

## Reduction of clinkerization temperature by using phosphogypsum

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Received 8 August 2005; received in revised form 13 December 2005; accepted 13 December 2005

Available online 13 March 2006

### Abstract

Valorization of phosphogypsum as mineralizer in the burning of Portland cement clinker was studied in our laboratory. X-ray fluorescence, optical microscope technique and powder X-ray diffraction were then used to characterize the synthesized clinker and its raw mixture in terms of chemical composition and clinker mineralogical composition. The effects of phosphogypsum on structural and morphological properties of clinker minerals and on the presence of alite were followed by scanning electron microscopy combined with microprobe analysis. The addition of phosphogypsum to the cement raw mixture shows that the burning temperature decreases and therefore improves the production process of clinker. The addition of 10% phosphogypsum permits a complete clinkerization at low burning temperature (1200 °C), instead of 1470 °C, which increases the cement factory efficiency by 25% and extends the service life of furnace fire brick. Structural and morphological analysis of clinker produced under the new conditions show that phosphogypsum preserve perfectly the crystalline structure of silicate phases, which leads to the improvement of physical and mechanical properties of cement.

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**Keywords:** Mineralizer; Phosphogypsum; Clinker; Structure; Hydraulic Properties

### 1. Introduction

Mineralizers are inorganic compounds which accelerate the process of reactions in solid phase, liquid phase and solid–liquid interface [1]. They lead to major impacts on the determination of burning zone, the composition and formation of clinker minerals [2,3].

The effect of different mineralizers on the decrease of burning temperature of Portland clinker was the object of many researches. Fluorosilicates improve the chemical activity of clinker mixture minerals and accelerate the reactions of clinkerization at low temperatures (1300–1350 °C) [4,5]. Fluorides, according to different authors [6–8], have also a favorable action on the formation of clinker minerals by decreasing the thermal energy consumption. Various researches related to the study of

oxides effect on the decrease of clinker burning temperature. Alkaline oxides, alkaline-earth oxides and heavy metal oxides, according to their percentage in the mixture and their nature, act differently on the clinker formation reactions [9–15]. Chlorides, carbonates, sulfates and phosphates present also an adequate mineralizer effect on the clinker formation [16–19].

The effect of these mineralizers on the clinker properties was also studied by many researchers [20–42], which determined the influence of mineralizers on chemical, mineralogical, structural, textural, mechanical and physical properties of clinker minerals.

The mineralizer effect of previous pure compounds led the researchers to study industrial wastes containing proportions of such mineralizers studied above. They tested the effect of some industrial pollutant wastes on burning temperature of clinker and their effect on the cement properties, like blast-furnace slag [43], fly ash [44], borogypsum [45], fluogypsum [44] and phosphogypsum [46–53].

Phosphogypsum is a by-product of the fertilizers industry, obtained by etching natural calcium phosphates by sulfuric acid. In this process, the residue is a dihydrate calcium sulfate (phosphogypsum) containing different impurities (Co, V, As, Cu, Cr,

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Pb, Ni, Hg, Cd, F and PO<sub>4</sub>), often toxic, found in the raw materials or produced during the treatment. Its elimination creates a serious problem, which increases with the production increase.

In Algeria, there are two major processes to dispose of phosphogypsum: pouring it into the sea or rivers and burying it. Both processes cause great environment problems and pollution risks of phreatic surface-water table, vegetable soil, rivers and seawater.

In this work, the valorization of phosphogypsum in the cement production is studied. Its influence on the burning temperature of clinker, produced in laboratory using Algerian raw materials (limestone and marl), was examined. The effect of phosphogypsum on clinker minerals and hydraulic properties of the cement derived from this new clinker was also determined.

## 2. Experimentation

### 2.1. Sample preparation

The development of clinker formation was followed mainly on the basis of free lime (CaO) contained in burnt samples. It is the most used procedure so far because calcium oxide, initially formed by dissociation of CaCO<sub>3</sub>, is gradually consumed to give clinker phases. The formation of the latter will be complete when free lime content tends to zero.

To prepare 6 g of mixture, 1–10% of phosphogypsum (PG) was added to the laboratory raw mixture (ML), prepared from limestone and marl (Table 1), according to the raw calculation. After homogenization in a mixer during 20 min, the mixture was introduced into a platinum crucible and placed in a muffle furnace with a heating rate of 30 °C/min. The sample was maintained at the desired burning temperature during 30 min, then quickly cooled by air and crushed. The burned mixture was analyzed by the traditional method (glycerine–alcohol), at the laboratory of Zahana factory, according to the European standard (NE-2-1-015-1984), to determine the residual free lime content.

### 2.2. Sample testing

The chemical compositions of raw materials, mixtures and synthesized clinkers were determined by X-ray fluorescence (PW 1404X) and the morphology by scanning electron microscopy, using a Philips XL30 microscope. The mineralogical composition of these clinkers was determined from the optical microscope observations by using the polished section

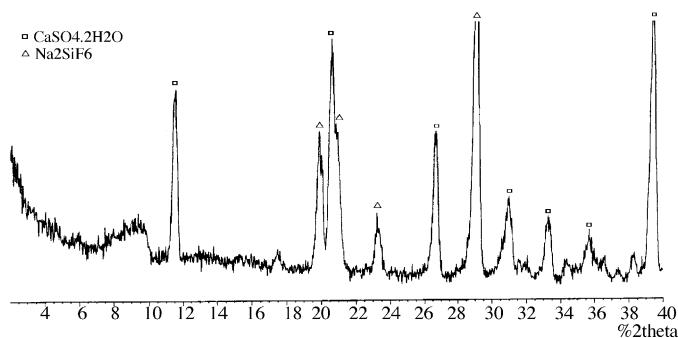


Fig. 1. X-ray pattern of phosphogypsum.

method. Thermal analyzer (DTA-TG) was used to study the mineral mixture transformations during the decarbonation process between 25 and 1100 °C.

The chemical composition of alite (3CaO·SiO<sub>2</sub> or C<sub>3</sub>S) in the synthesized clinkers was determined by scanning electron microprobe analysis on a Casting type (CAMEBAX) electron microscope. Crystallized phases in the clinker minerals were identified by X-ray diffraction with a Philips PW 1800 diffractometer equipped with a variable slit opening using the Cu K $\alpha$  radiation.

Mechanical and physical tests on cements derived from this clinker were carried out according to the French standards (NF P15-431, 432, 442, 451, 461). The addition effects on the setting time, expansion, density, specific area, mechanical strength and hydration heat of these products were determined. These cements were prepared at the Zahana factory, in accordance with the standardized method (NF P15-301) used in the industry, by adding 5% gypsum and 15% pozzolana to the synthesized clinkers. The mineralizer effectiveness was compared to the clinker without phosphogypsum (CML) and the ordinary clinker produced by the Zahana factory (COZ).

### 2.3. Raw materials characterization

The chemical compositions of phosphogypsum (PG), raw materials (limestone, marl), cement additives (natural gypsum, pozzolana) and the laboratory raw mixture (ML) determined by X-ray fluorescence are reported in Table 1. Minerals present in phosphogypsum were identified by X-ray diffraction. As shown in Fig. 1, PG contained gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and sodium fluorosilicate (Na<sub>2</sub>SiF<sub>6</sub>).

Table 1  
Chemical composition (wt.%) of raw materials

Material	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	F	F.S.	LOI
Limestone	53.59	1.26	0.58	0.30	1.85	0.28	0.09	0.22	–	–	–	41.55
Marl	13.86	45.70	11.39	4.88	3.79	0.74	0.37	2.23	–	–	–	16.86
PG	31.18	0.88	0.10	0.03	0.06	40.90	1.32	0.12	0.87	1.20	3.10	20.08
ML	43.14	10.52	3.08	2.88	2.21	0.39	0.29	0.46	–	–	–	36.68
Gypsum	32.03	3.15	0.75	0.46	0.35	41.31	0.01	0.20	–	–	–	21.70
Pozzolana	9.96	47.46	18.13	9.18	4.58	0.09	2.90	1.01	–	–	–	3.82

LOI: loss on ignition; F.S.: fluorosilicates.

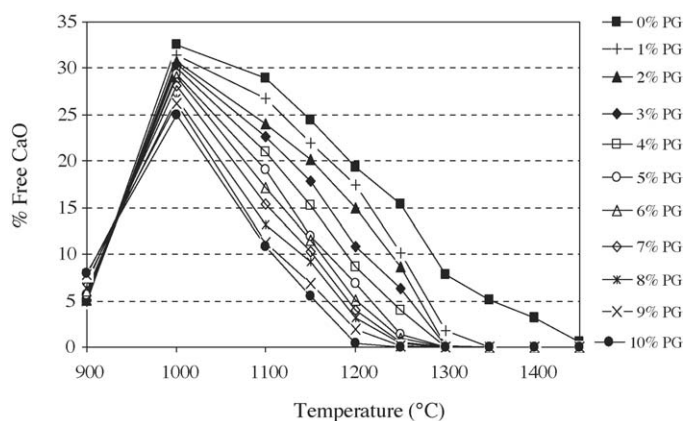


Fig. 2. Phosphogypsum effect on the clinker-free lime content at different temperatures.

### 3. Results and discussion

#### 3.1. Phosphogypsum effect on the decarbonation process

The decarbonation and the burning processes of various raw mixtures (with and without mineralizer), expressed by the variation of free lime content versus heating temperature, are shown in Fig. 2. The variation of free CaO content is a function of added phosphogypsum percentage.

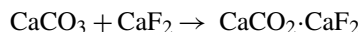
The free lime formation is not observed above 900 °C in mixtures containing more than 3% of phosphogypsum, although the limestone decarbonation starts from 750 °C in the clinker raw mixture [54], according to the reaction:



The absence of CaO is registered in spite of the strong decarbonation, confirmed by thermal analysis (TDA-TG): high mass loss is observed in the vicinity of 800 °C, which confirms the CO<sub>2</sub> departure of the CaCO<sub>3</sub> structure (Fig. 3).

This is explained, on one hand, by the immediate combination of lime (CaO) released by CaCO<sub>3</sub> decomposition, with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, fluorides and fluorosilicates contained in the mixture to form metastable minerals, as calcium silicates, calcium aluminates, calcium aluminoferrites and cal-

cium fluosilicates [55,56]. On the other hand, calcium carbonate can easily combine, in presence of phosphogypsum, with silica, alumina and iron oxide, before its decomposition. Phosphogypsum contains sodium fluorosilicate (Na<sub>2</sub>SiF<sub>4</sub>) (Fig. 1), which gives F<sup>-</sup> and forms calcium fluoride (CaF<sub>2</sub>). The calcium fluoride reacts with calcium carbonate (CaCO<sub>3</sub>) at temperatures lower than 600 °C, according to the reaction [57]:



Above 850 °C, the compound (CaCO<sub>2</sub>·CaF<sub>2</sub>) breaks up into CaO·CaF<sub>2</sub> which combines easily with other compounds in the mixture.

Over 900 °C, free lime starts to form (Fig. 2) and its amount is more significant in mixtures containing more phosphogypsum. This explains the effect of this mineralizer on the decarbonation process.

The reverse is noticed above 950 °C; free lime content in the mixture without mineralizer is higher than in the other mixtures. This difference is accentuated by the increase of phosphogypsum content in the mixture (Fig. 2). This is explained by the mineralizer capacity to make lime combine quickly with other compounds in the mixture, and forms calcium silicates, calcium aluminates and calcium aluminoferrite increasingly rich in CaO.

At 1000 °C, the decarbonation is completed by giving high free lime content, which is higher in the mixtures containing less phosphogypsum. At this temperature, all calcium carbonate is decomposed, which is proven by the mass loss halt in TG-pattern (Fig. 3), and part of resulting CaO is combined to form other minerals. The minerals formation is more significant at low temperatures in the mixtures containing more phosphogypsum, which explains the weak free CaO content in these mixtures at 1000 °C.

#### 3.2. Phosphogypsum effect on clinkerization process

The alite content in various burned mixtures was determined from the optical microscope observations by using the polished section method. Fig. 4 illustrates the variation of the formed alite (C<sub>3</sub>S) content in the mixtures containing different phosphogypsum contents versus burning temperature.

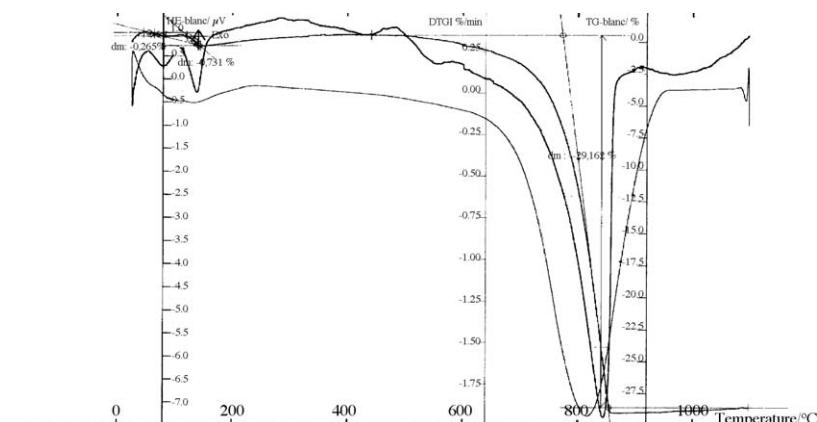


Fig. 3. TDA-TG pattern of phosphogypsum-clinker.

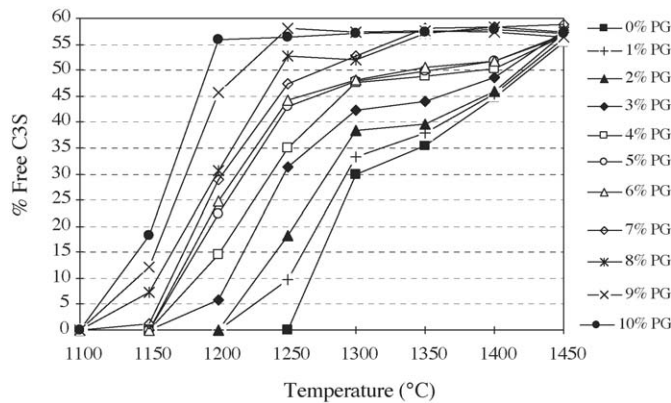


Fig. 4. Phosphogypsum effect on  $C_3S$  formation at different temperatures.

Above  $1000^\circ\text{C}$ , the free lime content starts to decrease. This reduction is more significant when the phosphogypsum percentage increases in the mixture (Fig. 2). This is due to the catalytic effect of the waste, which accelerates the lime combination process and leads to the alite formation at low temperature ( $1150^\circ\text{C}$ ) (Fig. 4).

As shown in Fig. 4, alite content quickly increases with burning temperature when phosphogypsum content increases in the mixture, and consequently, free CaO decreases (Fig. 2). The temperature of alite complete formation, which is clinker formation temperature, decreases versus the phosphogypsum content. Thus, for 10% phosphogypsum, the clinker contains 56% alite (Fig. 4) with a negligible free CaO content (0.4%) at low burning temperature ( $1200^\circ\text{C}$ ) (Fig. 2). This temperature permits to form a clinker, rich in alite and poor in free lime, by addition of 10% phosphogypsum to the raw mixture.

The clinker, containing 10% phosphogypsum, was retained to study the mineralizer effect on its chemical, mineralogical, structural, morphological, physical and mechanical properties.

### 3.3. Chemical composition of studied clinkers

The results of X-ray fluorescence chemical analysis of clinker with phosphogypsum (CPG), clinker without phosphogypsum (CML) and Zahana ordinary clinker (COZ) are reported in Table 2.

A reduction in the percentages of CaO,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and increase in those of  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$ , are noticed in the clinker containing phosphogypsum, which are due to the waste chemical composition and its content in the mixture.

Table 2  
Chemical composition (wt.%) of studied clinkers

Clinker	CaO	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{SO}_3$	$\text{P}_2\text{O}_5$
CPG	62.92	22.90	3.52	3.47	1.24	0.63	1.39	3.52	0.07
CML	64.77	22.43	4.76	4.20	1.54	0.18	0.11	1.67	–
COZ	65.24	23.16	4.55	3.92	1.19	0.21	0.25	1.04	–

Table 3  
Mineralogical composition (wt.%) of studied clinkers

Clinker	Burning $T$ ( $^\circ\text{C}$ )	Alite	Belite	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$	A.P.
CPG	1200	56	25	7	12	17.53
CML	1450	54	29	7	10	20.61
COZ	1470	52	29	8	11	19.54

### 3.4. Mineralogical composition of studied clinkers

The mineralogical composition of these clinkers was determined from the optical microscope observations by using the polished section method. The results are reported in Table 3.

The weight percentages of clinker minerals [alite ( $\text{C}_3\text{S}$ ), belite ( $\text{C}_2\text{S}$ ),  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  ( $\text{C}_3\text{A}$ ) and  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$  ( $\text{C}_4\text{AF}$ )] are calculated in comparison to the crystallized mass. While the percentage of the amorphous phase (A.P.) is given compared to the total mass of the sample, by using the following Bogue method:

- If the alumina modulus:  $\text{AM} = \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3} > 1.38$ :

$$\% \text{AP} = 6.1(\% \text{Fe}_2\text{O}_3) + \% \text{MgO} + \% \text{SO}_3 + \% \text{K}_2\text{O}$$

- If  $\text{AM} \leq 1.38$ :

$$\% \text{AP} = 8.2(\% \text{Al}_2\text{O}_3) - 5.22(\% \text{Fe}_2\text{O}_3) + \% \text{MgO} + \% \text{SO}_3 + \% \text{K}_2\text{O} + \% \text{Na}_2\text{O}$$

The phosphogypsum–clinker presents the greatest alite content in spite of its low burning temperature ( $1200^\circ\text{C}$ ). This is owing to the catalytic effect of this waste containing some mineralizers, in particular  $\text{Na}_2\text{SiF}_6$  and  $\text{CaSO}_4$ , known by their great effect on the  $\text{C}_3\text{S}$  formation by solid-state reactions [21,30,47,58]. The low amorphous phase amount in CPG is due to the low clinker burning temperature ( $1200^\circ\text{C}$ ).

### 3.5. Chemical composition of alite in the studied clinkers

Alite is the most wanted mineral in the clinker, because it determines the hydraulic properties of Portland cement, in particular the mechanical strength. This characteristic is related to its structure and chemical composition. The results of the alite chemical composition, obtained by EDAX, for different clinkers (CPG, CML and COZ) are given in Table 4.

The measured  $\text{CaO}/\text{SiO}_2$  ratio in CPG alite is smaller than that in COZ or CML. This is explained by the fact that in the alite phase, there are small quantities of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{F}^-$ ,



Table 4  
Chemical composition (wt.%) of alite in studied clinkers

Clinker	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	CaO/SiO <sub>2</sub>
CPG	62.67	25.45	2.24	0.51	2.34	1.93	0.25	4.61	2.46
CML	70.29	25.51	1.30	0.58	1.21	0.41	–	0.70	2.76
COZ	72.35	24.69	1.11	0.30	1.16	0.13	–	0.26	2.93

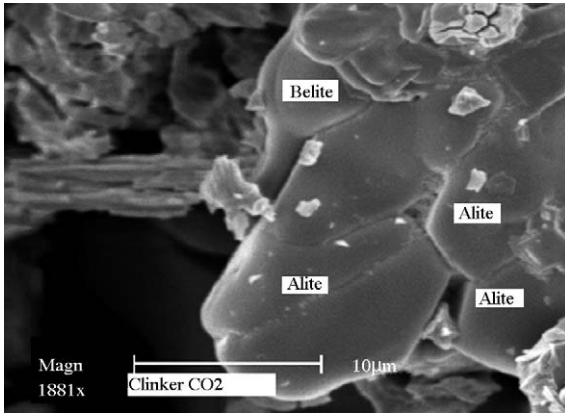


Fig. 5. Scanning electron micrograph of COZ burned at 1470 °C.

which induce a decrease in Ca content, but the phenomenon of Si<sup>4+</sup> substitution by Al<sup>3+</sup>, Fe<sup>3+</sup> and SO<sub>3</sub> is not clear. It is possible that they fill the interstices present in the alite phase. Because of its larger diameter (1.68 Å), Ca<sup>2+</sup> ion gets substituted by the smaller-diameter Na<sup>+</sup> (0.98 Å) and Mg<sup>2+</sup> (0.78 Å) ions, and therefore reducing the alite crystal cell parameters. The amount of SO<sub>3</sub> solid solution in CPG alite is higher than in the others, which is generated by the presence of fluorosilicate in this clinker [21,58].

### 3.6. Characterization of clinkers by scanning electron microscopy

The effect of phosphogypsum on the calcium silicates (alite and belite) morphology was analyzed under scanning electron microscope. The micrographs of clinkers without phosphogypsum (COZ and CML) show that tricalcium silicate (alite) and dicalcium silicate (belite) are characterized by hexagonal and circular shapes, respectively (Figs. 5 and 6). In clinker with phosphogypsum (CPG), this morphology is irregular (Fig. 7), which is due to the presence of fluorine in this clinker [2]. The alite crystal size becomes smaller than in clinkers without mineralizer. This is owing to the Ca substitution by smaller ions (Table 4) and the low liquid mass formation (Table 3), which inhibits crystals agglomeration.

### 3.7. Characterization by X-ray diffraction

To study the effect of phosphogypsum on structural properties of clinker, the synthesized clinkers (COZ, CML and CPG) were characterized by X-ray diffraction (Figs. 8–10).

The high peak intensities in the XRD pattern of phosphogypsum–clinker (Fig. 10) confirm the adequate crys-

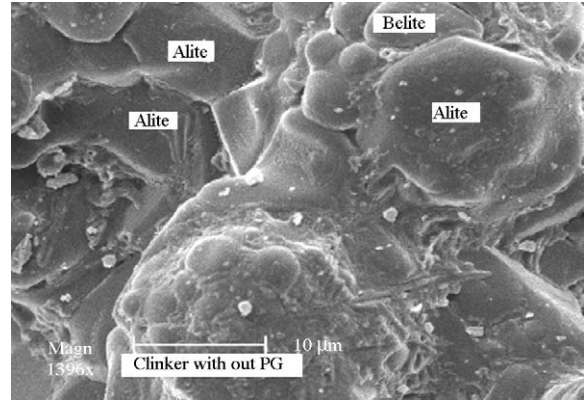


Fig. 6. Scanning electron micrograph of CML burned at 1450 °C.

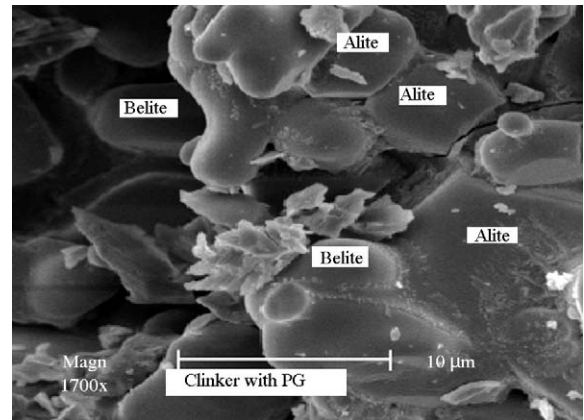


Fig. 7. Scanning electron micrograph of CPG burned at 1200 °C.

tallization of calcium silicates solid solutions, in particular the alite phase, in spite of the low burning temperature (1200 °C). The alite phase in this clinker is different from 3CaO·SiO<sub>2</sub>, as shown by the interreticular distances (Table 5). These distances are definitely weaker in CPG than those of pure C<sub>3</sub>S or in the

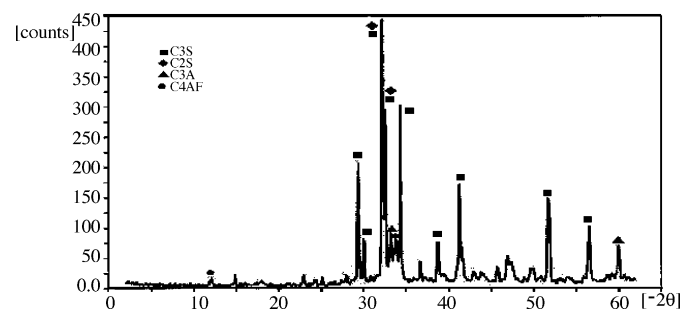


Fig. 8. X-ray pattern of Zahana ordinary clinker (COZ) burned at 1470 °C.

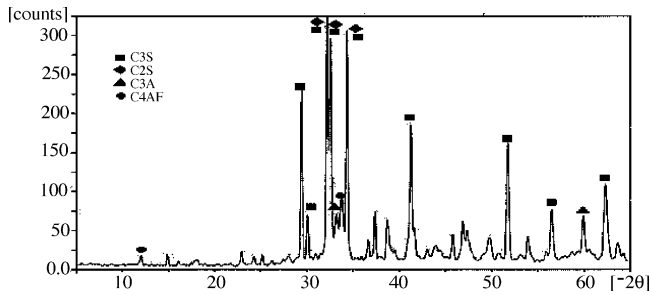


Fig. 9. X-ray pattern of laboratory mixture clinker (CML) burned at 1450 °C.

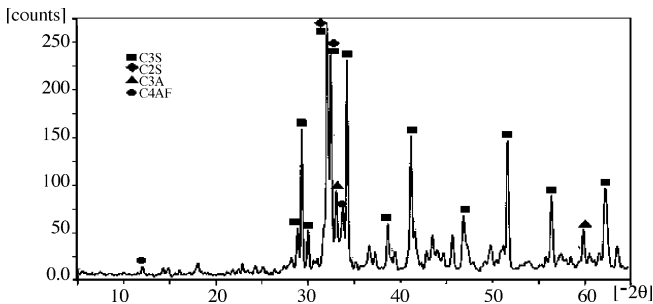


Fig. 10. X-ray pattern of phosphogypsum-clinker (CPG) burned at 1200 °C.

Table 5  
Main interreticular distances of alite crystal lattice in different studied clinkers

Clinker	Main interreticular distances of alite (C <sub>3</sub> S)					
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
CPG	3.0416	2.7836	2.7495	2.6163	2.6090	2.1886
CML	3.0425	2.7854	2.7517	2.6165	–	2.1924
COZ	3.0461	2.7845	2.7575	2.6176	–	2.1924
Pure C <sub>3</sub> S	3.0590	2.7883	2.7676	2.6392	2.6122	2.2153

other clinkers (CML, COZ). This is owing to the Ca substitution by Mg, Na or F, supported by the presence of sodium fluorosilicate and gypsum contained in phosphogypsum. This substitution decreases the CaO/SiO<sub>2</sub> ratio in alite phase by increasing the impurities content in its crystal lattice (Table 4), which improves the hydraulic reactivity of this clinker [21,59].

Belite in phosphogypsum-clinker is crystallized in β-modification and the corresponding peaks shift from their usual positions (Fig. 10). This is due to the presence of fluorine and sulfates which support the insertion of some impurities in belite structure [21]. γ-C<sub>2</sub>S is not crystallized in this clinker, in spite of the fluorine presence which supports this phase formation. This is explained by the existence of SO<sub>3</sub> that plays the role of

Table 6  
Main diffraction angles and peak intensities of C<sub>3</sub>A and C<sub>4</sub>AF

Clinker	C <sub>3</sub> A				C <sub>4</sub> AF			
	Peak 1		Peak 2		Peak 1		Peak 2	
	2θ (°)	III <sub>0</sub> (%)	2θ (°)	III <sub>0</sub> (%)	2θ (°)	III <sub>0</sub> (%)	2θ (°)	III <sub>0</sub> (%)
CPG	33.070	29.5	59.835	8.5	12.050	13.0	33.795	22.0
CML	33.240	19.9	59.910	7.4	12.035	11.5	33.755	19.9
COZ	33.170	18.6	59.915	6.5	12.060	7.3	33.810	15.8

Table 7  
Grindability of studied clinkers

Clinker	Burning T (°C)	SSB (cm <sup>2</sup> /g)	Grinding time (min)
CPG	1200	3500	19
CML	1450	3500	30
COZ	1470	3500	26

β-C<sub>2</sub>S structure stabilizer, in which its incorporation is higher than in alite phase [21].

Some spots are noticed on calcium silicate crystals of phosphogypsum-clinker (Fig. 7), due to the precipitation of SO<sub>3</sub> liquid phase: presence of gypsum and fluoride in the mixture [22,58].

C<sub>3</sub>A and C<sub>4</sub>AF seem to be better crystallized in CPG (Fig. 10) than in CML (Fig. 9) and COZ (Fig. 8), as deduced from their peak intensities (Table 6). This crystallization is due to the low burning temperature (1200 °C), which is close to that of the melting temperature of these phases [21].

The main peak intensity of C<sub>3</sub>A (Fig. 10, peak at 2θ = 33.07°) is stronger than that of C<sub>4</sub>AF (Fig. 10, peak at 2θ = 33.79°) in phosphogypsum-clinker (Table 6). This is explained by the simultaneous presence of fluorosilicate and SO<sub>3</sub>, which supports C<sub>3</sub>A crystallization [58].

The X-ray diffraction angles of C<sub>3</sub>A in CPG are lower than those in the other clinkers (Table 6), which is explained by the presence of fluoride and sulfate in crystals, by forming 11CaO·7Al<sub>2</sub>O<sub>3</sub>·CaF<sub>2</sub> or 4CaO·Al<sub>2</sub>O<sub>3</sub>·SO<sub>3</sub> [21,22,58].

Consequently, phosphogypsum preserves the silicate phases crystallinity of clinker produced at low burning temperatures, by supporting the alite formation with a great number of inclusions and belite in the variety β, which improves the clinker hydraulic activity [21,59].

### 3.8. Effect of phosphogypsum on the hydraulic properties of clinker cements

To study the physical and mechanical properties of selected cements, great quantities of clinker were synthesized to carry out the hydration and hardening tests.

The mixture made of 80% synthesized clinker, 5% natural gypsum and 15% Algerian natural pozzolana (Table 1), was crushed and mixed, in accordance with the used factory method, to obtain Portland cement (CPJ or CEM II), according to standard (NF P15-301). Then 450 g of this cement was mixed with 1350 g of standardized sand and 225 g of water, to obtain mortars for the physical and mechanical analyses.

Table 8  
Physical properties of studied clinker cements

Cement of	Burning $T$ ( $^{\circ}\text{C}$ )	Density (g/ml)	Expansion (mm)	Setting time, $H$ (min)		Hydration heat (Cal/g)		
				Initial	Final	3 days	7 days	28 days
CPG	1200	1.13	00	5:30	7:30	56.3	81.1	94.7
CML	1450	1.24	00	3:14	4:30	71.4	75.4	92.2
COZ	1470	1.23	00	3:55	4:45	60.7	68.6	88.4

Table 9  
Mechanical strength of studied clinker cements

Cement of	Burning $T$ ( $^{\circ}\text{C}$ )	Flexural strength (MPa)			Compressive strength (MPa)		
		2 days	7 days	28 days	2 days	7 days	28 days
CPG	1200	1.87	3.0	8.3	10.84	21.7	45.15
CML	1450	3.50	6.25	7.0	16.9	33.2	43.1
COZ	1470	3.75	5.63	7.0	16.37	30.46	42.0

### 3.8.1. Effect of phosphogypsum on the clinker grindability

The grindability of the produced clinkers was studied by grinding 100 g of the material, precrushed to 1–2 mm, in a small laboratory swing mill and by determining the grinding time to obtain clinker with a  $3500\text{ cm}^2/\text{g}$  Blaine specific area (SSB). The results are summarized in Table 7.

There is a great difference between the grindabilities of the individual clinkers. The grindability of clinker containing phosphogypsum is easier than the others. This is owing to the low amorphous phase (A.P.) amount in this product (Table 3), and consequently the clinker porosity increases which decreases the clinker grain hardness. The decrease of grinding time is also explained by the presence of sufficient amount of  $\text{SO}_3$  in clinker minerals [21,58].

### 3.8.2. Physical properties of studied cements

Physical tests used to determine the expansion, setting time and hydration heat of the clinker cements, according to the French standards (NF P15-432), (NF P15-431) and (NF P15-461) successively, led to the results presented in Table 8.

The hydration heat of CPG-cement evolves quickly with time. This heat, related mainly to the content of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$ , reaches high values after 7 days of hydration, by comparison with other cements (Table 8). The low hydration heat in the short time is due to the ettringite formation, which precipitates on the minerals surface and decreases the  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  exothermic reactions [61]. This is owing to the high  $\text{SO}_3$  content in this clinker. After 3 days, the ettringite crystal lattice is destroyed and the clinker minerals continue their hydration, which accelerates the heat release. The hydration heat becomes more significant in cement of phosphogypsum–clinker. This is explained by the high  $\text{C}_3\text{S}$  content in this clinker (Table 3), the low size of its crystals (Fig. 7) and its disturbed structure, by the substitution of Ca by Na, Mg and F, and by the insertion of other foreign elements like Al, Fe and S (Table 4) [21,61].

The lower density of CPG-cement is due to the low amorphous phase and the high porosity of phosphogypsum–clinker. This clinker, as shown in Fig. 7 and Table 5, is characterized

by small crystals and low amorphous phase which improves the product porosity.

The CPG-cement is characterized by setting time higher than the others. This is owing to the presence of  $\text{SO}_3$  in clinker minerals, in particular  $\text{C}_3\text{A}$  and  $\text{C}_3\text{S}$ . The high presence of  $\text{SO}_3$  in calcium aluminates decreases the cement hydration, by the ettringite formation on crystal surface [60].

On the other hand, the fast cooling of clinker obtained at low temperature allows the formation of crypto-crystalline  $\text{C}_3\text{A}$ , which reacts slowly with water [62].

### 3.8.3. Mechanical properties of studied cements

Because it is one of the most important properties for practical use, the strength development of cements was tested. Test specimens of mortars ( $40\text{ mm} \times 40\text{ mm} \times 160\text{ mm}$ ) with water/cement ratio of 0.5 and an aggregate/cement ratio of 3, according to standard (NF P15-451), were produced from cements of studied clinkers. The results of compressive and bending strengths are given in Table 9.

The mechanical strength of CPG-cement (compressive and flexural strengths) is lower than that of control cements at early ages. After 7 days, the evolution speed of these strengths increases to reach values at 28 days higher than those of the other cements, which is in agreement with the literature [60]. This is explained by the presence of  $\text{SO}_3$  on the clinker minerals surface, in particular  $\text{C}_3\text{S}$  (Table 4 and Fig. 7), which decreases the hydration and consequently the cement hardening, by the precipitation of sulfoaluminates and sulfosilicates on the alite surface. This leads to some expansion and deformation inside mortars [48,58,60]. During the hydration process, water destroys these layers and the cement continues energetically its hardening reactions, which accelerate the strength development to become higher than this of ordinary cement.

## 4. Conclusion

Phosphogypsum allows a complete clinkerization at low temperature ( $1200\text{ }^{\circ}\text{C}$ ). It is distinguished perfectly from the usual

mineralizers by its catalytic effect on the decarbonation and burning processes of clinker raw mixture.

The addition of 10% of this waste in clinker raw mixture permits to decrease the free lime content in the clinker to 0.4% for burning temperature of 1200 °C. The very satisfactory result is due to the mineralogical composition of this by-product composed of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and sodium fluorosilicate ( $\text{Na}_2\text{SiF}_6$ ). The structural and morphological analysis of the clinker, produced under these conditions, showed that this mineralizer preserves, at low burning temperature (1200 °C), the silicate phases crystallinity usually acquired at high temperatures (higher than 1450 °C).

The phosphogypsum–clinker, containing high alite content and  $\beta$ -belite, is characterized by low size crystals of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , generating a great number of inclusions. These characteristics are at the base of the improved mechanical and physical properties of this clinker cement.

The low amorphous phase amount in this clinker increases its porosity and consequently, facilitates its grinding and improves its specific area. This leads to the improvement of its hydraulic properties.

This clinker is characterized by high hydration heat and good mechanical strength at 28 days, in spite of low values at early ages. The prolonged setting time of this cement is owing to the high sulfate amount in its clinker.

The results of this study show that phosphogypsum, under the optimal conditions, influences positively the technological parameters of clinker. It is thus advised to use it as mineralizer in the raw mixtures, since it enables to reduce the burning temperature by almost 250 °C. This generates the reduction of fuel expenditure, the increase in the revolving kiln productivity, the reduction of the electric power expenditure, the increase of the working life of refractory materials and the improvement of the cement quality.

Moreover, the valorization of this polluting industrial waste enables to contribute to the improvement of ecological balance and the environmental protection by its recovery and incineration in the production of clinker Portland cement and by the reduction of the exhausted  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{SO}_x$  due to the decrease of clinker burning temperature.

## Acknowledgments

The authors thank Dr. L. Josien, from the Laboratoire de Matériaux à Porosité Contrôlée for his technical assistance, and thank Dr. A. Mhamedi (Mostaganem University) and Dr. H.H. Al Douri (USTOran University) for reviewing the text.

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