

EFFECTS OF THE SECONDARY MINERALS ON THE POZZOLANIC ACTIVITY OF CALCINED CLAY: CASE OF QUARTZ

Wafa Mechti ^{1,*}, Thameur Mnif ¹, Basma Samet ² & Med Jamel Rouis ¹

¹ Unité de Recherche de Géotechniques Environnementale et Matériaux Civil, Ecole Nationale d'Ingénieur de Sfax, BP W 3038, Sfax, Tunisia

² Laboratoire de Chimie Industrielle, Ecole Nationale d'Ingénieur de Sfax, BP W 3038, Sfax, Tunisia

ABSTRACT

This study aims to document the potential effect of quartz as a secondary mineral on the pozzolanic activity of local kaolinitic clay (from the region of Tabarka, Tunisia). Purification of clay was carried out using the centrifugation process in order to decrease the rate of secondary minerals. Our research was based on two samples: a crude sample and a centrifuged one, and both of them were characterized by several methods. The pozzolanic activity of the two samples was evaluated by compressive strength measurements in mortars containing calcined clays, lime and sand. In addition, the identification of the hydrated phases in pastes was done by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The comparison between crude and centrifuged samples through this analysis associated with laser granulometry showed that the presence of quartz with particle size lower than 20 µm contributed to the pozzolanic reaction: the pozzolanic activity of the crude sample with high content of quartz was higher than that of the centrifuged sample.

The results of the last part of the paper proved the pozzolanic reactivity of crystallized quartz with fineness 20µm, the introduction of 10% of grinding quartz as Portland cement replacement improved the cement paste compactness by increasing compressive strength and hydration.

Keywords: *Clays, Strength and testing of materials, Centrifuge modeling.*

1. INTRODUCTION

Today, the high energy consumption by Portland cement industry causes environmental damage due to the release of high quantities of greenhouse gases [1]. Hence, several research activities are directed towards partial or full substitution of Portland cement with the pozzolanic binder in some applications [2,3]. In recent years, the use of calcined clays as a pozzolanic material for mortar and concrete has received considerable attention [4,5].

One of such materials is metakaolin, which is obtained by thermal treatment of kaolin clays in the range of 600-800°C [6,7] and mixed with lime or cement, metakaolin acts as a highly reactive pozzolana [8,9]. Furthermore, the development of pozzolanic properties in fired clays depends mainly on the nature and abundance of clay minerals in raw materials, the calcination conditions and the final product fineness [10,11,12]. However, it is very common to find secondary minerals such as calcite, iron, quartz, feldspar... resulting from the alteration of primary minerals associated with clays. Only, a few studies have investigated the potential effect of these secondary minerals on the pozzolanic activity of these materials. For instance, He et al. [13] studied the effect of quartz on the pozzolanic reaction of six principal clay minerals. In addition, Türkmenoglu et al. [14] investigated the quartz potential effect on the tuff pozzolanic activity. In a recent study, Habert et al. [15] illustrated the effect of calcite on the strength development of pozzolanic mortars.

In this context, the goal of this study is to determine the potential effect of quartz as a secondary mineral on the pozzolanic activity of local Tunisian clay for future use as a supplementary cementitious material.

2. EXPERIMENTAL

2.1. Materials

- The mortar mixtures prepared in this study were composed of three materials:
- Clay: the studied clay is a local one, collected from the region of Tabarka and calcined at 700°C. It is used in hand-made pottery.
- Standard sand: the graded standard sand complied with the European standard EN-196-1 [16].
- Lime: the lime used was commercial analytical grade calcium hydroxide (minimum 95% of purity).

2.2. Sample preparation

This purpose work aims to study the effect of one secondary mineral (quartz) on the pozzolanic activity of local clay. In order to reduce the amounts of non-clayey minerals, a wet sieving was carried out (sieve 63 µm). The crude

and purified samples were characterized by physicochemical methods. For all analyses, it could be noticed that by sieving, the results showed no difference between crude and purified samples: it seems that with this process, we cannot separate clayey particles from non-clayey fractions (secondary minerals). So, we must choose a more effective process such as centrifugation to predict the potential effect of the secondary minerals on the pozzolanic activity of kaolinitic clay.

The two clays used in this study were a crude sample noted Tb referring to Tabarka and a centrifuged sample noted Tbc obtained by centrifugation in water of whole clay by putting 15 to 30 g of the crushed clay sample in 50ml of distilled water in a 250ml flask and mix thoroughly until all particles were dissolved. Then, we centrifuged the solution at 2500 rpm for 10 min [17].

In order to study the pozzolanic activity of these clays, the samples Tb and Tbc were heated in a laboratory programmable furnace during 5h at 700° C [18].

2.3. Experimental techniques

The chemical composition of samples Tb and Tbc was determined by X-ray fluorescence (ARL 8400). The clays were also submitted to blue methylen test (for specific surface area determination) in compliance with the French standard NF P 18- 592 norms.

X-ray diffraction (XRD) was carried out to determine the mineralogical composition of the crude and the centrifuged samples. The X- ray diffractometer used in this investigation was a Philips X 'Pert Pro System. The generator settings were 45 kV and 40 mA and the wavelength (λ) was 1.5418 Å (CuK). The scanning rate was 2 θ per min from 0 to 60°. In order to identify more precisely the nature of the clay minerals, the clay fraction was separated from the whole sample by centrifugation of the < 2 μ m fraction on a glass slide [19,20], and mounted as an oriented aggregate mount. This could be a very useful technique for the identification of clayey minerals. The clay samples in oriented mounts were run under three separate conditions: air-dry state, after ethylene glycol treatment (for the checking of the extent of d-spacing expansion of certain clay minerals) and after heating at 550° C for 1 hour according to the Protocol [21]. Whereas, by calcination of kaolinitic clay at 700°C, the crystal structure is destroyed and an amorphous structure was formed, developing pozzolanic properties [22]. The pozzolanic activity of the calcined clays was assessed using a mechanical method (compressive strength testing). In this regard, the calcined clays (CC) were mixed with calcium hydroxide (CH), sand and water with a CC/CH ratio equal to 3 by weight (3 parts of sand, 1 part [(CH, CC)]. Experiments were carried out on standard mortar mix: 1:3 binder-standard sand were cast in compliance with the EN 196-1 norm [16], the water/solid ratio being equal to 0.75. All sample preparations were processed in a similar manner according to European standard EN-196-1 [16].

Water was first introduced in the mechanical blender. The dry mix solids (calcined clay + calcium hydroxide) were then added to the water solution and mixed for 30 s at low speed; sand was added and mixed for 30 s. Then, the mixing proceeds in a sequence of three steps: 30 s mix at high speed, 90 s in rest and 60 s mix at high speed. The samples were cast in mini-cylinder molds (diameter 20mm, height 40 mm), demolded after 7 days and then cured in water at 20° C for 28 days. The mini-cylinders were tested in compression in compliance with the EN 196-1 norm. The fragments of the compressive strength were submitted to XRD after a 28-day curing in order to identify the hydration products of the pozzolanic reaction.

In addition, The morphology of the hydration products was studied using a scanning electron microscope (Philips XL 30, USCR MEB/03) equipped with an energy-dispersive X-ray analysis (EDXA) system indicating the chemical composition of the observed points. Finally, to study the average size of quartz particles contained in the decanted phase separated by centrifugation, a Mastersizer 2000, Malvern instrument was used to determine the Particle Size Distribution (PSD) of the decanted material rich in non-clayey phase after the centrifugation process.

3. RESULTS AND DISCUSSION

3.1. Chemical study

The chemical composition of the crude clay and the centrifuged material determined by X-ray fluorescence are reported in table1. It is not surprising to notice that some non-clay fractions remain in the clay sample(Tbc), as most of the quartz could be removed by centrifugation. The blue methylen test confirms this result. Indeed, we recorded a specific surface (SS) of 94 (m²/g) for Tb and of 126 (m²/g) for Tbc: the presence of associated minerals in the raw material could be the cause of the reduction of this surface: SS Tb < SS Tbc. In addition, we noticed that Al₂O₃ content increased in response to centrifugation. This result confirms the concentration of clayey minerals through the latter.

Table 1. Chemical composition of clays

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	MgO	Na ₂ O	L.O.I at 500°C
Tb	0.85	58.38	27.08	2.60	0.03	0.88	1.14	0.11	6.26
Tb _c	0.04	55.72	30.22	2.77	0.03	0.98	1.22	0.10	7.64

ASTM Standard C 618-98 (American Society of Testing and Materials [23]) set a minimum value of 70% for the sum of silica, alumina and iron oxide of the total compounds making up the pozzolanic material with sulfur dioxide less than 4% and loss on ignition of less than 10%. In connection with these criteria, Indian Standard stated that for good pozzolans, the CaO content should not be greater than 10% and the total SiO₂ and Al₂O₃ should be greater than 50% [24].

The chemical criteria for pozzolanic activity of Tb and Tb_c were reported in table 2. It can be seen that the clay of Tabarka with and without centrifugation can produce a good pozzolana. However, it is important to note that the chemical composition cannot be used as a single factor for determining the clay pozzolanic activity of the clays but only as a guide for the potential reactivity [25].

Table 2. Chemical criteria for pozzolanic activity of Tb and Tb_c

	ASTM requirement			Indian requirement	
	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ > 70%	SO ₃ < 4%	PF < 10%	CaO < 10%	SiO ₂ + Al ₂ O ₃ > 50%
Tb	88.06	0.03	6.26	0.85	85.46
Tb _c	88.71	0.03	7.64	0.04	85.94

For this reason, we tried to quantify kaolinite in samples before and after centrifugation by using XRF analysis. The results showed that Tb_c was richer in kaolinite (75%) than Tb (67%). It is well known that the pozzolanic activity is directly related to the percentage of kaolinite present in samples [26]. Therefore, we predicted that Tb_c would have the best pozzolanic activity.

3.2. X-ray diffraction study

The X-ray fluorescence was conducted to determine the oxide content. On the other hand, the XRD of clay fraction (< 2μm) was carried out to determine the nature of the clayey minerals in sample Tb (fig 1).

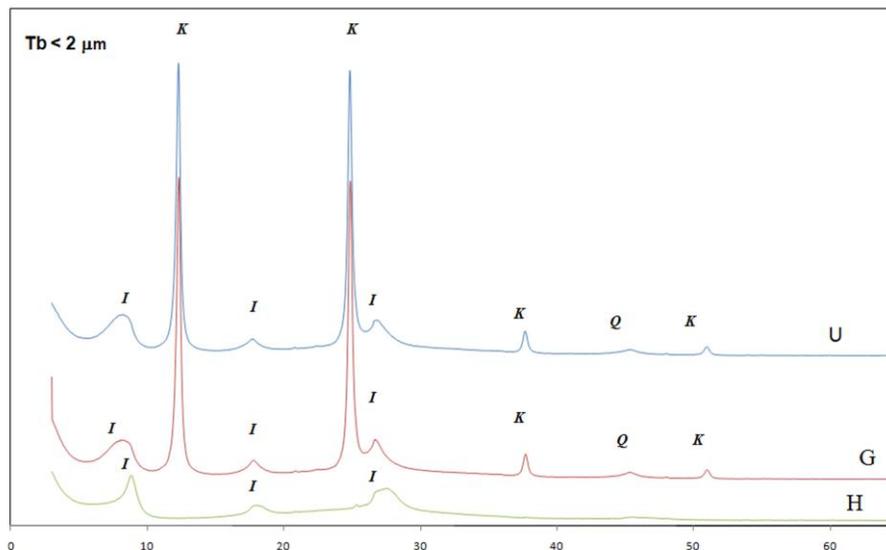


Figure 1. X-ray diffractograms of separated clay fraction (< 2μm) after various diagnostic treatments (U: untreated, G: glycolated, H: heated; K: kaolinite, I: illite, Q: quartz)

The results of X-ray diffractograms of separated clay fraction (< 2μm) indicate that:

- Kaolinite is the major clay present in this sample; it is represented by basal reflections at 7.14 Å, 3.58 Å and 2.38 Å. The collapse of Kaolinite structure to an amorphous material takes place on heating to 550°C: all peaks of kaolinite are destroyed.

- Illite is identified by a series of basal reflections at 10.1 Å, 4.98–5.01 Å and 3.33 Å. On glycolation, illite is essentially non-expanding. Heating illite at 550 °C, the (001) peak may show a slight collapse.
- In addition, X-Ray diffraction patterns on the centrifuged samples (< 2 µm particles) reveal the presence of an associated mineral (quartz) in a small quantity indicating that the clays are not pure. It should be mentioned that the so called < 2 µm particle samples were in the form of a paste as it was the result of a centrifugation process to collect the smaller particles. Therefore, the stacking of the clayey particles induces preferential orientations for diffraction and the signal in the basal phases increases. This can be a very useful technique for the identification of clayey minerals as randomly distributed particles may not allow peaks coming from different clayey phases to be distinguished [27].
- In order to identify associated minerals, we recorded the XRD patterns of the studied samples before and after purification by centrifugation.
- The XRD analysis shows (fig 2) that the raw material is rich in kaolinite and little illite, which is associated with non-clay mineral quartz and very little anatase (TiO₂).

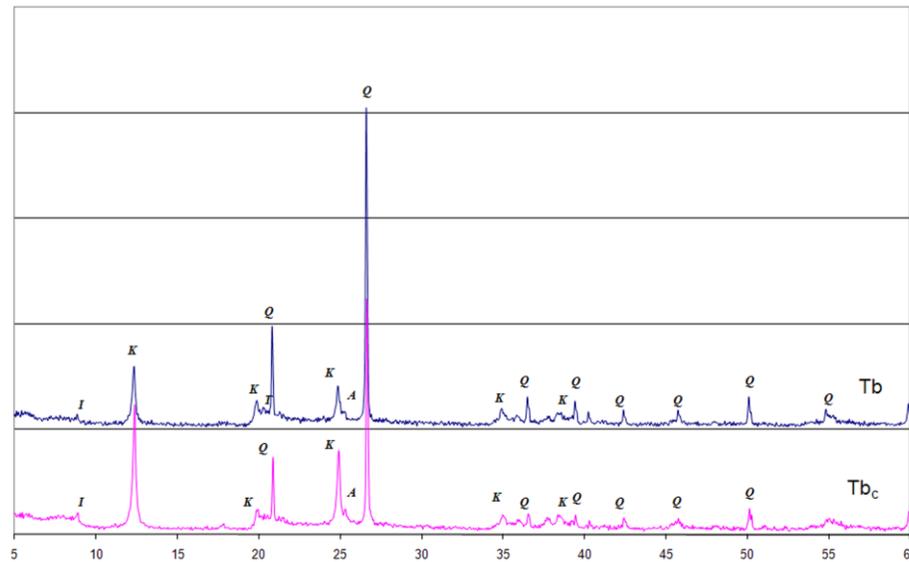


Figure 2. X- ray diffractogram of the raw and the centrifuged clay: K: kaolinite, I: illite, Q: quartz, T: titanium oxide, A: anatase.

- The comparison of the diffractograms of Tabarka clay before and after centrifugation shows clearly that the intensity of the peaks corresponding to clayey phases increased after centrifugation. On the other hand, the purification by centrifugation strongly decreased the rate of quartz. So, we can conclude that centrifugation reduced the quartz quantity and increased subsequently the amount of clayey minerals: kaolinite and illite.

3.3. Evaluation of the pozzolanic activity by a mechanical method: compressive strength

According to Sayanam et al. [28], the strength development in lime-pozzolana-sand mortars is the best and safest method for measurement of pozzolanic activity.

The obtained compressive strengths of calcined clays Tb and Tb_c after 7 and 28 days of hydration are presented in table 3. The obtained results indicate that the compressive strength of mortars containing Tb_c is lower than that containing Tb despite its higher kaolinite content. Because quartz was the main component removed by centrifugation, we can conclude that the presence of quartz has a beneficial effect on the pozzolanic activity. This result agrees with previous investigations which indicate that the origin of pozzolanic activity lies in the high content of reactive silica in pozzolans [29].

Table 3. Compressive strengths of mortars made with calcined clays

Clay	Compressive strength (MPa)	
	7 days	28 days
Tb	7.8	11.9
Tb _c	4.1	8.3

3.4. Laser granulometry

It is well known that quartz, which is a well crystallized material, is not a potential pozzolan, but it seems that when quartz is finally ground, it could contribute to the pozzolanic reaction. For this reason, we proceeded to the granulometric analysis of the decanted material separated by centrifugation.

The grain-size distribution shows the presence of two particle-size ranges: (fig 3):

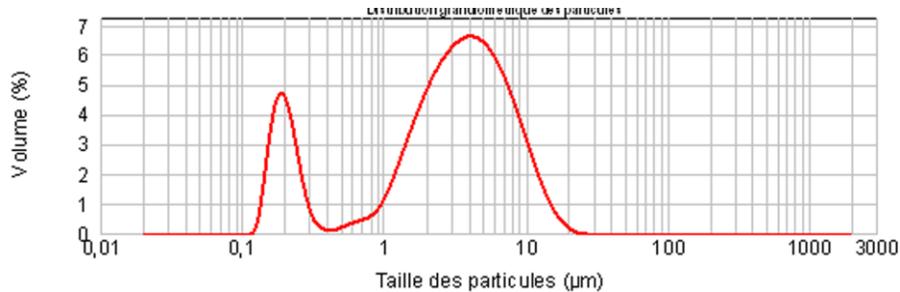


Figure 3. Particle size distribution of decanted fraction of clay of Tb

A class between 0.1 and 0.3 µm which corresponds to the elimination of a clayey fraction: Kaolinite (size of the particles: 0.2 µm) [30].

A class between 1 and 20 µm which corresponds to quartz. So, the abundance of quartz in the decanted material confirms the XRD results and the fact that centrifugation removes essentially quartz due to its relatively large size. We can conclude that the principal difference between Tb and Tb_c is the relatively high content of quartz with particles lower than 20 µm in the crude sample. Thus, the higher pozzolanic activity of the clay rich in quartz could be explained by two facts:

- The quartz grains act as grinding bodies and contribute to the mechanical activation of kaolinite [31], which is largely consistent with previous results of Frost et al. [32].
- The finally ground quartz can be dissolved in alkaline solution (in presence of Ca (OH)₂) to generate soluble silica which contributes to the pozzolanic reaction.

Consequently, we can conclude that quartz with particles size lower than 20 µm has a beneficial effect on the pozzolanicity of Tabarka clay.

In order to explain the differences in the mechanical behaviour between Tb and Tb_c, the sediments of the compressive strength were preserved in acetone for 24 hours then in oven at 60°C for 1h to remove the residual water and to stop subsequently the hydration. The obtained fragments were submitted to XRD analysis and SEM observations.

3.5. Identification of hydration products by XRD

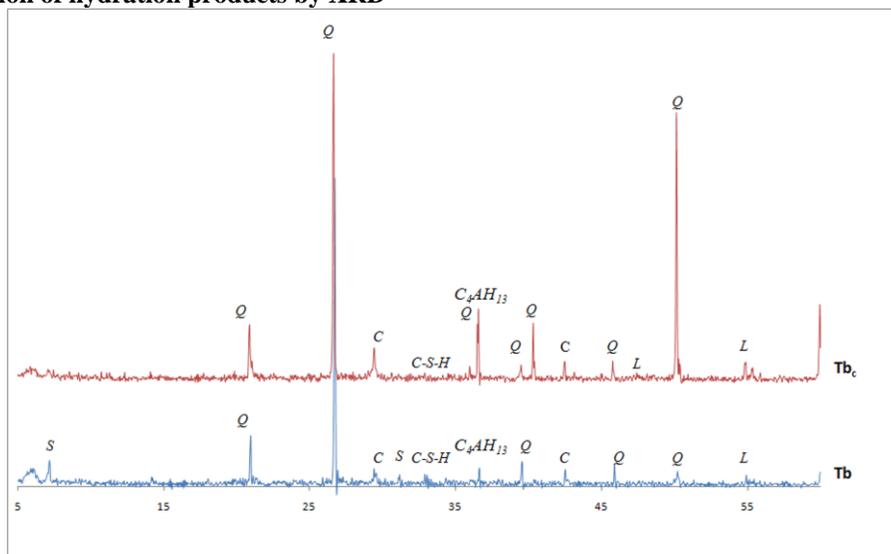


Figure 4. X- ray diffractograms of the raw and the centrifuged samples-lime-sand mixtures after 28 days of hydration (S: stratlingite, L: lime, Q: quartz, C: calcite, C-S-H: Calcium silicate hydrate, C₄AH₁₃: tetra calcium aluminate hydrate)

The analysis of the mortars XRD patterns for both samples after 28 days of hydration (fig 4) shows:

- Relatively intense peaks relative to quartz existing in sand and in the clay: the amount of residual sand is higher in mortars made with Tb_c .
- Peaks relative to residual lime and calcite (formed by carbonation of remaining lime). It is interesting to note that the intensities of both residual lime and calcite are higher in mortars made with Tb_c , which proves that the pozzolanic activity of Tb_c is lower than that of Tb .
- Peaks corresponding to C_4AH_{13} which is a hydration product of the pozzolanic reaction; its intensity is higher in mortars made with Tb_c in spite of its saturation with residual lime. This fact is in agreement with the observations made indicating that the formation of C_4AH_{13} phase at $20^\circ C$, in a metakaolin/lime system, is not clearly associated with the evolution of the lime content [33].
- In addition to C_4AH_{13} , we note the presence of stratlingite C_2ASH_8 in mortars containing Tb . The presence of this phase is caused by a higher source of Si in the solution. This fact proves that the fine quartz particles were dissolved by the alkaline solution and contributed to the C_2ASH_8 formation.
- Some peaks relative to C-S-H which is generally an amorphous material: this phase seems more evident in mortars with Tb .
- These results agree with previous investigations: when metakaolinite reacts with calcium hydroxide, cementitious products are formed. It has been reported that the main phases produced during the pozzolanic reaction at ambient temperature are C-S-H, C_2ASH_8 and C_4AH_{13} [34,35,36], depending on Si/Al ratio: the most dominating reaction products are C-S-H and C_4AH_x in various concentrations, indicating that both Si and Al from the clay participate in the pozzolanic reaction [13].

3.6. Scanning electron microscopy

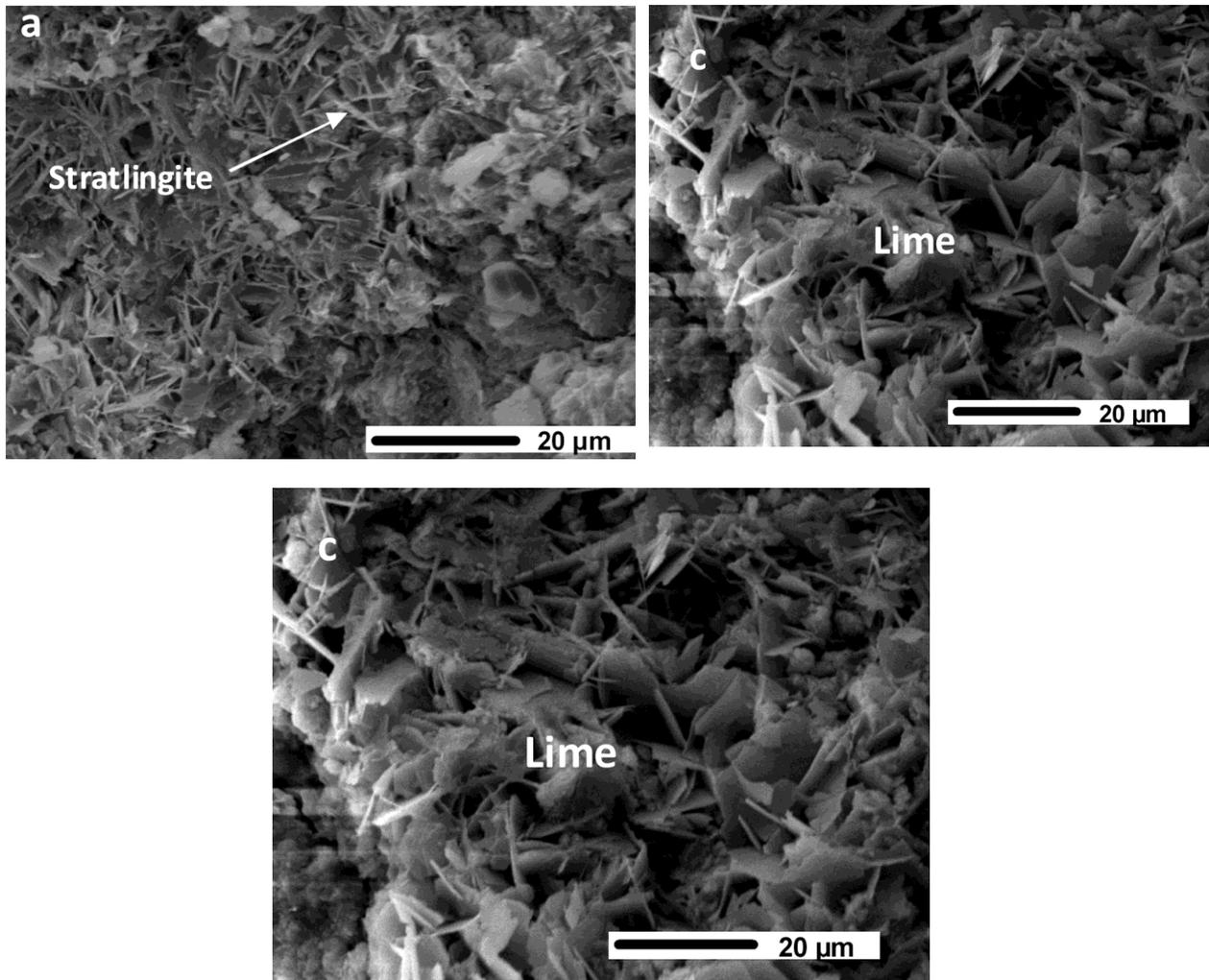


Figure 5. Observation by SEM : Tb -a: bundle of stratlingite needles, Tb -b: snowy structure (C-S-H gel), Tb_c -c: lath shaped lime phase

The microscopic observation of fractures of the mixtures (calcined clay + lime + sand) of T_b and T_{b_c} hydrated for 28 days showed that:

The structure of T_b is more compact than that of T_{b_c} , indicating a good evolution of the reaction of hydration: the presence of a bundle of stratlingite needles (Fig 5a), a snowy structure: C-S-H gel (fig 5b). Fig 5-c, however, shows an example of a residual lime phase: ideal crystals with lath shaped morphology. These findings totally agree with previous results of identification of hydration products by XRD.

4. IDENTIFICATION OF REACTION MECHANISMS OF QUARTZ POZZOLANIC REACTIVITY

In order to confirm previous results and justify the pozzolanic effect of crystallized quartz with particle size lower than $20\mu\text{m}$, we selected three mass percentages (10%, 15% and 20%) of grinding quartz with different finesses equivalent to their mean diameter in μm : Q_{20} , Q_{40} , and Q_{80} for addition to ordinary Portland cement (OPC). The required objective is to evaluate through experiments the effect of these mineral admixtures on hydration and compressive strength of cement pastes.

4.1. Materials and mix proportions

- Portland cement: the cement that was used is an ordinary Portland cement (OPC, CEM I 42.5 Mpa; Clinker is produced by CAT (Ciments Artificiels Tunisiens) plant, Tunisia by a dry process.
- Quartz: the quartz is crystallized silica content of more than 97%. This is a grinding quartz. The crushing is carried out using a conventional ball crusher.

The mixture composed by OPC and (10%, 15% and 20%) respectively of quartz was cast in cubic specimens ($20 \times 20 \times 20 \text{ mm}$). The cement pastes were prepared in accordance with French standard NF EN 196- 1. After 24 h moist curing, the specimens were demolded and cured in water at 20°C till testing at 7 and 28 days for compressive strength.

For all mixtures, the ratio water/binder was maintained constant, equal to 0.35.

4.2. Results and discussion

4.2.1 Compressive strength

According to these results (fig.6-7), one notices that compressive strength depends on all measurable parameters: time of tests, percentage and fineness of grinding quartz.

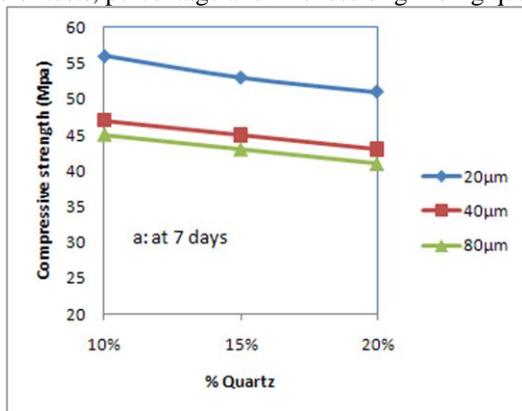


Figure 6. Variation in compressive strength at 7 days of cement pastes as a function of fineness and percentage of quartz

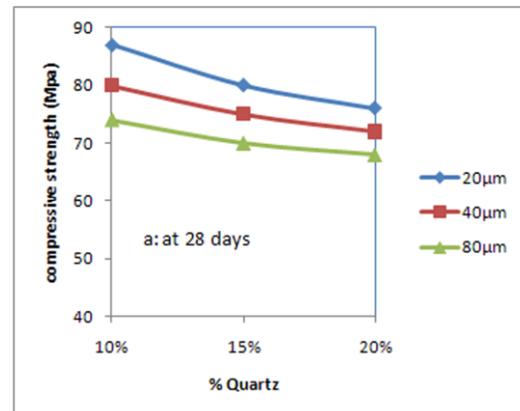


Figure 7. Variation in compressive strength at 28 days of cement pastes as a function of fineness and percentage of quartz

A global observation of the results shows that after 28 days, the compressive strength at 10, 15 and 20 % of quartz is greater than the strength of the Portland cement (69 MPa). The maximum compressive strength can be achieved when the percentage is about 10 %. That translates the chemical effect of crushed quartz and confirms its pozzolanic activity. These results are confirmed by several studies. The introduction of fine siliceous particles equipped with a certain pozzolanic role contributes to the increase in the resistance and the durability of the concretes to which they are built-in [37,38].

The increase in strength is the consequence of various effects which act simultaneously and in a complementary way on the compressive strengths of cement pastes [39]: the two main ones being the filler effect and the pozzolanic effect [39,40].

Filler effect: an improvement of the compressive strengths by a thickening of the cementing matrix.

The pozzolanic effect relates to the capacity of quartz to react with lime provided in the case of Portland cement and water to form new mineral phases and increase resistances by refining capillary pores.

Concerning the influence of the fineness of grinding quartz, we see clearly that the compressive strengths of cement pastes at any age, increase with the fineness of quartz.

The highest strength is observed for the fraction lower than 20 μm . The finer the particles are, the more effective their role is. These results are in agreement with the suggestions of the works [41,42,43,44], that there is an optimum quartz PSD which gives the highest strength and confirms well the previous conclusions of the first part that quartz with particles lower than 20 μm contributes to the pozzolanic reaction.

4.2.2 Mineralogical analysis

Figure 8 presents the XRD diffractograms for the crushed quartz (fineness equal to 20 and 40 μm). We can notice that the two diagrams are similar. They present a crystalline structure of quartz. The only difference resides in the emergence of a small peak at 3.24 \AA attributed to an amorphous quartz. This indicates the effect of the grinder. According to Tkacova et al. [45], the grinder is considered as a reactor that changes the surface structure of particles. Similarly, De Larrard [46] showed that the quartzes crushed deemed crystal, are amorphised on surface (nothing is ultra-fine inert). Afterwards, quartz can be associated with lime according to its classic pozzolanic reactivity.

As regards the evolution of mixture hydration (90 % OPC + 10 % Q) as a function of time, to clarify the effect of this mineral admixture (quartz) in Portland cement, we followed mixture hydration pastes (100 % OPC) and (90 % OPC + 10 % Q with fineness 20 μm) by XRD (figure.9)

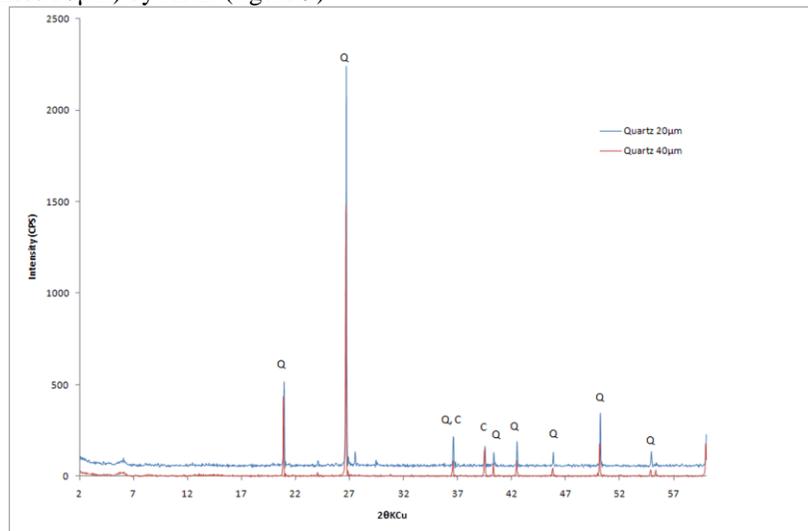


Figure 8. X- ray diffractograms of quartz with fineness 20 and 40 μm

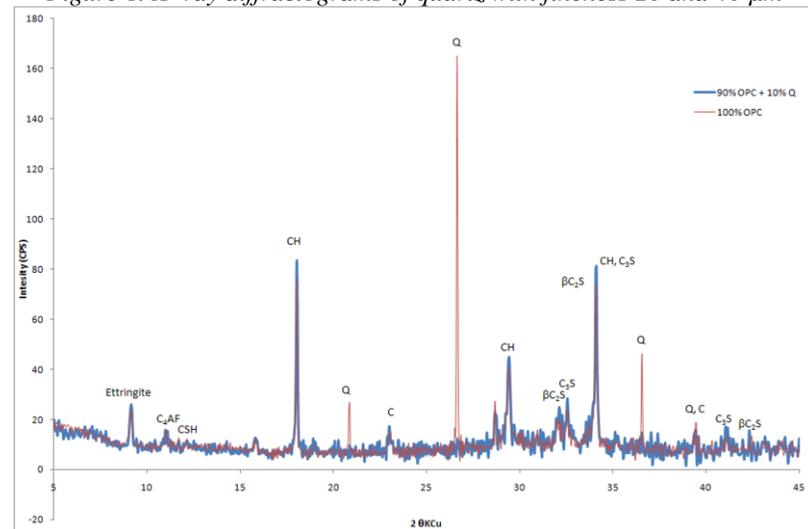


Figure 9. X- ray diffractograms of mixtures hydration (100% OPC) and (90% OPC + 10% Q with fineness 20 μm) at 28 days

It can be observed that in the presence of grinding quartz, the line intensities of lime (4.90 Å, 3.03 Å, 2.62 Å) decreased as compared to the Portland cement, which explains the lime fixing by the silica grains to form C-S-H. Knowing that, the pozzolanic activity is evaluated by the lime consumption. So, the XRD analysis is the most reliable chemical analysis which proves the quartz pozzolanic reactivity.

In the same way, the line intensities of cement minerals (Ettringite, C_3S and βC_2S) decreased and C-S-H appearances in the mixture hydration with quartz at 28 days, which proves the pozzolanic reactivity of quartz particles lower than 20 μm . This confirmed the previous results which totally agree with those confirming the pozzolanic reactivity of grinding quartz mixed with lime [47].

5. CONCLUSION

This paper aims to compare the pozzolanic activity of the whole and the centrifuged clays Tb and Tb_c and show the pozzolanic effect of secondary minerals: quartz.

From the results presented in this paper, we can conclude that:

- The X-ray diffraction is an important tool to identify the nature of the clayey minerals and secondary minerals.
- The pozzolanic activity assessed by mechanical tests showed that the activity was directly related to the percentage of quartz present in samples: the higher the quartz content, the better the compressive strength.
- The granulometric analysis of the decanted material separated by centrifugation showed that quartz with particles size lower than 20 μm had a beneficial effect on the Tabarka clay pozzolanicity.

The analysis of the mortars XRD patterns of the hydrated pastes showed that the reaction products were C_4AH_{13} with intensity peaks higher in mortars made with Tb_c and C_2ASH_8 , formed in presence of high silica concentration only detected with clay rich in quartz: Tb.

The results of the final part suggests that:

- The use of quartz as a substitute for Portland cement improves the compressive strengths. This change is a function of fineness and percentage of these mineral admixtures. The latter has an optimum effect on compressive strengths when the percentage is about 10 % and a 20 μm fineness of crushed quartz.
- At 28 days of hydration, in the presence of quartz, intensity rays of lime and cement minerals decreased as compared to 100 % OPC. This explains the hydration of calcium silicate and confirms the quartz pozzolanic reactivity with particles lower than 20 μm .
- Finally, we can conclude that despite its crystalline structure, quartz presents a pozzolanic reactivity.

6. ACKNOWLEDGMENTS

I wish to thank Mr. Jamil JAOUA, Founder and former Head of the English Unit at the Sfax Faculty of Science, for having proofread this paper.

The Authors would like to thank the “Société des Ciments de Gabès”, Tunisia for its collaboration. The Authors are grateful to Mr. Moumen Marzouki from the INRAP (Institut National de Recherche Et d'Analyse Physico-chimique), Tunisia for undertaking the XRD.

7. REFERENCES

- [1]. H. Klee, The cement sustainability initiative, In: 3rd International symposium sustainability in cement concrete, Istanbul, Turkey, 21-23 May (2007).
- [2]. B. Ural, L. Turanlı, Studies on blended cements containing a high volume of natural pozzolans. *Cement and Concrete Research* **33**, 1777-81 (2003).
- [3]. C. Fortes-Revilla, S. Martinez-Ramirez, M. Blanco-Verela, Modelling of slaked lime-metakaolin mortar engineering characteristics in terms of process variables. *Cement and Concrete Composites* **28**, No. 5, 58-67 (2004).
- [4]. A.A. Al Rawas, A.W. Hago, D. Al Lawati, A. Al Battashi, The omani artificial pozzolans (Sarooj). *Cement and Concrete Aggregates* **23**, No1, 19-26 (2001).
- [5]. A. Shvarzman, K. Kovler, I. Schamban, G. Grader, G. Shter, Influence of chemical and phase composition of mineral admixtures on their pozzolanic activity. *Advances in Cement Research* **14**, No.1, 35-41 (2002).
- [6]. C. Shi, An overview on the activation of reactivity of natural pozzolans. *Canadian Journal of Civil Engineering* **28**, 778-786 (2002).
- [7]. J. Torres, R. Mejía deGutiérrez, F. Puertas, Effect of kaolin treatment temperature on mortar chloride permeability. *Materials of Construction* **57**, 35-43 (2007).
- [8]. G. Kakali, T. Perraki, S. Tsvivilis, E. Badogiannis, Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. *Applied Clay Science*, Vol. **20**, pp. 73-80 (2001).

- [9]. A. Shvarzman, K. Kovler, G.S. Grader, G.E. Shteret, The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. *Cement and Concrete Research* **33**, 405-416 (2003).
- [10]. J.A. Kostuch, V. Walters, T.R. Jones, High performance concretes incorporating metakaolin: a review, in: R.K. Dhir, M.R. Jones, (Eds.), *Concrete 2000: Economic and Durable Construction Through Excellence*, E & FN SPON, London, pp. 1799-1811 (1996).
- [11]. B.B. Sabir, S. Wild, J. Bai, Metakaolin and calcined Clays as pozzolans for concrete: a review. *Cement and Concrete Composites* **23**, 441 (2002).
- [12]. P. Stroeven, P. Dau, Effect of blending with kaolin or diatomite on characteristics of Portland cement paste and mortar, In: R. K. Dhir, T.D. Dyer, (Eds.), *Modern Concrete Materials: Binders, Additions and Admixtures*. Thomas Telford, London, pp. 139-149 (1999).
- [13]. C. He, B. Osbaeck, E. Makovicky, Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects. *Cement and concrete Research* **25**, No. 8, 1691-1702 (1995).
- [14]. A.G. Türkmenoglu, A. Tankut, Use of tuffs from central Turkey as admixture in pozzolanic cements. Assessment of their petrographical properties. *Cement and Concrete Research* **32**, 629-637 (2002).
- [15]. G. Habert, N. Choupay, J.M. Montel, D. Guillaume, G. Escadeillas, Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity. *Cement and Concrete Research*, Vol **38**, 963- 975 (2008).
- [16]. EN 196-1, Methods of Testing Cement: Part 1. Determination of Strength, European Committee for standardization, Brussels (1995).
- [17]. F.W. Larque, Ph. Techniques de préparation des minéraux argileux en vue de l'analyse para diffraction des rayons X, Laboratoire de Géologie et de Paléontologie, CNRS, Strasbourg, (1978).
- [18]. A. Chakchouk, B. Samet, T. Mnif, Study on the potential use of Tunisian clays as pozzolanic material. *Applied Clay Science* **33**, 79-88 (2006).
- [19]. E. Barahona, Arcillas de ladrilleria de la provincial de Granada, Evaluacion de algunos ensayos en materias primas. Ph D. Thesis, Universidad de Granada, pp. 398 (1974).
- [20]. G.W. Brindley, Order-disorder in clay mineral structure, In: G.W. Brindley, G. Brown, (Eds.), *Crystal Structures of Clays Minerals and their X- Ray identification*. Mineralogical Society Monograph. vol. 5. London, pp. 126-189 (1984).
- [21]. G. Brown, G.W. Brindely, X-ray diffraction procedures for clays minerals identification, In: G.W. Brindley, G. Brown, editors. *Crystal structures of clays minerals and their X-ray identification*. London: Mineralogical Society, pp. 305-59 (1980).
- [22]. V.S. Ramachandran, *Concrete admixtures handbook, properties, science and technology*. 2nd ed. New Jersey, USA: Noyes Publications (1995).
- [23]. American Society of Testing and Materials, "ASTM C618", Specifications for Fly Ash and Raw or Calcined Natural Pozzolan for Use as Mineral Admixture in Portland Cement Concrete, pp. 375-378 (1980).
- [24]. R.S. Varshney, *Concrete Technology*, IBH Company, Oxford, (1982).
- [25]. W.H. Price, "pozzolans - a review" *American Concrete Institute journal*, Vol. **5**, pp. 225-232 (1975).
- [26]. B. Samet, A. Chakchouk, T. Mnif, A. Tagnit, Influence of mineralogy of Tunisian clays on pozzolanic activity-assessment by differents methods. *Advances in Cement Research* **19**, No. 2, 57-65 (2007).
- [27]. R. Lopez, *Calcined Clayey Soils as a Potential Replacement for Cement in Developing Countries*, thesis, EPFL Suisse (2009).
- [28]. R.A. Sayanam, S.K. Mehta, K. Kalsotra, Studies on the lime reactivity with thermally activated clay from Jammu Region (India). *Journal of Thermal Analysis* **37**, 11-17 (1991).
- [29]. F. Massazza, Pozzolanic cements. *Cement and Concrete Composites*.**15**, 185-214 (1993).
- [30]. D. Tessier, Recherches expérimentales sur l'organisation des particules dans les argiles, Application à l'étude de 4 pâtes argileuses « calciques » en voie de dessiccation. Thèse pour l'obtention du diplôme d'ingénieur CNAM, laboratoire de géologie appliquée, (1975).
- [31]. E. Mako, R.L. Frost, J. Kristog, E. Horvath, The effect of quartz content on the mechanochemical activation of kaolinite. *Journal of Colloid and Interface Science*, Vol. **244**, pp. 359-364 (2001).
- [32]. R.L. Frost, E. Mako, J. Kristof, E. Horvath, J.T. Klopogge, Modification of kaolinite surfaces by mechanochemical treatment. *Langmuir* **17**, 4731- 4738 (2001).
- [33]. M. Frias, J.Cabrera, Industrially interesting approaches to "low-CO₂" cements, cement and concrete research, **31** 519 (2001).
- [34]. M.A. Serry, A.S. Taha, S.A.S. El-Hemaly, H. El-Didamony, MK-lime Hydrations products. *Thermochemica acta* **79**, 103-110 (1984).
- [35]. M. Murat, Hydration reaction and hardening of calcined clays and related minerals. *Cement and Concrete Research* **13**, No. 2, 259-266 (1983).

- [36]. M.A. Serry, Influence of calcination conditions on the hydration of MK- lime. *Silicates. Industriels* **52**, No. 5-6, 83-87 (1987).
- [37]. M. Buil, Comportement physico-chimique du système ciment-fumée de silice. *Annales de l'ITBTP*, Paris 485 19-29 (1990).
- [38]. P.C. Aïtcin, *Bétons Hautes Performances*, édition EYROLLS, Paris, 683 (2001).
- [39]. S. Guettala, B. Mezghiche, B. Belounnar, The influence of the content of cement the sand of dune finely crushed, on the characteristics of the concrete. Séminaire National sur la Gestion Intégrée des Déchets, Thème III, 29 et 30 Mai, ENSET d'Oran; p. 195-202 (2007).
- [40]. S. Guettala, B. Mezghiche, L'influence de l'ajout du sable de dune finement broyé au ciment, sur les performances mécaniques et de durabilité des pâtes. Séminaire International sur la Normalisation et Qualité dans la Construction, 18-19 Novembre, 128-138, Tlemcen (2006).
- [41]. K. Hamano, Y.-H. Wu, Z. Nakagawa, M. Hasegawa, Effect of grain size of quartz on mechanical strength of porcelain bodies. *J. Ceram. Soc. Jap. Int.* 99, 149-153 (1991).
- [42]. J.C. Benezet, A. Benhassaine, The influence of particle size on the pozzolanic reactivity of quartz powder. *Powder Technol.* **103**(1):26-9 (1999).
- [43]. K. Arroudj, M.N. Oudjit, Influence of the sand of dune finely crushed on the hydration of cements. 2ème Colloque Maghrébin en Génie Civil, Biskra, Algérie; 10 et 11 Décembre. p. 119-27 (2002).
- [44]. K. Arroudj, M.N. Oudjit, M.T. Lanez, Carayon Demonstration by X-ray diffraction C-S-H second generation, 1ère Séminaire sur les Technologies du Béton, le Béton Perfection et Incertitudes, Algérie, 18-19 septembre, 1-8 (2004) .
- [45]. K. Tkacova, N. Stevulova, *Powder Technol.* **52** 161-166 (1987).
- [46]. F. De Larrard, Formulation and properties of concrete with high performance, Rapport de Recherche L.P.C n °149, Laboratoire Central des Ponts et Chaussées: Paris, France Mars; (1988) .
- [47]. S. Guettala, B. Mezghiche, Compressive strength and hydration with age of cement pastes containing dune sand powder. *Construction and Building Materials* **25**, 1263-1269 (2011).

LIST OF NOTATIONS

Tb: crude sample from Tabarka
 Tb_c: centrifuged sample from Tabarka
 L.O.I: loss on ignition
 CC: calcined clays
 CH: calcium hydroxide
 PSD: Particle Size Distribution
 EN 196- 1: European standard norm
 XRD: X-ray diffraction
 SEM: Scanning Electron Microscopy
 NF P 18- 592: French standard norm
 EDXA: energy-dispersive X-ray analysis
 SS: specific surface
 ASTM: American Society of Testing and Materials
 C-S-H: calcium silicate hydrate
 C₂ASH₈: stratlingite
 C₄AH₁₃: tetra calcium aluminate hydrates