

## new eco-friendly hydraulic binder based on a combination of inorganic additions and organic admixture: formulation and characterization

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### Abstract

This work aims to valorize a mineral and a natural resources such as the Limestone Fillers (F-Limi) and the Natural Pozzolan (PN) by introducing them into the formulation of cement and / or concrete matrix, to minimize CO<sub>2</sub> emissions into the atmosphere, to reduce the energy consumption and raw materials and as well as, to improve the physical and mechanical properties. In this work, we substituted the clinker by the combination between the F-Lime and NP at 40% by weight of cement with steps of 5% in the presence of two types of superplasticizers. The influences of the incorporation of these additions on the physical properties and mechanical performance of mortar and/or concrete in the fresh cement paste and hardened state were evaluated. The obtained results by different formulations developed to show that the replacement a part of clinker by the combination between the F-Lime and the PN has produced a new hydraulic binder eco-friendly and durable with improving the physical and the mechanical properties, namely increasing the fineness, decreasing the density, reduced the water demand, minimizing the porosity and the capillary absorption. The setting times and the compressive strength have been improved.

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## 1. Introduction

The country of Yemen contains, in appreciable quantities, of a mineral and a natural materials among these materials, we find the Natural Pozzolan (PN); of volcanic origin from the Difan-Amran deposit north of Sana'a in Yemen, [1, 2] and the Limestone Fillers (F.Lime), which is found in several regions of Yemen, namely, Hadramaout, El maharah, Sana'a, Amran, Etc .. [3, 4]. The valorization of these resources by introducing them as an additive in the manufacture of cement and various types of concretes has both benefits economic and environmental; to reduce the energy consumption and raw materials used in the manufacture of clinker and/or cement on one hand and to minimize the greenhouse gas emissions into the atmosphere on the other hand [5–7]. These mineral additions by their fineness and their reactivity in the presence of cement lead to significant changes in the physical properties of the fresh cement paste and the mechanical performance of mortars and/or concrete in the hardened state [8–12]. The presence of inorganic and/or organic (F.Lime, PN and/or superplasticizers) additions in the cement and/or mortar (concrete) matrix modifies the structure of granular skeleton (granular effect) and the friction between the solid components in the liquid phase [13–16]. In the same way, during the setting and hardening [17–20], the additions particles interact in the cement hydration process while modifying the structure of the hydrated products and for some may react chemically (effects physical chemical and microstructure) at cementitious environments, in order to form a new hydrated products which have an additional binding character (improvement of physical properties and mechanical performances). Originally, the mechanisms of these modifications appear to be particularly complex [19, 21, 22], agree to distinguish three main effects of additions in the formulation of a cementitious material.

- A granular effect resulting from the modifications introduced by the addition of the granular structure of this material in presence of water and optionally of admixture which acts on the rheological properties and the porosity of the cementitious materials in the fresh and hardened state.
- A physical chemical and microstructural effect generated by the multiple interactions between the particles of the addition and the process of hydration of cement which acts on the evolution of the hydration of cement during the setting and the hardening.
- A purely chemical effect specific to certain additions in the cementitious environments which acts during the hydration of the cement and which interact strongly with the physical-chemical and microstructural effect.

The combination between the organic and inorganic additions makes it possible to increase the hydration rate of mortars and/or concretes while modifying the W/C ratio and to improve the mechanical performance, namely porosity and capillary absorption [2, 23–25]. This improvement finally influences the mechanical of compressive strength. Indeed, when the molecules of the superplasticizers (SP103 and/or SP402) are introduced into a suspension of concrete formulated by the combination of the F.Lime and the NP, a large part of them is fixed to the surface of the cement particles (adsorption)[16, 26, 27]. This adsorption that makes in the interface of grains of cement is explained by the creation of repulsive forces between the particles and by the reduction or total elimination of the attractive forces of interactions that exist between the atoms of the different particles. While the other part is intended to disperse the grains of the cement from one another[28–30]. In this work, different formulations have been developed while partially substituting the clinker by the combination between the F.Lime and the PN at 40% by weight of cement with a step of 5%, in the presence of two types of superplasticizers of high water reducer (accelerator (SP402) and/or retarder (SP103) of setting). The influence of the incorporation of these additions on the physical properties and the mechanical performances in the fresh and hardened state were studied. The obtained results from the various formulations elaborated show that the substitution a part of clinker by the combination between the F.Lime and the PN in the presence of two types of superplasticizers enabled us to manufacture of a new hydraulic binder with improved

physical-chemical and mechanical properties, while reducing the cost of production, minimizing CO<sub>2</sub> emissions into the atmosphere, reducing the use of mixing water.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Cement

The type of cement used in this work is (CMI-42.5), this is a Portland cement as a resulting of simultaneous grinding at (95%) of clinker and (5%) of gypsum according to the standard EN 196-1. It is from of a cement factory of Amran - Yemen. The chemical compositions (clinker, gypsum, and cement) and mineralogical (clinker) determined by X-rays fluorescence (XRF) are presented in the tables (1 and 2). The physical and mechanical characteristics of cement are shown in Table (3).

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

Chemical name	Chemical formula	Cement nomenclature	Clinker	Gypsum	Cement
Lime	CaO	C	62.76	33.40	61.29
Silica	SiO <sub>2</sub>	S	21.00	0.70	19.99
Alumina	Al <sub>2</sub> O <sub>3</sub>	A	5.84	0.36	5.57
Ferrite	Fe <sub>2</sub> O <sub>3</sub>	F	3.00	0.09	2.85
Magnesia	MgO	M	1.96	0.63	1.89
Sulfur trioxide	SO <sub>3</sub>	S	0.90	47.20	3.22
Potassium oxide	K <sub>2</sub> O	K	1.21	0.03	1.15
Sodium oxide	Na <sub>2</sub> O	N	0.20	0.10	0.20
Chlorine	Cl <sup>-</sup>	Cl	0.02	0.01	0.02

**Table 2:** Mineralogical composition of clinker

Chemical name	Mineral name	Chemical formula	Cement nomenclature	Content
Tricalcium silicate	Alite	Ca <sub>3</sub> SiO <sub>5</sub>	C <sub>3</sub> S	47.70
Dicalcium silicate	Balite	Ca <sub>2</sub> SiO <sub>4</sub>	C <sub>2</sub> S	25.10
Aluminate tricalcium	Aluminate	Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	C <sub>3</sub> A	10.40
Tetracalcium Aluminoferrite	Ferrite	Ca <sub>4</sub> AlFeO <sub>5</sub>	C <sub>4</sub> AF	9.10

**Table 3:** Physical and mechanical properties of cement used

Designations	Values	Units
Absolute Density	3.14	g.cm <sup>-3</sup>
Refusal of the sieve 45 µm	12.50	%
Refusal of the sieve 90 µm	1.50	%
Specific surface Blaine	3240.00	cm <sup>2</sup> .g <sup>-1</sup>

#### 2.1.2. Inorganic additions

##### ❖ Limestone Fillers (F.Lime)

They are mineral materials which spread in several regions in Yemen, such as Hadramaout, Sana'a, Amran and etc.

### ❖ Natural pozzolan (PN)

The PN used is of volcanic origin, extracted from Difan-Amran deposit of Yemen located in the north of Sana'a. It consists essentially of slag and pumice stones well stratified its color varies from red to black.

### ➤ Physical-chemical characteristics

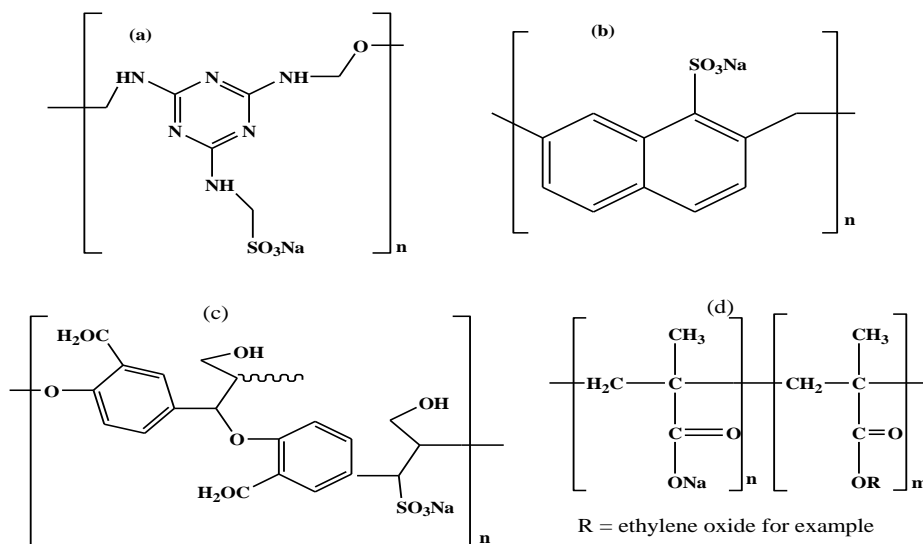
The results of the analysis by X-ray fluorescence (XRF) of F.Lime and PN are represented in the table (4). From the results shown in the table (4), we observed that the F.Lime of Bani Qais-Amran-Yemen contained 54.96% of Lime (CaO)/0.62% of Silica (SiO<sub>2</sub>)/0.12 of alumina (Al<sub>2</sub>O<sub>3</sub>)/0.16 iron of (Fe<sub>2</sub>O<sub>3</sub>). The sum of the percentages is equal to 56.36% and the remainder represents the loss on ignition (LOI), which presents the water and CO<sub>2</sub>. These fillers have a specific surface Blaine 4776 cm<sup>2</sup>.g<sup>-1</sup> and a density 2.13 g.cm<sup>-3</sup>. However, we observed that the PN contained 41.43% of silica (SiO<sub>2</sub>) /16.16% of alumina (Al<sub>2</sub>O<sub>3</sub>)/9.41% iron (Fe<sub>2</sub>O<sub>3</sub>)/8.8% lime (CaO). These percentages represent an amount equal to 85.13% and the rest means the loss on ignition (LOI). These pozzolans have a specific surface 4576 cm<sup>2</sup>.g<sup>-1</sup> and a density 2.81 g.cm<sup>-3</sup>.

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

Content (%)	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Cl <sup>-</sup>	LOI
F.Lime	54.96	0.62	0.12	0.16	0.41	0.08	0.01	0.00	0.00	43.63
PN	8.8	41.43	16.16	9.41	4.79	0.128	0.9	3.47	0.04	14.87

### 2.1.3. Chemical admixtures

The admixtures “superplasticizers” are polymers in liquid form especially synthesized for the concrete industry. They are based on sodium or sulfonated naphthalene-formaldehyde “SNF” (figure.1 “a”), sulfonated melamine formaldehyde “SMF” (figure.1 “b”), high purity liginosulfonate (figure.1 “c”) or acrylate ester copolymer (polyacrylate) (figure.1 “d”) [EN 934 - 2].



**Figure 1:** Families of superplasticizers; “a”: Sulfonated melamine formaldehyde (SMF), “b”: Sulphonated naphthalene-formaldehyde (SNF), “c”: Lignosulphonate of high purity and “d”: acrylate ester copolymer (polyacrylates)

These superplasticizers are delivered by the company CONMIX Ltd of Sharjah, United Arab Emirates. They are incorporated during the mixing of concrete at doses equal from 0.5% to 4% by weight of cement with a step of 0.5%.

In this work we used two types of superplasticizers:

- High Range Water Reducing And Accelerating Superplasticiser “SP103”;
- Advanced SuperPlasticiser for Prolonged Slump Retention “SP402”.

The physical properties of the two superplasticizers (SP103 and SP402) collected at the table (5).

**Table 5:** Physical properties of superplasticizers

Name	Nature	Color	Density(g.cm <sup>-3</sup> )	Area training (%)	Chloride content
SP103	Liquid	Brown	1.20	0.50 – 1.00	Nil
SP402	Liquid	Brown	1.23	0.50 – 1.00	Nil

#### 2.1.4. The mixing water

The water used to mix the mortar and/or concrete is tap water. The main characteristics of these waters are summarized in table (6).

**Table 6:** Main features of the mixing water

Components	Unity	Values
pH	-	7.00
Turbidity	(mg/L)	450.00
CO <sub>3</sub> <sup>-2</sup>	(mg/L)	216.00
HCO <sub>3</sub> <sup>-</sup>	(mg/L)	0.00
Ca <sup>+2</sup>	(mg/L)	56.40
Mg <sup>+2</sup>	(mg/L)	52.40
Conductivity	μS/cm	692.00

#### 2.1.5. Sand

To make our mortar and /or concrete, we used standard sand according to the norm EN 196-1, delivered by the new French company of the Littoral. Its particle size analysis is illustrated in figure (2).



**Figure 2:** Curve granulometric of sand

## 2.2. Methods

### 2.2.1. The density

The density of cement is measured by the displacement of an inert liquid with respect to the cement inside a graduated vessel. It is measured using a “Le Chatelier” apparatus according to the specification of the norm EN 196-6 / ASTM C188 / NM 10.1.004. It was calculated using the equation (1).

$$\rho = \frac{\text{Mass of cement (g)}}{\text{Absolute volume of cement (cm}^3\text{)}}; \frac{\text{g}}{\text{cm}^3} \quad \text{Equation 1}$$

### 2.2.2. The fineness by the method of specific surface Blaine

It is the total surface area of the grains contained in a powder mass. The Fineness is measured using the Blaine apparatus according to standard 10.1.005 NM. The finesse was calculated according to the equation (2).

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

Where:  $\rho$ : Absolute density of cement; K: Apparatus constant; e: Porosity (in general: 0.50); t: Measured time in seconds;  $\eta$ : Dynamic viscosity of air at the test temperature.

### 2.2.3. The report of water/cement “W/C”

The aim of this test is to determine the optimum quantity of mixing water to obtain a good mortar. This test is carried with the Vicat apparatus, according to the standard 196-3.

### 2.2.4. Setting time

This is the time required for the cement paste solidifies. This experiment was carried out with the Vicat automatic apparatus according to the standard 196-3.

### 2.2.5. The porosity

The porosity is an essential feature of the mortar or concrete at hardened State. It is a part of the factors that determine the durability of concrete. It is obviously calculated using the equation (3).

$$P = \frac{V_P}{V_T} \quad \text{Equation 3}$$

With: P: The porosity  $V_P$ : The pore volume of the specimens;  $V_T$ : The total volume of the specimens, that is to say, the sum of the volume of solid and the volume of the pores.

### 2.2.6. The capillary absorption

The capillary absorption (CA) of our formulations at different percentages of PN was calculated by using the equation (4). It is expressed in g.mm<sup>-2</sup>.

$$CA = \frac{M_f - M_i}{S} \quad \text{Equation 4}$$

With: CA: The capillary absorption (g.mm<sup>-2</sup>)  $M_f$ : The mass of the specimen after conservation for 2 days, 7 days and 28 days, in grams;  $M_i$ : The mass of the specimen before conservation under the water in grams; S: The area of the specimens in (mm).

### 2.2.7. Compressive strength

To achieve the objective of our study, we have prepared a reference mortar without additions whose compositions are inspired by that of the normal mortar defined by the norm EN 196-1, with a quantity of water adjusted to obtain a reference consistency. And other mortar with mineral additions and superplasticizers, always keeping the standardized consistency fixed. For each mortar having acquired this consistency, we have prepared prismatic specimens with dimensions (40x40x160) mm<sup>3</sup>. The compressive strengths were measured at a young age (2 days), in median age (7 days) and long-term (28 days) using a bending test machine to break the specimen into two halves and each party is responsible the subject of compressive using a hydraulic testing machine. The value of the resistance is considered as the average of the crushing stress of three test pieces (6 halves). The compressive strength was calculated using the equation (5). The formulations of various tests carried out by maintaining the content of gypsum 5% by weight of a total of cement with 40% of the combination the Fillers Limestone (F.Lime) and the Natural Pozzolan (PN) are presented in the tables (7 and 8).

$$\text{Compressive strength} = \frac{\text{Load, in "N"}}{\text{Area, in "mm}^2\text{"}}; \text{MPa} \quad \text{Equation 5}$$

**Table 7:** Formulation matrix of cement paste formula by the combination between F.Lime and PN

Content	Cement (%)	F.Lime (%)	PN (%)	Addition sum (%)	W/C Report
1	60	40	0	40	0.32
2	60	35	5	40	0.308
3	60	30	10	40	0.292
4	60	25	15	40	0.28
5	60	20	20	40	0.27
6	60	15	25	40	0.256
7	60	10	30	40	0.246
8	60	5	35	40	0.234
9	60	0	40	40	0.21

**Table 8:** Formulation matrix of mortar and/or concrete in the hardened state the combination between F.Lime and PN

Content	Cement (%)	F.Lime (%)	PN (%)	Addition sum (%)	Sand (g)	W/C Report
1	60	40	0	40	1350	0.54
2	60	35	5	40	1350	0.52
3	60	30	10	40	1350	0.51
4	60	25	15	40	1350	0.5
5	60	20	20	40	1350	0.49
6	60	15	25	40	1350	0.47
7	60	10	30	40	1350	0.46
8	60	5	35	40	1350	0.43
9	60	0	40	40	1350	0.42



### 3. Results and discussion

#### 3.1. Influence the combination between of F.Lime and PN on the Physical-chemical properties of fresh cement paste

The table (9) shows the physical-chemical properties of fresh cement paste formulated by the combination between of the F.Lime and the PN.

**Table 9:** Physical-chemical properties of the cement paste formulated by the combination of F.Lime and PN as a function of the mass fraction of these additions

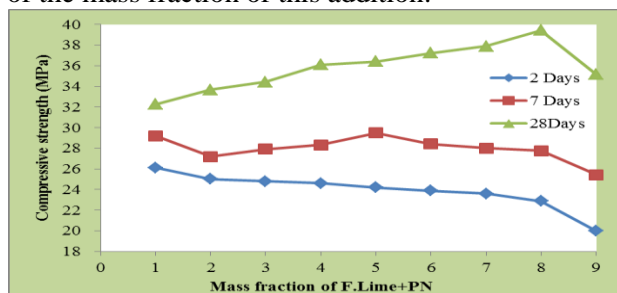
Content (%)		1	2	3	4	5	6	7	8	9
Density "g .cm <sup>-3</sup> "		3.02	3.02	3.02	3.02	3.02	3.01	3.01	3.01	3.00
Fineness by specific surface"cm <sup>2</sup> .g <sup>-1</sup> "		4 050	3 940	3 900	3 830	3 770	3 710	3 680	3 650	3 630
Setting time"min"	Initial	40	70	90	110	120	120	125	125	130
	Final	80	110	130	140	150	160	170	180	180
W/C		0.54	0.52	0.51	0.50	0.49	0.47	0.46	0.43	0.40
expansion		0.5	0.33	0.32	0.325	0.335	0.345	0.376	0.42	0.45

From Table (9) we have found that the density of cement formulated by the combination between the F.Lime and the PN decreases as a function of the increase in the mass fraction of these additions. This decrease is generally due to the density of these additions (for Pozzolan is 2.81 g.cm<sup>-3</sup>, while that of the Limestone Fillers is 2.13 g.cm<sup>-3</sup>), which is usually lower than that of cement. We have noticed that the fineness by the specific surface (Blaine) of cement formulated by the combination between the F.Lime and PN increases with the increase in the mass fraction of these additions. This increase is mainly due to the fineness of F.Lime which is 4776 cm<sup>2</sup>.g<sup>-1</sup> and that of the PN is 4576 cm<sup>2</sup>.g<sup>-1</sup>. We observed that the initial and the final times decrease with (40%) of the addition of F.Lime. This decrease is due on one hand to the chemical and mineralogical compositions of these fillers which are rich in CaO and poor in Al<sub>2</sub>O<sub>3</sub> (physical-chemical effect) and on the other hand is due to the fineness of these fillers which fills the voids between the particles of cement and that of the aggregate (granular effect) "The addition of F.Lime gives our materials the role of the setting accelerator". Subsequently, the setting time increased considerably with the increase in Pozzolan content and the decrease in the F.Lime proportion. This increase in setting time is generally due to the chemical / mineralogical compositions of the NP which is very rich in aluminum oxide (16.16% Al<sub>2</sub>O<sub>3</sub>) and silicon dioxide (41.43% SiO<sub>2</sub>) and low in an oxide of calcium (8.8% CaO), (physical-chemical effect). These compositions promote the pozzolanic reaction which occurs between the reactive silica of the NP and the calcium hydroxide Ca(OH)<sub>2</sub> released by the cement during the hydration of the mixture, which slows down the hydration phenomena "The addition of PN gives our materials the role of the setting retarder". We also found that the W/C ratio of the cement paste formulated by the combination between the F.Lime and the PN decreased with increasing the PN proportion and decreased the F.Lime content. Indeed, when the water reacts chemically with the lime released by the cement during the hydration of the mixture, the water will be absorbed slowly for form calcium hydroxide Ca(OH)<sub>2</sub> on one hand. On the other hand, the decrease is generally due to the chemical and mineralogical compositions of these additions (the PN is poor in CaO, despite, the limestone fillers are rich in CaO). Finally, we distinguished that the expansion of the cement paste formulated by the combination between the F.Lime and the PN increases slightly as a function of the mass fraction of these additions. This increase does not exceed the limit (5 mm) given by standard NF EN 196-3 + A1.



### 3.2. Influence the combination between the F.Lime and PN on the compressive strength

The figure (3) illustrates the compressive strength of mortar and/or concrete formulated by combining between the F.Lime and the PN as a function of the mass fraction of this addition.



**Figure 3:** The compressive strength of mortar and/or concrete formulated by the combination between F.Lime and the PN as a function of them mass fraction

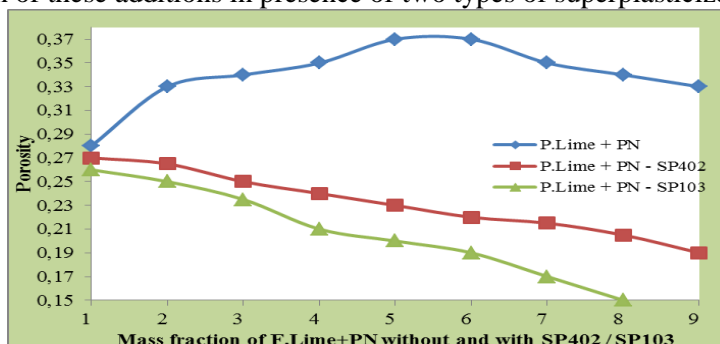
At the figure (3), we have noted that the compressive strengths at the young age (2 days), the middle ages (7 days) and the long-term (28 days) of all the mortars formulated by the combination between the F.Lime and the PN increase steadily with age and shows no fall. However, the compressive strengths decrease slightly with the addition of 40% of the F.Lime. This decrease is generally due to the chemical and mineralogical compositions of F.Lime which is rich in CaO. Then, the compressive strengths are increased with increasing the mass fraction of the Natural Pozzolan and decreasing the proportion of fillers in the formulation matrix. This increase in compressive strength is explained by the fact that the interaction between the reactive silica found in the vitreous part of the PN and the calcium hydroxide Ca (OH)<sub>2</sub> released by the cement during the hydration of the mixture, promotes the physical-chemical effect of this addition and contributes to the consumption of the lime present in the cement by subsequently improving the compressive strength.

### 3.3. Improvement of physical properties and mechanical performance

In order to improve the physical properties and mechanical performance of mortar and/or concrete formulated by the combination between the F.Lime and the PN, we have incorporated into the different formulation matrix two types of superplasticizers of different nature, a high water reducer and setting accelerator (SP103 with 2.5% by weight of cement) and the second is a high water reducer and setting retarder (SP 402, with a rate of 3.5% by weight of cement).

#### 3.3.1. Influence on porosity

The figure (4) illustrates the porosity of concrete formulated by the combination between the F.Lime and the PN as a function of the mass fraction of these additions in presence of two types of superplasticizers.

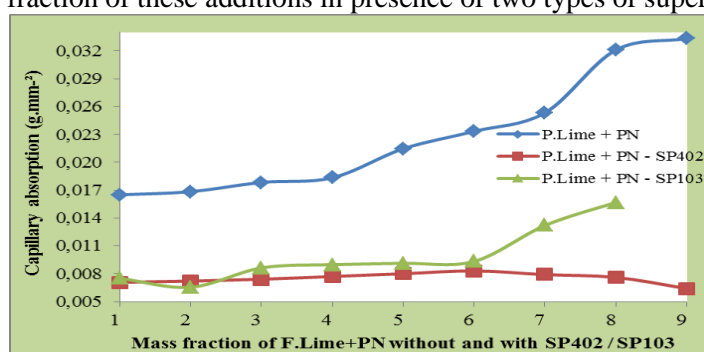


**Figure 4:** Porosity of mortar and/or concrete formulated by the combination between the F.Lime and the PN as a function of the mass fraction of these additions with superplasticizers.

From the figure (4), we have found that the porosity of concrete formulated by the combination between the F.Lime, the PN, and superplasticizers “F.Lime+PN /F.Lime+PN-SP103 /F.Lime+PN-SP402” Increases slightly according to their different percentages. In the second and third cases (F.Lime+PN-SP402 / F.Lime+PN-SP103), we observed a strong decrease in porosity. This decrease is due to the effect of the combination of the organic additives (superplasticizers: SP402 and SP103) and inorganic additions (F.Lime + PN) which disperse the cement grains from one another. On the other hand, it can be explained by the fact that the combination between the F.Lime and the PN (very fine materials) in the presence of superplasticizers fill interstitial voids; between the cement and aggregate particles; (Physicochemical and microstructure effects).

### 3.3.2. Influence on capillary absorption

The figure (5) shows the capillary absorption of concrete formulated by the combination between the F.Lime and the PN as a function of the mass fraction of these additions in presence of two types of superplasticizers.

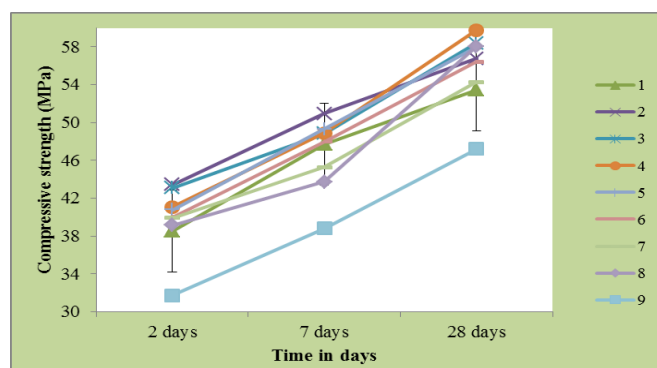


**Figure 5:** Capillary absorption of mortar and/or concrete formulated by the combination between the F.Lime and the PN as a function of the mass fraction of these additions with superplasticizers

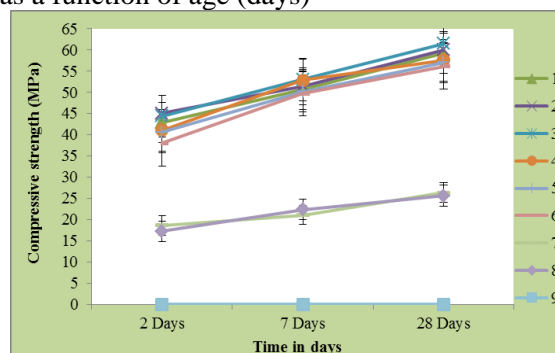
From the figure (5), we have observed that the capillary absorption of concrete formulated by the combination between the F.Lime and the PN (case: P.Lime + PN) increases with respect to the control mortar. On the other hand, we have found that the incorporation of superplasticizers in the concrete formulation matrix based on the combination of the F.Lime and the PN (case: P.Lime + PN -SP402 / case: P.Lime + PN-PS103) decreases the capillary absorption. This decrease can be explained on one hand by the fact that the capillary absorption of mortar is influenced by the porous structure and the level of superplasticizers. The latter can contribute to the reduction of the capillarity by the formation of a polymer film and reduce the capillary pressure. On the other hand, it is linked to the initial role of superplasticizers which disperses the grains of cement from each other and also to the fineness of these additions (P.Lime + PN) which fill the voids between the particles by subsequently participating in the reduction of the capillary absorption of the concrete in the hardened state.

### 3.3.3. Influence on mechanical performance

The figures (6 and 7) show the evolutions of the compressive strength of mortar or concrete formulated by the combination between the F.Lime and the PN in the presence of two types of superplasticizers.



**Figure 6:** The compressive strength of mortar and/or concrete formulated by the combination between the F.Lime and PN with superplasticizers (SP402) as a function of age (days)

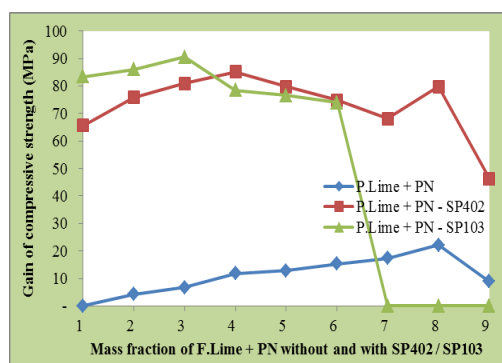


**Figure 7:** The compressive strength of mortar and/or concrete formulated by the combination between the F.Lime and PN with superplasticizers (SP103) as a function of age (days)

From the figures (6 and 7), we found that the compressive strengths of all the mortars formulated by the combination between the F.Lime and the PN in combination with two types of superplasticizers (SP402 / SP103) increase steadily and show no drop. These increases can be explained by the fact that the combination between the F.Lime and the PN (very fine materials) with their fine fills fill voids between the cement particles and granules (granular effect) on one hand. And on the other hand, the increases are related to the role of the addition of superplasticizers (SP103/SP402) which disperse the grains of cement from one another (physicochemical effects). In fact, when the organic molecules (SP402 / SP103) are introduced into a suspension of the cementitious material formulated by the combination between the F.Lime and the PN, a large part of them is fixed by adsorption to the surface of the cement particles (physicochemical and microstructural effect). The latter reduces the attractive forces of interaction between the particles and the atoms of the different constituents (possibly chemical effects). The superplasticizer admixture by their chemical effects modifies the interparticle forces, that is to say, to minimize the porosity by influencing the increase in the compressive strength.

### 3.4. Gain in compressive strength at 28 days

We also calculated the gain in compressive strength at 28 days (figure.8) of mortar and/or concrete formulated by the combination between the F.Lime and the PN with and without superplasticizers. From the (8), we observed that the combination between the F.Lime and the PN in the mortar and / concrete or matrix with superplasticizers (SP402/SP103) improves the compressive strength at a young age, middle age, and long term. These results show that we have succeeded in improving the physical properties of fresh cement paste and the mechanical performance of mortar and/or concrete in the hardened state by the combination between the F.Lime and the PN in the presence of two types of superplasticizers (SP402/SP103).



**Figure 8:** Gain in compressive strength at 28 days of concrete formulated by the combination between the F.Lime and PN with and without superplasticizers

## 4. Conclusion

In this work, we studied the influence of the partial substitution of clinker by the combination between the Limestone Fillers and the Natural Pozzolan (P.Lime + PN) at 40% by weight of cement with a step of 5% in presence of two types of superplasticizers with a high water reducer (accelerator /retarder setting). The influence of the incorporation of these additions on the physical properties of the fresh cement paste and the mechanical performances in the hardened state were studied. The obtained results from the various formulations elaborate show that granular, physical chemical and microstructural effects have been distinguished. These effects influence the physical-chemical and mechanical properties, namely the reduction of the quantity of water used. Similarly, density and expansion have been decreased. In addition, fineness by surface area and setting time were increased. We found that porosity and capillary absorption were decreased (granular and microstructural effects). However, we have observed that compressive strengths at young ages (2 days), medium ages (7 days) and long-term (28 days) have been improved in the presence of superplasticizers compared to the controls (physical-chemical and mechanical). Our study contributes to, the valorization of mineral and natural resources such as Natural Pozzolan (PN) and Limestone Fillers (P-Lime) in the Amran region of Yemen, the minimizing greenhouse gas emissions, to reduce the energy and the raw material consumption, and to manufacture durable cementitious material again; ecological with mechanical and physical-chemical properties improved.

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