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Comparative study of the influence of inorganic additions on the physical-chemical properties and mechanical performance of mortar and/or concrete

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Abstract

In this work, we studied the comparative between the effect of inorganic additions such as the P.Lime and the PN on the physical-chemical properties of cement and the mechanical performances of mortar and/or concrete, while partially substituting the clinker by these materials, at various percentages ranging from 5% to 40% of each add by weight of cement with an interval of 5%. The obtained results by the different formulations elaborated show that the substitution a part of clinker by PN and/or P.Lime produced a new durable hydraulic binder with the physical-chemical and mechanical properties improved, namely the increases in the fineness by specific surface, the density is decreased, the setting time decreased as a function of the increase in the percentage of P.Lime and increased with the increases in the percentage of PN, the report of water/cement decreased as a function of the mass fraction of PN and increased with the percentage of P.Lime. The compressive strength at a young age (2 days), median age (7 days) and long term (28 days) improve with the percentage of P.Lime and/or PN was increased.

Keywords: *Natural Pozzolan; Pure limestone; Adding inorganic; Physical properties; Mechanical performance, Hydraulic binder.*

1. Introduction

The recent developments in the field of cementitious materials show that the incorporation of fine and ultrafine mineral additions lead, generally, to the reduction of the amount of water of the mixing [1, 2], to minimize the emissions of CO_2 into the atmosphere, to reduce the energy and the raw materials consumed [3] and consequently to improve the physical properties and mechanical performance [4- 6]. The Yemen has a significant amount of a mineral additions and natural rocks, among these materials, we found that the natural pozzolan (PN), and the pure limestone (P.Lime) which in the presence of water reacts chemically with the calcium hydroxide at ambient temperature to form a compound having binding properties. The pozzolanic materials are the silico-aluminous minerals of volcanic origin, extracted from the deposit of Difan-Amran in north of Sana'a [1, 7 - 9]. And the pure limestone is also a mineral obtained by grinding of sedimentary rocks soluble in water, composed of calcium carbonate “$CaCO_3$” and magnesium carbonate “$MgCO_3$”, extracted from the deposit of Amran also in Yemen [1, 10-12]. The valorization of these active resources by introducing them in the manufacture of cement and concrete has economic and environmental advantages at the same time; the reduction of production costs and the minimization the emissions of CO_2 in the atmosphere [2, 3, 9, 13-14] on one hand. On the other hand, to improve the properties of these materials in the fresh state such as the workability/the fluidity/the water content/ the homogeneity and the compactness as well as the compressive strength in the hardened state [5 - 7, 15 - 20]. The use of these additions in the formulation of cementitious material or concrete promotes to reduce the porosity which translates a series of effects very advantage of the reduction of the permeability of water, the calcium hydroxide content and also to improve the compressive strength of sulfates, chlorides [7, 11, 14, 19, 21-24]. In this work, we have been realized in scientifically collaboratively between the laboratory of agro-resources polymers and process engineering in the faculty of sciences, Ibn Tofail University, Kenitra-Morocco and the laboratory of cement and quality control of Amran-Yemen, different formulations have been developed all by partially substituting the clinker by the pure limestone and/or the natural pozzolan at different percentages ranging from 5% to 40% by weight of cement with a step of 5%. The influence of the incorporation of these additions on the physical properties of cement in fresh cement paste has been studied on one hand and on the mechanical performance in the hardened State has been evaluated on the other. The obtained results from the different formulations developed show that the substitution a part of clinker by these additions from produce us a new durable hydraulic binder with to improve the physical-chemical properties, namely, the reduction of the quantity of water used / the decrease in the density /the increase in the finesse by specific surface /the decrease in the setting time as a function of the percentage of P.Lime and crossing it with the increase in the percentage of PN. The compressive strength at a young age (2 days), median age (7 days) and long-term (28 days) have also improved in function of the increase in the P.Lime and/or PN.

2. Experimental

2.1. Materials

In order to evaluate the effect of the natural pozzolan and/or the pure limestone on the physical properties of the fresh cement paste and on the compressive strengths of mortars and/or concretes, we have started this work by characterizing of the materials used in order to understand the phenomena which occur at the time of mixing and their hardening.

2.1.1. Cement

The type of cement used in this work is (CMI-42.5). This a Portland cement as a resulting from simultaneous at (95%) of clinker and (5%) of gypsum accordance to the standard EN 196-1. It is from of a cement factory of Amran -Yemen.

The chemical compositions (clinker, gypsum, and cement), mineralogical (clinker) determined by X-rays fluorescence (XRF) and their physical properties are presented in tables (1, 2 and 3).

Table 1: Elementary chemical compositions of clinker, gypsum, and cement in weight of atomic

Content (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Cl^-
Clinker	62.76	21.00	5.84	3.00	1.96	0.90	1.21	0.20	0.02
Gypsum	33.40	0.70	0.36	0.09	0.63	47.2	0.03	0.10	0.01
Cement	61.29	19.99	5.57	2.85	1.89	3.22	1.15	0.20	0.02

Table 2: Mineralogical composition of clinker

Chemical name	Mineral name	Chemical formula	Cement nomenclature	Content
Tricalcium silicate	Alite	Ca_3SiO_5	C_3S	47.70
Dicalcium silicate	Balite	Ca_2SiO_4	C_2S	25.10
Aluminate tricalcium	Aluminate	$Ca_3Al_2O_6$	C_3A	10.40
Tetracalcium Aluminoferrite	Ferrite	$Ca_4Al_2Fe_2O_{10}$	C_4AF	9.10

Table 3: Physical properties of clinker and cement

Physical properties	Unity	Value	
Specific surface Blaine	$cm^2.g^{-1}$	Clinker	3360
		Cement	3240
Density	$g.cm^{-3}$	Clinker	3.17
		Cement	3.14

2.1.2. Inorganic additions

Pure limestone (P.Lime)

It is a mineral material that is spread in several regions in Yemen, such as Hadramaut, Sana'a, and Amran, etc. (fig. 1).

Figure 1: Deposit of extract of pure limestone in Bani Qais-Amran -Yemen

Natural pozzolan

The natural pozzolan (PN) used is of volcanic origin, extracted from the deposit of Difan – Amran-Yemen (figure 2), located north of Sana. It consists essentially of slag and well-stratified pumice stones, color varies from red to black.

Figure 2: Deposit of extract of natural pozzolan in Difan-Amran-Yemen

Physical-chemical characteristics

The chemical compositions of pure limestone (P.Lime) and natural pozzolan (PN) after grinding determined by the XRF are illustrated in the table (4).

Table 4: Elementary chemical compositions of P.Lime and PN determined by XRF in weight of atomic

Content (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Cl^-	LOI
P.Lime	54.96	0.62	0.12	0.16	0.41	0.08	0.01	0.00	0.00	43.63
PN	8.80	41.43	16.16	9.41	4.79	0.13	0.90	3.47	0.04	14.87

From the table (4), we found that the P.Lime of Bani Qais-Amran - Yemen contains 54.96% of lime (CaO) /0.12% of alumina (Al_2O_3) /0.16% of iron (Fe_2O_3) /0.62% of silica (SiO_2). On the other hand, the PN of Difan-Amran contains 41.43% of silica (SiO_2) /16.16% of alumina (Al_2O_3) /9.41% of iron (Fe_2O_3) /8.80% of lime (CaO). The mineralogical analysis by X-ray diffraction (XRD) of P.Lime and PN are shown in the figures (3, 4).

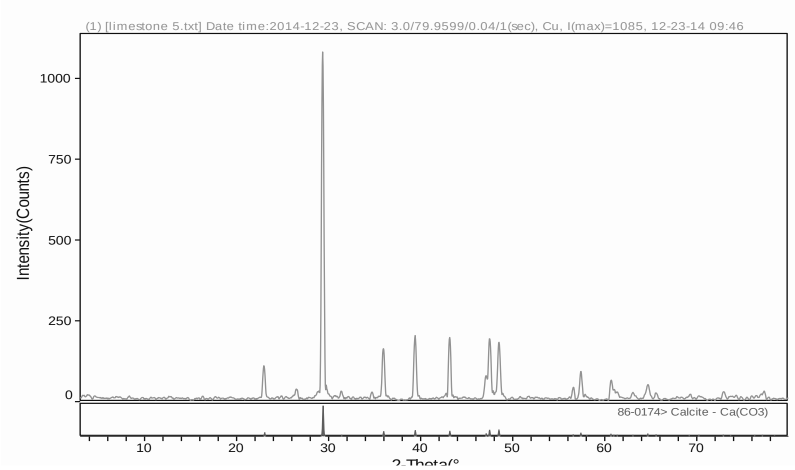


Figure 3: Spectrum of P.Lime by X-ray diffraction

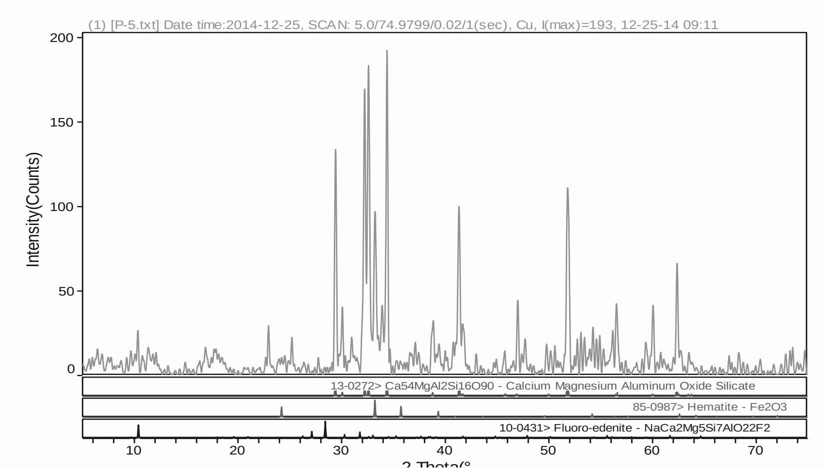


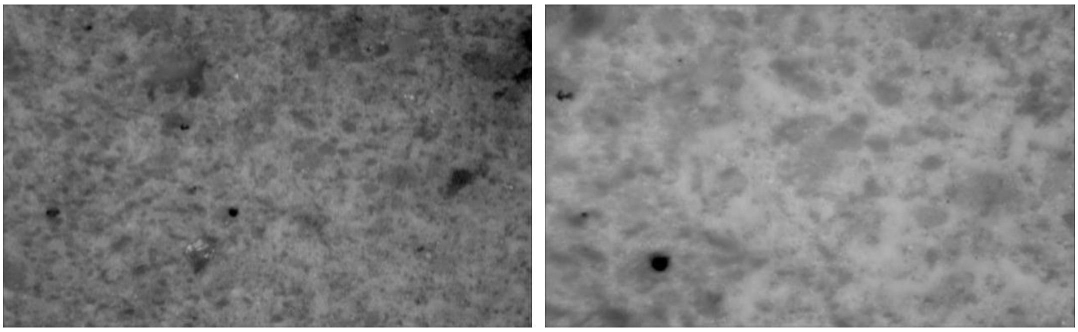
Figure 4: Spectrum of PN by X-ray diffraction

According to the figures (3, 4), we have deduced the following comments:

- The P.Lime present in figure (3) reveals the strong presence of calcite ($CaCO_3$), then by the Dolomite ($CaCO_3/MgCO_3$), afterward the magnesium carbonate ($MgCO_3$) and the magnesium hydroxide "Mg $(OH)_2$".
- The PN shown in figure (4) reveals the strong presence of Feldspar plagioclase (Anorthite: $CaOAl_2\ O_3\ 2SiO_2$) followed by the pyroxene (Augite: $(Mg, Fe)_2\ 2SiO_6$) then the Volcanic glass of Analcime (zeolite) Chlorite:

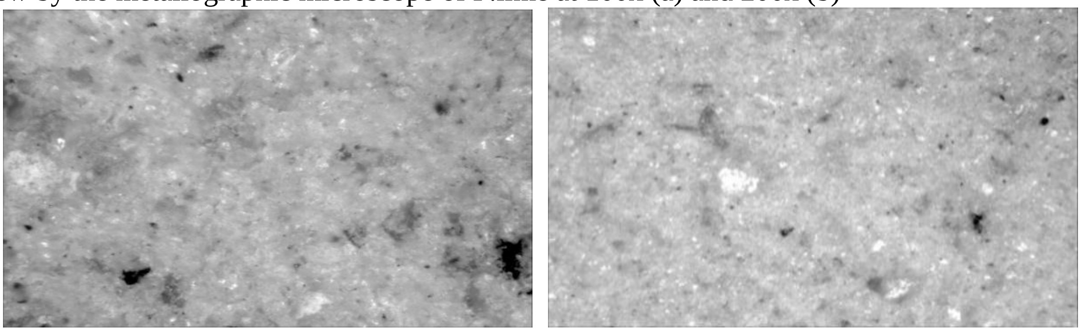
(6 Mg_5 $AlSi_3$ O_{10}) (OH) and some traces of Hematite: Fe_2 O_3, also that the Magnetite: Fe_2 O_3 OTF, as well as the Biotite: 2 K (Fe, Mg)$_3$ $AlSiO_{10}$ (OH) and traces of minerals: basalts, calcite, Dolomites, clays, etc.

The analysis by the metallographic microscope of P.Lime and PN is presented in figures (5, 6).



(a) (b)

Figure 5: View by the metallographic microscope of P.lime at 100x (a) and 200x (b)



(a) (b)

Figure 6: View by the metallographic microscope of PN at 100x (a) and 200x (b)

The particles of limestone and pozzolan are presented in the form of rosettes. They are exposed in the figures (5, 6) using a metallographic microscope to two expansions (100 x and 200 x).

The physical properties

The physical properties of P.Lime and PN are given in table (5):

Table 5: Physical properties of P.Lime and the PN

Physical characteristics	Unity	Value	
		P.Lime	PN
Specific surface Blaine	$cm^2.g^{-1}$	4776	4576
Density	$g.cm^{-3}$	2.13	2.81

2.1.3. The mixing water

To prepare our mixture, we used tap water (wells), its main features are gathered in the table (6).

Table 6: Main features of the mixing water

Components	pH	Turbidity	CO_3^{-2}	HCO_3^-	Ca	Mg^{+2}	Conductivity
Unity	-	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	µS/cm
Value	7.00	450.00	216.00	0.00	56.40	52.40	692.00

2.1.4. Sand

To make our mortar, we used standard sand according to the norm EN 196-1, delivered by the new French company of Littoral. Its particle size analysis is illustrated in figure (7).

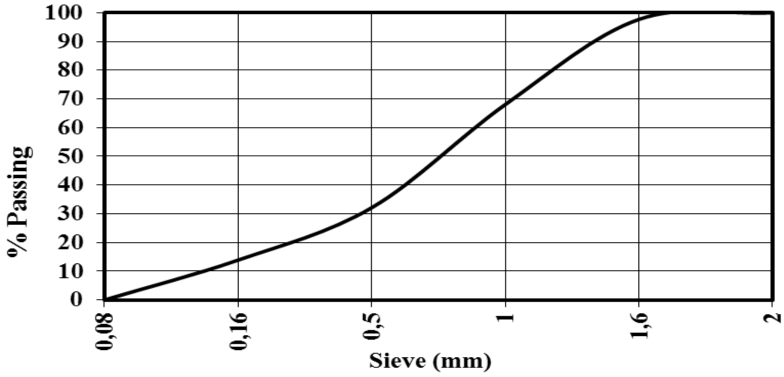


Figure 7: Curve granulometric of sand

The particle size analysis presented in figure (7) there is that used sand grains are distributed in a systematic way according to the specifications of the standard EN 196-1.

2.2. Methods

2.2.1. Method of preparation of the State cement powder

The density

The density of cement is measured by the displacement of an inert liquid with cement within a graduated container. It is measured using a Le Chatelier device according to a specification of norm EN 196-6 and calculated using the equation (1).

$$\rho \frac{\text{Mass of cement (g)}}{\text{Absolute volume of cement}\left(\text{cm}^3\right)}; \frac{g}{cm^3} \qquad (1)$$

Finesse by specific surface Blaine

It is the total surface of the grains contained in a mass of powder, it is measured using the Blaine device and calculated according to the equation (2).

$$S = \frac{K}{\rho} \times \frac{\sqrt{e^3}}{1-e} \times \frac{\sqrt{t}}{\sqrt{0,1\eta}}; \text{cm}^2/\text{g} \qquad (2)$$

With: ρ: Absolute density of cement; K: Apparatus constant; e: Porosity (in general: 0.50); t: Measured time in seconds and η: Dynamic viscosity of air at the test temperature.

2.2.2. Method of preparation of fresh cement paste

The experimental protocols used to determine the physical properties are given by EN 196-3. The formulations of different matrix of the fresh cement paste at the base of PN and /or P.Lime show in the table (7).

Water demand

The objective of this test is to determine the optimal amount of mixing water. This test is carried out by the Vicat unit according to the norm EN 196 - 3.

Setting time:

This is the time required for the cement paste solidifies. It is measured using the Vicat apparatus.

Table 7: Formulations matrix of fresh o cement paste at base of PN and / or P.Lime

Content	Cement	W/C	
	%	PN	P.Lime
0%	100	0.28	0.28
5%	95	0.27	0.29
10%	90	0.26	0.29
15%	85	0.25	0.29
20%	80	0.24	0.30
25%	75	0.23	0.31
30%	70	0.22	0.31
35%	65	0.21	0.32
40%	60	0.21	0.32

2.2.3. Methods of preparation of mortar and /or concretes in the hardened State

To achieve the objectives of our study, we prepared a reference mortar and other mortar with mineral additions which compositions are inspired by that of the normal mortar that defined by the standard EN 196-1, with adjusted the water, that show in the table (8).

$$\text{Compressive strength} = \frac{\text{Load ,in "N"}}{\text{Area, in "}mm^2\text{"}}; \text{MPa} \quad (3)$$

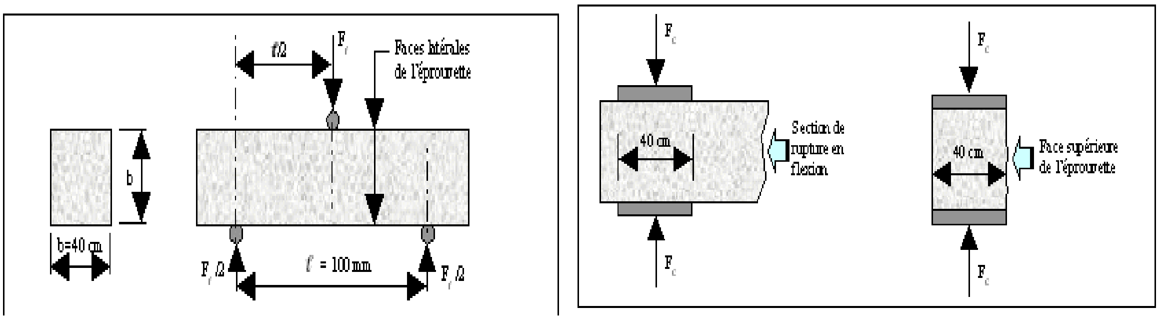


Figure 8: Device of bending and compressive load of specimens mortar

Table 8: Formulations matrix of mortar and/or concrete in the hardened State at the base of PN and / or P.Lime

Content of add	Cement	Sand	Water (W/C)	
%	%	Mass (g)	PN	P.Lime
0	100	1350	0.50	0.50
5	95	1350	0.49	0.50
10	90	1350	0.48	0.51
15	85	1350	0.47	0.52
20	80	1350	0.45	0.52
25	75	1350	0.44	0.53
30	70	1350	0.42	0.53
35	65	1350	0.40	0.54
40	60	1350	0.40	0.54

The procedures followed for the preparation of these mortars begin with the mixing of the hydraulic binder (cement with the different percentages of addition of pure limestone "P.Lime" and/or Pozzolan "PN"), sand and water, and then we filled the mold (4 x 4 x 16) cm^3. Then we shook the mortar in this mold that is obtained by introducing the paste twice and applying, to the mold 60 shocks every time. After the mold is covered with a plate of glass and stored in the wet room. After 20 h or 24 h from the start of mixing, the test pieces are molded and stored in water at 20 °C±1°C until the breaking test. On the scheduled day, the 3 test pieces are broken in flexion and compression (figure 8). The results of compressive strength are calculated using the equation (3).

3. Results and discussion

3.1. Influence of (PN and/or P.Lime) additions on the physical properties

3.1.1. Influence on the density

The figure (9) illustrates the density of cement based on the mass fraction of the additions of P.Lime and/or PN.

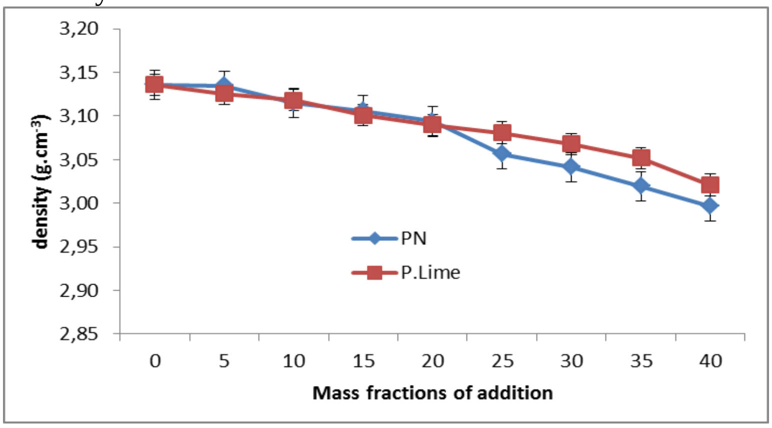


Figure 9: Variation of the density as in function of the mass fraction of the additions of PN / P.Lime

From the figure (9), we found that density of cement based on mass fractions of additions P.Lime and/or PN decreases. This decrease is explained by the fact that these additions (pure limestone "P.Lime" and/or natural Pozzolan "PN") have the lowest densities compared to Portland cement. Those lowest densities are habitually due on one hand to the density of the various oxides which constitute them and on the other hand to the high proportions of voids of the addition of the pure limestone and the natural Pozzolan.

3.1.2. Influence on the finesse by the specific surface

The figure (10) displays the finesse by the specific surface of cement based on the mass fraction of additions (pure limestone and/or natural pozzolan).

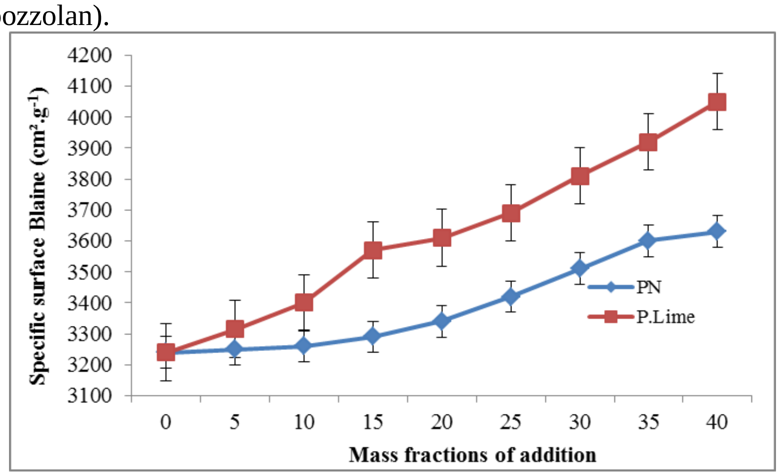


Figure 10: Variation of specific surface as in function of mass fraction of the additions of PN / P.Lime

At the figure (10), we have noticed that the finesse of cement by specific surface increases with the mass fraction of the additions of P.Lime and /or PN was increased. This is usually due to the fineness of these additions, which provided a very greater contact of the cement grains and a high reactivity during hydration on one hand. And which fills the voids between particles of cement and that of sand on the other.

3.1.3. Influence on the W/C ratio

The figure (11) shows the evolution of the W/C ratio as a function of the mass fraction of additions.

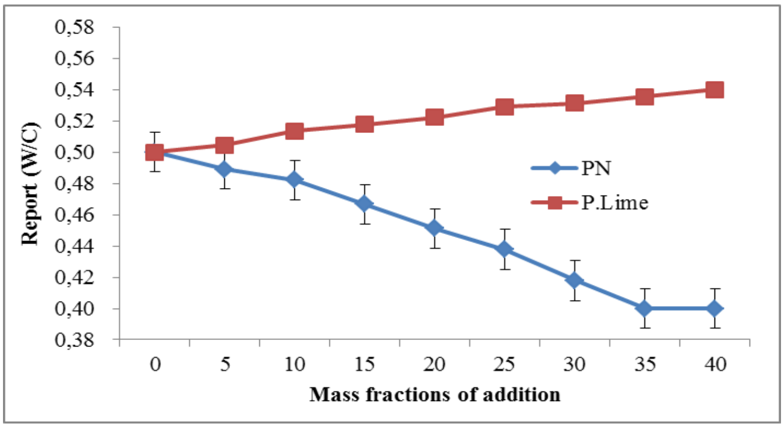


Figure 11: Variation of the W/C report as in function of the mass fraction of the additions of PN / P.Lime

The results presented in the figure (11) show that the of W/C ratio of cement paste increases with the mass fraction of P.Lime and decreases with the mass fraction of PN. These variations are usually due to the chemical and mineralogical compositions of our additions. Indeed, in the case of the addition of pure limestone "P.Lime", is rich in CaO; the presence of high levels of calcium oxide in the pure limestone addition (rich in this mineral phase) has an influence on the phenomenon of hydration, which will require more water. However, in the case of the addition of natural Pozzolan "PN" the W/C ratio decreases as a function of the increase in the mass fraction this one. This could be an indication of the consumption of the lime present in the cement by the SiO_2 existing in the vitreous part of the natural Pozzolan. Indeed, when the water reacts with the lime released by the cement during the hydration of the mixture, it will be absorbed slowly to form calcium hydroxide $Ca(OH)_2$. The decrease in the quantity of water is also due to the chemical and mineralogical compositions of the CaO-poor natural Pozzolan; the presence of decreased CaO in natural Pozzolan (poor in this mineral phase) tends to have a lower water demand compared to controls.

3.1.4. Influence on the setting time:

The figure (12) gives the changing of initial and final setting time of fresh cement paste as a function of the mass fraction of the P.Lime and PN.

From the figure (12), we deduced the following comments:

- We found that the initial and final setting time of fresh cement paste increase, according to the percentage of PN. This is usually due to the chemical and mineralogical compositions of natural Pozzolan on one hand and on the other hand, it could be due to the pozzolanic reaction which consumes the calcium hydroxide or Portlandite, Ca(OH), and which forms the hydrated calcium silicates, similar to those produced by the hydration of tricalcium silicate (C_3S) (C_3A. SiO_2). This gave us our binder the role of retarder in setting time.
- We have noticed that the initial and final setting times of fresh cement paste decrease considerably with the percentage of the P.Lime. This decrease is due usually to the chemical and mineralogical compositions of

our addition which is rich in CaO and low in Al_2O_3. The presence of P.Lime in the mixture releases with the calcium hydroxide "Ca $(OH)_2$". However, the tricalcium aluminate phase (C_3A) ($Ca_3Al_2O_6$) increase, which gave us our binder the role of an accelerator in setting time.

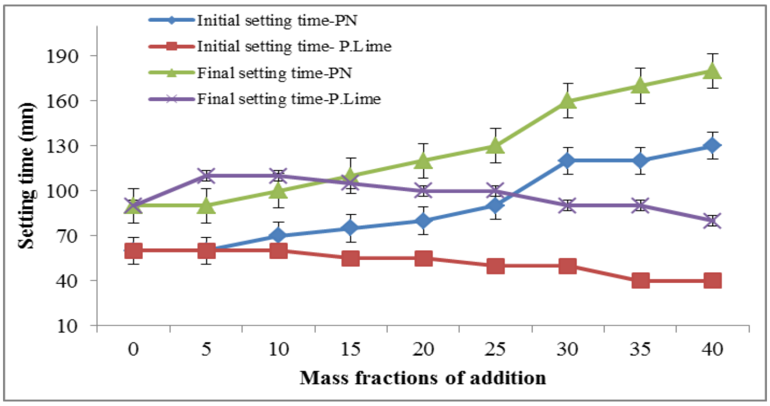


Figure 12: Variation of the setting time as in function of the mass fraction of the additions of PN / P.Lime

3.2. Influence of additions (PN and/or P.Lime) on mechanical performance

The figures (13 and 14) present the variation of compressive strength as a function of age in days.

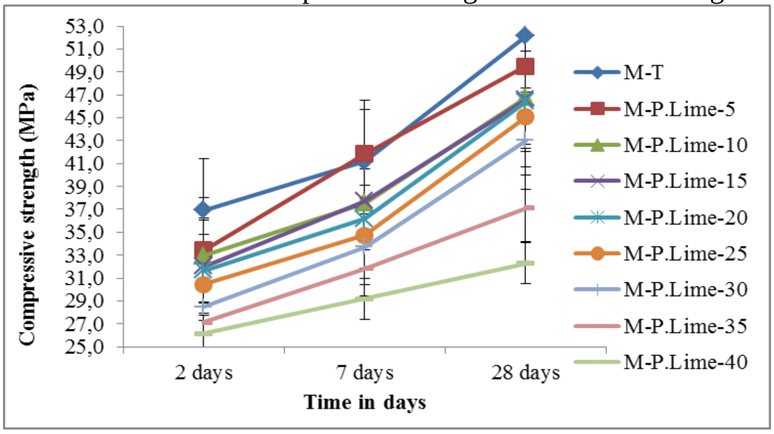


Figure 13: Variation of compressive strength as a function of the time en days

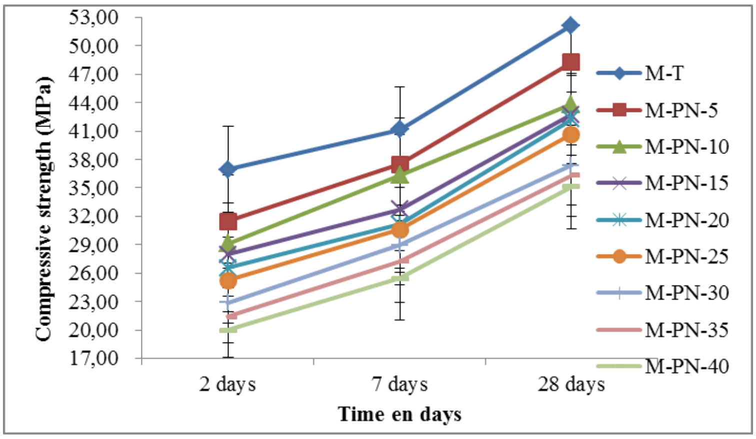


Figure 14: Variation of the compressive strength as a function of the time en days

According to the figures (13 and 14), we found that the compressive strength of all mortars formulated by the P.Lime and/or PN increase regularly with age. These increases are awarded generally by several reasons amongst which, we found that the chemical and mineralogical compositions of these additions, promote the Pozzolanic reactions that

occur between the reactive silica in the part of vitreous of natural pozzolan and that of the calcium hydroxide Ca $(OH)_2$ released by the cement during the hydration of mixture according to the following chemical reactions on one hand:

$3CaO.SiO_2+H_2O$ —> $CSH+Ca(OH)_2$ (hydration reaction of Portland cement);

$CaO+SiO_2+H_2O$ —> CSH (Pozzolanic reaction).

And on the other hand is explained by the fact that additions of PN and/or P.Lime by their fines, had to fill the gaps existing between the cement particles and that of sand which improves the porosity and which subsequently affects the mechanical performance.

4. Conclusion

During this work, we compared the effects of the incorporation of inorganic additions to know the pure limestone (P.Lime) and the natural pozzolan (PN) on physical properties in fresh cement paste and the performance mechanical of mortar and/or concrete in hardened State. By partially substituting the clinker by these additions at different percentages ranging from 5% to 40% by weight of cement for each addition with an interval of 5%. The obtained results by different formulations developed show that the replacement of a part of clinker by these additions (PN and/or P.Lime), we have produced a new hydraulic binder with the physical-chemical and mechanical properties significantly improved namely:

- The increase of the finesse by the specific surface, which facilitates hydration of the mixture during mixing;
- The reduction of the density, which enabled us to produce a lightweight concrete;
- The descending of the initial and final time of fresh cement paste as a function of the percentage of the P.Lime, which gave us our binder the role of the accelerator of setting time. However, they setting time increases with the increase in the percentage of PN, which has given our binder the role of retarder in setting time;
- The reduction in the demand for water;
- The improvement of the compressive strength at a young age (2 days), median age (7 days) and long-term (28 days) in function of the increase of the P.Lime and/or PN.

Our contribution participle clearly to minimize the emissions of CO_2 into the atmosphere, to reduce the energy and the raw materials consumption, and to produce a new material cementitious sustainable, environmentally friendly (less CO_2, less energy consumed) less expensive.

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