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Research Paper

Influence of thermal activation of natural pozzolan on the mechanical behavior of cement pastes

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ABSTRACT

This experimental work focused on the thermal activation of natural pozzolan (NP) from the town of Beni-Saf, in order to improve its reactivity. The present study consists of using natural pozzolan as partial replacement of ordinary Portland cement, with 10 to 40% by weight of cement. Various curing temperatures were used to assess the influence of thermal treatment on the mechanical properties of the pozzolan pastes. For this purpose, three curing modes were chosen, namely the normal curing at the temperature $T = (20 \pm 2) ^\circ\text{C}$, taken as a reference, the curing at $40 ^\circ\text{C}$, and another one at $60 ^\circ\text{C}$. The experimental results obtained showed that the 40% natural pozzolan paste, which was stored at $40 ^\circ\text{C}$, exhibited much better strengths than those of ordinary cement (CEM I), which was kept at room temperature. This finding leads us to consider that the replacement rate of 40% of NP, stored at the temperature of $40 ^\circ\text{C}$, constitutes the best conditions for preparing an efficient eco-material. Natural pozzolan pastes thermally treated at $60 ^\circ\text{C}$ gives better mechanical strengths with larger amounts of natural pozzolan.

1 Introduction

Today, manufacturers are required to limit the release of carbon dioxide CO_2 into the atmosphere in order to limit air pollution and reduce the greenhouse effect that is increasingly warming the planet. The cement industry is one of the primary producers of carbon dioxide that is released into the atmosphere. With a world production of up to two billion tons, the cement industry emits more than 7% of CO_2 in the atmosphere, 54% of which comes from limestone calcination; the remainder originates from the fuel used [1]. Mineral additions are an interesting alternative to reduce the emission of gases into the atmosphere, since the use of one ton of mineral additive helps prevent the emission of one ton of CO_2 gas [2, 3]. It is

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interesting to note that replacing 5% of cement by a mineral addition leads to a reduction of 75 million tons of CO₂ in the atmosphere Esc. The natural pozzolan is a prominent candidate for use as a mineral addition.

Natural pozzolan (NP) is a natural rock made up of volcanic rocks and scoria. It has a scoriaceous and alveolar structure, and is ordinarily red or black, and exceptionally gray. Natural pozzolan consists essentially of silica (SiO₂), alumina (Al₂O₃) and ferric oxide (Fe₂O₃). The sum of all three oxides (SiO₂ + Al₂O₃ + Fe₂O₃) must be greater than 70% [4, 5]. The natural pozzolan from the region of Beni-Saf is the basic material for several cement manufacturers in western Algeria. Several researchers have worked on that type of pozzolan as they were particularly interested in the durability of mortars based on this pozzolan [4-6] they also looked into the possibility of using it as an aggregate for the manufacture of lightweight concrete [7], as well as in self-compacting concretes (SCC) [8] due to its instantaneous and delayed mechanical characteristics, to prevent the alkali-silica reaction (ASR) [9]. All the studies conducted on this matter, proved the effectiveness of pozzolan. This natural pozzolan, which has an activity index of 0.82 for a substitution rate of 25% [10], showed an average reactivity. Some studies [11] have shown, based on a lime consumption test, [4-9] that pozzolan from the town of Beni-Saf has a relatively low pozzolanic activity, and this currently remains a major challenge for many researchers. In order to overcome this problem, it was considered essential to accelerate the early-age pozzolanic reactivity, through the use of different possible activation methods such as the chemical activation (use of alkaline solutions to modify the setting and hardening of concrete) [12-16], mechanical activation (high binder grinding) [17, 18], or thermal activation (acceleration of chemical reactions by raising the curing temperature [19, 20]).

The thermal activation consists of accelerating the chemical reactions by raising the temperature. This type of activation occurs through two different modes, namely calcination or curing temperature elevation. Escalante-Garcia and Sharp [21] reported that, in the microstructure of cement containing 22% of volcanic ash and stored at 60 °C, calcium hydroxide is entirely consumed due to the accelerated reactions which lead to an appreciably high porosity. This would lead to a crossing between the curve representing the strengths of a concrete that hardens at high temperature and that of concrete that cures at ambient temperature. Such behavior is known as the crossover effect. It has been demonstrated that, over a wide range of curing temperatures, e.g. 20, 40, 60 and 80 °C [22], 40 °C is the ideal curing temperature to obtain optimum fly ash cement strength. Other studies [22] concluded that 30 °C is the best temperature for achieving optimum strengths of slag-based cement. Escalante-Garcia [23] investigated the effect of the curing temperature on the compressive strength in two series of natural pozzolan mortars. In series A, the specimens underwent an isothermal cure at temperatures equal to 20, 40 and 60 °C; whereas in series B, the specimens were subjected to varying curing temperatures. The latter curing method consists in exposing the mortars to high temperatures, i.e. 40 or 60 °C, for 1, 3 and 7 days; after that, the specimens are put back to the reference temperature of 20 °C. The results obtained showed that high temperature curing, during the first seven days, is the ideal method for improving the strength of pozzolanic mortars. Ezziiane [24] reported that increasing the temperature from 10 to 50 °C made it possible to improve the tensile and compressive strengths as well as the modulus of elasticity of concrete in the short term, and at low temperatures. Furthermore, all the results obtained above remained unchanged in the long term, except for the temperature of 35 °C which gave acceptable results at any age, and in the short and long terms. Day et al. studied lime-pozzolan pastes treated at room temperature and tested at 7 days. These pastes gave strength values of about 0.8 MPa; on the other hand, when they were treated at 52 °C, values around 6 MPa could be obtained [25]. These findings were also confirmed by Day [26]; they confirmed the effect that the curing temperature has on the strength development in lime-pozzolan pastes without activator. High curing temperatures greatly accelerate the early age strength development. The pastes showed a measurable strength value only after about four days, and at 23 °C. After one day only, and at the temperature of 65 °C, they showed strength values around 2.5 MPa.

Within the same study, Shi and al. [27] prepared pastes with 20% lime and 80% pozzolan activated with 4% Na₂SO₄, at different curing temperatures. They showed that the effect of thermal activation of Na₂SO₄-activated lime-pozzolan pastes appears to be less effective at temperatures below 50 °C. According to the most interesting works on pozzolan-based pastes, three parameters are to be considered: the temperature and the curing time with two modes, i.e. at constant temperature and at variable temperature. The variable temperature mode gave the best results.

Our research addressed the results from an experimental study on the thermal activation of natural pozzolan in order to emphasize the possibility of accelerating the pozzolanic reactivity of natural pozzolan, particularly at early age, by thermal treatment, and consequently to increase the amount of natural pozzolan substituted to cement. The choice of the three temperatures, i.e. 20, 40 and 60°C, was made with the aim of highlighting the possibility of accelerating the pozzolanic reactivity of natural pozzolana, particularly at a young age, by heat treatment, and consequently to increase the rate of natural pozzolan substituted for cement.

Over a wide range of curing temperatures, i.e. 20, 40, 60 and 80°C [24], it has been shown that 40°C is the optimum curing temperature for fly ash cement strengths. Other works [28] have concluded that 30°C is the optimum curing temperature for the development of the resistances of a cement composed of slag.

Furthermore, the literature review [25-27] allowed showing that the temperature of 40°C is the ideal temperature because it adapts better with the natural pozzolan to develop maximum resistance in the long term, i.e. after 28 days of cure. The question that currently arises is whether this is also the case for the natural pozzolana of Beni-Saf.

Previous work [24-27, 29] has indicated that if one wants to increase the resistance in the short term, one must use a temperature above 40°C. For this, it was deemed necessary to choose the following three temperatures. The first (20°C) is room temperature, next 40°C to study long-term resistance, and finally 60°C to study resistance at young age. Temperatures between 80 and 100°C have been ruled out in order to avoid aberrant and unnecessary energy expenditure. In addition, these temperatures are difficult to achieve in our sites; they can even damage the materials.

2 Experimental Study

2.1 Characteristics of the materials used Title

2.1.1 Natural pozzolan

The study material is the local natural pozzolan, extracted from the deposit of Bouhamidi in the region of Beni-Saf. After crushing, bake-out, and grinding, the resulting powder was recovered. The results of its physico-chemical analysis are presented in Tables 1 and 2.

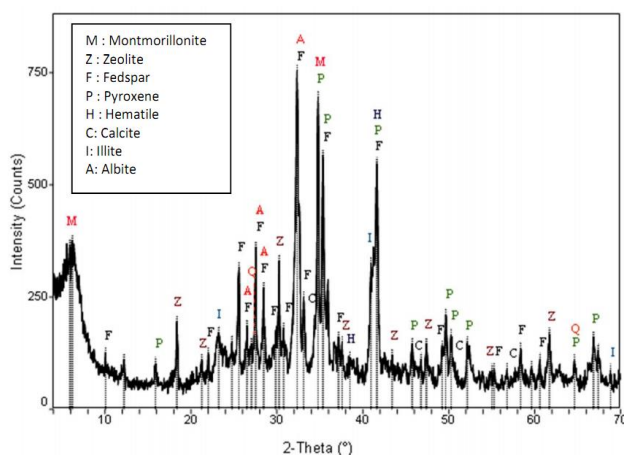


Fig. 1 – X-ray diffraction spectrum of natural pozzolan from the town of Beni-Saf

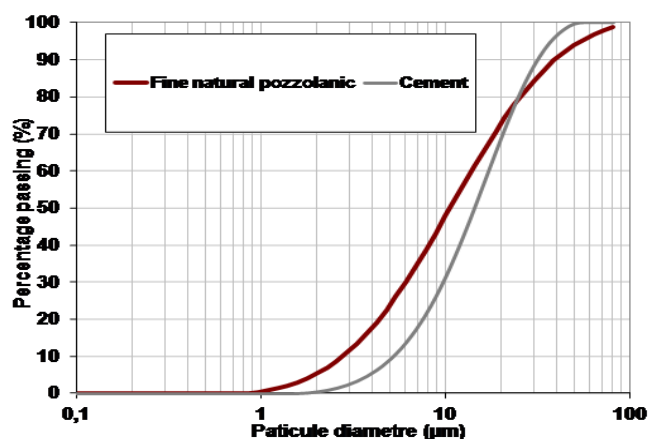


Fig. 2 – Laser granulometry of cement and natural pozzolan

Table 1 – Chemical characteristics of natural pozzolan

Element	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O
(%)	46,6	18,8	9,2	10,5	3,8	0,5	0,8

The structural analysis by X-ray diffraction (Fig.1) showed that this type of pozzolan consists of crystalline minerals rich in silica, alumina, iron and magnesium (feldspar plagioclase, pyroxene, quartz ...), in addition to some clayey minerals (montmorillonite, ...) buried in an amorphous mass (volcanic glass). The particle size analysis of natural pozzolan was carried out using the Fritsch model Analysette 22 Compact granulometer which analyzes the particle size between 0.3 µm and 270 µm by laser diffraction. The particle size distribution is shown in Fig.2.

Table 2 – Physical characteristics of natural pozzolan

Physical characteristics	values
Apparent density (g/cm ³)	0.98
Absolute density (g/cm ³)	2.69
Specific surfaces area (Blaine) (cm ² /g)	6193
PAF (%)	6,50

2.1.2 Cement

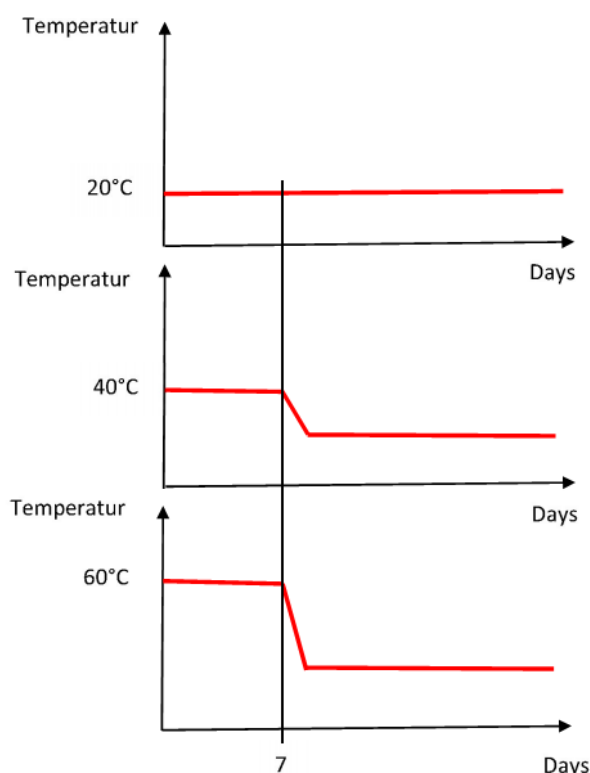
The cement CRS-CEMI 52.5 from Zahana plant (western Algeria) was used in the present study. The particle size distribution is shown in Fig. 2. The chemical and mineralogical composition of this cement, which contains no secondary additions, is given in Table 3.

Table 3 – The chemical and mineralogical composition of the cement CRS-CEMI 52.5

Chemical composition (%)							Mineralogical composition (%)			
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Insoluble residue	PAF	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
21.28	3.95	4.58	64.77	1.28	0.53	1.16	59.18	16.69	2.73	13.94

2.2 Manufacture of paste specimens

To study the effect of curing temperature on the evolution of the strength of pozzolan-modified portland cement (cement + natural pozzolan), a series of tests were carried out on pastes containing different amounts of natural pozzolan, namely 0, 10, 20, 30 and 40% by weight of cement, with a constant water to binder ratio ($W/B = 0.27$). The mixtures were prepared and mixed according to NF EN 196–1 [30]. The specimens went through heat treatment, at various temperatures, as shown in Figure 3. The curing process consisted in exposing the paste to high temperatures, i.e. 40 °C and 60 °C, during the first 7 days; it was then returned back to the reference temperature of 20 °C.

**Fig. 3 – Different curing modes used in the thermal activation of natural pozzolan-cement pastes.**

All fifteen specimens, which were supposed to be crushed at 3 and 7 days, were removed from the oven one hour before the compression test, and were then stored in a desiccator to be cooled.

3 Results and discussions

The development of the compressive strength of cement paste (100% CEM I), stored at different curing temperatures (20, 40 and 60 °C), is illustrated in Figure 4.

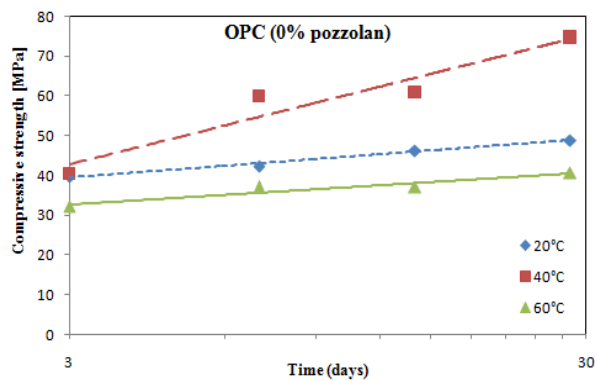


Fig. 4 – Influence of the curing temperature on the compressive strength of Cement paste containing no pozzolan (CEM I).

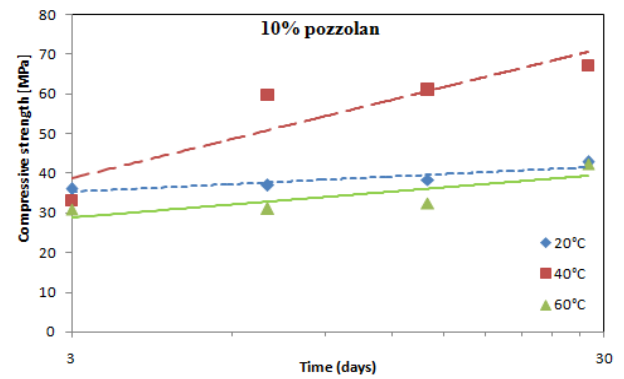


Fig. 5 – Influence of the curing temperature on the compressive strength of the paste containing 10% pozzolan.

According to Figure 4, the overall analysis of the compressive strength of pastes made with 100% of cement (CEM I) gives higher strength values for the curing temperature of 40 °C as compared to the normal curing temperature of 20 °C, due to the higher kinetics over time. This evolution is indicative of accelerated hydration reactions at the curing temperature of 40°C. The latter offers a gain on strength of 2% at 3 days. This strength gain can increase up to 42% at 7 days, and even to 53% after 28 days, as compared to the normal curing (20 °C). A significant decrease in the strength of cement paste, maintained at 60 °C, was noted, as compared to that obtained with normal curing (20 °C), with a difference of about 10 MPa (at each age). This strength decline was around 19% at 3 days, 13% at 7 days, 20% at 14 days and 16% at 28 days from these results, it appears that rising the temperature up to 60 °C has less influence on the evolution of the strength of cement. Shi and Day [27] studied the influence of temperature increase on mortars without additions. They found that, in the long term, the temperature of 20 °C gave the best strength for mortars containing cement only, without additions [31–37]. The strength decline at the temperature of 60 °C, as compared to that obtained at 20 °C, was probably due, according to [31], to the no uniform distribution of hydrates within the microstructure. However, at low temperatures, these hydrates have sufficient time to diffuse and precipitate relatively more uniformly through the cement matrix [27, 29] showed that mixtures without mineral additions, and treated at temperatures below 20 °C, gave better mechanical strengths over the long term. On the other hand, for temperatures above 20 °C, these mixtures gave better strengths over the short term. It is interesting to note that for mixtures containing mineral additions, the opposite occurs.

Figure 5 shows the influence of the curing temperature (20, 40 and 60 °C) on the development of the compressive strength of the paste containing (10% natural pozzolan + 90% CEMI), at the ages of 3, 7, 14 and 28 days.

The strength of paste containing 10% pozzolan evolved progressively with age, from 3 to 28 days, for the curing temperature of 40 °C. It can clearly be seen that the kinetics of strength development was higher at 40 °C [27]. On the other hand, this kinetics was lower for the curing at 20 °C and 60 °C, as compared to that noted at 40 °C. At 3 days, there was a slight decrease in strength with the increase in temperature of the order of 8 % and 14 % for the cures at 40 °C and 60 °C, respectively, as compared to that obtained at 20 °C. Overall, it was observed that strength increased for the curing at 40 °C; it exhibited gains of 61%, 59%, and 56% at 7, 14 and 28 days, respectively, with respect to that obtained with pastes stored at room temperature (20 °C). On the other hand, the compressive strength of the paste with 10% pozzolan, stored at 60 °C, did not exceed the value obtained at a normal cure (20 °C). The pozzolanic cement paste showed mechanical strength drops of the order of 16% and 15% at 7 and 14 days, respectively. However, it can easily be seen that at 28 days, the strength

reached the value obtained at 20 °C. Comparing the two Fig. 4 and 5, one can clearly see that the mechanical strength difference between the paste with 0% pozzolan (Fig. 4) and that with 10% pozzolan (Fig. 5) decreased due to the presence of pozzolan.

Figure 6 shows the evolution of the compressive strength of pastes containing (20% natural pozzolan + 80% CEMI) as a function of the curing temperature (20, 40 and 60 °C), at the ages of 3, 7, 14 and 28 days.

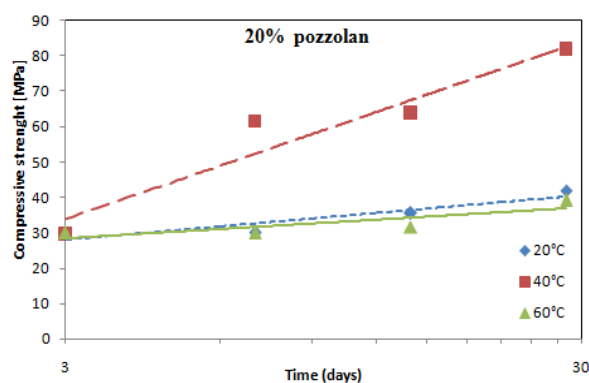


Fig. 6 – Influence of the curing temperature on the compressive strength of paste containing 20% pozzolan

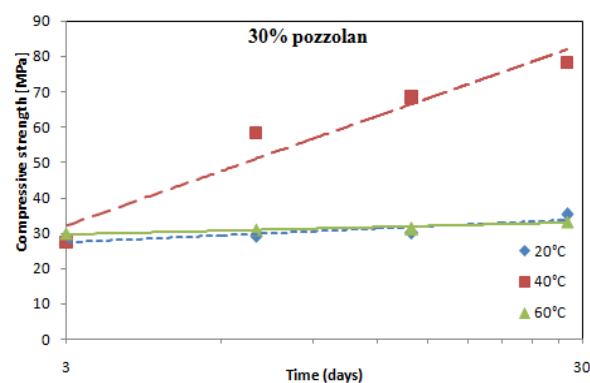


Fig. 7 – Influence of the curing temperature on the compressive strength of the paste containing 30% pozzolan.

For 20% replacement by natural pozzolan, one can note that the kinetics of the evolution of strength as a function of time was very high for the curing at 40 °C. However, it was found to be low at 60 °C and 20 °C. In the short term (3 days), the curing temperatures of 20, 40 and 60 °C gave almost the same strength value; it was of the order of 30 MPa. Increasing the temperature to 40 °C accelerated the yield of the pozzolanic reaction, which resulted in very high strengths, about twice that obtained with an ordinary cure at 20 °C. This strength gain was around 104% and 95% at 7 and 28 days, respectively. The cure at 60 °C of the pastes prepared with 20% natural pozzolan allowed for the increase in strength in such a way that the strength deviation from that obtained at 20 °C decreased. The strength values observed at 3 and 7 days are comparable to those obtained with the curing at 20 °C. However, at 14 and 28 days, these values decreased only by 11% and 6%, respectively. This shows the beneficial effect of natural pozzolan with a 20% content, at the temperature of 60 °C [29].

Figure 7 shows the influence of the curing temperature (20, 40 and 60 °C) on the compressive strength of the paste containing (30% natural pozzolan + 70% CEMI) at the dates of 3, 7, 14 and 28 days.

It can be seen from figure 7 that the strength value of the paste maintained at 60 °C is almost identical to the one obtained with a normal curing temperature (20 °C); a slight strength increase of 4%, 7%, 4% with respect to that obtained at 20 °C was also obtained at 3, 7 and 14 days. As a result, when the pozzolan content was increased to 30%, at the temperature of 60 °C, the mechanical strengths were improved by a level between 4% and 7%. The heat treatment at 40 °C proved to be very beneficial for the development of the compressive strength of the paste containing 30% of pozzolan. Indeed, it allowed for a considerable strength increase, as compared to that of the normal curing temperature (20 °C), except at 3 days, where the gain of the maximum strength was greater than 100%. This means that the strength was more than doubled as compared to that obtained in the case of the normal curing temperature (20 °C). The recorded gains were of the order of 101%, 128%, and 122% at 7, 14 and 28 days, respectively. These improvements may be attributed to the activation of the pozzolanic reactions at the curing temperature of 40 °C. This means fixing the portlandite $\text{Ca}(\text{OH})_2$ which is released by the hydration of the CEM I cement to ultimately give rise to additional hydrated calcium silicates (CSH). As for Dali Bendar et al. [38], they studied the pozzolanic reactivity of five types of natural pozzolana and pozzolana subjected to heat treatment, at different curing temperatures, in order to determine the effect of the nature of the pozzolana used. They found that their chemical compositions and crystal structures favor the formation of the geopolymer gel. The results obtained then make it possible to compare their effectiveness in the production of geopolymer cement [35].

Fig. 8 shows the evolution of the compressive strength of the pastes containing (40% natural pozzolan + 60% CEM I) as a function of the curing temperature (20, 40 and 60 °C) at 7, 14 and 28 days.

At 3 days, an improvement of about 17% was noted for the cure at 60 °C, as compared to that reached at the normal cure (20 °C). On the other hand, a slight strength drop, of the order of 13%, was observed for the cure at 40 °C. After 3 days, the strength at 60 °C was found to be almost identical to that of the normal cure of 20 °C, but with a slight improvement. The strength gains were of the order of 11% and 4% at 7 and 28 days, respectively. On the other hand, it was found that all pastes which had undergone a heat treatment (40 °C) exhibited excellent strength gains as compared to the normal curing of 20 °C (91%, 83%, 77% at 7, 14 and 28 days).

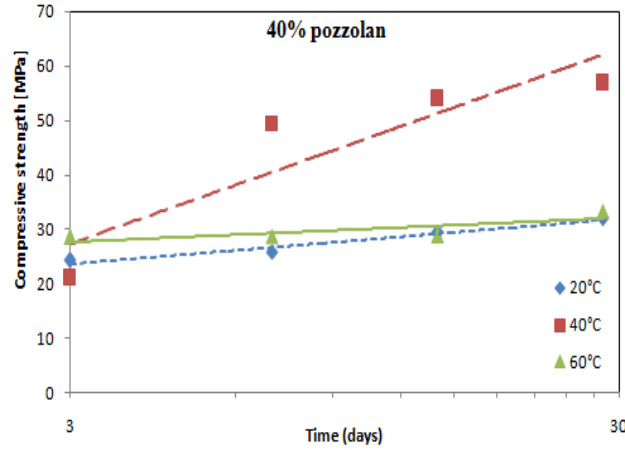


Fig. 8 – Influence of the curing temperature on the compressive strength of the paste containing 40% pozzolan.

3.1 Study of the efficiency of the curing temperature

In order to study the influence of the curing temperature (40 °C and 60 °C), the different mechanical compressive strength deviations from the curing temperature of 20 °C were calculated according to the formulas 1 to 6 . The results obtained are illustrated in Figures 9 and 10.

$$E_{(40^{\circ})} = \frac{[R_{pp(40^{\circ}c)} - R_{pp(20^{\circ})}]}{R_{pp(20^{\circ}c)}} \times 100 \quad (1)$$

$$E_{(60^{\circ})} = \frac{[R_{pp(60^{\circ}c)} - R_{pp(20^{\circ})}]}{R_{pp(20^{\circ}c)}} \times 100 \quad (2)$$

$$E_{cement(40^{\circ})} = \frac{[R_{cement(40^{\circ}c)} - R_{cement(20^{\circ})}]}{R_{cement(20^{\circ}c)}} \times 100 \quad (3)$$

$$\Delta_{(40^{\circ}c)} = E_{40^{\circ}c} - E_{cement(40^{\circ}c)} \times (100 - P) \quad (4)$$

$$E_{cement(60^{\circ})} = \frac{[E_{cement(60^{\circ}c)} - R_{cement(20^{\circ})}]}{R_{cement(20^{\circ}c)}} \times 100 \quad (5)$$

$$\Delta_{(60^{\circ}c)} = E_{(60^{\circ}c)} - E_{cement(60^{\circ}c)} \times (100 - P) \quad (6)$$

Where $E(40^{\circ}C)$, $E(60^{\circ}C)$ represent the mechanical compressive strength deviations of pozzolanic pastes maintained at 40 °C and 60 °C respectively from the curing temperature of 20 °C, $E_{cement}(40^{\circ}C)$, $E_{cement}(60^{\circ}C)$ represent the mechanical compressive strength deviations of pastes with 100% cement maintained at 40 °C and 60 °C respectively. R_{pp} is the compressive strength of paste containing a fixed quantity of natural pozzolan at a given age, and R_{cement} represents the

compressive strength of paste with 100% cement at the same age and conserved at the same curing temperature. $\Delta_{(40^{\circ}\text{C})}$, $\Delta_{(60^{\circ}\text{C})}$ difference between the compressive strength deviations. P is the amount of natural pozzolan used [35].

It can be seen from Fig. 9A that, at 40 °C, the presence of cement without pozzolan gives better mechanical strengths than at 20 °C. Moreover, in Fig. 9B, the presence of pozzolan has a positive effect up to 30% pozzolan. Also, it can be seen that beyond this level (30%), the mechanical strength decreases. Thus, an optimum (dosage/resistance) is found around the rate of 30% pozzolan.

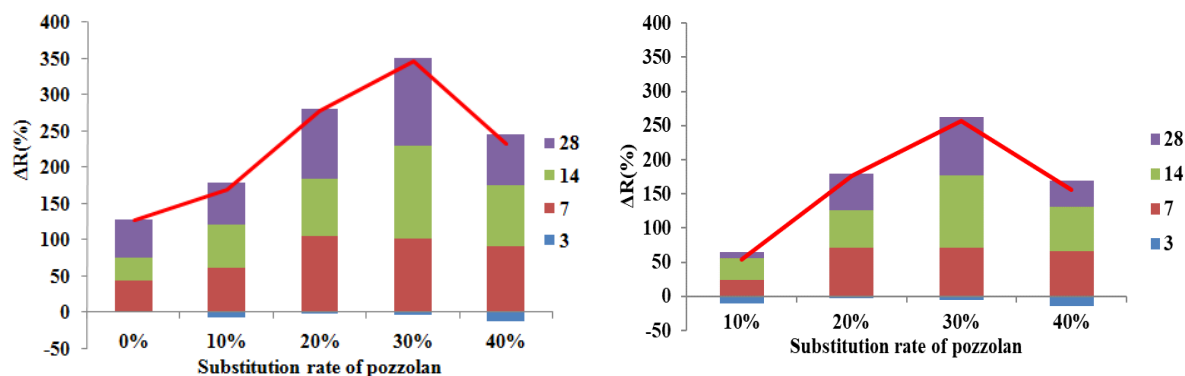


Fig. 9 – (A): Influence of the curing temperature on the development of the compressive strength at 40 °C, as compared to that obtained at 20 °C, with different amounts of natural pozzolan, (B): Efficiency of natural pozzolan at 40°C

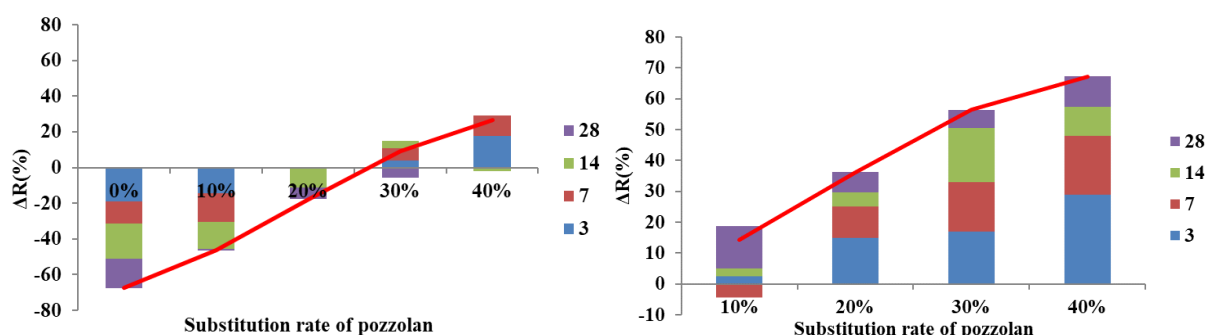


Fig. 10 – (C): Influence of the curing temperature at 60 °C on the deviation of the compressive strength, (D): Efficiency of natural pozzolan at 60°C.

From Figure 10 C, it is noted that the presence of cement without pozzolan is less effective. Moreover, when the pozzolan content increases from 10 to 40%, the mechanical strength also rises. In Fig. 10D, the contribution of pozzolan alone, with dosages between 10 and 40%, is clearly observed, and an optimum is detected around the rate of 40% of natural pozzolan (maximum dosage used) [28].

Figures 9 and 10 show the strength deviations between the curing temperatures of 40 °C and 60 °C as a function of the natural pozzolan content. The improvement in strength, as compared to that at 20 °C, is due to the presence of the mineral addition, which in this case is the natural pozzolan from Beni-Saf. It contains 46.6% of silica and 18.8% of alumina, which gives a total of 65.4%; their ratio is equal to 2.4. The high presence of silica in natural pozzolan makes it possible to reduce the Ca/Si ratio and to increase the amount of calcium silicate hydrates. These elements are among the main factors for the mechanical strength improvement [33]. According to [4-9] natural pozzolan favors the formation of secondary calcium silicate hydrates. This type of situation has a direct application in the field of prefabrication.

3.2 Comparison of the three curing methods used

Figure 11 (A, B, C and D) displays a comparison of the results of the compression strength obtained for each curing temperature used, i.e. 40 °C and 60 °C, with those of the normal cure at 20 °C as a function of the different substitution rates of pozzolan, at different maturities (3, 7, 14 and 28 days).

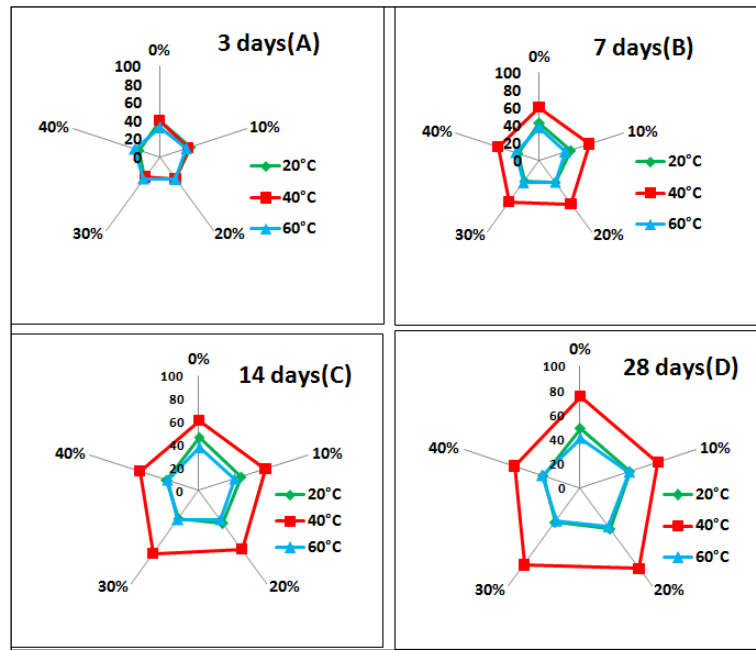


Fig. 11 – Evolution of the compressive strength as a function of the variation in the curing temperature, for different substitution rates of natural pozzolan from Beni-Saf, at 3 days, 7 days, 14 days and 28 days.

Fig. 11 clearly shows that for the different amounts of natural pozzolan, with the different curing temperatures for each age, the strengths of all pastes maintained at the curing temperature of 40 °C exceeded those of the pastes kept at ambient temperature. This is certainly due to the acceleration of the pozzolanic reaction as a result of the rise in the curing temperature. [22, 25, 27-35, 38] confirmed the improvement in strength with the increase in temperature in the presence of the mineral additions.

The heat treatment at 60 °C did not significantly improve the strength of pastes containing 10% and 20% of natural pozzolan, as compared to those obtained at room temperature (20 °C). This could be the reason of the influence of temperature which disrupted the chemical reaction during the hydration of cement and consequently stopped or delayed the pozzolanic reaction [31]. According to [29] this is due to the poor diffusion of calcium silicate hydrates (C-S-H) in the cement paste, at 60 °C. The temperature of 40 °C was found to be more suitable for this type of addition.

Escalante-Garcia [24] reported that thermal treatment inferior to 7 days has a beneficial effect on the development of long-term mechanical strength. This suggests that 40 °C is the optimum temperature for developing the strength of paste containing natural pozzolan.

3.3 Evaluation of the contribution of the substitution rate of natural pozzolan to the development of mechanical strengths

In order to evaluate the contribution of natural pozzolan to the improvement of the strengths of pastes maintained at different curing temperatures by the pozzolanic effect, it seemed interesting to calculate the ratio of strengths (R_t), which is defined by the equations 7 to 9.

$$R_{t(20^\circ)} = \frac{R_{pp(20^\circ c)}}{R_{cement(20^\circ c)}} \quad (7)$$

$$R_{t(40^\circ c)} = \frac{R_{pp(40^\circ c)}}{R_{cement(40^\circ c)}} \quad (8)$$

$$R_{t(60^\circ c)} = \frac{R_{pp(60^\circ c)}}{R_{cement(60^\circ c)}} \quad (9)$$

where R_{pp} is the compressive strength of paste containing a fixed quantity of natural pozzolan at a given age, and R_{cement} represents the compressive strength of paste with 100% cement at the same age and conserved at the same curing temperature. $R_{t(20^{\circ}C)}$, $R_{t(40^{\circ}C)}$, $R_{t(60^{\circ}C)}$ represent the strength ratios of pastes maintained at 20 °C, 40 °C and 60 °C, respectively.

3.3.1 Development of the strength ratio at 20 °C

Fig. 12 shows the development of the strength ratios as a function of age for the various percentages of pozzolanic additions at 20 °C.

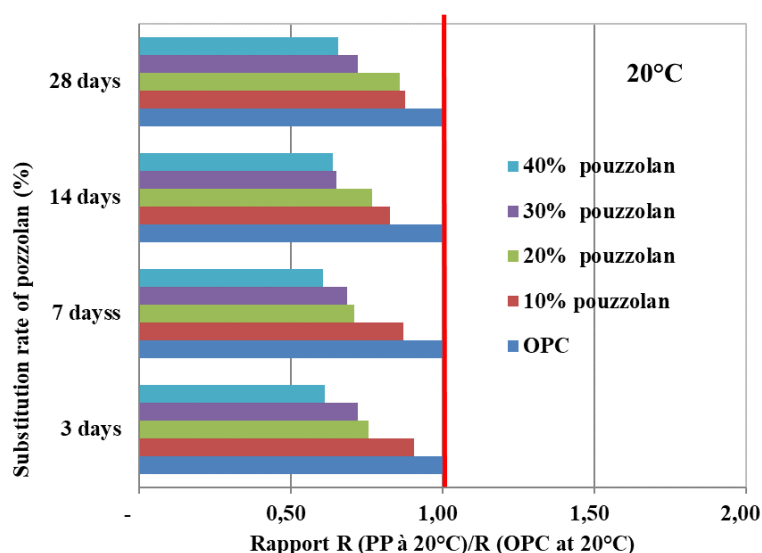


Fig. 12 – Evolution of the ratios of compressive strengths given by the formulas (from 7 to 9) for different substitution rates of the natural pozzolan from Beni-Saf at 20 °C as a function of time.

The results presented in Figure 12 show that the development of the compressive strength as a function of age depends on the substitution rate of cement. It was found that the presence of natural pozzolan reduced the compression strength at early age and middle age (between 3 and 28 days); indeed, the higher the replacement rate, the greater the strength difference.

This strength decrease was mainly due to the slow reaction between the reactive silica of the vitreous part of pozzolan and the lime released during the hydration of the CEM I [39]. Several researchers have shown that the pozzolanic reaction is not predominant at the early age, which leads to less intense hydration at the young age, and this induces a weak strength. On the other hand, in the long run, particularly at 90 days, the pozzolanic reaction continues its effect by forming additional C-S-Hs which improve the paste-aggregate interface and decrease the capillary porosity of concrete [17]. Nevertheless, it is important that the cement reach satisfactory strength level in a short time. Therefore, it becomes necessary to carry out a heat treatment in order to accelerate the pozzolanic reactions.

3.3.2 Development of the strength ratio at 40 °C

Figure 13 shows the development of strength ratios as a function of age for the various contents of pozzolanic addition at 40 °C.

From Fig. 13, one can see that the compressive strength of cement with pozzolan is lower than that of cement CEM I even at high curing temperatures. This depends on several factors, including the replacement rate. It was noted that at three days, all the pastes showed an increasing loss in strength, depending on the pozzolan content (the ratio is between 0.82 and 0.52 when the pozzolan replacement rate increases from 10% to 40%). At 7 days, the pastes containing between 10% and 30% of pozzolan developed slightly better compressive strengths, which tended to approach that of the CEM I cement paste at the same curing temperature (ratio ≈ 1). After 7 days, the strength ratio increased when the substitution rate of pozzolan went up. This proves that the pozzolanic reaction was clearly influenced by the increasing curing temperature, which gave rise to strengths comparable and sometimes even higher than those of the reference paste [40]. In particular, the pastes containing 20% and 30% of pozzolan gave better strengths than those of the control paste, which resulted in ratios greater

than 1. On the other hand, the paste prepared with 40% of pozzolan did not reach the strength value of the reference paste at all ages. The drop in strength for this paste may be attributed to the insufficient quantity of lime released during the hydration of the CEM I cement and consequently to incomplete chemical reactions.

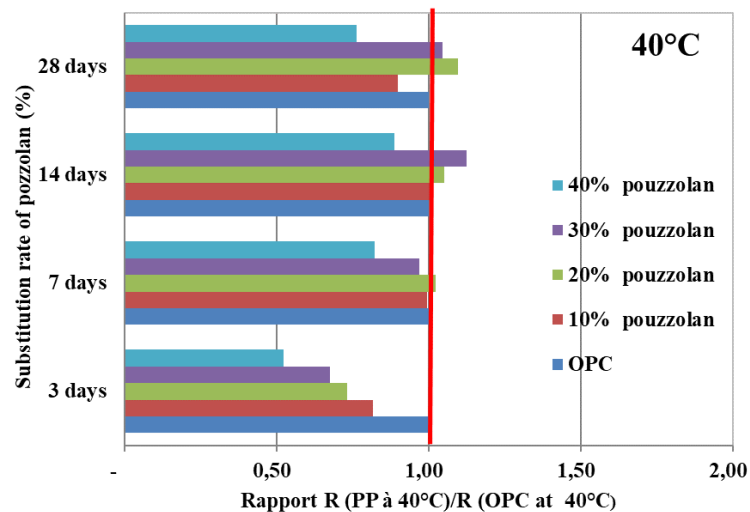


Fig. 13 – Evolution of the ratios of compressive strength, for different substitution rates of natural pozzolan from Beni-Saf at 40 °C, as a function of time

3.3.3 Development of the strength ratio at 60 °C

Fig. 14 shows the development of the compressive strength ratio as a function of the age of pastes containing different amounts of natural pozzolan and maintained at a curing temperature of 60 °C.

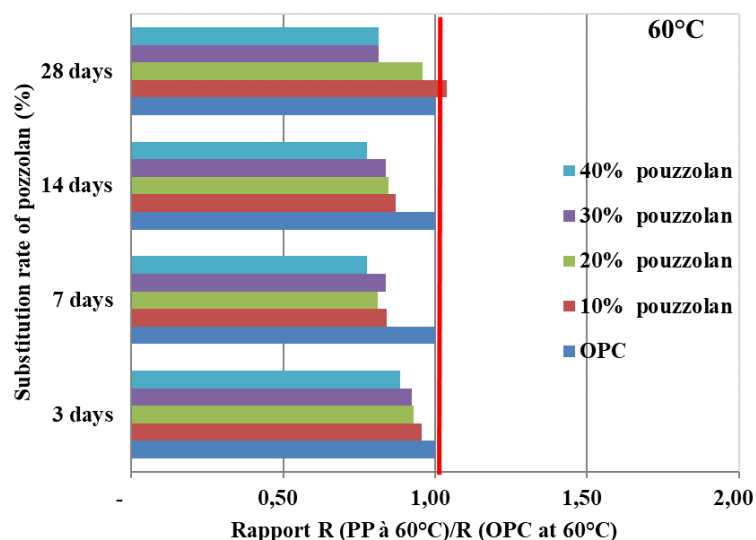


Fig. 14 – Evolution of the compressive strength ratio for different substitution rates of natural pozzolan from the town of Beni-Saf, at 60 °C, as a function of time.

It can clearly be observed from this figure that the compressive strength decreases with the rise of natural pozzolan substitution rates. However, this drop in strength between various pozzolan replacement levels was not very significant between the 3rd and the 14th days, since all the pozzolan pastes developed mechanical strengths that were nearly similar at 3, 7 and 14 days, with strength ratios around 0.90, 0.80 and 0.80 at 3, 7 and 14 days, respectively. However, it is worth mentioning that only the paste containing 10% of natural pozzolan developed a strength value that was comparable to that of

the reference paste at 28 days. In general, the curing at 60 °C does not significantly favor the pozzolanic reaction, as compared to that at 40 °C.

3.4 Evaluation of the contribution of the pozzolan substitution rate and the curing temperature to the development of the mechanical strength

In order to quantify and show the positive effect of heat treatment of pozzolanic pastes, in comparison with that of cement CEM I at 20 °C, the ratios $R_{p(40^{\circ}\text{C})}$ and $R_{p(60^{\circ}\text{C})}$ were calculated using the formulas 10 and 11; R_{pp} is the compressive strength of paste containing a fixed amount of natural pozzolan at a given age and $R_{\text{Cement } 20^{\circ}\text{C}}$ represents the compressive strength of the paste with cement CEM I at 20 °C, and at the same age.

$$R_{p(40^{\circ}\text{C})} = \frac{R_{pp(40^{\circ}\text{C})}}{R_{\text{cement}(20^{\circ}\text{C})}} \quad (10)$$

$$R_{p(60^{\circ}\text{C})} = \frac{R_{pp(60^{\circ}\text{C})}}{R_{\text{cement}(20^{\circ}\text{C})}} \quad (11)$$

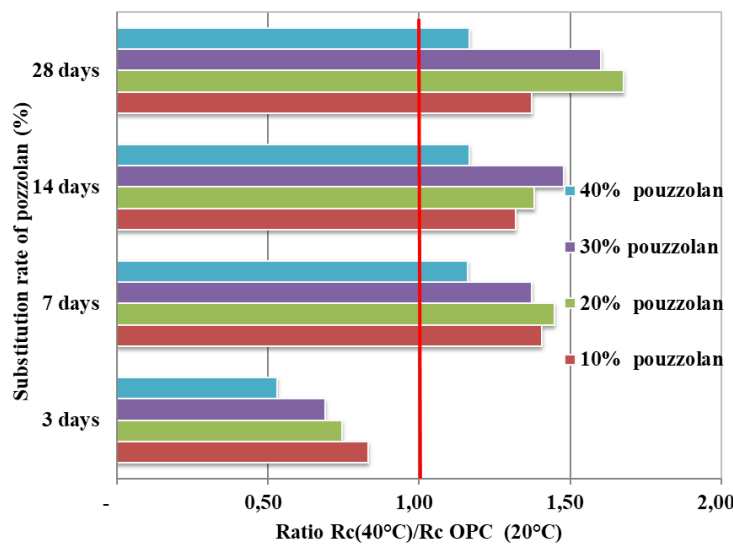


Fig. 15. Evolution of the ratio between the compressive strengths of the pozzolanic pastes, maintained at 40 °C, and that of the reference paste (OPC, at 20 °C), as a function of time.

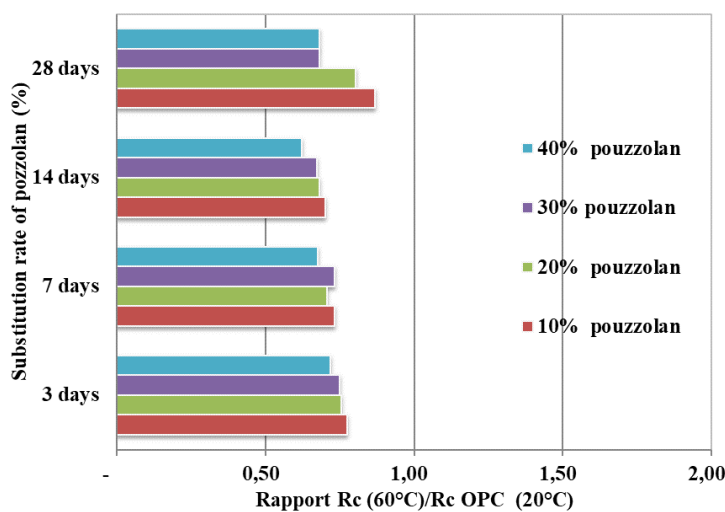


Fig. 16 – Evolution of the ratio between the compressive strengths of the pozzolanic pastes, maintained at 60 °C, and that of the reference paste (OPC, at 20 °C), as a function of time.

Fig. 15 and 16 show a comparison between the strength ratios of the pastes prepared with 10%, 20%, 30% and 40% of natural pozzolan, with a thermal cure at 40 °C and 60 °C, for 7 days, and that of cement CEM I paste which underwent a normal thermal curing (20 °C). For the curing temperature of 40 °C, the strength ratio was seen to decrease as the pozzolan level increased, at the young age (3 days). Beyond that date, the mechanical performances of all pozzolanic pastes, maintained at 40 °C, were superior to that of the reference paste for the 20 °C isothermal cure (ratio ≥ 1). The pastes prepared with 20% and 30% of natural pozzolan gave the best strength values, with ratios greater than 1.5. Similarly, pastes with 10% and 40% of pozzolana showed ratios greater than 1 as of the seventh day of curing. Thus, the optimum pozzolan replacement rate was about 40% for a curing temperature of 40 °C, which means that it is possible to save up to 40% of Portland cement when the curing temperature of 40 °C is used, as compared to the normal curing temperature of 20 °C. On the other hand, strengths of the pozzolanic pastes were seen to decrease at the temperature of 60 °C, whatever the pozzolan rate used (ratio ≤ 1). Therefore, it is possible to go well beyond 10% of substitution of the cement by pozzolana. This substitution level has been recommended by the Algerian standard NA 442 (2003) [41] for the manufacture of cement CEM II 42.5, with the aim of reducing the quantity of cement used and fight against CO₂ emission and thus contribute to reducing the greenhouse effect. This solution adapts quite well to the field of prefabrication where heat treatment is very important to have a cost-effective formwork.

4 Conclusion

The present experimental work was aimed to study the influence of curing at high temperatures, between 40 and 60°C, on the development of the resistance of pozzolanic pastes containing 10%, 20%, 30% and 40% natural pozzolana. The results obtained made it possible to draw the conclusions given below:

- The beneficial effect of heat treatment of pozzolanic pastes was not noticed during the first three days for the temperature at 40°C. Beyond 7 days, a significant improvement in resistance is observed.
- In the short term (3 days), the curing temperatures of 20, 40 and 60°C gave almost the same resistance value, of the order of 30 MPa.
- The mechanical resistances in the dough with substitution rates of 0, 10, 20, 30 and 40% dropped for temperatures equal to 20 and 40°C. On the other hand, they improved for the temperature of 60°C after a cure of three days.
- In the long term, for a replacement of 20% natural pozzolan, the evolution of the resistance as a function of time was considerable for a cure at 40°C, which is not the case for temperatures of 20°C and 60°C.
- The heat treatment at 40°C proved to be very beneficial for the development of the resistance to compression of the paste containing 30% pozzolan.
- Gains in compressive strength recorded were of the order of 101%, 128%, and 122% at 7, 14, and 28 days, respectively. These improvements can be attributed to the activation of pozzolanic reactions at the cure temperature of 40°C. This is certainly due to the fixation of the portlandite Ca(OH)₂ released by the hydration of the CEM I cement, which contributed to the formation of the additional hydrated calcium silicates (CSH).
- For a replacement rate of 40% at 3 days, an improvement of approximately 17% was noted for the cure at 60°C compared with that obtained at the normal cure (20°C). On the other hand, a slight drop in resistance, of the order of 13%, was observed for the cure at 40°C. In the long term, the strength obtained at 60°C was found to be almost identical to that of the normal cure at 20°C, but with a slight improvement. Strength gains were 11% and 4% at 7 and 28 days, respectively.
- On the other hand, it has been found that all the pastes having undergone heat treatment (40°C) exhibited excellent strength gains compared to what is obtained at 20°C. The deviations recorded were of the order of 91%, 83%, 77% at 7, 14 and 28 days.
- It is suggested that 40°C is the optimum and most appropriate temperature for the development of the strength of pastes containing natural pozzolan, regardless of the age of the material.
- The curing temperature of 60°C has a beneficial effect on the development of the mechanical resistance of pozzolanic pastes with a replacement rate of 20%.
- Natural pozzolan is more effective for high temperatures of 40°C and 60°C. Therefore, it is recommended to carry out the thermal activation of natural pozzolan for the manufacture of eco-materials.
- With the hydrothermal treatment, it is possible to go far beyond 10 % replacement of cement by pozzolan. This is recommended by the Algerian Standard NA 442 standard for the manufacture of an eco-cement. This technique

allows reducing the quantity of cement used, limiting the quantity of CO₂ released in the atmosphere, and attenuating the greenhouse effect.

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