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A STUDY OF PHOSPHOGYPSUM-CRUSHING SAND BASED BRICKS GRADE NEGLIGIBLE WEATHERING

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Housing is a great problem in today's world. The most basic building material for construction of houses is the usual burnt clay brick. A significant quantity of fuel is utilized in making these bricks. Also, continuous removal of topsoil, in producing conventional bricks, creates environmental problems. A feasibility study was undertaken on the production of full bricks by using of crushing sand-natural hydraulic lime-cement-phosphogypsum (CS-NHL-C-PG) to solve the problems of housing shortage and at the same time to build houses economically by utilizing industrial wastes. The compressive strength, flexural strength water absorption, density and speed of sound of these bricks are investigated. It is observed that these bricks have sufficient strength for their use in low cost housing development. Tests were also conducted to study the relationship between ultrasound pulse velocity (UPV) with strength of bricks. The results suggest that compressive and flexural strength values may approximately be determined without a destructive testing by using the non-destructive UPV measurements.

Keywords: *Phosphogypsum, Full brick, Strength, Durability*

1. Introduction

There is a general exodus of rural population to the cities with the rapid industrialization in developing countries. The infrastructure to support these cities, such as buildings for housing and industry, mass transit for moving people and goods, and facilities for handling water and sewage will require large amounts of construction materials. Enhanced construction activities, shortage of conventional building materials and abundantly available industrial wastes have promoted the development of new building materials.

Phosphogypsum is an important by-product of phosphoric acid fertilizer industry. It consists of [$CaSO_4.2H_2O$] and contains some impurities such as phosphate, fluoride, organic matter and alkalis. In Tunisia, for several years, a set of phosphoric acid production factories have produced PG in large great quantities (approximately 10 million tons per year [1]. Currently, the PG is stored into piles in the vicinity of the factory, by dry or wet process. The storage of PG causes the pollution of the water table and the soils by acid and heavy metals infiltrations.

Its valorization leads to environmental protection and to minimization of the storage costs. Several researchers had studied the use of PG in various fields. The PG was treated to be used in the plaster manufacture. It has been found that the PG is suitable for making good quality plaster showing similar proprieties to natural gypsum plaster [2-4]. This field is advantageous for the countries which do not have natural quarries such as Japan and India. The PG has been sought also to be used in agriculture [5]. It is as effective as the crushed natural gypsum. However, the quantities used are limited and moreover the health standards became increasingly restrictive. But the most interesting use of the PG is for the cement manufacturing: either by natural gypsum substitution (about 5%), which will play the role of a set retarder [6, 7], or in the burning process of clinker, to reduce the clinkerization temperature [8]. The PG was also used in soil stabilization [9]. Finally phosphogypsum PG has been studied to be used in hollow blocks [10] and light brick [11].

In Tunisia, the PG was studied to be used in similar fields. The most successful application so far is in the manufacture of cement; by substitution of the gypsum. The obtained product is known under the name of cement ultimo. It showed good performances but the used quantity is low [12, 13]. Moussa et al [14] had studied the possibility of the use of the PG in the embankments. The PG is studied in order to use it like a fill. This study showed a behavior to the compaction not similar to that of a soil. Furthermore, the fill showed also a continuous settlement because of the PG solubility.

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Moreover, Kuryatnyk and Angulski-Ambroise- Pera [15] have employed the phosphogypsum to be used as a hydraulic binder. But formation of ettringite led to cracking and strength loss. Finally, Sfar [16] has explored the PG for a road use. The study proposed the following formulation: 46.5% of PG, 46.5% of sand and 7% of cement. But this study was conducted in the Tunisian south region, where the rainfall is low.

In this paper, at first, compressive strength, flexural strength water absorption, density and speed of sound of phosphogypsum- crushing sand-lime-cement bricks grade NW are investigated. The second part deals with the relationship between ultrasound pulse velocity (UPV) with strength of bricks.

2. Experimental program

2.1 Materials

2.1.1.Chemical composition of phosphogypsum

The chemical analyses, considered most relevant to the prospect use in commercial brick making, were undertaken on the PG. The results of these analyses are presented in Table 1. The PG contains primarily (about 77%) calcium sulfate ($CaSO_4$). The remaining components are present in low percentage. It should be noted that the pH of PG samples has been found to be around 2.9, indicating a high acidity of this.

2.1.2. Grain density

The real densities of the grains were determined by the pycnometer method. The studied PG presents a density of about 2300 kg/m3. The crushing sand presented a density of about 2740 kg/m^3. This value is higher than the one of phosphogypsum.

2.2. Mix proportion

Shrinkage cracking and spalling are a major weakness in phosphogypsum-based bricks. Shrinkage cracking can be minimized by keeping the water content of binder as low as possible. Hence, in the present study, a low slump mix was used to limit the shrinkage. The water contents of phosphogypsum-crushing sand-lime mixtures were fixed respectively to 4 %. Bricks produced with more than 4 % showed cracks after fabrication due to excessive water.

The mix proportions of phosphogypsum, riddled crushing sand (CS), lime and cement (cement HRS 42.5) for bricks are given in Table 2. The mix proportions are given in terms of dry weights of the ingredients.

2.3. Manufacturing processes

A mixer, as shown in appendix Figure 1, is used for mixing materials. The dry phosphogypsum was sieved through 1 mm sieve. The weighed quantity of phosphogypsum, sand, lime and cement were first thoroughly mixed in dry state for a period of 10 minutes to uniform blending. The required water was then gradually added and the mixing continued for another 5 min.

All full bricks were made on a bench model, semiautomatic press having a capacity of 25 tons, as shown in appendix, to produce bricks of 51×95×203 mm in size under a static compaction of 15MPa.

2.4. Testing methods

All bricks were dried to the free air for a period of 28, 56 and 90 days. Compressive strength, density, water absorption, saturation coefficient and leaching tests of bricks from different mixes of phosphogypsum, sand, lime and cement with available mixing water content were determined.

Compressive strength of the units was determined according to ASTM C67 [17]. Tested bricks consist of half bricks with full height and width. Flexural strength tests on the bricks were performed according to ASTM C 67 [17]. Test specimens were taken as full-size brick units.

The absorption qualities of brick are taken

Table1

Chemical composition of phosphogypsum

Elements (%)								
CaO	SO_3	P_2O_5	F	SiO_2	Fe_2O_3	Al_2O_3	MgO	Ignition loss at 1000°C
32.8	44.4	1.69	0.55	1.37	0.03	0.11	0.007	22.3

Table 2

Mix proportions of WS-NHL-C-PG full bricks

Mix désignation	Constituant materials (% w)			
	Phosphogypsum	Sand (WS)	Cement	Lime
M-1	60	33	5	2
M-2	60	30.5	7.5	2
M-3	60	28	10	2
M-4	70	23	5	2
M-5	70	20.5	7.5	2
M-6	70	18	10	2
M-7	80	13	5	2
M-8	80	10.5	7.5	2
M-9	80	8	10	2

as a part of the acceptance measurement of the durability of the material. ASTM specification C67 describes a method by which absorption of building clay brick can be measured. First, the samples are immersed for 24 hours in cold water. The amount of water absorbed is then recorded as a percentage of the total weight of the dry unit.

In order to determine the density of each brick, dry bricks were weighed accurately and their volumes were measured.

The direct UPV values are measured on the flexural strength samples having direct path length required by BS1881 [18].

The leaching tests had been performed according to the French norm NF EN 12457-3 [19] at ambient temperature (20 ± 5°C). The specimens (three different samples for each mix-design) were crushed and an amount of 0.175 kg was taken to be analyzed. The distilled water was added to obtain a liquid/solid ratio of 10 l/kg.

The compressive and flexural strength and speed of sound of phosphogypsum-based bricks were tested after 28, 56 and 90 days of curing. Water absorption, density, and leaching test were determined on bricks tested after 28 days of casting.

3. Results and discussion

3.1. Dry density

The densities of CS-NHL-C-PG full bricks are shown in Table 3. These densities range from 1446 to 1700 kg/m^3 (Table 3). Therefore the CS-NHL-C-PG full bricks have high density.

3.2. Water absorption

The water absorption is a principal factor for the durability of the product and its behavior to natural environment. Table 4 presents the results of the bricks water absorption. It was observed that the water absorption of bricks decreased with the cement content increase. It was observed also, that the values obtained were favorable in comparison with those of clay bricks (0 to 30%) [20].

3.3. Compressive strength

The results, obtained as an average of measurements performed on three specimens, are shown in Figures 1-3. The BS6073-Part 1 [21] requires minimum compressive strengths of 7.0 MPa and 11.7 MPa after a curing period of 28-day for load-bearing concrete masonry units. All of the 28-day-cured investigated mixtures in this study satisfied the [21] standard for compressive strength.

Table 4

Water absorption of CS-NHL-C-PG full bricks

Mix designation	Water absorption after 24 hr curing in cold water (%)
M1	22
M2	26.3
M3	25.1
M4	26.6
M5	25.5
M6	24
M7	25.3
M8	24
M9	23

For all the studied cases, the strength of full bricks after 90 days was higher than 10.3 MPa, which is the minimum strength imposed by the standards [22]. Cement and lime as a source of reactive calcium silicates and aluminates are given silicate and aluminate hydrates, which are responsible for the development of strength.

The Figures 1-3 show also increase in the strength with the cement content. This result confirms the water absorption test outcome, where it has been indicated that the addition of cement produces a decrease in the internal pore size. Thus, the brick becomes less porous and as consequence, mechanical strength increases.

CS-NHL-C-PG bricks with more than 5 % cement are found to be conforming to physical requirements of clay or shale building brick grade NW (negligible weathering), bricks with little resistance to cyclic freezing-thawing but which are acceptable for applications protected from water absorption and freezing [22] (ASTM international: C62-08). Therefore, CS-NHL-C-PG bricks can replace the clay or shale bricks grade NW.

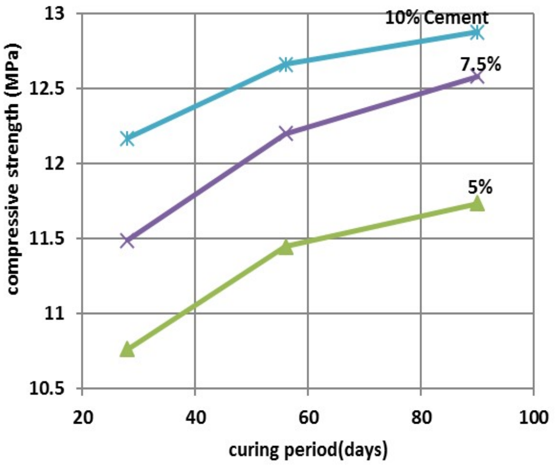

Fig.1 -Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=60%).

Table 3

Dry densities (kg/m^3) of WS-NHL-C-PG full bricks

Dry densities (kg/m^3)								
M1	M2	M3	M4	M5	M6	M7	M8	M9
1446	1523	1564	1556	1594.5	1613.5	1619	1636	1700

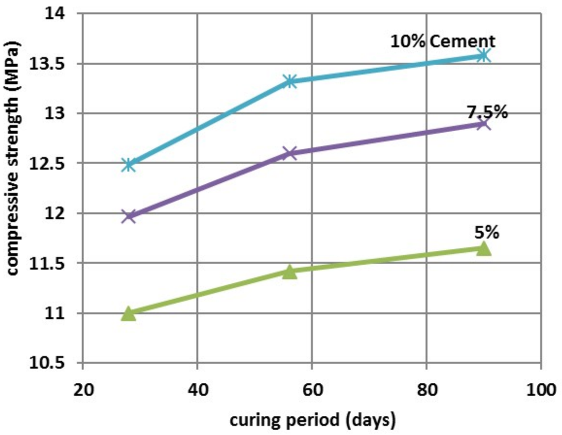

Fig.2 - Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=70%).

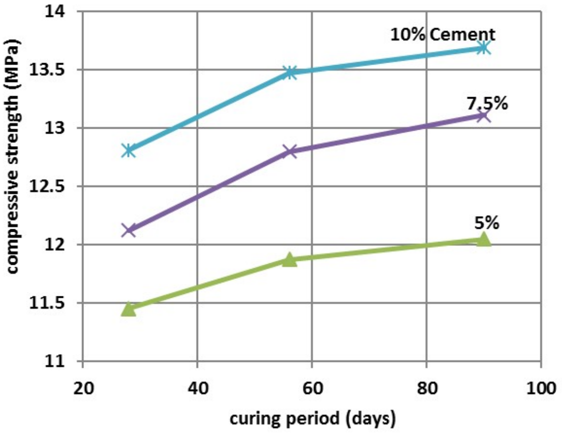

Fig.3 - Compressive strength of CS-NHL-C-PG full bricks (phosphogypsum=80%).

3.4. Flexural strength

The results, obtained as an average of measurements performed on three specimens, are shown in Figures 4-6. The code ASTM does not specify a requirement for flexural strength. However the values obtained were favorable when compared with the minimum flexural strength required by BS6073-Part 1[18] (0.65 MPa) after a curing period of 28-day, which was surpassed by all the samples.

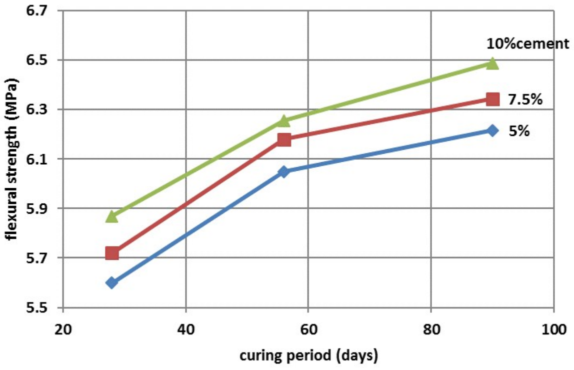

Fig.4 - Flexural strength of CS-NHL-C-PG full bricks (phosphogypsum=60%).

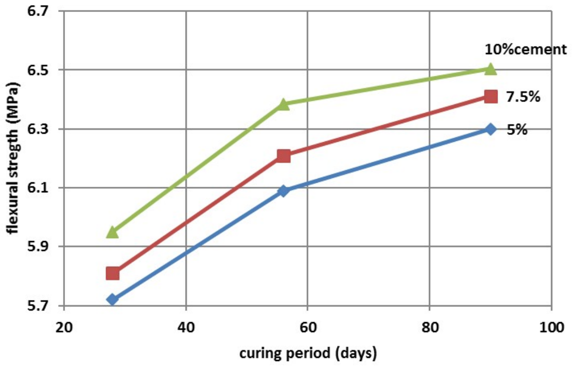

Fig.5 - Flexural strength of CS-NHL-C-PG full bricks (phosphogypsum=70%).

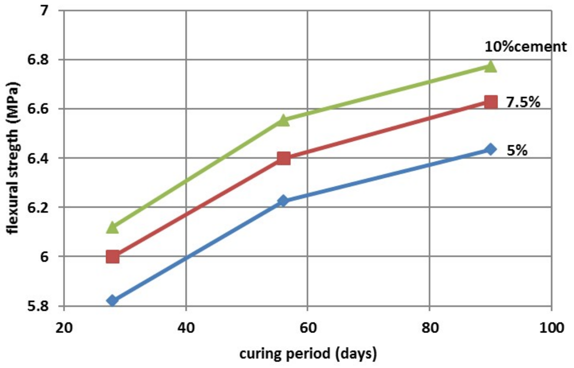

Fig.6 - Flexural strength of CS-NHL-C-PG full bricks (phosphogypsum=80%).

3.5. Ultrasonic pulse velocity (UPV)

Table 5 shows the results of the direct UPV values obtained for investigated bricks. The data show an increase of UPV with the cement content and curing time.

Relationships between the UPV and mechanical characteristics of bricks have been evaluated with respect to compressive and flexural strength. The significance of these correlations has been tried to explain.

UPV-compressive correlation has been investigated by using the compressive strength=f (UPV) relationship and applying linear regression to the data obtained from compressive tests of bricks. The linear regression coefficient (Rc) of the correlation between UPV and compressive strength of bricks containing 80 % phosphogypsum, NHL, C and crushing sand was determined r2 = 0.907 (Fig.7). High correlation coefficient indicates a strong relationship between compressive strength and values of UPV bricks. The correlation indicates the homogeneity of bricks.

Likewise, relationship between UPV-flexural strength have been investigated using experimental data with linear regression, and the evaluations are made under conditions similar to those of the compressive strength tests.

Here too, a strong relationship can be

Table 5

UPV of CS-NHL-C-PG full bricks

Mix designation	UPV (m/s) (28 days)	UPV (m/s) (56 days)	UPV (m/s) (90 days)
M1	3160.8	3300	3325.3
M2	3260.2	3320.3	3340.5
M3	3330.6	3420	3439
M4	3284.7	3330	3360
M5	3342.9	3400	3425
M6	3435	3489	3510
M7	3380	3420	3430
M8	3410	3470	3490.2
M9	3485	3520	3540

Table 6

Leaching test results, in mg/kg for L/S = 10 l/kg

Eléments	M1	M2	M3	M4	M5	M6	M7	M8	M9	Limit values acceptable as inert	Limit values acceptable as non hazardous
Cr	0.08	0.077	0.76	0.07	0.068	0.07	0.058	0.059	0.053	4	50
Ni	0.078	0.073	0.063	0.069	0.064	0.056	0.064	0.06	0.058	0.4	10
Zn	0.058	0.056	0.054	0.054	0.052	0.05	0.05	0.048	0.046	4	50
Pb	0.1	0.095	0.09	0.095	0.093	0.09	0.092	0.09	0.088	0.5	10
Cu	0.12	0.098	0.096	0.099	0.096	0.094	0.09	0.094	0.09	2	50
Cd	0.07	0.067	0.062	0.06	0.04	0.035	0.045	0.031	0.03	0.04	1

established between UPV and flexural strengths of bricks. As in the case of compressive strengths, the correlation between UPV and flexural strength has high value for 80% phosphogypsum content brick within (r2= 0.999) (Figure 8).

Flexural strength, such as compressive strength also indicates the homogeneity of the bricks based phosphogypsum made under a pressure of 15 MPa.

Correlation UPV - water absorption (after 24 h immersion in water) was studied using the relationship of water absorption = f (UPV) and applying the relationship linear regression on the data obtained from water absorption tests.

Bricks with a higher water absorption give lower values VS. There is an inverse relationship between the speed of sound and the water absorption for the bricks. Therefore there is an inverse relationship between the speed of sound and porosity. An inverse relationship between porosity and UPV is also indicated in the literature [23, 24]. The linear regression coefficient (r2) of the correlation between UPV and water absorption bricks containing 80% and 70% phosphogypsum, in mixtures with CHN, C and crushing sand was determined r2 = 0.999 (Fig. 9). High correlation coefficients indicate a strong relationship between water absorption and VS values of bricks.

3.6. Leaching tests

The average values of the leaching test are presented in Table 6. The concentrations of the selected metal species, i.e., Cd, Cu, Zn, Ni, Pb,

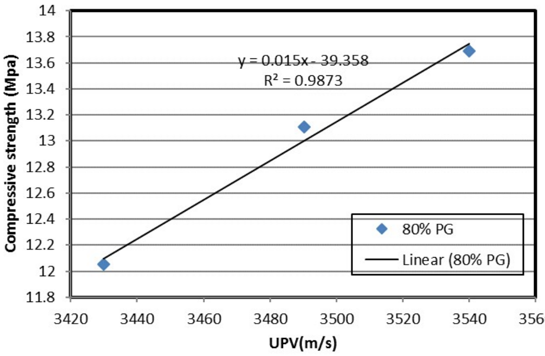

Fig.7 - Correlation between UPV and compressive strength for CS-NHL-C-PG full bricks (phosphogypsum=80%)

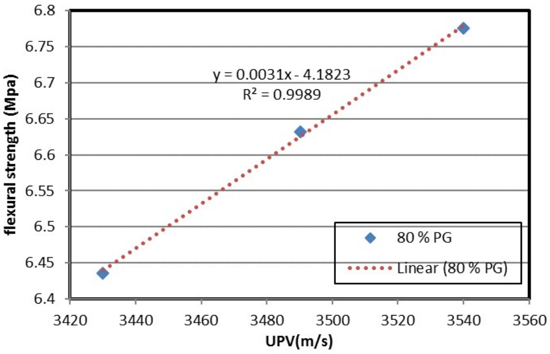

Fig.8 - Correlation between UPV and flexural strength for CS-NHL-C-PG full bricks (phosphogypsum=80%).

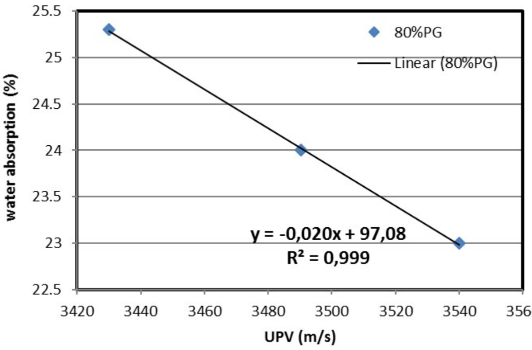

Fig.9 - Correlation between UPV and water absorption of CS-NHL-C-PG full bricks (phosphogypsum=80%).

and Cr, for all mixes, were well below the regulatory limits. Thus, these results indicate that PG amended brick specimens can be considered as non hazardous materials.

4. Conclusions

Based on the experimental investigation data reported in this paper, following conclusions can be drawn:

(1) A unique possibility exists for the utilization of phosphogypsum in producing bricks in the proximity of phosphoric acid fertilizer industries

(2) The CS-NHL-C-PG bricks have sufficient strengths and could be considered as a replacement for load-bearing concrete masonry units and clay or shale brick grade NW.

(3) Phosphogypsum has more pronounced binding action than crushing sand.

(4) The increase of PG and cement content in mixtures resulted in increase of the mechanical strengths of bricks.

(5) Mixture compositions with 80% phosphogypsum content shows low water absorption and better compressive and flexural strength and thus is suitable for use in construction industry.

(6) High correlation coefficients indicate a strong relationship between VS values of bricks and compressive strength, flexural strength and water absorption respectively.

REFERENCES

1. H. Sfar Felfoul, P. Clastres, GA. Carles, M. Ben Ouezdou, Amelioration des caractéristiques du phosphogypse en vue de son utilisation en technique routière. Waste Sci Tech; 2002 **28**, 21[in French].
2. M. Singh, Treating waste phosphogypsum for cement and plaster manufacture. Cem Concr Res; 2002, **32**(7), 1033.
3. M. Singh, Effect of phosphatic and fluoride impurities of phosphogypsum on the properties of selenite plaster. Cem Concr Res; 2003, **33**(9), 1363.
4. M. Singh Role of phosphogypsum impurities on strength and microstructure of serenity plaster. Constr Build Mater, 2005, **19(**6), 480.
5. G.L. Mullins, CC. Mitchell, Wheat forage response to tillage and sulfur applied as PG. In: Proceedings of the third international symposium on PG, Orlando, USA, 1990, vol. I. Publication FIPR no. 01-060-083; 362.
6. J.H. Potgieter, S.S Potgieter, R.I. McCrindle, C.A. Strydom., An investigation into the effect of various chemical and physical treatments of a South African phosphogypsum to render it suitable as a set retarder for cement. Cem Concr Res. 2003, **33**, 1223.
7. I.A. Altun, Y. Sert, Utilization of weathered phosphogypsum as set retarder in Portland cement. Cem Concr Res; 2004,**34**, 677.
8. L. Kacimi, A. Simon-Masseron, A. Ghomari, Z. Derriche, Reduction of clinkerization temperature by using phosphogypsum. J Hazard Mater; 2006, **B137**, 129.
9. N. egirmenci, Utilization of phosphogypsum as raw and calcined material in manufacturing of building products. Constr Build Mater; 2008, **22**, 1857.
10. K. Sunil, Fly ash-lime-phosphogypsum hollow blocks for walls and partitions. Building and Environment; 2003, **38**, 291.
11. Y.K Abalı, M.A Yurdusev, M.S. Zeybek, A.A. Kumanlıog˘lu., Using PG and boron concentrator wastes in light brick production. Constr Build Mater ; 2007, **21**, 52.
12. M.A. array, R. Mensi, Etude de la Deformabilite des Poutrelles en Beton Arme a base du Ciment Ultimax. Ann Batiment Travaux Publics; 2000, **2**, 5 [in French].
13. F.F. Charfi, J. Bouaziz, H. Belayouni Valorisation du phosphogypse de Tunisie en vue de son utilisation comme substituant au gypse naturel dans la fabrication du ciment. *Dechets Sci Tech*; 2000, **20**, 24 [in French].
14. D. Moussa, J.J. Crispel, C.L. Legrand, B. Thenoz Laboratory study of the structure and compactibility of Tunisian phosphogypsum (Sfax) for use in embankment construction. *Resour Conserv*; 1984, 11(2), 95 [in French].
15. T. Kuryatnyk, C. Angulski da Luz, J. Ambroise, J. Pera Valorization of phosphogypsum as hydraulic binder. J Hazard Mater; 2008, **160**(2-3), 681.
16. H. Sfar Felfoul, Etude du phosphogypse de Sfax (Tunisie) en vue d'une valorisation en technique routiere. 2004, PhD thesis, Department of Civil Engineering, National Engineering School of Tunis/INSA Toulouse.
17. BH. Ahmadi, Use of high strength by product gypsum bricks in masonry construction. PhD dissertation, University of Miami, Coral Gables, Florida, USA. (1989), 245p.
18. BS 1881. Recommendations for measurement of pulse velocity through concrete. London: British Standards Institute; 1997 (Part 203).
19. AFNOR. Lixiviation– Essai de conformité pour Lixiviation des déchets fragmentes et des boues. 2002, NF EN 12457-3; [in French].
20. S. Deboucha, R. Hashim, AA. Aziz, Engineering properties of cemented peat bricks Scientific Research and Essays 2011, **6**(8), 1732.
21. BS 6073: Part 1: precast concrete masonry units, Part 1. Specification for precast concrete masonry units. British Standards Institution, 1981
22. ASTM international: C62-08, 2008, Standard specification for building brick: Solid Masonry Units Made from Clay 4p
23. Z. Lafhaj, , M.Goueygou, , A.Djerbi, , M.Kaczmarek, , "Correlation between porosity, permeability and ultrasonic parameters of mortar with variable water/cement ratio and water content", Cement and Concrete Research, 2006, **36,** 625.
24. M.G Hernández,., M.A. Izquierdo., A. Ibanez, , J.J. Anaya,., L. Gomez-Ullate, "Porosity estimation of concrete by ultrasonic NDT", Ultrasonic**,** 2000, **38**, 531.

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