Engineering Properties of Wade Sand-Lime-Cement-Phosphogypsum Building Brick Grade MW

Lamia Bouchhima, Mohamed Jamel Rouis, Mohamed Choura

Abstract-This study concerns the analysis of wade sand - natural hydraulic lime-cement-phosphogypsum (WS-NHL-C-PG) solid bricks grade MW. In Tunisia, for several years, a set of phosphoric acid production factories have produced a waste product such as phosphogypsum (PG) in large quantities (approximately 10 million tons per year). Currently, in Sfax (Center-East of Tunisia), the PG is stored into piles in the vicinity of the factory, by dry or wet process. The storage of PG, even though presenting a low radioactivity, causes pollution to the water table and to the soil (due to the infiltration of acid and heavy metals). After treatment, the Tunisian PG was presented in the full bricks with different mass percentages of 60, 70 and 80%. The study involved physical, chemical, mechanical and environmental tests on the obtained bricks.

The obtained results showed that WS-NHL-C-PG bricks successfully satisfied the standard requirements of bricks grade MW. Notwithstanding the techno-economic virtues, phosphogypsum-based bricks comply with the criteria for environmentally friendly products manufactured with industrial by-product and the manufacturing process is totally energy conservative.

Keywords: Phosphogypsum; Full brick grade MW; strength; Durability

I. INTRODUCTION

The management of the industrial Phosphogypsum (PG) is environmental problem which concern several countries [1]. Considering the high produced quantities and the chemical composition of waste, this problem is worldwide since the phosphoric acid production is all around the world (Florida ‘‘USA”, India, Jordan, Turkey, Morocco, Senegal, etc.). 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 [2]. 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.

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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 [3], [4], [5]. 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 [6]. 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 [7-8], or to reduce the clinkerization temperature [9]. The PG was also used in soil stabilization [10]. Finally phosphogypsum PG has been studied to be used in hollow blocks [11] and light brick [12].

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 [13]-[14]. Moussa et al., (1984) had studied the possibility of the use of the PG in the embankments [15]. 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. Moreover, Kuryatnyk and Angulski- Ambroise- Pera (2008) have employed the Gabes and Skhira PG to be used as a hydraulic binder. But formation of ettringite led to cracking and strength loss [16]. Finally, Sfar et al have explored the PG for a road use [17]-[18]. 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, we start work the treatment of the Tunisian PG by adding wade sand and natural hydraulic lime. We deal in the second part with the valorization of PG in full bricks. This study scrutinizes the manufacturing process and tests for WS-NHL-C-PG bricks characterization.

II. EXPERIMENTAL PROGRAM

A. Characteristics of the studied PG

The characteristics of a PG depend on its composition and on its manufacturing process and control. Samples are obtained from the PG piles in the vicinity of the factory of Sfax (Center-East of Tunisia). The studied PG is characterized through its granularity, grains density, radioactivity and chemical composition.

2.1.1 Particule size

Fig. 1 presents the granulometric curve of the studied PG. The granular distribution of PG is obtained by laser diffraction (laser granulometry). This figure shows that the studied PG appears like fine sand, of a granulometry lower than 250 µm. The granular distribution of PG depends on the quality and the reaction of the time of the phosphate attack. The test allowed calculating the Coefficient of Uniformity (Cu) and the Coefficient of Conformity (Cc).

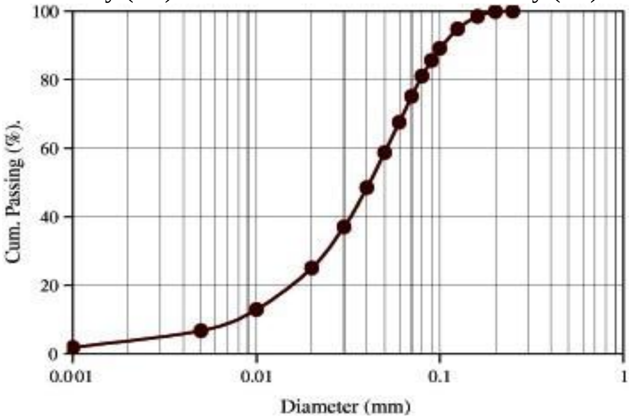

Fig. 1. Granulometric curve of the studied Tunisian PG.

The Cc (resp. Cu) was evaluated at 8 (resp. 3.125). Fig. 1 shows also a suitable uniform granulometry, consequently, it gives an optimum compactness which influences the strength, mainly in compression. The PG is considered to have a fine granulometry which is similar to sand. The Tunisian PG presents a percentage of fines of about 80% [17]-[18].

Grains density

The real densities of the grains were determined by the pycnometer method, by using water saturated with gypsum. The studied PG presents a density of about 2300 kg/m3. This value is the same as for the natural gypsum (2320 kg/m3). This value is also close to that indicated for the Brazilian PG (2308 kg/m3) [19]. But this density is lower than the one of the Turkish PG (2890 kg/m3) [20]. Theses high values are explained by a strong presence of impurities.

Chemical composition

The chemical analyses, most relevant to the prospect use in commercial brick making, are undertaken on the PG. The results of these analyses are presented in Table I. The PG is primarily (about 77%) made up of calcium sulfate (CaSO4). The remaining components are present at low percentage. It should be noted that the pH of PG samples are around 2.9, indicating a high acidity of the PG.

Table I. Chemical composition of phosphogypsum

Elements	(%)
CaO	32.8
SO_3	44.4
P_2O_5	1.69
F	0.55
SiO_2	1.37
Fe_2O_3	0.03
Al_2O_3	0.11
MgO	0.07
Ignition loss at 1000°C	22.3

B. Characteristics of the wade sand

Granularity

Fig. 2 presents the granulometric curve of the wade sand. The granular distribution of wade sand was obtained by dry sieving. The Cc (resp. Cu) was evaluated at 1.14 (resp. 3.11). Fig. 2 shows also a suitable uniform granulometry, consequently, it gives an optimum compactness which influences the strength, mainly in compression.

Grains density

The real densities of the grains were determined by the pycnometer method. The studied ridded wade sand presented a density of about 2630 kg/m3. This value is higher than the one for phosphogypsum.

C. Mix proportion

The mix proportions of phosphogypsum wade sand (WS), lime and cement (cement HRS 42.5) for bricks are given in table II.

The optimization of the mixes is based on the results of the evolution of pH of Phosphogypsum- wade sand-lime mixtures. Fig. 3 show that the wade sand-mix increased slightly the pH without reaching neutralization. Therefore, a small adding lime is necessary.Fig.4 shows the evolution of pH values with adding natural hydraulic lime. These results indicate that the adding of lime has allowed the neutralization of Phosphogypsum- wade sand mixtures. Besides, treatment with 3% lime has contributed to the use of higher percentage of Phosphogypsum (up to 60%). This minor amount of lime (3%) was chosen due to the fact that the PG plays the part of grease-remover. The use of higher percentage of phosphogypsum allows an economical gain on the price of brick (nowadays, the PG is free). Actually, the use of PG would resolve the problem of its storage.These Phosphogypsum-wade sand-lime mixtures would facilitate basic cementitious reactions, the formation of CSH compounds and, therefore, the best opportunities for development as a building material.Shrinkage cracking and spalling are major weaknesses 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.

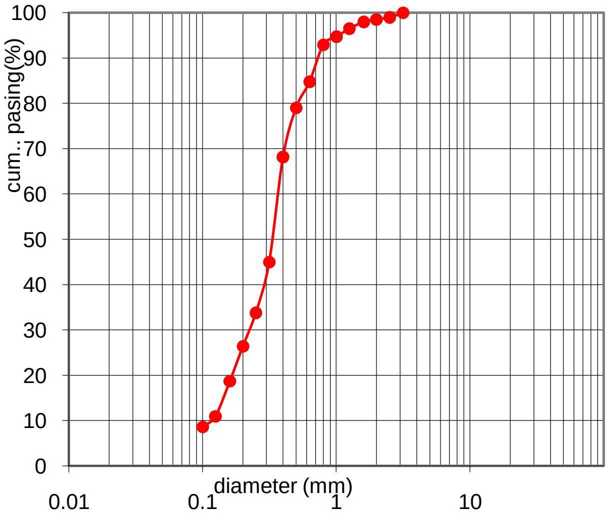

Fig 2. Granulometric curve of the waded sand.

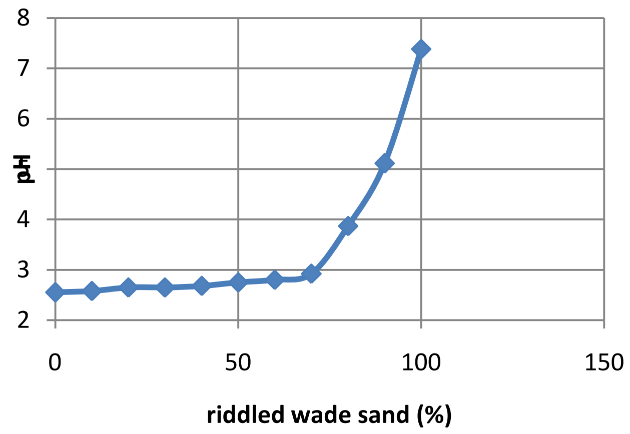

Fig.3. pH phosphogypsum-wade sand mixtures versus crushing sand proportioning

The water contents of Phosphogypsum-wade sand-lime mixtures were fixed to 4 %. Bricks produced with more than 4 % showed cracks after fabrication due to excessive water. All the formulations phosphogypsum-wade sand-lime presents white spots on the brick surface. To solve this problem, minor amounts of cement HRS 42.5 (3 to 10%) was introduced. The optimum composition of phosphogypsum-wade sand-lime-cement mixes is based on the results of the evolution of pH. Fig. 5 shows that the pH increases very slightly with the addition of 3 and 4% cement. A significant rise in pH is remarkable from 5% cement. Besides, the pH shows a significant rise for mixtures which contain 3% CHN, 5 to 10% cement, 60 to 80% phosphogypsum and the rest is that of wade sand. Mixtures containing 3% CHN, 5 to 10% cement, less than 60% of phosphogypsum and the rest wade sand, shows a very slight increase of pH. Thus the percentages are set to 3% CHN, 5, 7.5 and 10 of cement, 60 to 80% phosphogypsum and the rest is that of wade sand. The mix proportions of phosphogypsum, wade sand (WS), 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.

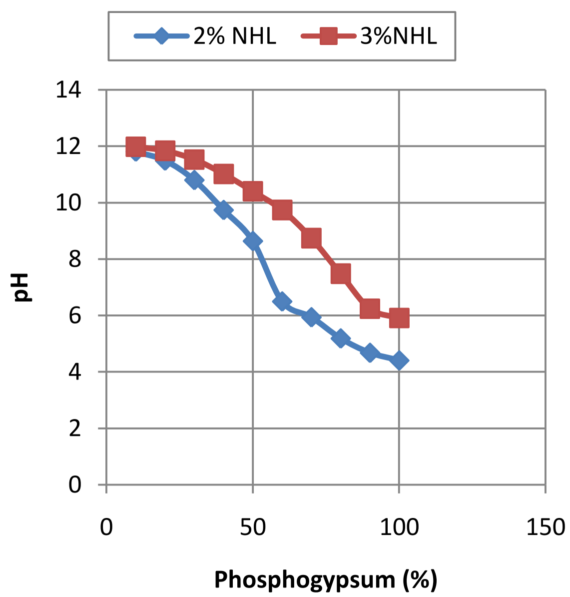

Fig.4. pH phosphogypsum-sand mixtures versus natural hydraulic lime (NHL) proportioning

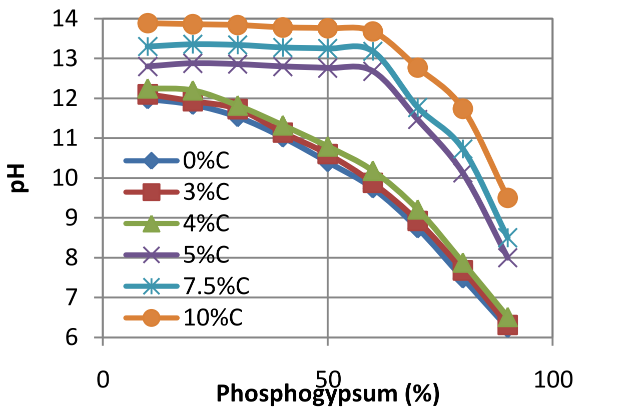

Fig.5. pH phosphogypsum-wade sand-lime-cement mixtures versus cement proportioning

D. Manufacturing process

Mixing of raw materials

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

Preparation of bricks

All full bricks were made on a bench model, semiautomatic press having a capacity of 25 tons, as shown in appendix figure A-2, to produce bricks of 0.051×0.095×0.203 m in size under a static compaction of 27MPa. The following operations are performed to produce one brick:

a. The material at the preset constituent proportions is fed into the mold.

b. The material fully occupies the space available in the mold (volumetric fill). At this point, the top surface is trimmed and the supply material is impeded.

c. The press ram compacts the material in the mold and immediately after, is raised.

d. The crick having a capacity of 5 tons fully extends to extrude the brick.

Table II. Mix proportions of WS-NHL-C-PG full bricks

Mix désignation	Constituant materials (Weight %)			
	Phosphogypsum	Sand (WS)	Cement	Lime
M-1	60	32	5	3
M-2	60	29.5	7.5	3
M-3	60	27	10	3
M-4	70	22	5	3
M-5	70	19.5	7.5	3
M-6	70	17	10	3
M-7	80	12	5	3
M-8	80	9.5	7.5	3
M-9	80	7	10	3

E. Method of curing

All bricks were dried to the free air for a period of 28, 56 and 90 days. The durability of phosphogypsum-based bricks was investigated by submersion in cold and boiling water.

F. Testing of bricks

Compressive strength, density, water absorption, saturation coefficient and leaching tests of bricks from different mixes of phosphogypsum, wade sand, lime and cement with available mixing water content were determined.

Compressive strength of the units was determined according to ASTM C67 [21]. Test bricks, as shown in appendix figure A-2, consist of a half brick with full height and width.

The absorption qualities of bricks are taken as a part of the acceptance measurement of the material durability. 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. After the cold water immersion, the unit is immersed in boiling water for 5 hours. Again the amount of absorption is recorded as a percentage of the total weight of the dry unit. The ratio of these two immersions is the cold water/boiling water ratio, or saturation coefficient. The test specimens were consisted of half bricks. Five specimens were tested.

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

The leaching tests had been performed according to the French Norm NF EN 12457-3 [22] at an 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 phosphogypsum-based bricks were tested after 28, 56 and 90 days of treatment. Water absorption, saturation coefficient, density and leaching test were determined on bricks tested after 28 days of casting.

III. TEST RESULTS AND DISCUSSION

A. Dry density

The densities of WS-NHL-C-PG full bricks are shown in table III. These densities range from 1598 to 1834 kg/m^3. Therefore the WS-NHL-C-PG full bricks have high density.

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

Mix désignation	Dry densities (kg/m^3)
M1	1598
M2	1631
M3	1660
M4	1615
M5	1638
M6	1652.5
M7	1731
M8	1753
M9	1834

B. Water absorption and saturation coefficient of studied bricks

The 24-h cold water absorption

The water absorption is a principal factor for the durability of the product and its behavior to natural environment. Table IV presents the results of the water absorption for the selected percentages of the bricks. The fact that the water absorption of bricks decreased with the increase cement and phosphogypsum contents was deduced. Moreover, the values obtained were favorable when compared with those of clay bricks (0 to 30%) [23].

The 24-h cold water absorption of each unit of a random sample of five WS-NHL-C-PG bricks exceeds 8%. So, the saturation coefficient requirement does apply [24].

The water absorption by 5 hours boiling test

The Water absorption after 24 hours in cold water+5hours in boiling water is shown in table IV. The fact that water absorption of bricks increased after 5hour boiling was noticed. The 24- hour submergence alone will not fill all the pores spaces in a brick, so more will be filled during the boiling stage.

Besides, the results show that the water absorption of phosphogypsum-based bricks is less than the maximum limit for clay building brick grade MW (moderate weathering) set by ASTM (22%).

The saturation coefficient

The saturation coefficient of those bricks is shown in table IV. This ratio is the proportion of total pore space that is easily filled with moisture. Since only a part of the total pore space of the brick is naturally filled with water in place, it is thus known that the room for expansion exists during freezing, without disrupting the wade sand-lime-cement-phosphogypsum body. This is the reason why this property becomes a partial measure of durability. The saturation coefficient of phosphogypsum-based bricks is less than the maximum limit for clay building brick grade MW set by (0.88). Therefore WS-NHL-C-PG bricks have moderate resistance to damage by freezing when wet.

Table IV. Physical characteristics of WS-NHL-C-PG full bricks

Mix designation	Water absorption after 24 hr cold water (%)	Water absorption after 24 hr cold water +5hr boiling (%)	Saturation coefficient
M1	19.71	22.4	0.88
M2	18.23	21.2	0.86
M3	16.88	20.1	0.84
M4	18.7	21.5	0.87
M5	17.25	20.3	0.85
M6	16.1	19.4	0.83
M7	17.74	20.63	0.86
M8	16.29	19.4	0.84
M9	15.04	18.35	0.82

C. Mechanical properties of studied bricks

The results, obtained as an average of measurements performed on three specimens, are shown in Figs. 6-8. For all the studied cases, the compressive strength of the 90 days cured full bricks was higher than 17.2 MPa which is the minimum strength of building brick grade MW [24]. According to literature sources, recommended wet compressive strength values of bricks and blocks are quite wide ranging, varying from country to country and from an author to another. The experimental values obtained here, however, can be well compared with most current brick and block standards. Some recommended minimum values are:

1.2 and 2.8 MPa [23]. Cement and lime as a source of reactive silica and alumina are given to silicate and aluminates hydrates, which are responsible for the development of compressive strength.

These Figures also shows increase in the compressive strength with the phosphogypsum and cement additions. This result confirms the water absorption test outcome, where it has been indicated that the addition of phosphogypsum produces a decrease in the internal pore size. Thus, the brick becomes less porous causing an increase in the mechanical strength.

WS-NHL-C-PG bricks are found to be conforming to physical requirements of clay or shale building brick grade MW (moderate weathering), bricks intended for use where moderate resistance to cyclic freezing damage is permissible or where the brick may be damp but not saturated with water when freezing occurs [24]. Therefore, WS-NHL-C-PG bricks can replace the clay or shale brick grade MW.

D. Leaching tests

The average values of the leaching test are presented in Table V. The concentrations of the selected metal species, i.e., Cd, Cu, Zn, Ni, Pb, and Cr, for all mix-design, were well below the regulatory limits. Thus, this result indicates that PG amended brick specimens can be considered as non hazardous materials.

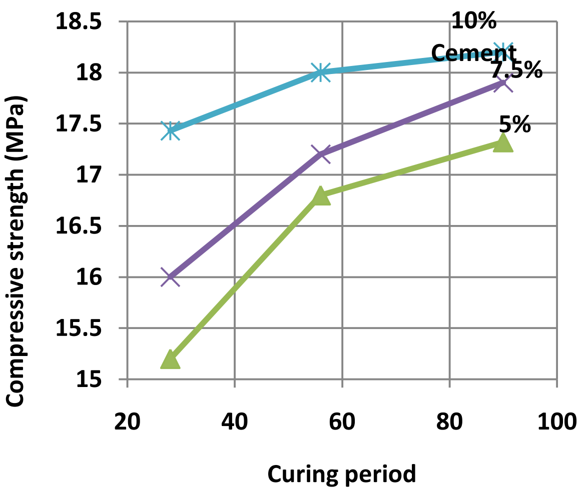

Fig.6 Compressive strength of WS-NHL-C-PG full bricks (phosphogypsum=60%)

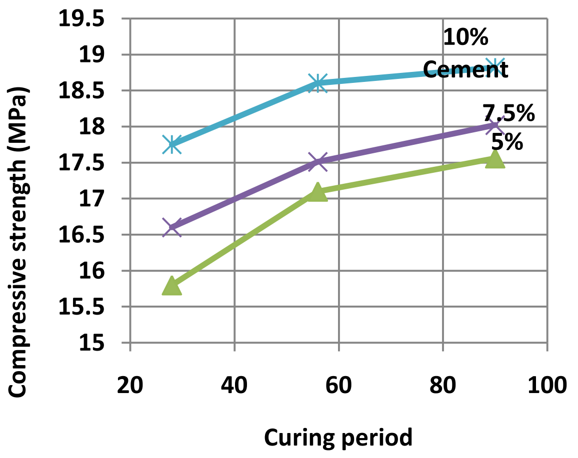

Fig.7. Compressive strength of WS-NHL-C-PG full bricks (phosphogypsum=70%)

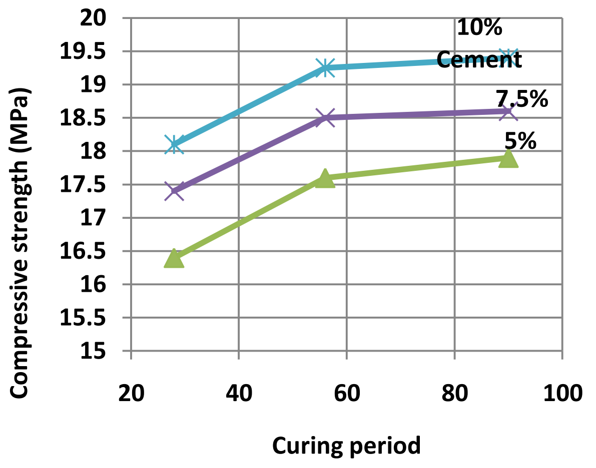

Fig.7 Compressive strength of WS-NHL-C-PG full bricks (phosphogypsum=80%)

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

Mix designation	Elements					
	Cr	Ni	Zn	Pb	Cu	Cd
M1	0.063	0.058	N	0.064	0.17	0.067
M2	0.057	0.045	N	0.053	0.15	0.055
M3	0.05	0.039	N	0.035	0.09	0.043
M4	0.055	0.046	N	0.06	0.12	0.053
M5	0.046	0.04	N	0.05	0.09	0.046
M6	N	0.035	N	0.03	0.063	0.037
M7	0.043	0.04	N	0.05	0.09	0.04
M8	0.035	0.035	N	0.045	0.055	0.02
M9	N	0.03	N	0.027	0.03	0.01
Limit values acceptable as inert	4	0.4	4	0.5	2	0.04
Limit values acceptable as non hazardous	50	10	50	10	50	1

IV. CONCLUSION

Based on the experimental investigation reported in this paper, following conclusions are drawn:

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

(2) The WS-NHL-C-PG bricks have sufficient strength and have potential as a replacement for conventional full clay bricks grade MW.

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

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

(5) Cementations binder with 80% phosphogypsum content shows low water absorption and better compressive strength and thus is suitable for use in construction industry. WS-NHL-C-PG bricks with 5% cement can be delivered after 56 days of manufacturing.WS-NHL-C-PG bricks with more than 7.5% cement can be delivered to the construction site after 28 days of manufacturing. This is can reduce the cost of storing the bricks.

(6) When subjected to a boiling test, the cementations binder which gave low water absorption after 24 hours in cold water and better compressive strength exhibited a low saturation coefficient.

APPENDIX

Fig.A-1. A mixer

The mixer was used for mixing materials. This type of mixer is suitable for mixing dry and lean mixes.

Fig.A-2. Bench model, semiautomatic press machine

The press machine was prepared specifically for this work. The model consists of a semi-automatic press, a mold, and a creek. The press has a capacity of 25 tons. The crick has a capacity of 5 tons.

Fig.A-3. Compressive strength test of the units

The size of test specimen is full height and width, and approximately one-half of a brick in length. The specimen is centered under spherical upper bearing block. The introduction of an eccentric load, if the specimen is not carefully centered, can result in a lower apparent compressive strength for the test specimen. Therefore, the specimens were carefully centered.

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