DEVELOPMENT OF NEW COMPOSITE CEMENT BASED ON WASTE ROCKS FROM DJEBEL ONK PHOSPHATE DEPOSIT (TEBESSA-ALGERIA)

Introduction. The mining waste produced continuously by the industrial activities is considered as major problems having a potentially negative impact on the environment and the economy of Algeria. The reuse of waste as an alternative raw material in building materials is a promising environmental solution. This way of valorization reduces large quantities of tailings and thus their environmental impact, as well as contributes to the preservation of non-renewable natural resources intensively used in construction (clays, limestone, sand, and others) [1, 2].

Algeria has a significant deficit in building materials, especially cement. Facing the seriousness of environmental problems due to overexploitation of resources, the Algerian government decided in 2001 to devote an important financial envelope to achieve the objectives set out in the National Action Plan for Environment and Sustainable Development [3].

In the context of sustainable development and, especially, respect for the environment, cement producers were interested in the incorporation into cement of certain industrial by-products, likely to develop hydraulic properties [1, 4].

The need to find different types of cheaper cement with required physic-mechanical properties leads manufacturers to produce cements containing secondary clinker additives (natural or industrial by-products), with more or less significant proportions (mineral additives are widely used in order to largely solve the problem of national self-sufficiency in cements, as well as that of the reduction of the energy cost, thereby the clinker consumption decreases according to the rate of additions used).

The mineral additives often used in the manufacture of cement are mainly blast furnace slag and pozzolan [5, 6], other materials can be used as industrial waste (brick waste, marble waste, flux waste, phosphogypsum, fibber waste). These types of waste can be considered not only as waste but as by-products and a source of one or more elements of commercial value [1].

The approach of our study involves, first of all, characterizing the waste rocks of Djebel Onk phosphate deposits, and then establishing a comparative study between the use of this type of waste as an addition in the production of cement and other additions such as blast-furnace slag (a by-product of steel industry) and pozzolan (of natural origin) and even their influence on the quality of the studied cement CPJ-CEM II 42.5 (on physical parameters such as consistency, measurement of setting time and mechanical parameters such as simple compression).

Characterization of waste rocks from Djebel Onk phosphate deposit (Tebessa). Geographical location. The Algerian phosphate is exploited by the Phosphate Mining Company (SOMI-PHOS) subsidiary of FERPHOS by the open pit method. This raw material is used largely for the manufacture of fertilizers and phosphoric acid. The Djebel Onk phosphate deposit is situated in Bir El-Ater about 100 km from Tebessa.

Characterization of phosphate waste rocks. The chemical and mineralogical composition of phosphate waste rocks is determined by using X-ray fluorescence and X-ray diffraction, respectively.

Chemical characteristics. The chemical analysis of the phosphate waste rocks of the different size fractions was carried out using a series of sieves nested on each other, whose opening dimensions are decreasing from top to bottom. Table 1 and Fig. 1 present the chemical analysis of particles size.

According to the chemical analysis data (Fig. 2) we note that the waste rocks contain all the elements found in limestone and clay (CaO, MgO, and SiO₂) However, limestone and clay do not contain P₂O₅. The phosphate waste rocks contain a very low P₂O₅ content so it is considered as a P₂O₅ poor material.

Mineralogical characterization. From Fig. 2 we see that the mineralogical composition of the original sample includes the following minerals: quartz, carbonate fluorapatite, albite, montmorillonite, orthoclase, dolomite, and calcite. However, it is noted that peaks of quartz, calcite and dolomite have a high intensity and are well expressed, which makes their identification easier.

Experimental part. In this work, we used the cement clinker of Ain Touta, the blast-furnace slag from El-Hadjar steel complex-Annaba(NE of Algeria), the pozzolan (a natural pozzolan of volcanic origin extracted from the Bouhamed de­posit located south of Beni-Saf-Ain Temouchent (NW of Al­geria), and the phosphate waste rocks from Djebel Onk phosphate deposit. Gypsum as a fundamental additive in the ce­ment is of local origin, we maintained a dosage of 4 %, for all the prepared cements for the following reasons:
the quality of the gypsum is average;  
- not to hide the influence of the additive content on the mechanical properties of the cement;  
- to regulate the setting.  

The chemical composition of the raw materials is given in Table 2.  

### Mineralogical composition of clinker.  
Based on certain hypotheses, Bogue (1929) developed a method that allows knowing the potential composition of main minerals (C₃S, C₂S, C₃A and C₄AF) of a clinker, or cement from its chemical composition.  

The numerical values of the mineralogical composition are given in Table 3.  

- C₃S = 4.07[CaO (T) – CaO (L)] – 7.6 (SiO₂ – RI) – 1.43Fe₂O₃ – 6.72Al₂O₃  
- C₂S = [2.865(SiO₂ – RI)] – [0.754C₃S]. RI = 0.21  
- C₃A = [2.650Al₂O₃] – [1.692Fe₂O₃]  
- C₄AF = 3.04Fe₂O₃  

### Preparation of the mixtures:  
To study the influence of the additions on the quality of the cement we have prepared six mixtures for each type of addition (phosphate waste rocks, slag, pozzolan) and a control sample (CWA).  
The starting mixtures are prepared according to the following proportions:  
- Mixture 1: Portland cement without added (96 % clinker + 4 % gypsum + 0 % additive), is named CWA (CPA).  
- For phosphate waste rocks addition CPWR:  
  - Mixture 2 : 91 % clinker + 4 % gypsum + 5 % waste rocks), is named CPWR5;  
  - Mixture 3 : 86 % clinker + 4 % gypsum + 10 % waste rocks), is named CPWR10;  
  - Mixture 4 : 81 % clinker + 4 % gypsum + 15 % waste rocks), is named CPWR15;  
  - Mixture 5 : 76 % clinker + 4 % gypsum + 20 % waste rocks), is named CPWR20;  
  - Mixture 6 : 71 % clinker + 4 % gypsum + 25 % waste rocks), is named CPWR25;  
  - Mixture 7 : 66 % clinker + 4 % gypsum + 30 % waste rocks), is named CPWR30.  
- For the pozzolan addition CP:  
  - Mixture 8 : 91 % clinker + 4 % gypsum + 5 % pozzolan), is named CP5;  
  - Mixture 9 : 86 % clinker + 4 % gypsum + 10 % pozzolan), is named CP10;  
  - Mixture 10 : 81 % clinker + 4 % gypsum + 15 % pozzolan), is named CP15;  
  - Mixture 11 : 76 % clinker + 4 % gypsum + 20 % pozzolan), is named CP20;  
  - Mixture 12 : 71 % clinker + 4 % gypsum + 25 % pozzolan), is named CP25;  
  - Mixture 13 : 66 % clinker + 4 % gypsum + 30 % pozzolan), is named CP30.  
- For the blast-furnace slag addition CS:  
  - Mixture 14 : 91 % clinker + 4 % gypsum + 5 % slag), is named CS5;  
  - Mixture 15 : 86 % clinker + 4 % gypsum + 10 % slag), is named CS10;  
  - Mixture 16 : 81 % clinker + 4 % gypsum + 15 % slag), is named CS15;  
  - Mixture 17 : 76 % clinker + 4 % gypsum + 20 % slag), is named CS20;  
  - Mixture 18 : 71 % clinker + 4 % gypsum + 25 % slag), is named CS25;  
  - Mixture 19 : 66 % clinker + 4 % gypsum + 30 % slag), is named CS30.  

### Physical characteristics of the cement paste.  
**Consistency.**  
The consistency to admit for having a good mortar is the quantity strictly necessary to obtain a plastic paste. The consistency

### Table 1  
Chemical composition of the phosphate waste rocks

| contents  | P₂O₅ | CaO | MgO | SiO₂ | Fe₂O₃ | K₂O | Na₂O | SO₃ | Cl | LOI |
|-----------|------|-----|-----|------|------|-----|------|-----|----|-----|
| (%)       | 1.69 | 28.04 | 14.39 | 25.28 | 0.88 | 0.25 | 0.31 | 0.18 | 0.017 | 28.70 |

### Table 2  
Chemical composition of materials by X-ray fluorescence

|        | SiO₂ % | CaO % | MgO % | Fe₂O₃ % | Al₂O₃ % | Cl % | K₂O % | Na₂O % | SO₃ % | P₂O₅ % | LOI % |
|--------|--------|-------|-------|---------|---------|------|-------|--------|-------|--------|-------|
| Clinker | 20.8   | 67.1  | 1.52  | 3.47    | 5.05    | 0.01 | 0.78  | 0.30   | 0.54  | 0.27   |
| Gypsum  | 8.1    | 34.1  | 3.32  | 1.11    | 3.06    | 0    | 0.58  | 0.04   | 39.5  | 10.0   |
| Slag    | 54.3   | 10.9  | 2.69  | 12.3    | 0.02    | 3.42 | 0.0   | 0.56   | 15.0  |        |
| Pozzolan| 37.8   | 14.9  | 2.69  | 14.39   | 15.4    | 0    | 1.29  | 1.70   | 0.56  | 17.8   |
| Waste rocks | 25.2   | 28.04 | 14.39 | 3.41    | 0.91    | 0.25 | 0.31  | 0.18   | 1.69  | 28.70  |
of the cement is necessary to determine the start and end times of setting.

Corresponding to the reading of the histogram (Fig. 3), it is noted that the increase in the percentage of slag addition in the cement decreases the amount of water; on the other hand, the water quantity increases with the rise in the rate of the phosphate waste rock additive and pozzolan.

The variation of the decrease and the increase in the quantity of water is not the same when phosphate waste rocks, pozzolan and slag are added.

Table 4 indicates that the change in normal consistency is consistent with the Algerian standard requirements NA 229 [7] for all types of studied cements. For phosphate waste rocks and pozzolan additives the consistency is proportional to the addition rates; the more the addition rate increases, the more the consistency increases.

Setting time. The setting time corresponds to the passage of the paste or cement mortar from the fluid state to a more or less consistent state (mechanically resistant solid), measurements carried out using the Vicat apparatus. The results of tests are illustrated in Figs. 4, a, b and c.

Based on Figs. 4, a, b and c we can say that: all the studied cements with additives have a setting time in accordance with Algerian standard requirements NA 442 [8], which imposes a minimum setting time of 60 minutes for the cement class CPJCEMII/A or B 42.5.

Tests of mechanical compressive strengths: mechanical resistance studies on pressure are performed by the Blinder mechanical strength device.

The study is summarized to calculate the mechanical resistance to simple compression, varying the percentages of the additions from 5 to 30 % with a step of 5 %, and respecting the Algerian standard requirements NA 234 [9] of composed Portland cements of the class (42.5).

In all tests, the Water/Cement ratio is maintained and equal to 0.5. Concerning the storage conditions, the test pieces were stored in a storage room at controlled temperature and humidity ($T = 20 °C ± 1 °C$, $H = 95 %$) until the day of measurement (2, 7 and 28 days).

The mortars are composed of: 1350 g of normal dry sand (from the Leucate region (France) with an extra fine quartz, 225 ml of water and 450 of cement they were prepared and poured into prismatic moulds of dimensions ($4 \times 4 \times 16$ cm) at the rate of six test pieces per test.

The results of the mechanical compression tests are reported in Table 5.

The analysis of the different types of additives Figs. 5, a, b and c Figs. 6, a, b and c, allows us to make the following comments.

The mechanical resistance to simple compression of the cement compound with different types of additives (CPJCEM II/A or B 42.5), are better compared to those of cement without additive (CWA-CEM I 42.5).

With fixation of age, it is noted that the more the percentage of addition increases (0 to 30 %), the more the mechanical strength to the cement compression CPJCEM II/A or B decreases.

All types of studied cement having resistances in accordance to the requirement of the Algerian standard NA 442 [8].

The phosphate waste rocks additive confers the better mechanical resistance to simple compression for all ages and for

### Table 3

| C4AF % | C3S % | C2S % | C3A |
|--------|-------|-------|-----|
| 10.55  | 74.22 | 3.26  | 7.51|

### Table 4

| Type of cement | CWA | Cement with phosphate waste rocks addition | Cement with added Pozzolan | Cement with added Slag |
|----------------|-----|-------------------------------------------|----------------------------|-------------------------|
| Consistency (%) | 26.8 | CPWR5 26.4 | CP5 27.2 | CS5 25.8 |
|                |     | CPWR 10 26.6 | CP10 27.4 | CS10 25.6 |
|                |     | CPWR 15 27.0 | CP15 27.8 | CS15 25.4 |
|                |     | CPWR 20 27.2 | CP20 28.2 | CS20 24.6 |
|                |     | CPWR 25 27.6 | CP25 28.2 | CS25 24.2 |
|                |     | CPWR 30 27.8 | CP30 28.4 | CS30 24.0 |

### Table 5

The setting time as a function of different addition rate:

- a – setting time as a function of phosphate waste rocks addition rate;
- b – setting times as a function of pozzolan addition rate;
- c – setting times as a function of slag rate addition.

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Conclusion. From the results of the various tests it is clear that the use of phosphate waste rocks as an additive in the manufacture of cement gives better compressive strengths for all ages and percentages compared to other additives; so this study has shown that it is possible to incorporate a considerable amount of phosphate waste rock from Djebel Onk deposit in the cement, since it also makes it possible to provide the cement with interesting physic-mechanical properties, even with a percentage of additions up to 30%.

According to the results of the tests it can be concluded that this type of cement can be used in: reinforced concrete usually poured on site or prefabricated rapid stripping, quick commissioning concrete steamed or self-parboiled.

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Розробка нового композиційного цементу на основі відходів порід fosfatного родовища Джебель Онк (Тебесса-Алжир)

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Цель. Основною целью нашей исследовательской ра­боты является описание характеристик и экологический менеджмент густой породы fosfatного месторождения Джебель Онк. Мы предлагаем валоризацию этого продукта как дополнение к технологии производства цемента (разработка нового композиционного цемента на ос­нове густой породы fosfatного месторождения Джебель Онк).

Методика. Проведено сравнительное исследование физико-механических параметров композиционного це­мента на основе fosфатных отходов горных пород с це­ментом без добавок (ПБД) и других видов цемента на основе добавок из пущолана и доменного шлака. Эти добавки составляют, соответственно, при массовом со­держании 5, 10, 15, 20, 25 и 30 % для каждой добавки.

Результаты. Проведенные исследования и испытания позволили нам сделать вывод: очевидно, что использо­вание fosфатных отходов в качестве добавки при произ­водстве цемента дает лучшие пределы прочности на сжатие по сравнению с другими добавками. Таким образом, это исследование показало, что можно включить в це­мент значительное количество fosфатных отходов по­рода месторождения Джебель Онк.

Научная новизна. Заключается в возможности сокра­тить количество fosфатных отходов порода Джебель Онк с экономической пользой и устранить их влияние с еко­логической точки зрения.

Практическая значимость. Повторное использование fosфатных отходов в качестве альтернативного сырья в строитель­ных материалах является многобenefициальным экологическим решением. Этот способ валоризации уменьшает большое количество "хвостов" и, следовательно, их воз­действие на окружающую среду, а также способствует сохранению невозобновляемых природных ресурсов, интенсивно используемых в строительстве (глины, изве­стняк, песок и т.д.).

Ключевые слова: фосфатні відходи порід, доменний шлак, пущолан, цемент, добавки, месторождение Джебель Онк

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