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Characterization of an Algerian natural pozzolan for its use in eco-efficient cement

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Abstract

The paper presents the characterisation of an Algerian natural pozzolan (NP) intended to for use in cement-based materials. The experimental programme was based on different tests on paste and mortar. The pozzolanic activity was assessed by the means of lime consumption over time of mixtures of lime-pozzolan (75% NP and 25% $Ca(OH)_2$, water-binder ratio of 0.45). The degree of reactivity was assessed by observing the crystallographic changes (XRD) and lime consumption (TG) up to 1 year of hydration. The effect of NP on cement-based mixtures was based on the measurement of the water demand and setting time of pastes, and on the compressive strength of mortars, up to one year. The replacement rates of cement by pozzolan were 5, 10 and 15%. A superplasticizer was used (0, 1, 2 and 3% of the binder mass). A calculation of the carbon footprint was investigated in order to assess if the natural pozzolan could be considered as eco-efficient when used in replacement of the clinker. The results showed that NP had a medium pozzolanic reactivity and with a medium-low silica content. The use of NP usually led to a small increase in the water/binder ratio (up to 10%) to maintain constant workability. The setting time was also increased by around 20%. Nevertheless, strength tests showed that the pozzolan had sufficient activity to counteract the water demand, since long-term compressive strength of the binary system (cement + pozzolan) were higher than those of cement alone. The use of NP in replacement of clinker involves a reduction in CO_2 emissions for transport up to 1800 km, which is compatible with sustainable development. The results are most promising from both a performance-based and an environmental point of view.

Keywords: *Natural pozzolan, Pozzolanic reactivity, Efficiency, CO_2 emission, Carbon footprint, Blended cement, Compressive strength, Setting time, Water demand.*

1. Introduction

Sustainable development has become a major preoccupation of our society. The construction field is no exception to the rule, and great efforts are being made, for instance to optimise the use of materials in order to maximise their beneficial effects in technical, environmental and economical ways.

In the case of cementitious materials, these efforts partly concern the use of local materials in replacement of a part of the cement. This could be particularly interesting in developing countries, where construction needs are great. Moreover, if these local materials are pozzolanic, their utilisation could lead to significant technological advantages, especially in terms of strength development and durability.

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Natural pozzolans (NP) have been widely used as supplementary cementing materials, especially in regions where there is a lack of other pozzolans such as fly ash, slag and silica fume. Many kinds of natural pozzolans can be found, and their origin, structure, chemical and mineralogical compositions vary widely. Usually, natural pozzolans are natural materials that exhibit pozzolanic activity without requiring any treatment other than grinding. Pozzolans are materials with an amorphous siliceous or siliceous and aluminous content that react with calcium hydroxide in the presence of water to form cementitious hydration products (calcium silicate hydrates and calcium silicate aluminate hydrates). Massazza [1] has proposed a system of classification in which NP are divided into three groups: (a) Pyroclastic rocks. This group of materials of volcanic origin includes unconsolidated materials such as Italian pozzolans [2-4], Santorin earth [5] and vitreous rhyolites [6]; it also includes consolidated materials, the most common being tuffs [7] and trass [8]. (b) Clastic rocks. These are composed of fragments of pre-existing rocks (mostly sedimentary) and include clays and diatomaceous earths. The calcination of clays significantly improves their pozzolanic properties. (c) Other materials of mixed origin. This category includes altered materials

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with high silica content. Italian white earths such as Sacrofano earths form part of this group.

Algeria is rich in volcanic tuff deposits. Some of them are currently used as pozzolans by local cement factories in blended Portland cement production. A large deposit (160 km long) of pyroclastic rocks is found in the north-west of Algeria, between the border of Morocco and the Oran' Sahel [9]. With pozzolan reserves estimated at 16 Mt in two deposits in the west, studies and trials are under way to expand the range of its use in the manufacture of construction materials. A few studies [10-12] have shown that these rocks might be pozzolanic, so the aim of this work is to evaluate the effect of this powdered rock in cement-based materials. This paper presents the results of an experimental programme mainly based on the measurement of lime consumption by the pozzolan, the setting time of pastes and water demand, and the compressive strength of mortars up to 9 months. The results concern pastes and mortars in which up to 15% of cement was replaced by pozzolan ground to finer than 80 µm. The final objective was to increase the commercial value of this natural and abundant resource, which is, for now, only partially exploited.

2. Materials and Experimental Procedures

2.1. Raw materials

The cement used was an ordinary Portland cement CEM I 32.5, according to Algerian standard NA 442-2003 [13] (equivalent to European Standard EN 197-1, 2001). It had a specific density of 3100 kg/m^3 and a Blaine specific area of 430 m^2/kg. Its chemical composition and physical properties are given in Table 1.

Table 1 Chemical, mineralogical and physical properties of cement and natural pozzolan

	Cement	Pozzolan
Chemical composition, % wt		
SiO_2	21.2	56.3
Al_2O_3	6.4	17.0
Fe_2O_3	4.6	8.6
CaO	64.3	9.8
CaO free	0.3	-
MgO	0.6	1.8
Na_2O	-	0.8
K_2O	-	0.5
SO_3	1.1	0.2
LOI	1.1	6.5
Physical properties		
Specific density (kg/m^3)	3100	2750
Blaine specific area (m^2/kg)	430	520

The natural pozzolan (NP) studied in this paper had the appearance of crushed pumice stone. It was composed of pyroclastic rocks resulting from the eruption of the Bouhamidi volcano, near Beni-Saf, in the north-west of Algeria (Fig. 1). Table 1 presents the chemical composition and physical properties of the sample used in this study, after the initial material had been crushed, ground (in a laboratory ball mill), dried and sieved at 80µm. Fig. 2 is a CaO-SiO_2-Al_2O_3 ternary diagram comparing the composition of the NP of this study and the compositions of several natural pozzolans, including Beni-Saf pozzolan described in other papers [14-17]. It can be seen that the composition of the NP of this study was: (a) in the range of class F fly ash and other natural pozzolans such as Italian pozzolans, but with a medium-low silica content [2, 4]; (b) similar to other Beni-Saf pozzolans reported in the literature, except that described by Belaribi et al. [14], who found a much higher silica content (75%).

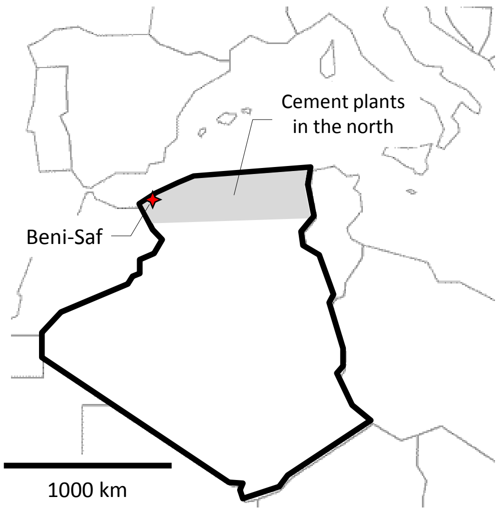

Fig. 1 Geographical location of natural pozzolan deposit, near Beni-Saf (Algeria).

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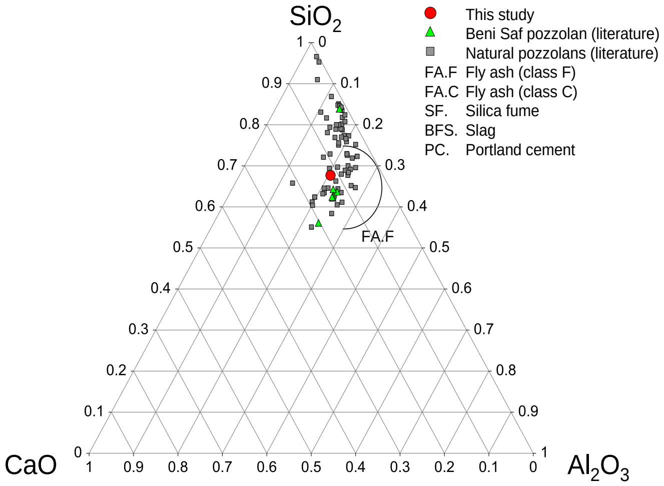

Fig. 2 Chemical composition of Beni-Saf pozzolan, presented in a CaO-SiO_2-Al_2O_3 ternary diagram. Comparison with other natural pozzolans and pozzolanic admixtures

The total content of SiO_2 and Al_2O_3 reached 73%, but was not completely in an amorphous form since a fraction of these oxides was included in crystallised, poorly reactive minerals. NP was composed of an amorphous phase (volcanic glass) and some crystallised phases known to be almost inert minerals in cement-based materials (quartz, feldspars plagioclase, pyroxene, calcite, etc.).

Commercial lime of high purity according to Algerian Standard NA 5011-2005 [18] (equivalent to European Standard EN 459-1, 2002) was used in the testing of the pozzolanic activity of NP.

The admixture (Medaplast SP 40) was a naphthalene formaldehyde sulfonated superplasticizer manufactured by Granitex. It had a relative density of 1.15 and a dry matter content of 35%.

The sand (0.08-2 mm) was a crushed limestone from the Kristel quarry of Oran in Algeria, with a mean diameter of 0.7 mm and a sand equivalent of 84% according to Algerian Standard NA 455-2006 [19] (equivalent to European Standard EN 933-8, 1999).

2.2. Test methodologies

2.2.1. Pozzolanic activity of NP

The pozzolanic activity of NP was studied by preparing lime-pozzolan mixtures and measuring the lime consumption over time (7, 28, 60, 90, 180, 245 and 365 days of curing). Pastes of NP, lime ($Ca(OH)_2$) and water (3:1:1.8, respectively, by mass) were made and the degree of reactivity was assessed by observing the crystallographic changes (XRD) and lime consumption (TG) versus time. The mineralogical properties were obtained by X-ray powder diffractometry using a Siemens D5000 diffractometer equipped with a rear monochromator and using cobalt radiation (Kα, $\lambda = 1.789$ Å). Measurements were made with a 2θ step of 0.02° (5°-70°) and an acquisition time of 10 s per step.

Thermogravimetric analyses (TG/DTG - Netzsch 409EP) were made in a static air atmosphere with a heating rate of 10°C/min from ambient temperature up to 1000°C, in order to investigate the $Ca(OH)_2$ consumption. TG measurements were performed on ~300 mg of powder.

2.2.2. Effect of NP in pastes and mortars

The consistency and setting time of cement pastes with and without pozzolan were assessed using the Vicat test (Algerian standard NA 230-2010 [20], equivalent to European Standard EN 196-3, 2006). The reference pastes without pozzolan were composed of cement, water and superplasticizer (SP, used at 0, 1, and 2% relative to binder mass). The cement replacement rates by the NP were 5, 10 and 15%.

The activity of the NP in cement-based materials was assessed by the mean of compressive strength tests on mortars. The mortar mixtures were prepared according to Algerian standard NA 234-2007 [21] (equivalent to European Standard EN 196-1, 2006). The reference mortar without pozzolan was composed of three parts of sand and one part of cement (by mass). The rates of cement replacement by the natural pozzolan were 0, 5, 10 and 15%. The superplasticizer was used at 0, 1, 2 and 3% relative to binder mass. The water content was determined for each mixture to obtain a constant spread of 45-50% using a flow table [22]. The mixtures were cast in 4x4x16 cm moulds for the first 24 h and then the mortar prisms were cured in a temperature controlled room at 18 ± 2°C. Some of the prisms were protected with an aluminium sheet and were put in plastic bags, in order to avoid any exchange of humidity (curing without moisture exchange). The others were kept in air at 18 ± 2°C and 50% R.H. Mechanical tests were performed on 4x4x16 cm prisms for the compressive strength [21], at 1, 3, 7, 14, 28, 45, 90, 180, and 270 days of curing time. Each result was the mean value of 6 tests.

3. Results

3.1. Pozzolanic activity

Fig. 3 illustrates the XRD diagrams of pastes containing NP and calcium hydroxide (portlandite), up to 365 days. The main changes concerned:

- The significant consumption of calcium hydroxide, characterised by the decrease in the peak intensity at 4.92 Å (20.9° 2θ Co). It cannot be excluded that a fraction of the calcium hydroxide was carbonated during the test.
- The production of hydrated calcium aluminates ($C_4A\check{C}H_{11}$ type) which were carbonated during the test and seen on the diagram at 13.6° 2θ Co (7.58 Å). The source of Al was probably the amorphous phase of NP (NP contained 17% of Al).
- The production of C-S-H, which was identified on XRD diagrams as a diffuse hump between 30° and 40° 2θ Co (see for example this area for 0 and 365d).

The consumption of calcium hydroxide was confirmed and quantified by thermogravimetric analysis (Fig. 4). The reaction involved the silica found in the amorphous phase of NP, and led to the formation of C-S-H, which was calculated on a semi-quantitative basis (Fig. 4) by using the surface of the diffuse hump on XRD diagrams (Fig. 3) over time.

The total content of SiO_2 and Al_2O_3 reached 73%, but was not completely in an amorphous form since a fraction of these oxides was included in crystallised, poorly reactive minerals. NP was composed of an amorphous phase (volcanic glass) and some crystallised phases known to be almost inert minerals in cement-based materials (quartz, feldspars plagioclase, pyroxene, calcite, etc.).

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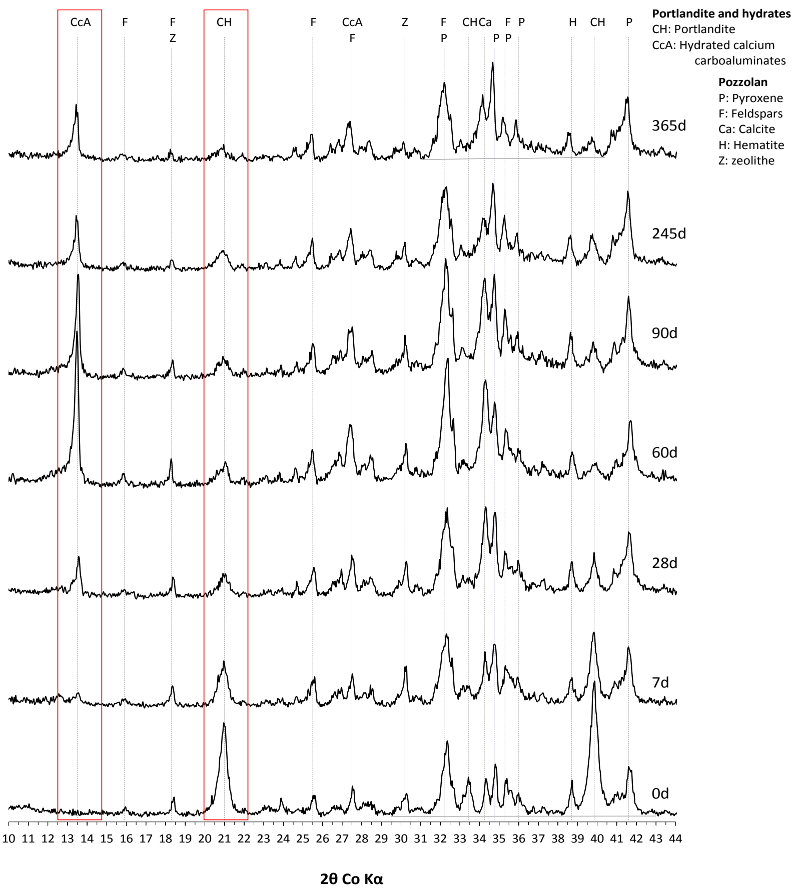

Fig. 3 XRD diagrams of pastes containing NP and calcium hydroxide, at 0, 7, 28, 60, 90, 245 and 365 days of hydration

Fig. 4 shows that the production of C-S-H was fast, since most of the production was effective within the first 3 months. It can also be seen that the consumption of CH followed a rapid kinetics, the decrease being fast in the first months of hydration. At the end of the test, only 3% of CH remained (but a small amount was probably carbonated). However, the active fraction of NP was not able to consume all the calcium hydroxide. The amount of calcium hydroxide consumed reached 23 and 27g of CH/100g of NP at 3 and 12 months respectively. For Japanese pozzolans used in similar mixtures (75% pozzolan and 25% of CH), Takemoto and Uchikawa [22] reported lime reaction in the range 22-32g of CH/100g of pozzolan at 3 months. However, these pozzolans usually contained more silica than the pozzolan studied here.

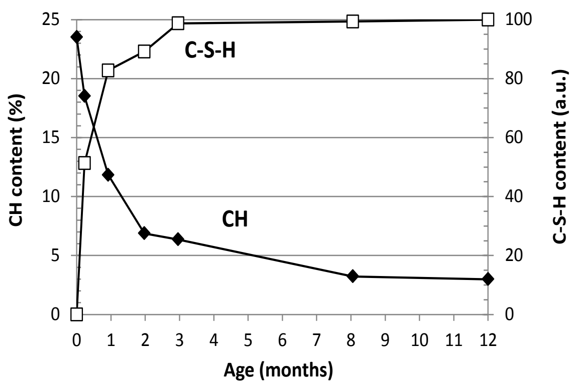

Fig. 4 $Ca(OH)_2$ consumed (%) calculated from TG measurements and C-S-H production (arbitrary units) calculated from the surface of the diffuse hump in XRD measurements. Pastes containing 75% of pozzolan and 25% of $Ca(OH)_2$

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3.2. Fresh and setting properties of pastes and mortars

3.2.1. Water demand

Fig. 5 presents the effect of the natural pozzolan (NP) and the superplasticizer (SP) on the water demand of both pastes and mortars. The water demand of the pozzolan is expressed in terms of water-binder ratio to obtain:

- The normal consistency of paste according to Algerian standard NA 230-2010 [20] (equivalent to European Standard EN 196-3, 2006), (Fig. 5a),
- A constant mortar spread of 45-50% on the flow table as specified in European Standard EN 1015-3 [23] (Fig. 5b).

The water content depended on the quantities of pozzolan and superplasticizer used. Obviously, an increase in the amount of superplasticizer led to a decrease of the water/binder ratio. The use of NP usually led to a small increase in the water-binder ratio, less than 5% for cement pastes. In the case of mortars, the use of 5% NP did not affect the water/binder ratio. However, the replacement rates of 10 and 15% involved an increase of the water demand ranging between 2 and 10%. So, for a given W/B, the use of 10 and 15% of NP required more SP to keep the workability constant.

These results could be explained by the higher specific area of the pozzolan compared to cement. Coarser particles would probably decrease the water demand, but would be unfavourable for the pozzolanic activity of the NP.

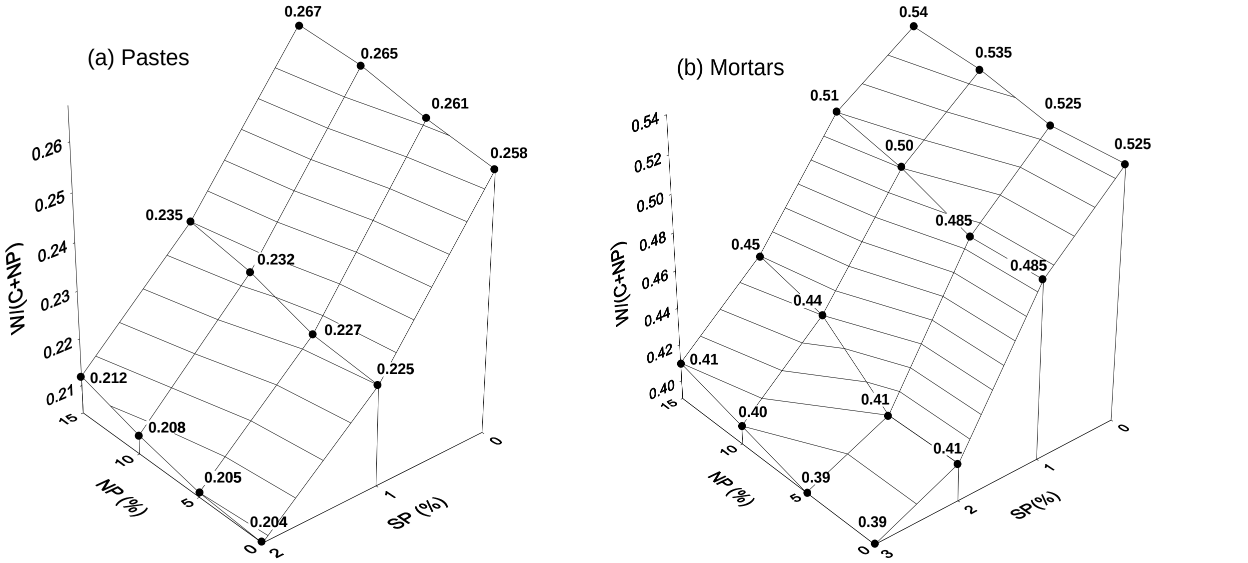

Fig. 5 Effect of replacement rate of cement by pozzolan and superplasticizer content on the water-binder ratio required to (a) obtain the normal consistency of paste and (b) keep the workability of mortars constant (45-50% on a flow table). Dots mark the experimental points

3.2.2. Setting time

Fig. 6 gives the setting time iso-curves of cement pastes at normal consistency (Fig. 5a) according to NP and SP contents (in % of the binder mass). The dots are the experimental points. It can be seen that increasing NP and/or SP involved an increase of the setting time: +60% (mean value) between mixtures with 0 and 2% SP and +20% (mean value) between mixtures with 0 and 15% NP.

The increase of the setting time is a known effect of some organic admixtures such as superplasticizers. In the case of NP, the delay in the setting time could be partly due to the increased amount of water in mixture with NP. A part of the delay could also be related to the dilution of cement when NP was used in mortars, since less cement implies less hydrate at young age and so a decrease in the shear resistance. The dilution effect has already been evoked by authors using other mineral admixtures, such as coal fly ashes [24].

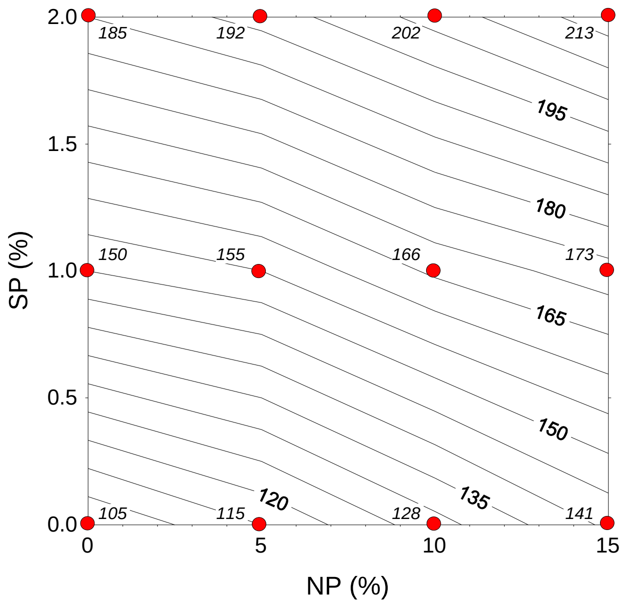

Fig. 6 Effect of replacement rate of cement by pozzolan and superplasticizer content on the setting time (iso-curves, in minutes) of paste having a normal consistency. Dots mark the experimental points (in minutes)

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3.3. Compressive strength of mortars

3.3.1. Constant workability, variable water content

Tables 2 and 3 present the compressive strength results, between 1 day and 9 months, of mortars having similar workability, cured in sealed bags (Table 2) and in air (Table 3). The bold numbers give the maximum strengths for each age. It is important to note that the comparison of unprocessed results was not favourable to the pozzolan, since it was necessary to increase the quantity of water in mixtures containing the pozzolan. Nevertheless, the results show that the pozzolan had a significant effect on mechanical performance since, between 7 and 28 days, the compressive strength of mortars containing pozzolan became systematically higher than those of the reference mortar.

Table 2 Compressive strengths of mortars cured in sealed plastic bags and containing 0 to 15% of NP, and 0 to 3% of SP (numbers in bold type correspond to maximum strengths for each series)

			Compressive strength (MPa) according to age (days)								
p (%)	W/B	W/C	1	3	7	14	28	45	90	180	270
					0% SP						
0	0.525	0.525	**2.8**	**15.1**	**32.8**	**35.8**	40.8	42.6	43.9	46.9	46.9
5	0.525	0.553	**2.8**	13.1	29.8	32.6	**45.8**	**50.4**	**52.0**	**52.1**	**52.1**
10	0.535	0.594	1.7	11.7	26.8	29.4	44.2	47.3	49.5	**51.6**	**51.6**
15	0.540	0.635	1.6	9.2	23.9	27.9	41.5	45.9	46.5	48.3	48.3
					1% SP						
0	0.485	0.485	**2.0**	**18.6**	**34.0**	**43.1**	41.6	43.1	47.2	49.9	49.9
5	0.485	0.511	1.0	16.2	33.5	40.5	**47.2**	**53.8**	**55.6**	**56.0**	**56.0**
10	0.500	0.556	1.0	14.9	33.2	39.8	**46.9**	**52.0**	**54.8**	**55.6**	**55.6**
15	0.510	0.600	1.0	13.3	32.0	37.0	45.0	50.6	52.2	53.3	53.3
					2% SP						
0	0.410	0.410	**1.8**	**27.1**	37.6	40.4	43.9	48.1	53.5	54.6	54.6
5	0.410	0.432	**1.8**	21.5	37.2	**45.7**	**49.2**	**53.6**	**56.2**	**57.9**	**57.9**
10	0.440	0.489	**2.0**	20.2	**41.6**	44.8	47.6	50.5	54.9	56.3	56.3
15	0.450	0.529	1.4	18.6	40.7	44.2	46.9	47.2	54.0	55.2	55.2
					3% SP						
0	0.390	0.390	**1.3**	**29.5**	39.2	42.9	46.0	50.6	56.2	56.9	56.9
5	0.390	0.411	**1.3**	25.2	38.8	**46.7**	**51.6**	**56.6**	**64.0**	**64.0**	**64.1**
10	0.400	0.444	0.8	23.2	**42.8**	**46.2**	50.2	53.2	58.9	59.0	59.1
15	0.410	0.482	0.9	21.8	41.7	44.8	49.5	54.0	57.6	57.9	58.0

Table 3 Compressive strengths of mortars cured in air and containing 0 to 15% of NP, and 0 to 3% of SP (numbers in bold type correspond to maximum strengths for each series).

			Compressive strength (MPa) according to age (days)								
p (%)	W/B	W/C	1	3	7	14	28	45	90	180	270
					0% SP						
0	0.525	0.525	**3.1**	**13.6**	**20.8**	**25.6**	33.8	36.3	38.0	38.5	38.6
5	0.525	0.553	**3.1**	12.9	18.9	24.9	**35.2**	**39.1**	39.2	39.2	39.3
10	0.535	0.594	2.1	10.0	16.1	23.0	34.4	**38.9**	**39.2**	39.2	39.3
15	0.540	0.635	1.6	8.0	13.9	21.2	32.6	38.6	**39.9**	**40.3**	**40.6**
					1% SP						
0	0.485	0.485	**2.5**	**15.4**	**25.4**	30.9	35.7	39.4	41.8	42.5	42.9
5	0.485	0.511	**2.5**	13.6	22.9	**33.2**	35.9	43.9	**44.0**	44.9	45.0
10	0.500	0.556	1.3	11.7	19.8	**32.9**	**36.1**	**44.9**	**44.2**	**45.6**	**46.0**
15	0.510	0.600	1.1	9.2	17.6	31.8	34.2	43.8	**44.0**	**46.0**	**46.6**
					2% SP						
0	0.410	0.410	**2.2**	**18.0**	**29.9**	34.2	38.2	41.6	43.9	45.6	45.9
5	0.410	0.432	**2.1**	16.3	25.8	**38.2**	39.8	**45.9**	**47.8**	48.6	49.1
10	0.440	0.489	**2.0**	14.4	22.8	**37.6**	**40.9**	**45.2**	46.4	**49.0**	**49.7**

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15	0.450	0.529	1.4	11.4	20.2	37.6	38.2	45.0	46.9	**49.8**	**50.1**
					3% SP						
0	0.390	0.390	**1.0**	**21.9**	**32.8**	37.3	39.9	43.2	45.3	46.8	47.9
5	0.390	0.411	**1.1**	19.4	28.2	**40.6**	40.2	**46.1**	**47.9**	**49.7**	**50.1**
10	0.400	0.444	**1.1**	17.7	26.6	**39.9**	**41.9**	**46.6**	**46.9**	**49.9**	**50.5**
15	0.410	0.482	0.8	16.6	23.4	39.2	**41.7**	**46.1**	**46.8**	**49.9**	**50.6**

Figs. 7a and 7b illustrate the evolution with age of the differences (in MPa) between compressive strengths of mortars with and without pozzolan cured in sealed plastic bags and in air, for SP content up to 3%.

- At young age (1 day), the replacement of cement led to a decrease of the compressive strength proportional to the replacement rate. The strength values given in Tables 2 and 3 show that 15% replacement of NP for Portland cement could reduce the early strength of the control cement by 40% (mean value). At one day, NP did not have a perceptible pozzolanic effect and only acted as inert filler, thus causing a simple dilution of the cement. The difference in compressive strength between mortars with and without pozzolan decreased with age and eventually disappeared or changed sign (Fig. 7). The moment of recovery depends on the fineness of both Portland cement [25], and pozzolan [26], as well as on the pozzolan activity. For this reason, the curing of pozzolanic concretes and mortars needs more care than that of Portland cement. It should be noted that the decrease in early strength caused by the partial replacement of pozzolan for Portland cement is a general occurrence [5,27-29].
- Between 3 and 14 days, there was a sudden and significant increase in the strength for all mixtures with pozzolan, leading to strengths higher than the reference. This increase was due to the development of a pozzolanic reaction. The ages of strength increase depended on the presence of SP: for the higher amounts of SP (2 and 3%), the pozzolanic effect appeared much earlier (3 days) than for 0 and 1% SP (14 days). Thus, the dispersing effect of the organic admixture was significant for the development of the pozzolanic reaction.
- For medium (28, 45, 90 180 days) and long terms (9 months), the compressive strengths of mortars containing pozzolan were greater than those of reference mortars. At 9 months, the strengths were up to 11% higher. In the conditions studied here, the higher strengths were obtained for a replacement rate of 5%. In this case, the quantity of water was the same as in the reference mortar. The mortars containing 10 and 15% NP also had higher strengths than the references, but the pozzolanic effect was counteracted by the higher water-binder ratios.

In summary, long-term strengths of mortars with pozzolan were always higher than those of the control mortar, despite the dilution effect of the cement and the increase in the W/C+NP. Thus it is possible and favourable to replace cement by this addition, since no loss of strength occurs.

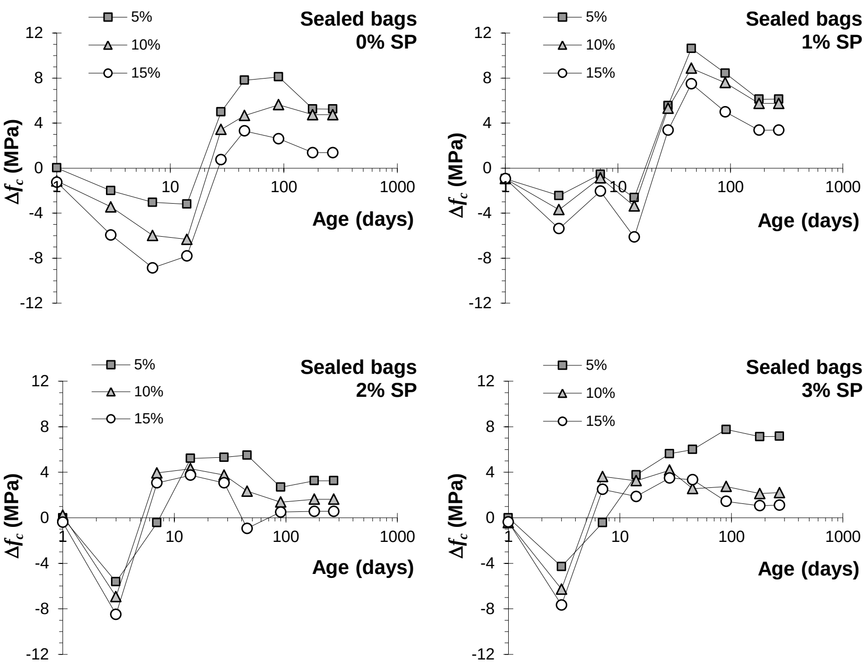

Fig. 7a Evolution with age of the differences (in MPa) between compressive strengths of mortars with and without pozzolan cured in sealed plastic bags

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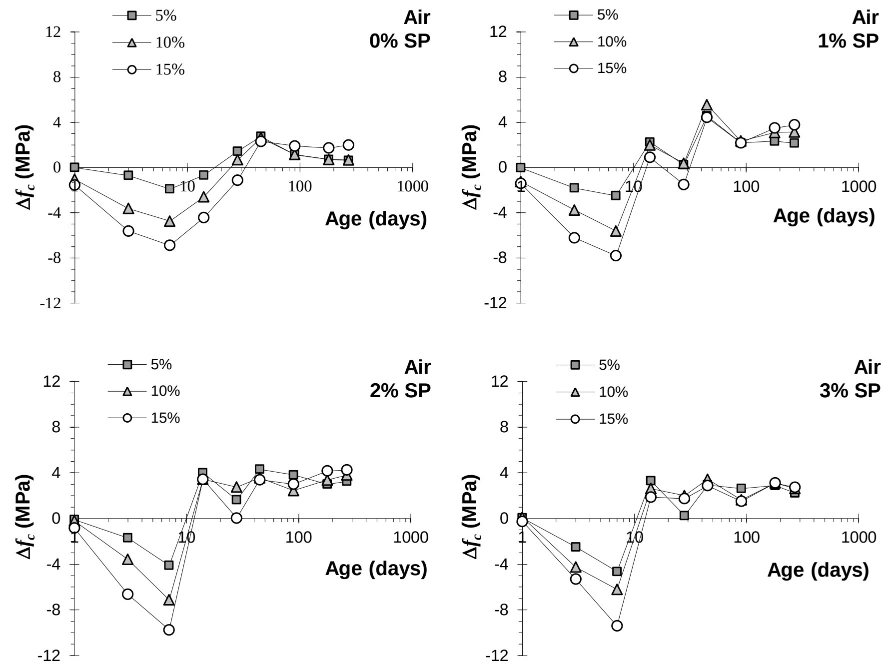

Fig. 7b Evolution with age of the differences (in MPa) between compressive strengths of mortars with and without pozzolan cured in air

3.3.2. Constant workability and water content, variable SP content

For mortars containing 10 and 15% of NP, more SP was needed to keep the workability constant. Fig. 8 shows the compressive strength of mortars up to 270 days according to the water-binder ratio. When the quantity of water was kept constant, the following observations were made:

- in the short term (3 days), the strengths of mortars with pozzolan were 3 to 5 MPa lower than those of the references;
- this tendency changed between 7 and 14 days;
- in the long term (28 days and after), the strengths were higher when the pozzolan was used;
- in almost all cases, the variations of strength between the three replacement rates were insignificant.

So, for a constant water-binder ratio, it is possible to replace up to 15% of cement by NP without affecting the performances of mortars, on condition that a sufficient amount of SP is used in order to maintain constant workability.

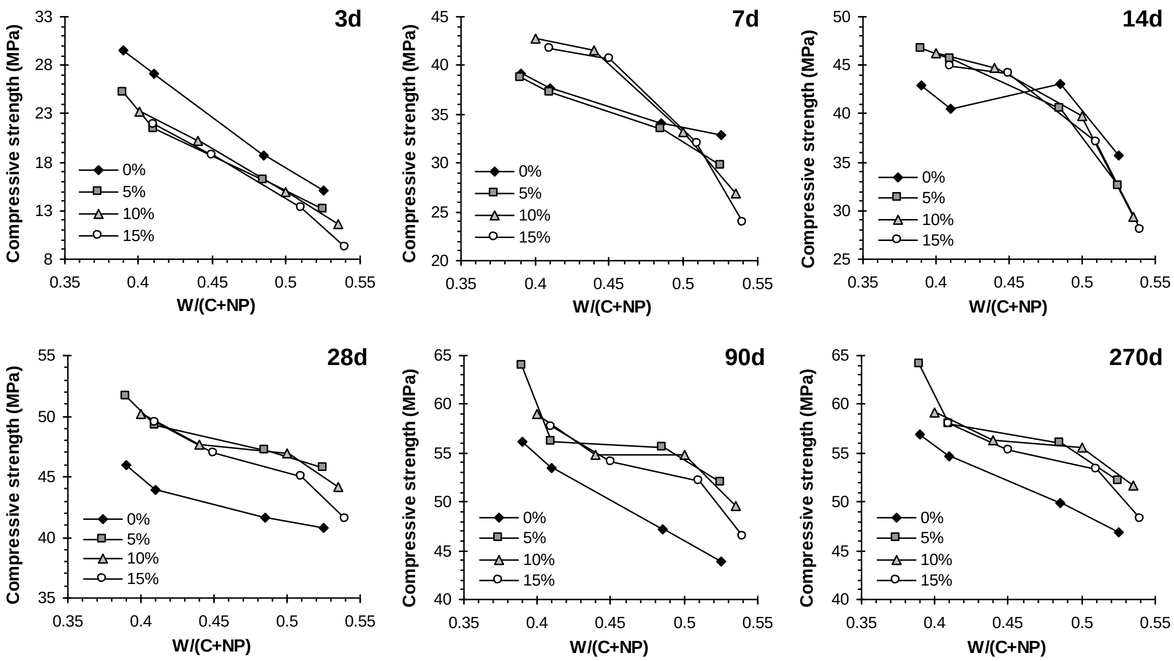

Fig. 8 Evolution of compressive strength with water-binder ratio (W/C+NP)

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3.4. Efficiency factor of NP

The efficiency of an SCM in mortar can be evaluated using the concept of cementitious efficiency factor, k [30]. This factor is defined as the number of parts of cement in a concrete mixture that could be replaced by one part of pozzolan without changing the property being investigated, which is usually the compressive strength.

In standards such as EN 206-1 [31], k is taken to have a fixed value, but non-normalised factors are also found. They are usually calculated from the compressive strength of mortars. In our case, the efficiency factors of NP were obtained by using an empirical equation, the Bolomey formula (equation 1).

$$f_c = K_B\left(\frac{C+kA}{W} - 0.5\right) \quad (1)$$

where f_c is the compressive strength of mortar (N/mm^2), C is the amount of cement in the mortar (kg/m^3), W is the mass of water, A is the mass of NP, and K_B is the Bolomey coefficient. K_B is calculated from the mixtures without pozzolan.

The efficiency factors of pozzolan were calculated for each cement dosage using K_B values. Fig. 9 illustrates the evolution of efficiency factors, k, of all mixes up to 270 days and calculated from equation 2. Higher values of the efficiency coefficients were obtained for mortars containing 5% and 10% NP (k around 2) and, for mortars containing 15% NP, an average value of this coefficient was around 1. This means that, at these levels of replacements, NP had a quite good pozzolanic effect and that 1 kg of cement could be replaced by 1 kg of NP without affecting the strength.

3.5. Carbon footprint

In order to assess whether the natural pozzolan (NP) could be considered as eco-efficient when used in replacement of the clinker, a calculation of the carbon footprint was made, by considering the transport of NP to the different cement production sites in Algeria.

3.5.1. Method of calculation of CO_2 emission

The determination of the binder's carbon footprint was based on a simple approach, which was to calculate the CO_2 emitted in the making of the binder from its composition, knowing the CO_2 emission of each individual component. The transport of the pozzolan was taken into account in order to evaluate the environmental interest of using such a product far from its extraction site (western Algeria). It should be noted that almost all cement plants in Algeria are located in the north of the country (Fig. 1). The distance between the extraction site of the natural pozzolan and the most distant existing plant in the east is around 1100 km. However, projects for the construction of cement plants in the south of the country would increase the distance to about 1500 km, or even 2500 km if the site was implanted in the extreme south.

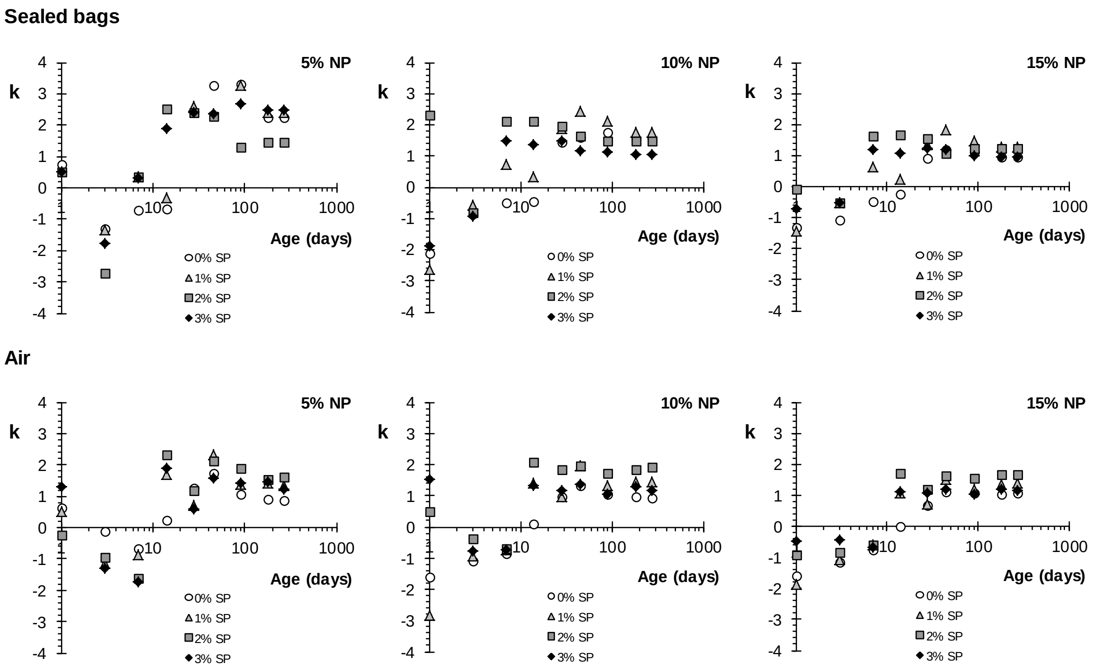

Fig. 9 Evolution of the efficiency factor, k, calculated using Bolomey's law

Table 4 gives the data used for the calculation of CO_2 emissions, which included the effect of the fuel used for the production of the materials [32-36]. The CO_2 release related to truck transport could be as much as 100 or 500 g of CO_2 per tonne of material per km (g/tonne·km), since the environmental impact could be very different depending on the quantity of material transported (Table 4) [33,36]. Generally speaking, for a given distance of transportation, the larger the load, the lower the CO_2 release per tonne of material.

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Table 4 Quantities of CO_2 emitted for the materials used in this study

	Matter*	Transport by truck**
	kg CO_2/tonne	g CO_2/tonne·km
Cement CEM I	914	between 79 (freight > 20 tonnes)
Natural pozzolan	11	and 500 (freight < 10 tonnes)

* According to data of [32]
** According to data of [33-35]

3.5.2. CO_2 emission of binders

The CO_2 emissions of the 4 types of dry binders (0, 5, 10 and 15% of NP) are reported in Fig. 10. All the results are expressed as kg of CO_2 per tonne of dry matter.

It can be seen that, at a distance near 0 km (i.e. use of NP at a cement plant close to the extraction site of NP), the CO_2 emission decreased significantly with the addition of NP in replacement of the cement: binders with 5, 10 and 15% NP led to 5, 10 and 15%, respectively, less CO_2 than Portland cement. These results were to be expected considering that NP released much less CO_2 than Portland cement (Table 4). Portland cement presents the double disadvantage of requiring a high firing temperature (1450°C), obtained mainly by the combustion of fossil fuel generating greenhouse gas emissions, and also of producing large amounts of CO_2 due to the decarbonation of calcite. The advantage of NP was that the only CO_2 released was due to the material extraction and grinding process.

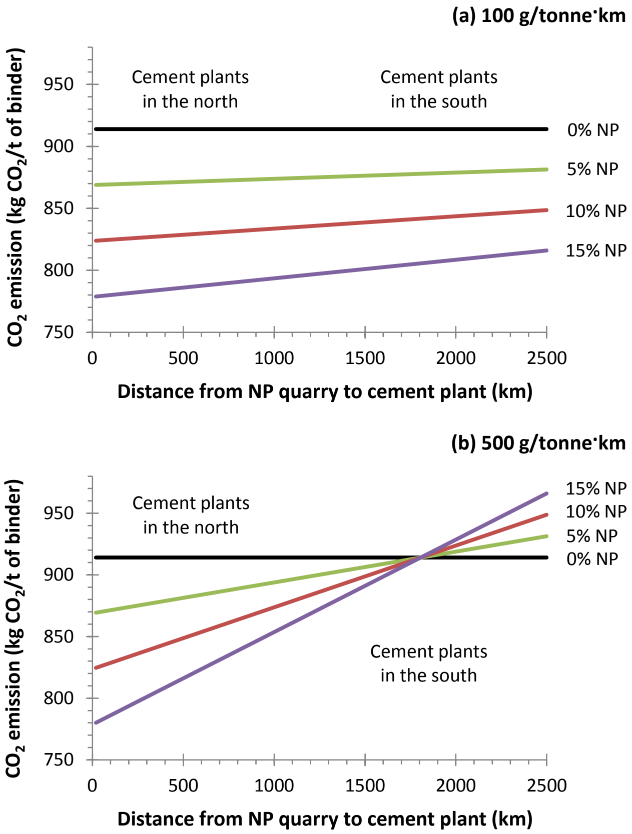

Fig. 10 CO_2 release of binders containing NP, compared to cement only, when the transport is taken into account

An increase in the transport distance of the pozzolan led to an increase in the CO_2 emissions.

At 100 g of CO_2 /tonne·km (Fig. 10a), the impact of transport was almost negligible compared to the effect of the cement content. At 500 g of CO_2 /tonne·km (Fig. 10b), the effect of transport was significant, especially for long distances. However, the binders with NP remained more environmentally friendly than cement alone for all cement plants located in the north of the country.

To reach an inversion in the environmental behaviour, it would be necessary to:

- increase the distance to 1800 km, which represents transport locations in the extreme south of Algeria. So in the pessimistic case, cement alone is less critical for the farthest cement plants.
- reach emissions of at least 0.8 kg of CO_2 per tonne per km, which is fairly typical for air transport (between 0.4 and 1.1 kg/tonne·km) [34].

4. Conclusion

Algeria has pozzolan reserves estimated at 16 Mt in two deposits in the west of the country.

This paper has reported results to evaluate the potential for using this natural pozzolan (NP) in cement-based materials. The following conclusions can be drawn from the study.

- The composition of NP was in the range of other natural pozzolans, e.g. Italian pozzolans, but with a medium-low silica content. NP was composed of an amorphous phase (volcanic glass) and some crystallised phases: quartz, feldspars plagioclase, pyroxene, calcite.
- This pozzolan consumed 27g of CH/100g of NP at 12 months, putting it in the range of medium reactive products.
- When used in pastes and mortars, this pozzolan led to an increase in the water demand and the setting time.
- However, its pozzolanic activity led to a significant increase of the compressive strengths of mortars, especially after 7-14 days. The use of a superplasticizer was particularly efficient in increasing the activity of the pozzolan.
- The efficiency of this pozzolan was good enough for it to be possible to replace 1 kg of cement by 1 kg of NP without affecting the strength (in the replacement range 5-15%).
- The CO_2 emissions (including transport effect) of binders containing the pozzolan were lower than for cement alone, for all cement plants in the north of Algeria.

References

[1] Massazza F. Chemistry of pozzolanic additions and mixed cements, Il Cemento, 1976, Vol. 1, pp. 3-38.

[2] Massazza F. Pozzolan and Pozzolanic Cements, Lea's Chemistry of Cement and Concrete, Fourth Edition, Arnold Publishers, London, 1998.

[3] Cook DJ. Natural pozzolans, Concrete Technology and Design, Cement Replacement Materials, Surrey

University Press, Glasgow, 1986, Vol. 3.
[4] ACI Committee 232, Use of Raw or Processed Natural Pozzolans in Concrete, Manual of Concrete Practice ACI 232.1R-00, 2000.
[5] Mehta PK. Studies on blended Portland cements containing Santorin earth, Cement and Concrete Research, 1981, No. 4, Vol. 11, pp. 507-518.
[6] Akman MS, Mazlum F, Esenli F. A comparative study of natural pozzolans used in blended cement production, Fourth International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Istanbul, ACI Special Publication 132, 1992, Vol. I, pp. 471-494.
[7] Sersale R. Analogic costituzionali fra il tufo giallo Napoletano ed il tufo giallo della Gran Canaria, Rendiconti dell'Accademia delle Scienze Fisiche e Matematiche della Società Nazionale di Scienze, Lettere ed Arti, Napoli, 1959, No. 4, Vol. 26, pp. 441-451.
[8] Sersale R, Aiello R. Richerche sulla genesi, sulla constituzione e sulla reattivita'del 'trass' Renano, Silicates Industriels, 1965, No. 1, Vol. 30, pp. 13-23.
[9] Sadran G. Les formations volcaniques tertiaires et quaternaires du Tell Oranais, Service de la Carte Géologique de l'Algérie, Algiers, 1958, [in French].
[10] Khelafi H, Rahal D, Frih M, Rahmani MC. Vers Un béton de haute résistance élaboré à partir de matériaux locaux, Revue Marocaine du génie civil, 1997, Vol. 70, pp. 33-39 [in French].
[11] Anon, Rapport préliminaire des résultats des essais de laboratoire et industries des ciments aux ajouts, Entreprise Nationale de Développement et Recherches Industriels des Matériaux de Construction, Unité Recherches et Etudes Géologiques, Boumerdes, Algeria, 1985, [in French].
[12] Harichane K, Ghrici M, Kenai S. Effect of curing time on shear strength of soft soils stabilized with combination of lime and natural pozzolana, International Journal of Civil Engineering, 2011, No. 2, Vol. 9, pp. 90-95.
[13] IANOR, Norme Algérienne NA 442-2003, Liants Hydrauliques - Ciments Courants, Composition, Spécification et Critères de Conformité, Algiers, 2003.
[14] Belas Belaribi N, Semcha M, Laoufi L. Influence of the beni-saf pozzolana on the mechanical characteristics of the concretes, Canadian Journal of Civil Engineering, 2003, No. 3, Vol. 30, pp. 580-584.
[15] Ghrici M, Kenai S, Meziane E. Mechanical and durability properties of cement mortar with Algerian natural pozzolana, Journal of Materials Science, 2006, Vol. 41, pp. 6965-6972.
[16] Mouli M, Khelafi H. Performance characteristics of lightweight aggregate concrete containing natural pozzolan, Building and Environment, 2008, No. 1, Vol. 43, pp. 31-36.
[17] Senhadji Y, Escadeillas G, Khelafi H, Mouli M, Benosman AS. Evaluation of natural pozzolan for use as supplementary cementitious material, European Journal of Environmental and Civil Engineering, 2012, No. 1, Vol. 16, pp. 77-96.
[18] IANOR, Norme Algérienne NA 5011-2005, Chaux de construction Partie 1: Définitions, spécifications et critères de conformité, Algiers, 2005.
[19] IANOR, Norme Algérienne NA 455-2006, Essais pour déterminer les caractéristiques géométriques des granulats – Evaluation des fines – Equivalent de sable, Algiers, 2006.
[20] IANOR, Norme Algérienne NA 230-2010, Méthodes d'essais des ciments - Partie 3: détermination du temps de prise et de la stabilité, Algiers, 2010.
[21] IANOR, Norme Algérienne NA 234-2007, Méthodes d'essais des ciments - Partie 1: Détermination des résistances mécaniques, Algiers, 2007.
[22] Takemoto K, Uchikawa H. Hydratation des ciments pouzzolaniques, Proceedings of the 7th International Congress on the Chemistry of Cement, Paris, 1980, Vol. I, IV-2/1-21.
[23] AFNOR, NF EN 1015-3. Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table), 2007.
[24] Dodson VH. The effect of fly ash on the setting time of concrete - Chemical or physical, Proceedings of Symposium on Fly Ash Incorporation in Hydrated Cement Systems, Materials Research Society, Boston, 1981, pp. 166-171.
[25] Costa U, Massazza F. Some properties of pozzolanic cements containing fly ashes, Proceedings of the 1st International Conference on the Use of Fly Ash, Silica Fume, Slag, and Other Mineral By-Products in Concrete, Montebello, ACI Special Publication 79, 1983, Vol. I, pp. 235-254.
[26] Sellevold EJ, Bager DH, Klitgaard JK, Knudsen T. Silica fume – cement pastes, hydration and pore structure, Report BML 82.610, Division of Building Materials, The Norwegian Institute of Technology, Trondheim, 1982, pp. 19-50.
[27] Abdul-Maula S, Odler I. Hydration reactions in fly-ash-Portland cements, Proceedings of Symposium N on Effects of Fly Ash Incorporation in Cement and Concrete, Materials Research Society, Boston, 1981, pp. 102-111.
[28] Massazza F, Costa U. Aspetti dell'attivita' pozzolanica e proprieta' dei cementi pozzolanici, Il Cemento, 1979, Vol. 1, pp. 3-18.
[29] Delvasto S. Pozzolanic activity and characteristics of Colombian materials, Proceedings of the 2nd International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Madrid, ACI Special Publication 91, 1986, Vol. I, pp. 77-89.
[30] Sánchez de Rojas Gómez MI, Frías Rojas M. Natural pozzolans in eco-efficient concrete, Eco-Efficient Concrete, 2013, pp. 83-104.
[31] AFNOR, NF EN 206-1, Concrete – Part 1: Specification, performance, production and conformity, 2012.
[32] San Nicolas R. Performance-based approach for concrete containing metakaolin obtained by flash calcination, Ph.D. Toulouse, Université de Toulouse, 2011. http://tel.archives-ouvertes.fr/tel-00756481 [in French].
[33] Morcheoine A. Transports de marchandises, énergie, environnement et effet de serre, Semaine Internationale du Transport et de la Logistique (SITL), Paris, 2006, [in French].
[34] RAC-F, Réseau Action Climat-France - Changement climatique et transports : manuel de recommandations à l'attention des acteurs territoriaux, 2007, [in French].
[35] Anon, Etude de l'efficacité énergétique et environnementale du transport maritime, January 2009, http://www.developpement-durable.gouv.fr/Etude-de-l-efficacite-energetique.html, http://www.shortsea.fr/synthesefinale.html [in French].
[36] Cyr M, Trinh M, Husson B, Casaux-Ginestet G. Effect of cement type on metakaolin efficiency, Cement and Concrete Research, 2014, Vol. 64, pp. 63-72.

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