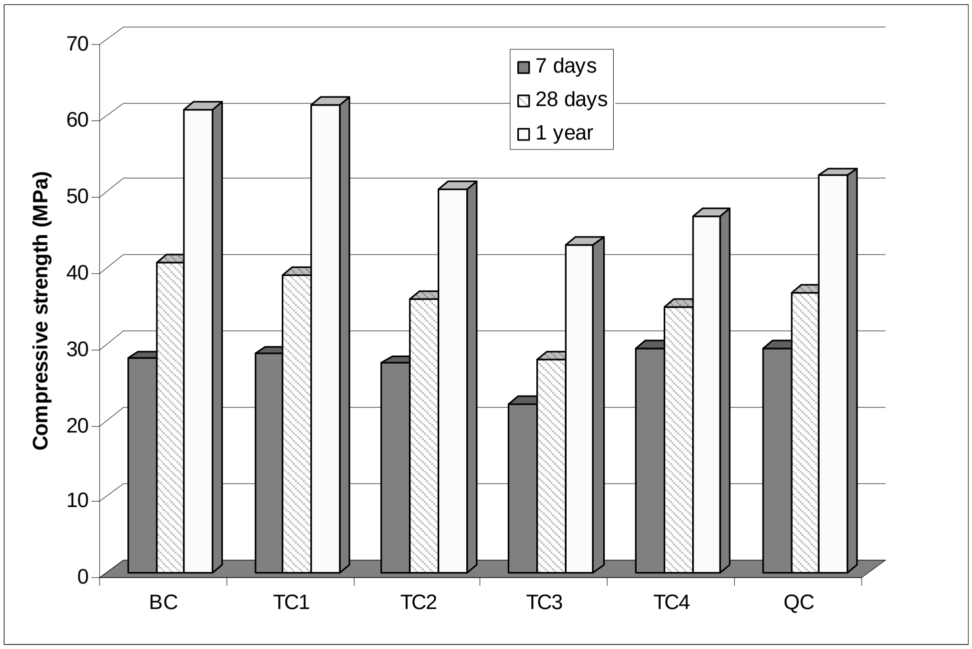

Figure 11. Evolution of compressive strengths.

The mortar strengths are acceptable at 28 days: between 5 to 6MPa in flexural test and between 28 to 41MPa in compressive test. These resistances improve clearly to reach very important performances after 1 year: between 7 to 9MPa in flexural test and between 43 to 61MPa in compressive test (strengths improvement about 50% between 28 days and 1 year). Highest strengths are obtained with slag addition (30%) BC. 5% replacement of slag by 5% of marble conduct to the same results (TC1 cement). Beyond 10% replacement of slag by marble (TC2 and TC3), we can observe an important decrease of strength (especially of compressive strength). Contrary to popular belief, the mortar with pozzolan (TC4 and QC) give the highest strength at short term. The quaternary cement (QC) gives similar strength at short term and quite correct strength at 28 days (equivalent CEM II32.5) and at long term (51 MPa).
The evolution of resistances according to time is explained by the latent hydraulic property of the hydration of the mineral additions (slag and pozzolan).

4.4 Internal Microstructure

The study of the microstructure, carried out by SEM and confirmed by microanalysis shows that after 28days and 1year, the hydration of the cementing matrix led to the formation of CSH (calcium silicate hydrate- gel-like flocks), small quantities of portlandite crystals CH and the ettringitte (fine needle-like crystals) C_3A, $3CaSO_4$,$32H_2O$ (Figs. 12 and 13).
We observe a less porous structure, explained by the specific surface of cement greater than 4100 cm^2/g, the addition of the industrial fillers (slag and marble powder) and the use of adjuvant. Whether with blast furnace slag or with Beni Saf pozzolan to a lesser extent, internal porosity observed by SEM is very low. The amount of portlandite is also low: in the both cases, it reacts to form a second generation of silicates and aluminates hydrated lime. These reactions conduct to a sealing of the porosity.
We can observe a very tight contact between marble grains and cement hydrates but the marble powder seems to be non reactive (no epithaxy between hydrates and $CaCO_3$). The marble grains

are known to be nucleation sites at the beginning of hydration process and contributes to block the porosity.

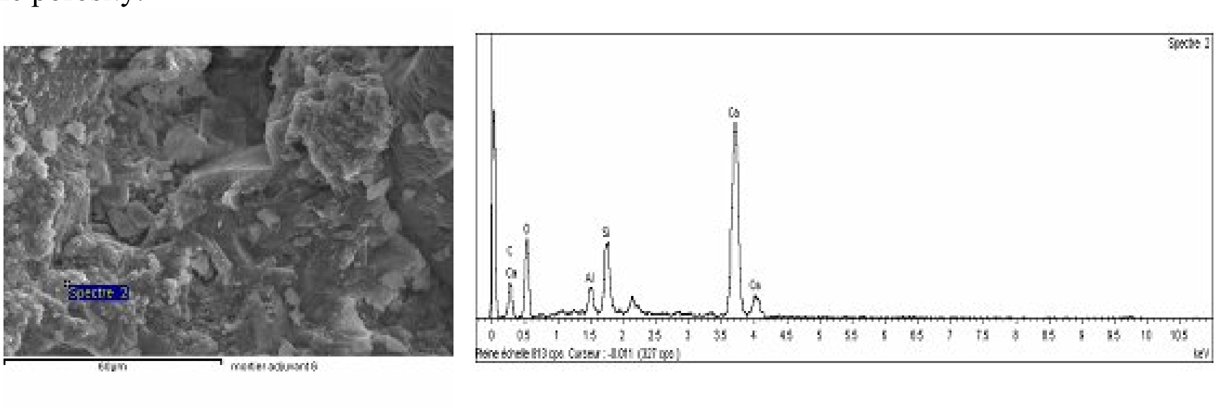

Figure 12. SEM observation of mortar containing quaternary cement (QC).

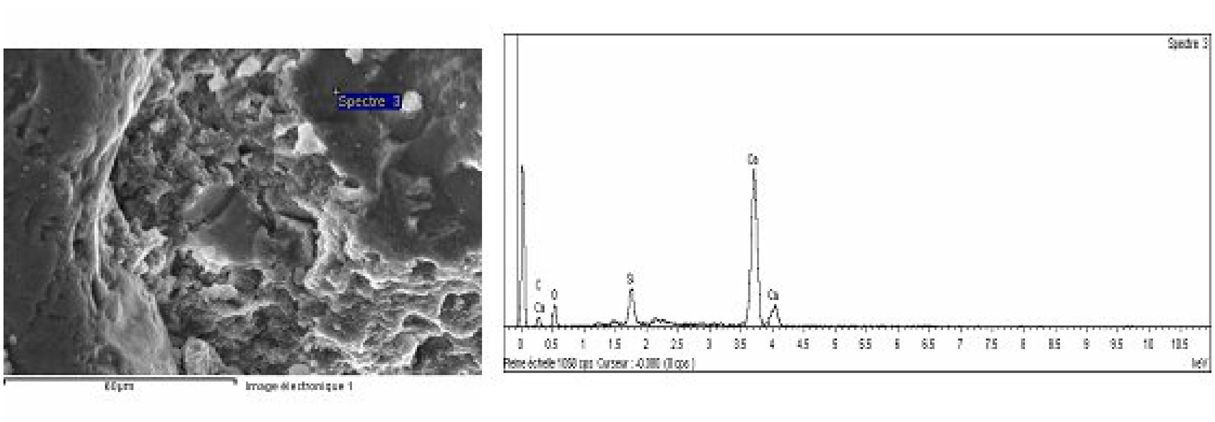

Figure 13. SEM observation of mortar containing ternary cement (TC1).

5. CONCLUSION

Results show that it is possible to obtain mortars with dune sand and local by-products: blast furnace slag, natural pozzolans (Beni Saf volcanic ashes) and marble powder.

These mortars are very economical due to the used of low cost materials: the volcanic pozzolan and marble powder are natural materials that only need a low energy grinding; the slag is a by-product from the steel manufacturing industry that needs a grinding with higher energy than the two previous. These three fillers do not need any calorific energy compare to clinker manufacturing.

From an environmental perspective, no more carbon dioxide is produce when these three materials are used. Furthermore, slag and powder marble are waste that should be stocked in adapted landfills.

The dune sand, an inexhaustible reserve in north African country, exhibits a very thin granulometry, that is not recommended for concrete mixes, but it presents a high content of quartz without argilous particle.

The proposed mortar compositions give acceptable strength at short and long terms. The highest strength are obtained with binary cement containing 65% clinker, 30% slag and 5% gypsum. The

replacement (up to 10%) of slag by marble powder conducts to an acceptable decrease of strength. The slag presents a latent hydraulicity induced by clinker hydration. The use of volcanic pozzolan gives to lower strength at long term but to higher strength at short term. Volcanic pozzolan are not hydraulic but reacted with lime released by clinker hydration (pozzolanic reaction). High short term strength can be due to the high reactivity of this pozzolan: pseudo-crystallized or amorphous siliceous components observed by X-ray diffraction.
SEM observations indicate a very low porosity. The initial porosity is low due to the low water to cement ratio and marble powder content. In a second time, the porosity is blocked by secondary hydrates (slag – lime reaction and pozzolan – lime reaction).
The quaternary cement proposed is a good compromise: it give high short term strength, normal strength at 28 days (similar to a CEMII 32,5) and good strength after 1 year.
Proposed cement with low porosity and low $Ca(OH)_2$ content should be resistant face to biological, physical and chemical attacks.

6. ACKNOWLEDGMENTS

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