UTILIZING CRUSHED LIMESTONE FINE WASTES IN ALGERIA AS FILLERS IN CEMENT

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Résumé

En Algérie, plus de mille unités produisent annuellement 68 millions de tonnes de granulats, pour l'essentiel de nature calcaire. Malheureusement, plus de 20% des sables fabriqués sont impropres à l'utilisation comme sable de construction du fait d'une teneur en fines supérieure à 12% (limite normative actuelle). De même, les fillers calcaires, qui résultent aussi du processus de concassage et de broyage des roches calcaires, sont considérés comme des résidus inutilisables et donc inexploités [1]. Pour améliorer la situation, il est important de valoriser au mieux tous les granulats et plus particulièrement les sables fillerisés et les fillers. Ceci intéresse non seulement l'économie du pays mais aussi la préservation de l'environnement.

Notre étude présente l'influence des caractéristiques de fines calcaires algériennes (dosage, finesse) sur les propriétés physiques et les performances mécaniques des pâtes de ciments confectionnées à différents rapports eau sur liant. Les résultats obtenus montrent que le remplacement d'une partie du ciment par ces fillers calcaires peut améliorer de manière sensible les résistances mécaniques et même l'ouvrabilité. L'étude montre aussi que les fillers calcaires n'ont pas seulement un effet physique mais présentent également une activité chimique, en donnant des nouveaux composés hydratés tels que les carboaluminates [2].

Mots clés **:** *Fillers calcaires, Pâte de ciment, Finesse, Résistance mécanique, Carboaluminate.*

Abstract

In Algeria, more than thousand of aggregate crushing station produces annually about 68 million tons of aggregates, essentially of calcareous nature. Unfortunately, more than 20% of manufactured sands are unsuitable to be used as construction sands because of their high fines content that largely exceed the current standard that limit the maximum value to 12%. Similarly, the limestone fillers, which also result from the limestone rocks crushing process, are regarded as inadequate residues and in consequence unexploited [1]. To improve the situation, it is important to improve all the aggregates and sands with a high filler content and more particularly sands and the limestone fillers itself. This has a favourable effect not only on the economy of the country but also the environment.

This paper shows the influence of the characteristics of Algerian limestone fine (proportioning, fineness) on the physical properties, the mechanical performance and durability of cements pastes made with various ratios of water to binder. Obtained results show that the replacement of part of cement by these limestone fillers can improve significantly the mechanical resistance, the workability. This study also shows that the limestone fillers not only have a physical effect but also an improved chemical activity by producing new hydrated compounds such as the carboaluminates [2]

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Keys words **:** *Limestone fillers, Cement paste, Fineness, Mechanical resistance, Carboaluminate.*

ملخص

توجد في الجزائر أكثر من ألف محجر ينتج سنويا ما يقارب 68 مليون طن من الحصى الكلسي. لكن للأسف أكثر من 20 % من الرمال المنتجة تبقى غير صالحة للاستعمال في مجال البناء، و هدا لاحتواء ها على نسبة عالية من الغبار و التي تفوق 12 % (القيمة الحدية للمواصفات المعمول بها). كما أن الغبار الكلسي الناتج عن عملية تفتيت الصخور الكلسية يعتبر كشوائب غير مستغل[1]. لتطوير و استغلال هده المواد يستوجب تثمين هده الرمال. مما يسمح بتنمية اقتصادية أحسن و المحافظة على البيئة.

هدا البحث يتطرق إلى دراسة تأثير خصائص الغبار الكلسي الجزائري (النسبة ، معامل النعومة) على الخصائص الفيزيائية و الميكانيكية لعجينة الإسمنت المصنوعة بنسب ماء إلى رابط مختلفة. النتائج المحصل عليها تبين استبدال جزء من الإسمنت بالغبار الكلسي يحسن بصيغة ملحوظ المقاومة الميكانيكية و سهولة وصعها في القوالب. هده الدراسة توضح أيضا أنه ليس فقط لهدا الغبار الكلسي تأثير فيزيائي بل و أيضا تأثير كيميائي وكذلك بتشكل هيدراتات جديدة كالكربو- أليمنات [2].

الكلمات المفتاحية : *الغبار الكلسي، عجينة الإسمنت ، النعومة، المقاومة الميكانيكية، كربو- أليمنات*

The production of building materials is typically accompanied by formation of secondary products (limestone fillers) or waste which has a direct impact on the environment and affects the quality of sands. The best way of minimizing their impact on the environment is finding a means to reuse the secondary product in a beneficial way.

The term fillers refers to rock particles (added to a binder) obtained by fine milling or crushing. In certain countries, limestone additions have been used for decades as partial cement replacement. Limestone fillers are generally added directly at the cement production plant. Research on the influence of limestone additions on the properties of hydrated cement-based materials indicates that their action is primarily physical in nature [3]. However, evidence of reaction with the aluminates-bearing phases usually found in cement systems has been reported [4, 5]. Calcite fines have also been used as a replacement for gypsum in Portland cement [6]. It has been shown that limestone additions can accelerate the hydration of the calcium silicate components of cement [7, 8].

The use of limestone fines results in products that have acceptable mechanical properties [3, 9]. These additions also have beneficial rheological effects [3]. The positive effects of limestone addition can explain why regulations world wide have permitted its addition to cement. However, depending on the country, the amount permitted varies from 0% to 35%. Debate on acceptable amounts of limestone addition to cement continues. The wide variety of practical cases of contact where concrete structures are directly in contact with chemically aggressive salt solutions and the expensive maintenance and repair of damaged structures account for the global interest in the durability of cement-based materials.

In the Western countries, the disposal of solid wastes, such as rubble, in refuse tips are strictly illegal, in France, for example, the law of 13 July, 1992 relating to the waste disposal and environmental protection. In Algeria, more than 20% of the manufactured sand in more than thousand plants that produce annually a total of 68 million tons of aggregate is not suitable for use as construction sand because of its fines content being higher than 12% (current normative limit). In the same way, limestone fillers, also are resulting from the process of crushing limestone rocks, are regarded as unusable residues and thus not exploited [1].

In civil engineering, the promotion of rejected quarry materials makes it not only possible to contribute to protecting the environment, but it also constitutes an attractive field of research about general executives of the solid waste treatments and the development of more economic hydraulic binders. To increase the production of cements with mineral additions (others that traditional additions fly-ash, silica fume, slag....) several investigations were carried out throughout the world in order to develop the use of the limestone fines [[6]

The various results show that the limestone fillers added to cement can have several roles:

- A filling role by correcting the size distribution of the fine elements of cement [10]
- A rheological role by their capacity fluxing on the interstitial paste [7, 10, 11]
- A chemical and physical role by increasing compressive strength and improvement of durability [1]. A chemical and physical role by formation of carboaluminates, germs that fix the hydrate [1, 3, 10, 12].The development of Portland-composite cements, using traditional and up-to-date mineral additions, is considered to be state of art in cement production. The initial aim was the reduction of cost but further objectives have been added, such as the improvement of performance, the energy saving, the use of conventional raw material or industrial by-products and the ecological benefits [3, 6], and to have many benefits, both technical and economical [3, 5, 7].

The European Standard EN 197-1 identifies four types of Portland-limestone cement containing 6–20% limestone (types II/A-L and II/A-LL) and 21–35% limestone (types II/B-L and II/B-LL), respectively [7]

The use of Portland-limestone cements seems to have many benefits, both technical and economical [4, 13, 14]. It is expected that the future world production of Portland- limestone cement will be continuously increased.

The wide use of limestone cement requires a thorough knowledge of the cement and concrete properties.

As far as the limestone cement is concerned, the research work is focused on three areas.

The first one is the effect of limestone on the cement performance [14, 15]. The second one deals with the participation of limestone in the hydration reactions of clinker [1, 16] while the third one is the production process and specifically the intergrading of clinker and limestone [11]. Although there is a disagreement on specific issues, the knowledge level is satisfactory and continuously extended.

It is thus essential to know the effects of the limestone fillers according to their contents and their smoothness on the cementing matrices and specifically on the hydraulic cement pastes. Thus, the objectives of this research are:

1. To present and examine the main part of the rheological and mechanical performances of cement pastes comprising Algeria limestone fillers in function the rate and finenesses.
2. To determine the optimum substitutions rate of cement by limestone fillers.

1. EXPERIMENTAL PROGRAM

1.1. Principle of the study

The objective of the study consists of making various cement pastes starting from cement CPA-CEM I and then substitute a part of this cement by limestone fillers having various finenesses. The parameters of study are:

Content of fines: 0%, 5%, 10%, 15%, 20%, 30% and 40% (substitutions in masse)

Fineness of fines: F5, F10, F15 and F29 respectively with the fillers diameter of 5 μm, 10 μm, 15 μm and 29 μm

Water to binder ratio: 0.24, 0.26 and 0.28

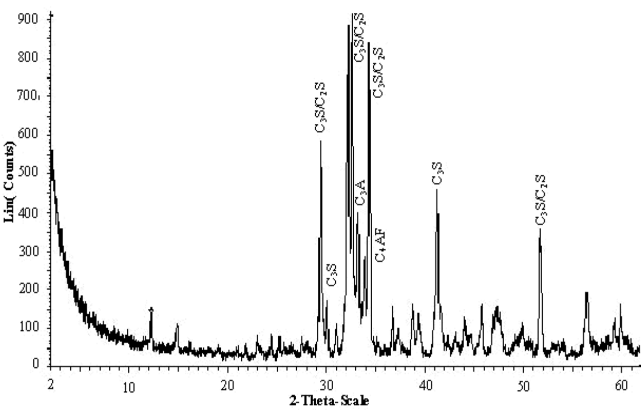

Figure 1 : X-rays diffractogram of anhydrous cement CPA-CEM I

1.2. Materials used

Cement

Cement used is CPA-CEMI. It comes from the Cement factory of Tebessa. The clinker shows good chemical and mineralogical characteristics. The laser grading analysis reveals a distribution of the various particle-size ranges of grains between 1 and 100 μm, a median diameter of 8 μm and a specific area of 2900 cm^2/g (use m^2/kg or mm^2/kg as per SI standards). The X-rays diffractogram of anhydrous cement is shown in figure 1.

Table 1 : Chemical and mineralogical analysis of cement, %

Chemical composition								
SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Cl	Na_2O	PF
20.01	2.97	4.65	64.01	0.62	2.15	0.015	0.24	4.34
Mineralogical composition								
C_3S		C_2S		C_3A		C_4AF		
61.3		15.9		8.0		9.6		

The chemical, mineralogical composition and characteristics of cement used are presented in Tables 1 and table 2.

Table 2 : Cements characteristics

Characteristic	Units	Type of cement CPA (CEMI)
Apparent bulk density	kg / m^3	1100
Absolute density	kg / m^3	3100
Normal consistency	%	25
Beginning of setting	h and min	2 h 15 min
End of setting	h and min	3 h 15 min
Shrinkage at 28 days	μm / m	810

Filler

The fillers come from the giant career E.N.G (national enterprise of aggregate). They are of limestone's nature having a higher content of $CaCO_3$ of 98% (analyzes by XRD figure 2).

The filler F5, F10, F15 and F29 are differed mainly by their median diameters which are presented in table 3. The characteristics of these fillers are gathered in Table 4.

Table 3 : Value of Blaine specific area and median diameters of fillers

Filler	F5	F10	F15	F29
Specific area (cm^2/g)	5400	3100	2800	2640
Median diameters (μm)	5	10	15	29
Apparent bulk density (kg/m^3)	810	870	980	1030
Absolute density (kg/m^3)	2700	2700	2700	2700

Table 4 : Chemical compositions of fillers

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	NaCl	PF
0.58	0.02	0.06	55.85	0.06	0.07	0.56	43.80

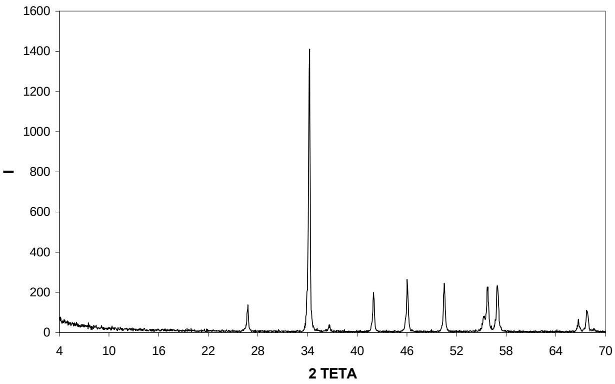

Figure 2 : X-rays diffractogram of filler

Laser grading of cement and filler is shown in figure 3

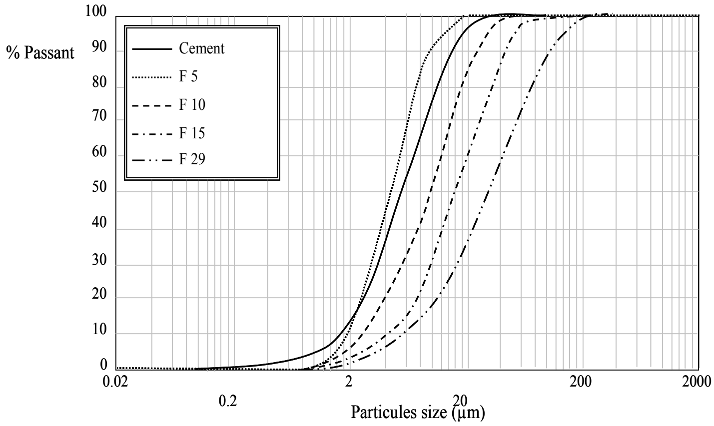

Figure 3 : Laser grading of cement and filler

Water

For the paste mixing, drinking water was used. Its quality is in conformity with the regulations of standard (NF P18 404). The results of the chemical analysis of water are shown in Table 5.

Table 5 : Chemical analysis of water

Ca	Mg	Na	K	Cl	SO_4	CO_2	NO_3	Insol.	PH
116	36	80	3	140	170	305	5	786	7.9

2. FABRICATION OF SPECIMEN AND METHODOLOGY OF TESTING

Production and mixing of the pastes studied were carried out according to standard NF P18-403. The first pastes obtained were used for the determination of normal consistency and the rheological study. Others pastes were carried out for the investigation of the performances of the hardened state. The release from the mould is made after 24h. The test-tubes obtained were preserved in a wet chamber HR=95% ± 5% and T=20°C until the testing ages of 28days.

The tests were carried out on four series of pastes. Each series corresponds to the one of the fillers F5, F10, F15 or F29 added to cement CPA-CEMI to proportions of 0%, 5%, 10%, 15%, 20%, 30% and 40% and ratios W/C=0.24, 0.26 and 0.28 respectively.

3. RESULTS AND DISCUSSED

Consistency

The normal consistency of cement CPA-CEMI without addition (figure 4) is reached for 25% of water content. For added filler to cement (figure 5), one notes that up to 15%, limestone fine F5 and F10 play the role of one flux. Beyond this percentage these fines have a thickening effect. Fines F15 and F29 have a weak effect with means on consistency.

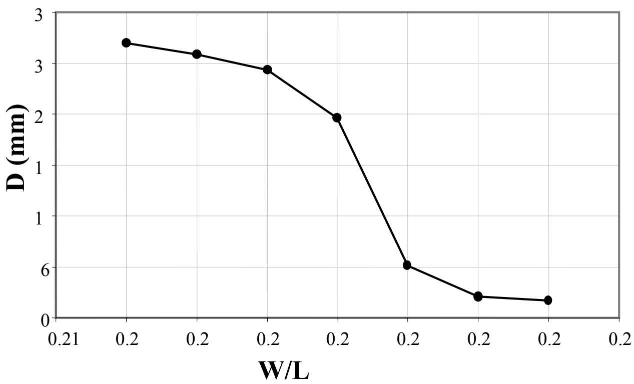

Figure 4 : Consistence of CPA-CEMI cement paste

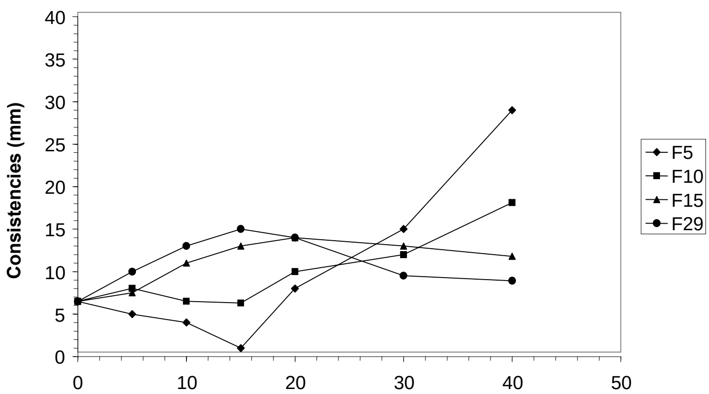

Figure 5 : Consistencies of the cement paste as function of percentage of substitution

Setting time

The influence of substitution rates of limestone fine is weak to means on the beginning and end of setting times in the interval 0% to 20% (Figures 6 and 7). Beyond this value, fines F15 and F29, the time of beginning and the end of setting rise from 20 to 90 minutes so fillers plays a retarding role on the setting time.

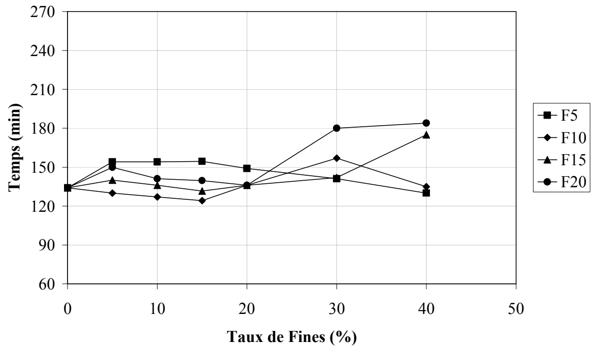

Figure 6 : Beginning of setting time

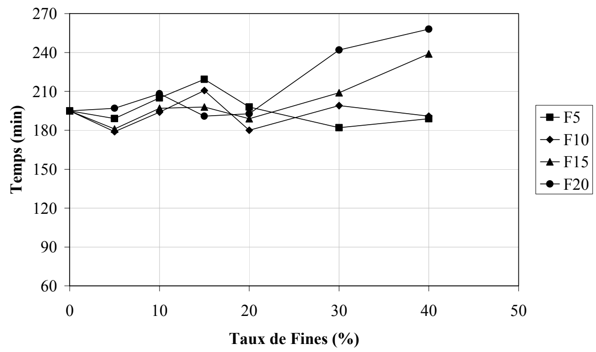

Figure 7 : End of setting time

Compressive strength

The incorporation of fines having high specific area such as the fillers F5 and F10 (figure 8) considerably improves the compressive strengths especially for values of substitution of about 15%. Beyond this value, the resistance decreases by about 45% for the fillers F29 to 40% of substitution.

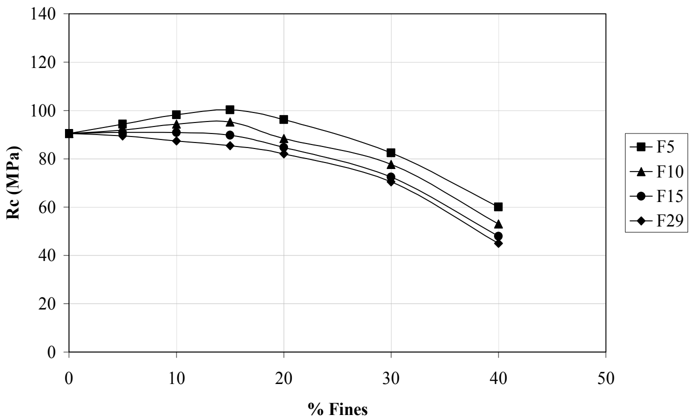

Figure 8 : Compressive strengths

The finest fillers (F5) improve a better resistance in compression. Choosing this type of fillers, the optimal value of 15%, is particularly well highlighted. The increase in resistance can be explained, as shown by x-ray diffraction (figure 9), by the formation of the Carboaluminate which appears from the seven days. The formation of monocarboaluminates in the paste with 15% of F5 filler content is very important compared to the paste with F29 filler. The limestone's fillers are thus active chemically and their activity influences the mechanical resistances of the binder [10, 12 et 14].

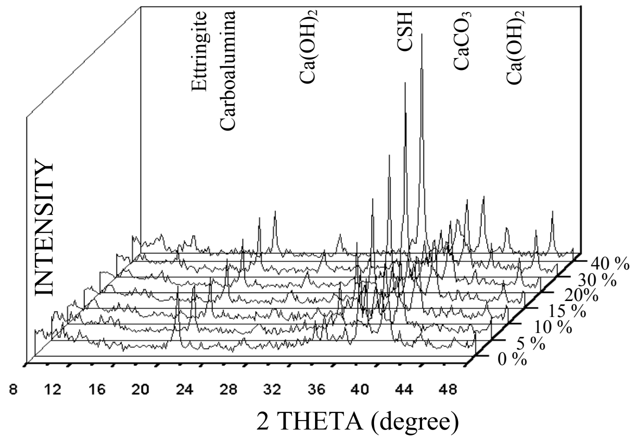

Figure 9 : X-rays diffraction of hardened cement paste

Tensile strength

The tensile strength (figure10) is affected almost in the same way as compressive strength. Except for the fines F5 and F10 for which the increase are more marked.

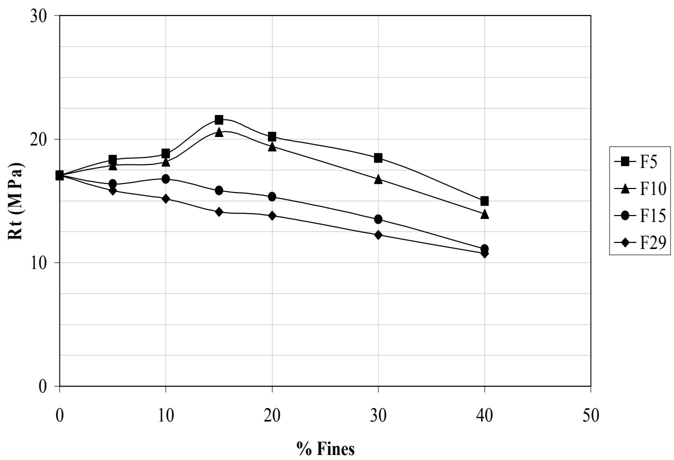

Figure 10 : Tensile strength versus of percentage of fines

Evolution of total porosity

For the pastes without addition (100% cement), a very tightened porosity was noted in a marked principal peak, between 10 and 100 µm, this peak is reduced by the incorporation of the very fine fillers F5 and F10 at a rate of 15%. So the hardened cement paste with 15% F5 filler seems as dense and homogeneous material which explains the improvement of the mechanical performances.

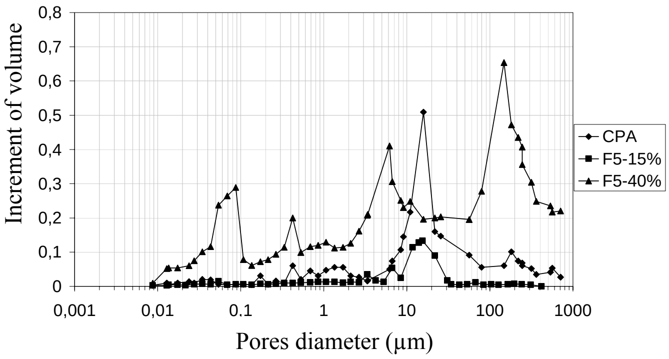

Figure 11 : Distribution of the pores according to the fine rate (F5 Fillers; W/C=0.24)

In addition, for the addition of F5 fillers to 40%, several families of pores are observed, which points that this paste is more porous and have porosity coarser than that observed on the paste with 15%.

CONCLUSION

In Algeria, limestone fines resulting from the aggregates crushing, have for long been considered as unusable residues and one of principal causes of rejection of the construction sand. However, they can have a beneficial role in the matrix cementing.

The various results obtained show well that the limestone's fillers can play several roles :

- A filling role by offsetting the cement lack on fine elements in the grading curve.
- A rheological role by their dispersing capacity on the grains of cement which results in a reduction in the water content at a constant hardness[16]
- A chemical and physical role by formation of carboaluminates, crystal nuclei (with acceleration of the hydration) [10, 12, 14].
- The variation of smoothness of the fillers practically does not have a significant influence on the demand for water.
- The influence of the fillers is marked favourably when their content is lower than 25%.
- Porosity of the pastes decrease with the addition of the limestone fillers up to 15% beyond that point an increase is observed either for fine smoothness and W/C ratio.

The present study, confirms that with a fillers contents of 15%, the mechanical performances of the cement pastes are clearly improved. The hardness of the cement pastes with this percentage of fine is slightly affected. The fineness of limestone fine to has a considerable role in the improvements of the rheological and mechanical performances of the cement pastes due to the formation the new compounds such as the carboaluminates [10, 11].

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