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Development of a new hydraulic binder (composite cement) based on a mixture of natural Pozzolan active 'PN' and Pure Limestone 'P,Lime': Study of the physical-chemical and mechanical properties

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- physical properties;
- Compressive strength

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Abstract

The aim of the present work is to valorize a local and natural sources, such as the natural Pozzolan (PN) and the pure limestone (P,Lime) of the region of Amran - Yemen in using them in the production of cement and concrete to reduce the energy and raw material consumed in a first time and minimize the emission of the greenhouse gases (GHGS). Therefore, in this work we have studied the influence of mineral additions in PN and P,Lime in cement, partially substituting the clinker by these materials in powder form and fine crushed, while fixing the total addition at 40% of the addition which make up the mixture in PN and P,Lime. The variation of the percentage was fixed at 5% to lead the following formulations: F1(0% PN + 0% P,Lime), F2(40% PN + 0% P,Lime), F3(35% PN + 5% P,Lime), F4(30% PN + 10% P,Lime), F5(25% PN + 15% P,Lime), F6(20% PN + 20% P,Lime), F7(15% PN + 15% P,Lime), F8(10% PN + 30% P,Lime), F9(5% PN + 35% P,Lime), and F10(0% PN + 40% P,Lime) in weight of clinker. The physical-chemical properties of the new formulations of cement based to PN and P,Lime, to know (the fineness by Blaine specific surface area, the density, the loss on ignition), the physical properties of fresh cement paste, such as (the setting time, the content water) and the mechanical strength of the mortar and/or concrete were studied. The obtained results by the different methods of physical-chemical analyses such as (XRF / XRD / calcination in the air, the absolute density, the fineness by the air permeability), physical properties (the Vicat of water content and setting time) and the mechanical properties of the different formulations show that there was an improvement in the fineness, the setting time and mechanical properties.

1. Introduction

The country of Yemen contains appreciable quantities of minerals and natural materials between these materials, we found the natural Pozzolan (PN); of volcanic origin, extracted from the deposit of Difan - Amran, North of Sana'a, Yemen, [1-2] and the pure limestone (P,Lime), which is located in several regions in Yemen, namely, Hadramout, Mahra, Sana'a, Amran, etc. [3-7].

The valuation of these natural sources active inserting them as an addition in the production of the cement with the different types of concrete by partially substituting the clinker by these materials, present the economic and environmental advantages in the same time; the reduction of energy and the raw materials consumed during the production of clinker on one hand and the minimization of the emissions of CO_2 into the atmosphere which is the main cause of the greenhouse on the other hand.

The incorporation of the mineral additions as the P,Lime and the PN remains so far a technically important for the improvement of the properties of concrete, such as the fluidity, the strength, the durability, [8-10], Etc. These mineral additions affect significantly on the rheology of the fresh cement materials, which is directly connected with the development of the mechanical resistance of compression [11] and subsequently of durability of the materials in the hardened state [12-13].

Several works were the subject of study on the influence of fillers of pure limestone or porcelain as an aggregate on only the mechanical performances of concrete [14-16]. But in this research work we have achieved in the laboratory of cement and quality control of Amran cement plant (Yemen) in collaboration with the laboratory of agro resources polymers and process engineering of the faculty of science, Ibn Tofail University (Kenitra-

Morocco), we have studied the possibility of developing a new hydraulic binder (composite cement) at base of pure limestone (P,Lime) of Bani Qais-Amran - Yemen and natural Pozzolan from scoria volcanic in the deposit of Difan-Amran - Yemen, while partially substituting the clinker by these natural material in powder form and finely crushed, however, fixing the total addition to 40% by weight of the clinker with a fixed the variation to 5% of the two additions constituting the mixture in PN and P,Lime. And studying the influence of the P,Lime and PN addition on the physical chemical characteristics of cement (the fineness of Blaine specific surface / the density / the loss on ignition), physical properties of fresh cement paste (the setting time / the water content) and the mechanical resistance of compression of the mortar and/or the concrete in the hardened state.

2. Materials and methods

2.1. Materials

2.1.1. Cement

The type of cement used in this work is (CMI / 42, 5) from the factory of AMRAN-Yemen is 95% of clinker and 5% of gypsum. The chemical composition determined by X-Ray Fluorescence (XRF), mineralogical and the physical properties are legendary in tables (1), (2) and (3):

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

Content (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	CL
Clinker	62,76	21	5,84	3	1,96	0,9	1,21	0,2	0,02
Gypsum	33,4	0,7	0,36	0,09	0,63	47,2	0,03	0,1	0,01
Cement	61,35	19	5,87	2,97	2,01	2,4	1,17	0,1	0,02

Table 2: Mineralogical composition of clinker

C_3S	C_2S	C_3A	C_4AF
47,7	25,1	10,4	9,1

Table 3: Physical properties of clinker and cement

Physical properties	Units	Values	
Blaine specific surface	cm^2/g	Clinker	3360
		Cement	3240
Absolute density	g/cm^3	Clinker	3,17
		Cement	3,14

2.1.2. Mineral additions

- *Pure limestone (P,Lime)*

The pure limestone (P,Lime) is an inorganic material that spread in many parts of Yemen, including Hadramout, Sana'a and Amran, etc. This material is occupying a volume about of 3,6 billion m^3. The chemical analysis determined by the X-Ray Fluorescence (XRF), mineralogical by X-Ray Diffraction (XRD) and physical of the P,Lime of Bani Qais-Amran (Yemen) after crushing, drying for 12h at 80°C and grinding are shown in the table (4 and 5) and the figure (2).

- *Natural Pozzolan (PN)*

The used Natural Pozzolan (PN) is a volcanic origin, extracted from the deposit of Difan – Amran, Yemen, figure (1) located in the north of Sana'a [1, 2, 17]. It consists essentially of scoria and well stratified pumice stones, with color vary from red to black. The chemical analysis determined by the XRF, mineralogical by the XRD and the physical of PN of Difan-Amran after crushing the slag Pozzolanic then put in the stove for 24 hours d for 24 hours at a temperature of 50 °C to remove the eliminate their moisture and grind until the obtained powder can pass through a sieve of 90 μm are shown in the table (4 and 5) and the figure (3).

- *Physical, chemical characteristics*

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

Figure 1: Deposit of Difan-Amran-Yemen extraction of the natural Pozzolan

Table 4: Elementary chemical compositions of P,Lime and PN determined by XRF

Content (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	Mgo	SO_3	K_2O	Na_2O	Cl
P,Lime	54,96	0,621	0,12	0,159	0,411	0,0799	0,0132	0	0,0006
PN	8,8	41,43	16,16	9,41	4,79	0,128	0,9	3,47	0,041

The mineralogical analysis by the XRD of the P,Lime of Bani Qais-Amran, Yemen and PN of Amran are scheming in the (Fig.2, 3).

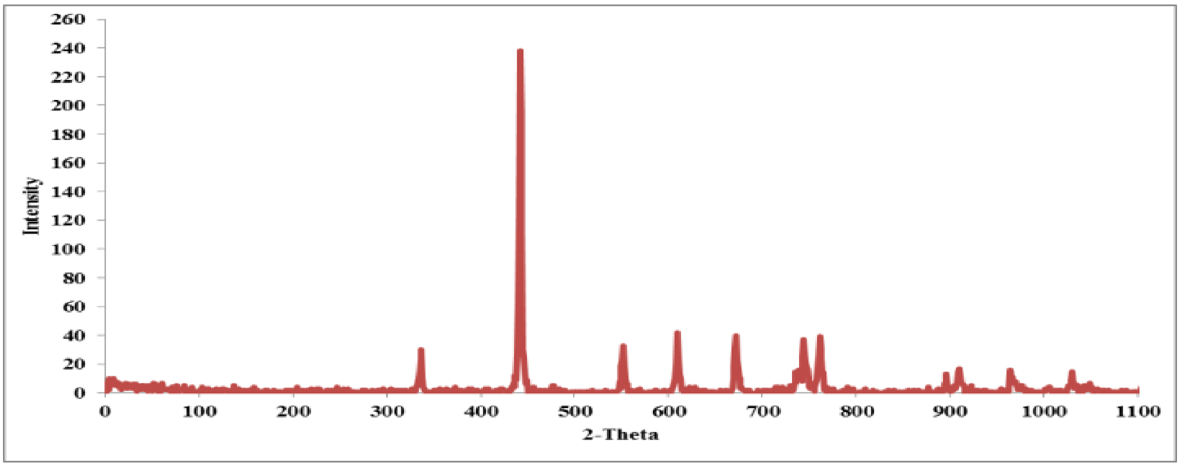

Figure 2: The spectrum by X Ray Diffraction of P,Lime

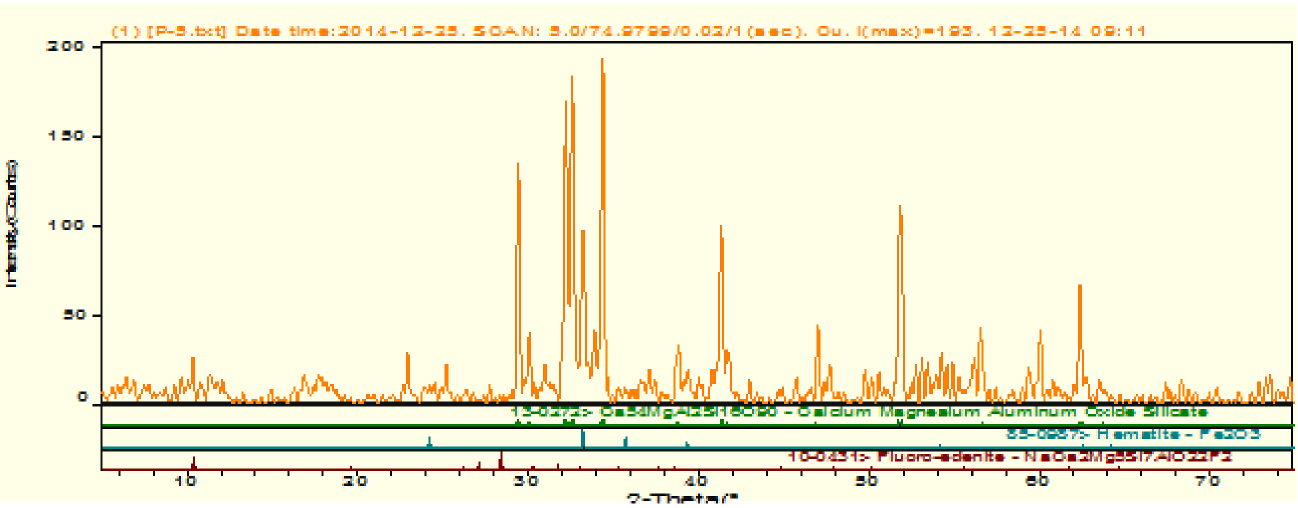

Figure 3: The spectrum by X Ray Diffraction of PN

According to the results shown in the table (4) we find that the P,Lime of Bani Qais-Amran, Yemen contains 54,96% lime (Cao) / 0,12 alumina / 0,159 iron / 0,621% silica and the Pozzolan of Difan-Amran contains 41,43% silica (SiO_2) / 16,16% of alumina (Al_2O_3) / 9,41% iron (Fe_2O_3) / 8,8% lime (Cao). The results of mineralogical analysis by X-Ray Diffraction (XRD):

- The present P,Lime in the figure (2) shows the strong presence of lime, followed by silica, then magnesium afterward of iron oxide and alumina.
- The natural Pozzolan shown in the figure (3) we note the strong presence of the quartz followed by the alumina after the calcite next the iron oxide and some traces of the magnesium [18].

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	Units	Values	
		P,Lime	**PN**
Blaine specific surface	cm^2/g	4776	4576
Density	g/cm^3	2,13	2,81

2.1.3. The mixing water

To spoil our mixture, we used tap water (well), its main characteristics are collected in a table (6).

Table 6: Main characteristics of the mixing water

Components	**PH**	**T, D, N**	**CO_3^{-2}**	**HCO_3^-**	**Calcium**	**Magnesium (Mg^{+2})**	**Conductivity**
Unit	**-**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**(mg/l)**	**ms/cm**
Value	7,0	450	216,0	0,0	56,4	52,4	692,0

2.1.4. Sand

To prepare our mortar, we used normalized sand conforming to norm EN 196-1, delivered by the French society Nouvelle of Littoral, its particle size analysis is illustrated in figure (4).

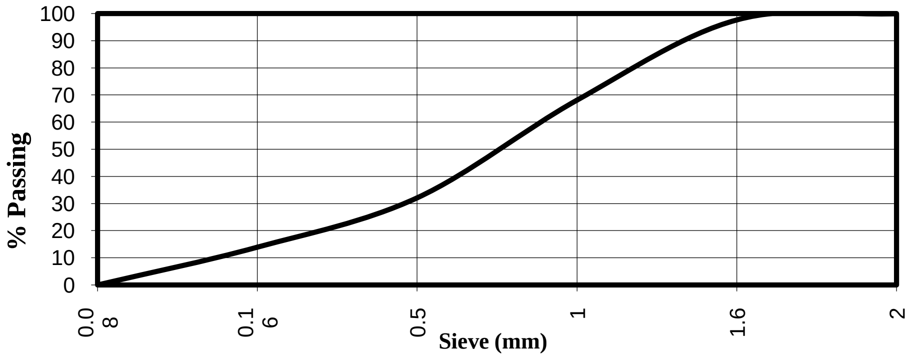

Figure 4: Grading curve of sand

The particle size analysis presented in figure (4) there is that used sand grains are distributed in a systematic way according to the specifications of the norm EN 196-1 [15].

2.2. Methods

The formulations of the different tests are prepared for the elaboration of the new hydraulic binder, while still maintaining the content of gypsum to 5% of the total weight of the cement with the addition of P,Lime and PN are presented in tables (7, 8 and 9).

Table7: Composition of cement used to prepare 500g of mixturesbased to the different percentages of adding PN and P,Lime

%	Cement	Pure Limestone		Natural Pozzolan		Sum of addition	
	Mass (g)	Mass (g)	%	Mass (g)	%	Mass (g)	%
C "0% PN + 0% P,Lime"	500	0	0	0	0	0	0
C "0% PN + 40% P,Lime"	300	200	40	0	0	200	40
C "5% PN + 35% P,Lime"	300	175	35	25	5	200	40
C "10% PN + 30% P,Lime"	300	150	30	50	10	200	40
C "15% PN + 25% P,Lime"	300	125	25	75	15	200	40
C "20% PN + 20% P,Lime"	300	100	20	100	20	200	40
C "25% PN + 15% P,Lime"	300	75	15	125	25	200	40
C "30% PN + 10% P,Lime"	300	50	10	150	30	200	40
C "35% PN + 5% P,Lime"	300	25	5	175	35	200	40
C "40% PN + 0% P,Lime"	300	200	0	200	40	400	40

Table 8: Composition of fresh cement paste based to adding of the PN and P,Lime

%	Cement	Pure Limestone		Natural Pozzolan		Sum of addition		Water	
	Mass (g)	Mass (g)	%	Mass (g)	%	Mass (g)	%	Mass (g)	W/C
P "0% PN + 0% P,Lime"	500	0	0	0	0	0	0	140	0,280
P "0% PN + 40% P,Lime"	300	200	40	0	0	200	40	160	0,320
P "5% PN + 35% P,Lime"	300	175	35	25	5	200	40	154	0,308
P "10% PN + 30% P,Lime"	300	150	30	50	10	200	40	146	0,292
P "15% PN + 25% P,Lime"	300	125	25	75	15	200	40	140	0,280
P "20% PN + 20% P,Lime"	300	100	20	100	20	200	40	135	0,270
P "25% PN + 15% P,Lime"	300	75	15	125	25	200	40	128	0,256
P "30% PN + 10% P,Lime"	300	50	10	150	30	200	40	123	0,246
P "35% PN + 5% P,Lime"	300	25	5	175	35	200	40	117	0,234
P «40% PN + 0% P,Lime»	300	200	0	200	40	400	40	105	0,210

Table9: Composition of mortars in the hardened state based to adding of the PN and P,Lime

%	Cement	Pure Limestone		Natural Pozzolan		Sum of addition		Sand	Water	
	Mass (g)	Mass (g)	%	Mass (g)	%	Mass (g)	%	Mass (g)	Mass (g)	W/C
M "0% PN + 0% P,Lime"	450	0	0	0	0	0	0	1350	225	0,50
M "0% PN + 40% P,Lime"	270	180	40	0	0	180	40	1350	243	0,54
M "5% PN + 35% P,Lime"	270	157,5	35	22,5	5	180	40	1350	235	0,52
M "10% PN + 30% P,Lime"	270	135	30	45	10	180	40	1350	228	0,51
M "15% PN + 25% P,Lime"	270	112,5	25	67,5	15	180	40	1350	225	0,50
M "20% PN + 20% P,Lime"	270	90	20	90	20	180	40	1350	221	0,49
M "25% PN + 15% P,Lime"	270	67,5	15	112,5	25	180	40	1350	213	0,47
M "30% PN + 10% P,Lime"	270	45	10	135	30	180	40	1350	205	0,46
M "35% PN + 5% P,Lime"	270	22,5	5	157,5	35	180	40	1350	193	0,43
M "40% PN + 0% P,Lime"	270	180	0	180	40	180	40	1350	180	0,40

3. Results and discussion

3.1. Influence the additions of P,Lime and PN on physical properties of fresh cement paste

3.1.1. *The density of cement with the addition of P,Lime and PN*

The density of cement is measured by the displacement of an inert liquid towards the cement inside a graduated container. It is measured using a Le Chatelier device preferably jolting according to the norm EN 196 - 6 / ASTM C188, NM 10.1.004 and presented in figure (5). The experimental study shown in the figure (5) indicates that the density of the cement is decreasing with the adding of P,Lime and PN in comparing with a witness of cement. This variation in the density of the cement based on P,Lime and PN is usually caused by the density of addition, which are 2,13 for the P,Lime and 2,81 for the PN.

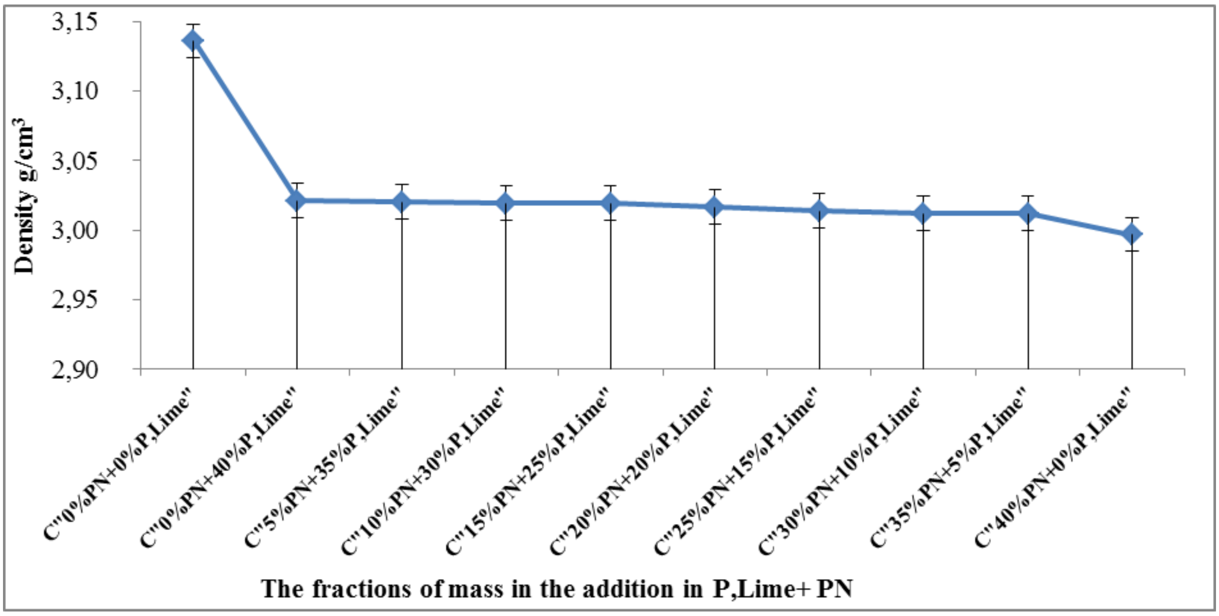

Figure 5: Variation of the density in function to the percentage in the addition of P,Lime+ PN

3.1.2. Finesse by air permeability (Specific Surface BlaineMethod)

The cement is presented in the form of powder, finely divided [19-22]. This fineness is an important characteristic, during mixing. More cement in contact with the water surface is great more hydration is rapid and complete. The Specific Surface Blaine (BSS) of the new hydraulic binder based on P,Lime and PN appears in figure (6) is determined using the air permeability device according to the norm NM 10.1. 005. [20-21].

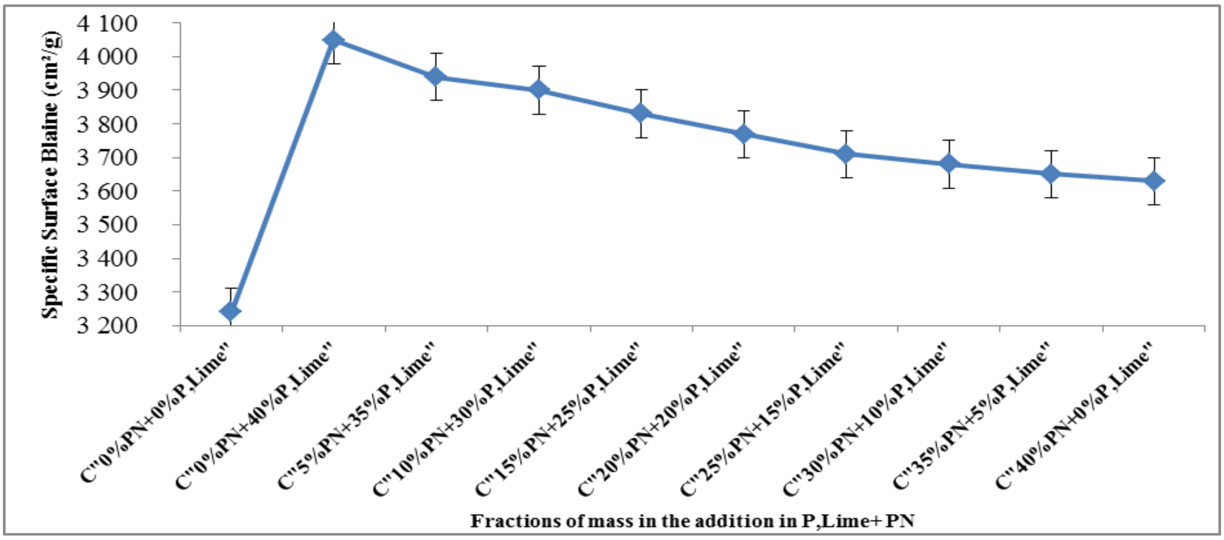

Figure 6: Variation of the Specific Blaine Surface in function to the percentage in the addition of P,Lime+ PN

After the figure (6) we realize that the BSS of cement increases with the addition of 40% of P,Lime, and then it decreased with the addition of P,Lime and PN. These changes are due primarily to the specific surface of P,Lime which is 4776 cm²/g with the PN that equals 4576 cm²/g.

3.1.3. Reduced of the water content

The consistency of cement paste is a characteristic which evolves over time. To be able to study the evolution of the consistency according to 40% addition of P,Lime and PN (partial substitution the clinker by P,Lime and PN at: P' 0% PN + 0% P,Lime' / P' 40% PN + 0% P,Lime' / P' 35% PN + 5% P,Lime'/ P' 30% PN + 10% P,Lime'/ P' 25% PN + 15% P,Lime' / P' 20% PN + 20% P,Lime'/ P' 15% PN + 15% P,Lime' / P' 10% PN + 30% P,Lime' / P' 5% PN + 35% P,Lime' / P' 0% PN + 40% P,Lime') should be able to go to a standard consistency that is the same for all studied pastes [15,19,23, 24]. The aim of this test which shows in the figure (7) is to determine the optimum quantity of mixing water for obtaining a good mortar. This test was performed with the Vicat device in conflict with the norm NE 196-3.

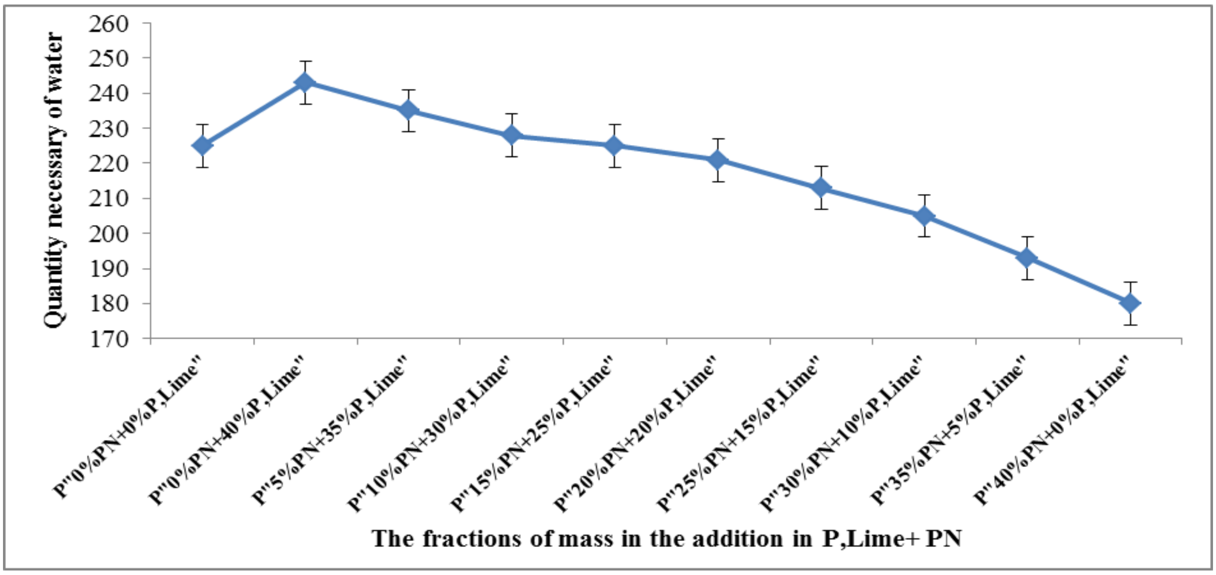

Figure 7: Variation of quantity, necessity of water in function with the percentage in the addition of P,Lime+ PN

According to the figure (7) we observed that the water content of the cement paste based on the addition of 40% in P,Lime and PN was increased with the addition of 40% of P,Lime. This generally increases due to the chemical composition and mineralogical of our addition of P,Lime which is rich in Cao, on one hand, the presence of CaO high rate influences on the phenomenon of hydration since this mineral phase-rich limestone tends to have a demand for more water and on the other hand the demand of water is linked to the fineness of the addition of P,Lime. Then water demand was reduced successively with the % increase in PN and decreases the P,Lime %. This decrease is due to the chemical composition and mineralogical of our adding of PN, which is poor in CaO. The presence of CaO decline rate influences on the phenomenon of hydration as a Pozzolan poor in this mineral phase to a tendency to be less in demand in the water.

3.1.4. The setting time

To perceive the influence of additions of P,Lime and PN in cement on the physical properties of the fresh cement paste in the initial and final time. We measured the initial and final time of fresh cement paste with 40% of all two additions in P,Lime and PN, using automatic Vicat apparatus complies with EN 196-3, are presented in the figure (8).

And after the figure (8) that illustrates the evolution of the initial and final time of the fresh cement paste state in 40 % of the addition of P,Lime and PN based on the fraction of these additions, we observe that the initial and final time decreased with the addition of 40% of P,Lime, this decrease in setting time is due generally to composition chemical and mineralogical P,Lime which is rich in Cao and poor Al_2O_3 on one hand and on the other hand it is grace to the fineness of limestone fillers that fills the gaps between the cement particles, which improves the compactness of concrete later. The time will increase considerably with the addition of PN increase and decrease of P,Lime. This increase is usually caused by chemical / mineralogical and the physical properties of PN and also the slow Pozzolanic reaction of the mixture

3.2. Influence of the additions of the P,Lime and the PN on the mechanical properties of mortar or concrete in the hardened state

Finally, we have evaluated the effect of the P,Lime and the PN additions on the mechanical performance of mortar or concrete by using the mechanical resistance of compression. The measurements of the mechanical resistance are on normal mortars (4 x 4 x 16) cm^3 sample according to the specification of the standard (NF EN 196-1) [23]. The specimens are removed after one day and kept under water among the period of crushing. The measurement of mechanical compression resistance was performed at 2 / 7 and 28 days to observe the gradual evolution of performance mechanical of our new hydraulic binder 40% addition of P,Lime and PN (partial substitution of clinker by P,Lime and PN of:M'0% PN + 0% P,Lime' / M'40% PN + 0% P,Lime' / M'35% PN + 5% P,Lime' / M'30% PN + 10% P,Lime' / M'25% PN + 15% P,Lime' / M'20% PN + 20% P,Lime' / M'15% PN + 15% P,Lime' / M'10% PN + 30% P,Lime' / M'5% PN + 35% P,Lime' / M'0% PN + 40% P,Lime').

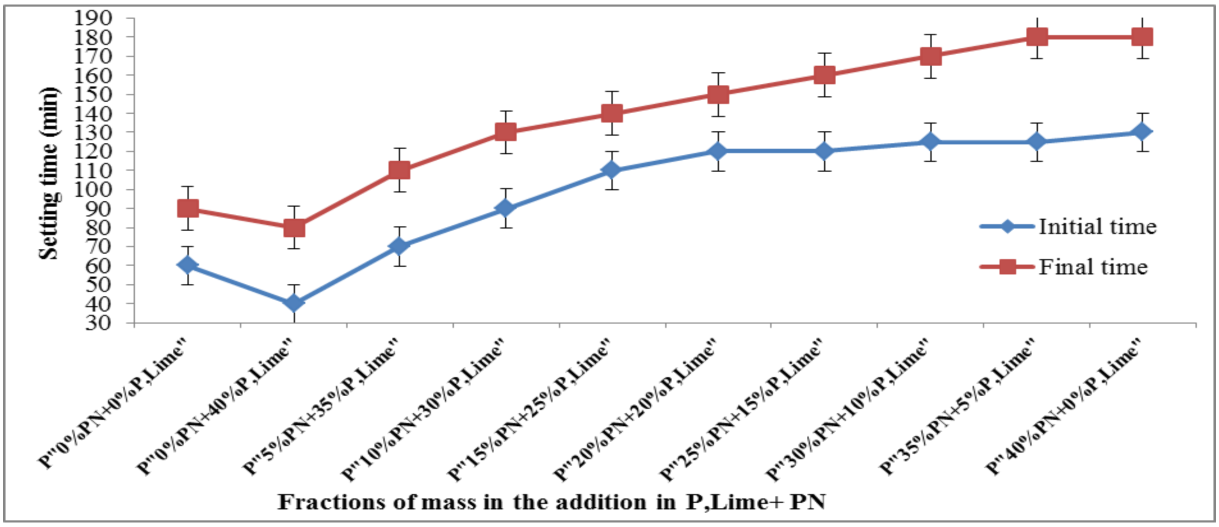

Figure 8**:** Variation of setting time in function with the percentage in the addition of P,Lime+ PN

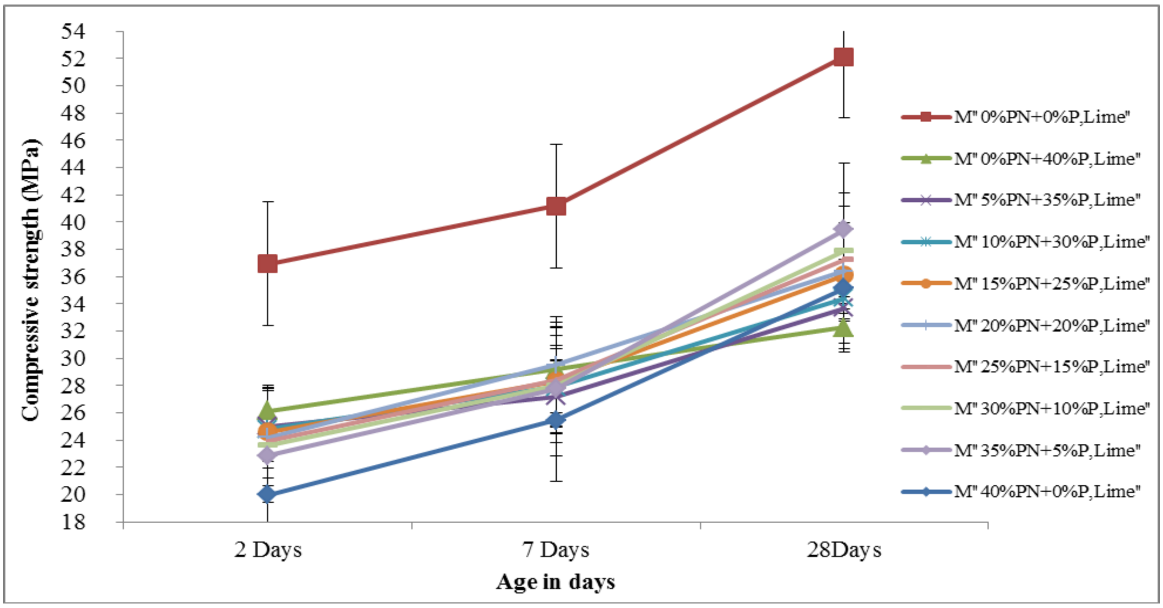

Figure 9: Variation of the compressive strength in function to the age in days

According to the figure (9) we can detect the following observations:

- The resistance of all mortars regularly increases with age and are no drop.
- The mechanical compression resistance decreased with the addition of 40% of P,Lime. This decrease is due generally to the chemical compositions and mineralogical of the P,Lime that is rich in content of Cao. However the mechanical compression resistance was increased with the addition of PN decrease, increasing the % of P,Lime. This increase in the mechanical resistance of compression is attributed primarily to the chemical composition and mineralogical which can be explained by the interaction between the reactive silica, which existed in the glassy part of natural Pozzolan and Ca $(OH)_2$ released by the hydration of cement, which gives the natural Pozzolan property to eat lime.

Conclusion

Through this work, we have studied the possibility of obtaining a new hydraulic binder base on the mineral materials, such as the pure limestone (P,Lime) and the natural Pozzolan, while partially substituting the clinker by these materials in powder form, finely divided and fixing the total addition to 40% by weight of the clinker with a fixed the variation of 5% of the addition constituting the mixture in a PN and P,Lime on one hand. And on the other hand to study the effect of these additions in P,Lime and PN on the physical chemical characteristics of cement, physical properties of fresh cement paste state and the mechanical performance of mortar and / or concrete in the hardened state.

The results obtained by the different developed formulations binders show that the partial substitution of clinker by the P,Lime and the PN provides significant improvements in the physical properties cement and mechanical resistance to compression of mortar or concrete, such as:

- ❖ The fineness by the specific Blaine surface which increases with the addition of 40% in P,Lime 4050 m^2/g. And then decreased with augmented the addition in PN and reduction of P,Lime.
- ❖ The density of cement based on the P,Lime and PN decreased from 3,14g/cm^3 to 3,00 g/cm^3compared with the control;
- ❖ The initial and final setting time of paste increase passing from 60 min at 130 min and 90 min at 180 min, respectively.
- ❖ The compressive strength by 28-day augmented from 32,27 MPa for mortar 0% PN + 40% P,Lime 40% P,Lime to 39,44 MPa for mortar 35% PN + 5% P,Lime.

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