Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2019, 11(8):55-65

Research Article

ISSN: 0975-7384
CODEN(USA): JCPRC5

Valorisation of Phosphogypsum in Concrete (Non-Load Bearing Concrete)

Omar Moudden[1,3*], Abdelwahed Chari[1,2], Omar Elfilali[3], Chawki Sadik[1] and Abdselam El Bouari[1]

[1]Laboratory of Physico-Chemistry of Applied Materials (LPCMA), Faculty of Sciences Ben M'sik, University of Hassan II of Casablanca, Driss El Harti, B.P 7955, Sidi Othmane, Casablanca, Morocco

[2]Center of Advanced Materials, EMINES, University Mohammed VI Polytechnic, Lot 660 Hay MoulayRachid, 43150, BenGuerir, Morocco.

[3]Structure & Rehabilitation Laboratory, Casablanca, Morocco

---

ABSTRACT

This work presents the first results of the use of phosphogypsum (rejection of the production of phosphoric acid) in the manufacture of concrete. We show that from the point of view of the physical characteristics and aspects required, mechanical performance tests performed on hardened concrete specimens manufactured in the laboratory at different addition dosage and ages have been shown. The introduction of this waste at mass percentages up to 15% gives encouraging behaviors of concretes formed for specific applications (non-load bearing concrete).

Keywords: Concrete; Cement replacement; Sustainability; Non-load bearing concrete

---

INTRODUCTION

Each production area and industrial process requires the use of raw materials and involves physical and/or chemical transformations in order to obtain end products. This generates wastes that will surely have bad impact on the environment [1-4].

Morocco is the world's second producer and exporter of phosphate with about 23 million ton per year. For that reason, phosphate mining and processing industries and resulting wastes constitute a field of scientific studies that is relevant nowadays. The volume and chemical characteristics of these materials generate serious problems. From one hand, they require large and safe storage spaces [5,6]. From the other hands, solutions for an environmental being degradation process should be seted up. Therefore, valorization of mine wastes will contribute directly to the protection of environment by reducing the amount of toxic species or transforming them into chemically stable products using several procedures. The treated products can be exploited for other industries [7,8].

Several phosphogypsum upgrades have been initiated in the chemical industry and in civil engineering, especially in backfill and construction materials (cement, road and agricultural industry, etc…). However, the phosphogypsum contains toxic and radioactive constituents.

Which reveal serious environmental problems mainly water pollution [9,10]. Up to now, phosphogypsum is used in the manufacture of Portland cement. It has also been used in large quantities since the 1950s in the manufacture of reinforced concrete [11,12].

In 1991, Ribas et al. published a patent on the co-production of clinker and sulfur dioxide destined to the production of sulfuric acid from calcium Sulphate [13]. In 1903, lunge et al. reported for the first time that calcium sulphate, heated with clay can directly decompose to sulfur dioxide and clinker cement. Subsequently, in 1908 [14] Hofman and Mostowithsch published two papers on the effect of temperature on the decomposition rate of CaSO4 in the presence of additives. In 1915 [15] Mueller studied the decomposition of CaSO4 with additives at the laboratory scale and the process was finally implemented on an industrial scale by Kuhne. Thus, in the 1920 [16] Muller-Kuhne technology developed in Europe with Marchon in England at Whitehaven and Billingham. Other countries implemented this process later, such as France, Austria, South Africa and Poland [17,18]. However, this process requires a very high investment cost and has proven to be economically viable only for industries with certain characteristics ie companies with a high sulfur requirement [19], located in an area with large quantities of gypsum (or phosphogypsum) and coal and when the price of sulfur or its import is high. In addition, with this process, some companies have experienced difficulties in operation and maintenance [20]. Moreover, the gas generated from this process contained only between 7 and 10% of SO_2 [21].

The aim of this project is the recovery of industrial wastes in concrete for non-load bearing structures and the use of phosphogypsum as a regulator of Portland cements in different proportions. Preliminary tests showed that the use of phosphogypsum does not affect the strengths of concrete after seven and twenty eight days of hydration.

MATERIALS AND METHODS

Materials

The phosphogyps (PG) used in this study is collected from the Moroccan phosphoric acid industry in the region of JORF LAS FAR EL JADIDA. After drying it in an oven at 80°C, the PG was sieved to have a particle size of less than 0.5 µm [12].

Characteristics

- Samples with grain size less than 80 µm were observed using a HIROX S4000 scanning electron microscope. Before introduction into the enclosure of the SEM, the samples have undergone carbon deposition in order to increase the electronic conductivity of the surface.
- The IR spectra of the samples were acquired in the frequency range 4000 - 400 cm^{-1} on a BRUKER TENSOR 27 spectrometer. The finely ground solid were mixed with KBr (1 mg per 100 mg KBr). After homogenization, the mixture is pressed to obtain pellets. These are kept away from the air until they pass through the appliance, in order to avoid any decomposition with air humidity.
- Energy dispersive X-ray spectrometry (EDS) analysis was performed at the Materials and Energy Research Center at Hassan II University using a Bruker EDS "Quantax Compact" spectrometer.

- Thermogravimetric and thermo-differential analysis (ATG/ATD) was performed using a Verstherme TGA thermoanalyzer (Thermoscientific), in a temperature range of 25-1000 °C, with a heating rate of 10°C/minute and a cooling rate of 30°C/minute.
- The X-ray diffraction analysis was carried out at the MOHAMMED V Rabat Faculty of Science on a BRUKER AXS type apparatus equipped with a copper anticathode (15,418 Å).

Phosphogypsum Characteristics

The phosphogyps (PG) used in this study is collected from the Moroccan phosphoric acid industry in the region of JORF LAS FAR EL JADIDA. After drying it in an oven at 80°C, the PG was sieved to have a particle size of less than 0.5 μm.

The chemical analysis of phosphogypsum indicates high content of calcium and sulfur (As indicated by reflections in the XRD diffractogram) as well as the presence of some traces of aluminum, phosphorus and sodium respectively coming from Al_2O_3, P_2O_5 and Na_2O. We also note the significant presence of Si, Mg and Fe due mainly to impurities from siliceous minerals in different forms: quartz (SiO_2), opal (SiO_2, nH_2O), and various silicates of iron alumina and magnesium. Elements pourcentage and morphology of the GP are presented in Table 1 and Figure 1.

Table 1. Chemical composition of PG

Elements	%Mass
SO_3	44.29
MnO	0.01
CaO	36.22
SiO_2	7.28
Na_2O	0.19
Fe_2O_3	0.05
Al_2O_3	0.22
P_2O_5	2.41
MgO	0.01
K_2O	0.01
TiO_2	0.06
P.A.F	8.46

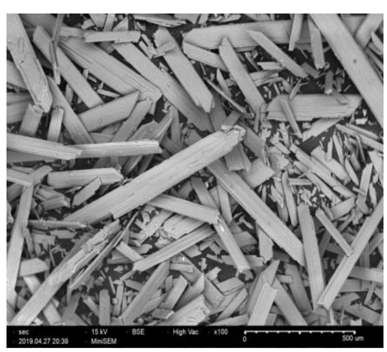

Figure 1. Morphlogical characterization of phosphogypsum by SEM

The mineralogical characterization was carried out by powder XRD (Siemens D500, λKCuα1=1.5406Å). The spectrum is shown in Figure 2.

Table 2. Indexation of phosphogypsum DRX diagrams

hkl	Presented phase
20	$CaSO_4$, $2H_20$
100	$CaSO_4$, $1/2H_20$
-121	$CaSO_4$, $2H_20$
40	$CaSO_4$, $2H_20$
130	$CaSO_4$, $2H_20$
-141	$CaSO_4$, $2H_20$
200	$CaSO_4$, $1/2H_20$
102	$CaSO_4$, $1/2H_20$
51	$CaSO_4$, $2H_20$
213	$CdSO_4$, $2H_20$ + $CaHPO_4$, H_2O
202	$CaHPO_4$, $2H_2O$+ $CdHPO_4$

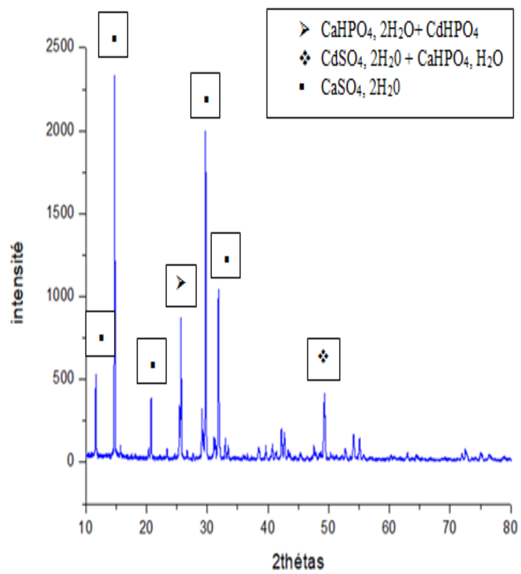

Figure 2. DRX diffraction spectrum of phosphogypsum

The indexing of the X-ray diffraction pattern lines made it possible to determine the values of inter-reticular distances. All of these results are presented in Table 2.

The analysis of the results in Table 2 shows that the phosphogypsum consists mainly of calcium sulfate dihydrate ($CaSO_4$, $2H_2O$) and hemihydrate ($CaSO_4$,$1/2H_2O$) with the presence of diffraction lines that correspond to the brushite ($CaHPO_4$,$2H_2O$).

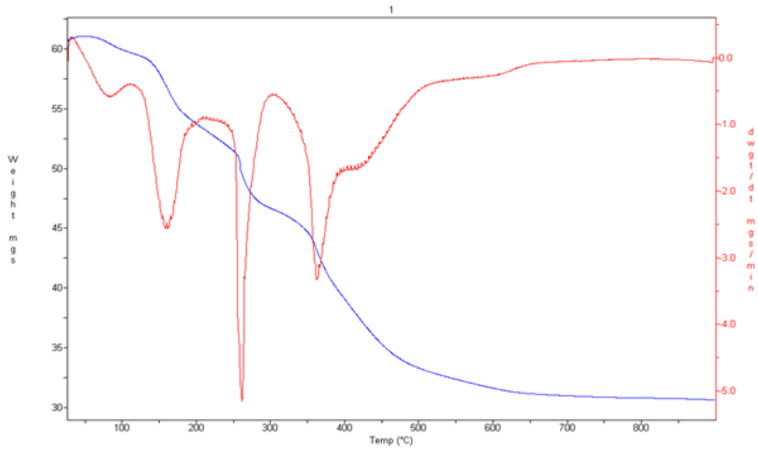

Figure 3. DTG/TGA curves of phosphogypsum

The TGA curve of phosphogypsum, recorded in inert atmosphere (argon) with a heating step of 10° C/min. From (Figure 3) exhibits a first endothermic peak around 150° C corresponding to the departure of water adsorbed on phosphogypsum. The second endothermic peak between 260 and 450° C corresponds to the pyrolysis of organic matter which consists of a transformation of a solid mass into a liquid/gas mixture. Another endothermic peak is observed around 600°C which represents the decomposition of the mineral matrix (carbonates). Figure 4 represents the infrared spectra between 4000 and 450 cm $^{-1}$ of the phosphogypsum at 40°C.

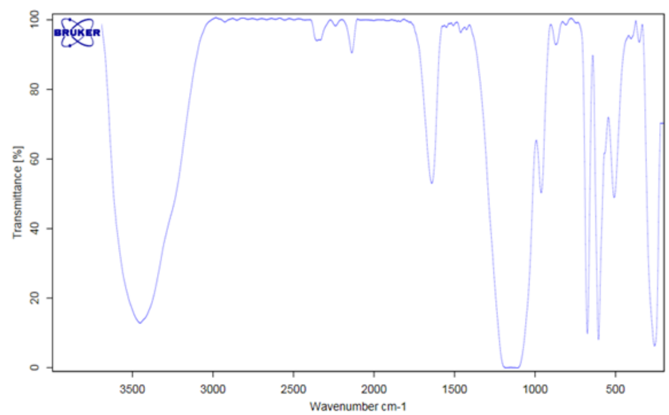

Figure 4. Infrared spectrum of phosphogypsum

The different vibration bands associated with phosphogypsum are detected at:

1- 602 and 668 cm^{-1}: are sharp and can be assigned to ν_4 SO_4^{-1}.

2- 1004 cm^{-1}: associated with ν_1 SO_4.

3- 1113 and 1150 cm^{-1}: are broad and intense and can be attributed to the vibration bands ν_3 SO_4.

4- 1623 and 1684 cm^{-1}: belong to ν_2 H_2O.

5- The band at 1623 cm^{-1} is quite marked, the one at 1684 cm^{-1} is weaker and the bands at 3545 and 3404 cm^{-1} are those of ν_1 H_2O [22].

Characterization of Constituents

The cement used in our study is a composite Portland cement obtained by the finely ground mixture of clinker and additions. Calcium sulphate is added as gypsum as a setting regulator. The cement comes from the Lafarge

Bouskoura factory (Casablanca region) The product has the following commercial identification CPJ-45 It has the following characteristics The starting time measured on pure paste is 62 minutes The compressive strength at 28 days is 45 N/mm^2 and the actual density is 3100 Kg/m^3.

The sand used is a granular fine granulates extending between 0 and 4 mm. It is a product, quarry Casablanca region, resulting from rock crushing of a massive limestone petrography.

According to the laboratory analysis, the results of the cumulative passers and the corresponding granulomere curve shown in Table 3 were obtained.

Table 3. Results of granulometric analysis of aggregates

Gravel		Sand	
Open sieves (mm)	Cumulative percentage of passers %	Open sieves (mm)	Cumulative percentage of passers %
4	100	16	100
2.5	94	12.5	72
2	85	10	33
1.6	75	8	5
1	56	6.3	2
0.8	49	5	1
0.5	37	4	1
0.2	23	0.063	0.5
0.1	18	--	--
0.063	14	--	--

The gravel used is a granular grade granulate extending between 4 and 16 mm (Figure 5), crushed product resulting from the crushing of the same rock used to produce 0/4 sand.

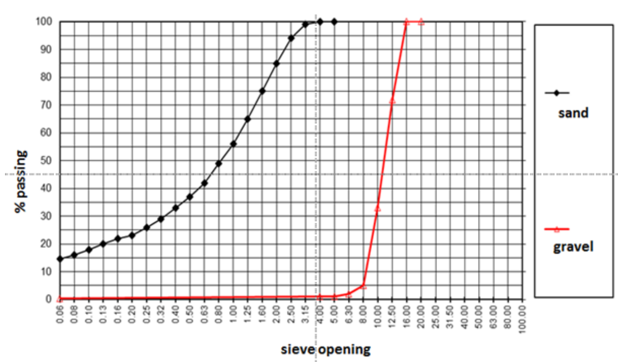

Figure 5. Grain size distribution curves for gravel and sand

It is observed that for this sand, the percentage of fines is a little high and that the equivalent of sand is less than 70%. A high FM fineness module with a value greater than 2.7, which makes this sand coarse sand.

RESULTS AND DISCUSSION

Formulation of concretes

The needs of our study lead us to prepare four concretes from mixtures of aggregates identified in the cement and Phosphogypsum laboratory with well-defined physicochemical characteristics. In what follows we give the definition and composition of each type of concrete. The control concrete is an ordinary mix prepared from 4/16 crushed chippings, 0/4 crushed sand, Portland cement and water and Phosphogypsum is substituted for cement. The method of composition used is the Dreux Gorisse method.

The process followed to prepare the concrete is summarised in the diagram in Figure 6.

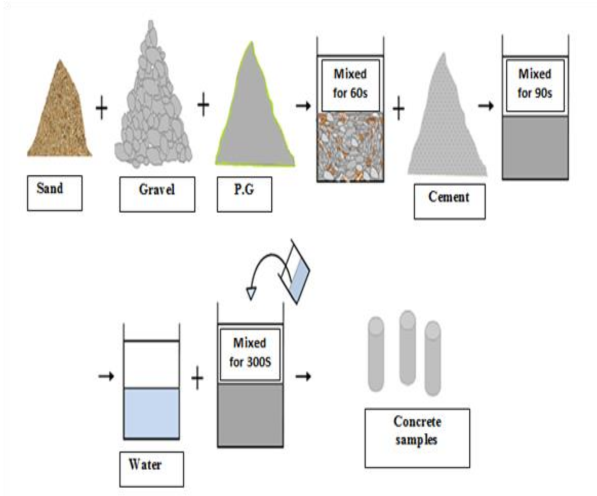

Figure 6. Concrete preparation

Following pre-selected percentages of Phosphogypsum, we obtained four types of concrete presented in Table 4.

Table 4. Concrete designation based on phosphogypsum percentage

Designation	Percentage of phosphogypsum/cement weight
Sample concrete (B_1)	0%
concrete 2 (B_2)	5%
concrete 3 (B_3)	10%
concrete 4 (B_4)	15%

The concrete control studied is a concrete with specified properties (BPS) which according to the standard NF EN 206-1, is designated by: BPS NF EN 206-1 C25/30 XC1 D_{max}=22.4 S Conformity to standard NF EN 206 -1. Resistance class C25/30; Exposure class XC1; Maximum dimension of aggregates D_{max}=22.4 mm; Consistency class S3.

The designation may also include the type and grade of cement if specified in accordance with the standard, eg CEM II/A 42.5 CPJ NA.

Concrete properties

- Resistance

Fck-cyl=25 MPa because it is the most common value in projects, for ordinary concrete.

If we accept an average coefficient of variation of the order of 15%, we can adopt the approximate rule for the average resistance to be targeted at twenty-eight days of σ'28=σ'n + 15%. With a nominal resistance σ'n (bars) for a C25/30, we have a value of σ'n=250 bars.

Hence σ '28=σ'n + 15%=250 + (15 × 250)/100=287.5 Bars

We get a (C/E)=(σ '28/G × σc) + 0.5=1.93 and therefore an E/C=0.52

- Maximum size of aggregates

For the reason of the present study we chose Dmax=16.0 mm

- Consistency

The slump value A=80 ms was obtained. With relative tolerance to consistency target values as follows:

According to the standard EN 206-1 for A=80 mm the tolerance is ± 20 mm which guides us to an acceptable sag between 70 mm and 100 mm.

- Cement dosage

The concrete mixes were dosed at a cement dosage of 400 kg/m^3 which is clearly higher than the minimum dosage prescribed by the European standard where it requires a minimum of 260 kg/m^3.

- The E/C ratio

When calculating the concrete formulation using the Dreux-Gorisse method, a water dosage of 207.25 liters and a cement dosage of 400 kg/m^3 are obtained. This gave us a water-to-cement ratio (W/C) equal to 0.52. By comparing the value obtained with the value specified in the European standard E/C=0.65, we find that the condition 0.52 ≤ 0.65 is satisfied (Table 5).

Table 5. Dosage of the prepared concrete

Percentage	Materials	Volume in L	Dry mass in kg	W%	Q.E existing	wet mass	Q.E Omar Moudden add
PG 0%	PG	---	---	---	---	---	---
	Gravier	357	960.3	0.3	2.9	963.2	---
	Sable	304	556.3	0.9	5	561.3	---
	Eau	211.25	211.25	---	7.9	---	203.35
	Ciment	---	400	---	---	---	---
PG 5%	PG	---	20	13	2.6	22.6	---
	Gravier	357	960.3	0.3	2.9	963.2	---
	Sable	304	556.3	0.9	5	561.3	---
	Eau	211.35	211.25	---	10.5	---	200.75
	Ciment	---	380	---	---	---	---
PG 10%	PG	---	40	13	5.2	45.2	---
	Gravier	357	960.3	0.3	2.9	963.2	---
	Sable	304	556.3	0.9	5	651.3	---
	Eau	211.25	211.25	---	13.1	---	198.15
	Ciment	---	360	---	---	---	---
PG 15%	PG	---	60	13	2.6	67.8	---
	Gravier	357	960.3	0.9	8.64	968.94	---
	Sable	304	556.3	0.9	5	561.3	---
	Eau	211.25	211.25	---	16.06	---	195.19
	Ciment	---	340	---	---	---	---

Application of mechanical tests hard specimens

Concrete Performance (Compressive Strength) The compression test was carried out on cylindrical specimens. The loading speed is constant. The test machine is a class "A" force press with a maximum capacity of 3000 KN in accordance with NF P 18-412 (NA 28)32.

Figure 7. Specimen of concrete

The specimens are stored without being moved within 24 hours. After demolding, the tested pieces were stored until the tests were carried out in the same ambient medium. The purpose of the test is to determine the compressive strength. The studied specimen was subjected to increasing load until rupture (Figure 7 and Table 6).

Table 6. Results of Compressive Strength of Concrete

Specimens	Age	Actual dimensions		Weight of the test piece (Kg)	Density (Kg/m^3)	Load at break (KN)	Resistance to compression (Mpa)
Reference		d (mm)	L (mm)				
0%	7 days	101.1	198.4	3.64	2282.95	156.71	19.5
0%	28 days	110.1	195.2	3.515	2020.08	243.03	25.5
5%	7 days	101.6	196.7	3.764	2357.74	125.79	15.5
5%	28 days	101	198.2	3.8472	2420.12	168.43	21
10%	7 days	102.4	201	3.8520	2324.50	82.44	11
10%	28 days	100.8	198.9	3.722	2342.39	167.76	21
15%	7 days	101	199.2	3.766	2357.15	80.20	10.5
15%	28 days	101.3	204	3.7549	2281.33	100.85	14.5

The conduct of the test is as follows: the test piece, once ground, must be centered on the test press with an error of less than 1% of its diameter. The loading must be carried out at a rate of 0.5 MPa with a tolerance of ± 0.2 MPa. For 16x32 cm test pieces, this means a load increase of 10 KN/s ± 4 KN/s. The breaking load is the maximum load recorded during the test. The compressive strength is the ratio of the breaking load to the cross section of the specimen.

After perfecting the specimen, they are allowed a period of 24 hours to harden it and put it in the preservation room for 7 days and are calculated after their compressive strength each test was carried out 3 times the results of the (Table 7) represent the average.

Table 7. Comparison of the results obtained with the standards

Handiwork	Minimum cement dosage	Concrete strength class	Reference documents
Industrial armored paving	320 Kg/m3 CPJ45	C25/30	NF P 11-213-2 (DTU 13.3. Part 2)
Armored paving building	400 Kg/m3 CPJ45	C20/25	NF P 11-213-3 (DTU 13.3. Part 3)
Concrete curb and gutter	330 Kg/m3	Compressive strength	Fascicule 31

	CPJ 45 ou 55	Classe A : 10 MPa ; Classe B : 7 MPa ; Classe C : 5.5 MPa ;	

Based on the results of the Summary (Table 7) on Low Lift Concrete Elements and Fascicle 31, it can be concluded that the prepared formulations can be used for application in Class A non-load bearing concrete (10Mpa) for formulation 4 (PG15%).

CONCLUSION

Phosphogypsum is a waste obtained in large quantities during the production of phosphoric acid. The untreated rejection of this waste produced in several phosphoric acid production units is not only an environmental threat because of the impurities it contains but also an economic loss. It is therefore ecologically necessary to find another route of elimination and recovery. On the basis of the experimental results of this study, the following conclusions can be drawn; In general, incorporation of phosphogypsum into the cementitious binder reduced the strength.

Experimental results have shown that introduction of 5% of the phosphogypsum with E/C=0.55, with a compressive strength for 7 and 28 days respectively and of the order of 15.5 MPa, 21 MPa

For a percentage of 15% phosphogypsum with an E/C ratio=0.62, with compressive strength for 7 and 28 days respectively and of the order of 10.5 MPa, 14.5 MPa, and according to the standard (Fascicle 31) the formulations prepares that can be used as non-structural class (A) concrete handiwork.

ACKNOWLEDGEMENTS

This work was supported by the University Hassan II of Casablanca and the Structure & Rehabilitation Laboratory.

REFERENCES

1) FC Fourati; J Bouaziz; H Belayouni. *Déchets Sci Tech,* **2000**, 1550.
2) Q Chen; Q Zhang; A Fourie. *J Environ Manage*, **2017**, 201, 19-27.
3) H Felfoul; P Clastres; M Ouezdou. Proprietes et perspectives de valorisation du phosphogypse l'exemple de la Tunisie, in Proceedings of International Symposium on Environmental Pollution Control and Waste Management, EPWCOM, **2002**, 510-520.
4) N Manal; A Samdi; K Elabassi; M Gomina; R Moussa. Recyclage de déchets industriels, phosphogypse et cendres volantes, dans des matériaux de construction, MATEC Web Conf, **2012**, 2, 01015.
5) L Dvorkin; N Lushnikova; M Sonebi. Application areas of phosphogypsum in production of mineral binders and composites based on them: a review of research results, MATEC Web Conf, **2018**, 149, 01012.
6) B Cantero; IF Sáez del Bosque; A Matías; C Medina. *Constr Build Mater,* **2018**, 185, 93-101.
7) M Garcia; L da; J Sousa-Coutinho. *Constr Build Mater,* **2013**, 41, 897-910.
8) J Sun. *Constr Build Mater*, **2013**, 44, 663-670.
9) K Mun; WK Hyoung; C Lee. *Constr Build Mater.* **2007**, 21, 1342-1350.
10) N Lam. *Earth Environ Sci*, **2018**, 143, 012016.
11) D Xuan; B Zhan; CS Poon; W Zheng. *Constr Build Mater*, **2016**, 113, 664-672.
12) F Karim; M Waqif; L Saâdi. Caractérisation physico-chimique du gypse synthétisé et du phosphogypse. **2013.**

13) Y Yang. *Appl Therm Eng,* **2018**, 128, 1494-1501.
14) B Gracioli. *Constr Build Mater.* **2008**, 22, 1857-1862.
15) A Akhtar; AK Sarmah. *J Clean Prod.* **2018**, 196, 411-423.
16) M Choura; M Keskes; D Chaari. *J Environ Sci Toxicol Food Technol.* **2015**, 9, 8-3.
17) A Kashani; T Ngo; A Hajimohammadi. *Cem Concr Compos*. **2019**, 99, 120-129.
18) Mécanique et chimiques sur les Briques cuites fabriquées à partir du phosphogypse, Procedia Environ Sci. 31, **2016**, 970-976.
19) Y Huang; M Zhang; J Lyu; H Yang; Q Liu. *Fuel*. **2018**, 221, 240-248.
20) A Juan-Valdés; D Rodríguez-Robles; J García-González; MI Guerra-Romero; J Morán-del Pozo. *J Clean Prod.* **2018**, 180, 482-493.
21) G Jiang; A Wu; Y Wang; W Lan. *Build Mater.* **2018**, 167, 263-270.
22) CA Takaya. *Waste Manag*. **2019**, 88, 56-70.