Ecological Cementitious Material Based on Combination Between Natural Pozzolan and Polymer Admixture

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1 Introduction

The valorization of natural pozzolan using it in cement formulation and concrete has economic and environmental benefits: to minimize the CO_2 emission into the atmosphere, to reduce the consumption of raw materials and energy, and to improve the physical properties and mechanical performance. The fine particles of this addition contribute to reducing the porosity and capillary absorption of concrete while improving the physical and mechanical properties [1–9].

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The incorporation of the polymeric admixture of polycarboxylate into concrete formulated by natural pozzolan has the advantage of being done as late as possible during the mixing of concrete, minimizing the amount of mixing water, improving the rheological properties of cement paste, and, subsequently, increasing its mechanical of compressive strength [1–3, 10, 11]. The combination of organic and inorganic additions makes it possible to increase the rate of hydration of mortars and concretes while modifying the *W*/*C* ratio and improving the mechanical performance, namely, the compactness and the capillary absorption [2, 4, 10–14].

In this work, different formulations have been elaborated while partly substituting the clinker by natural pozzolan in various percentages ranging from 5% to 40% by weight of cement with a step of 5% in presence of 3.5% of the polymeric admixture of polycarboxylate. The influences of incorporation of these additions on physical properties and mechanical performances in the fresh and hardened state have been studied.

The obtained results from the different formulations elaborated show that the partly substitution of clinker by natural pozzolan in presence of admixture of polycarboxylate allowed us to develop new durable hydraulic binder with improved physical–chemical and mechanical properties while reducing the cost of production, minimizing the CO_2 emissions into the atmosphere, decreasing the use of mixing water, and improving the physical properties and mechanical performance of concrete in fresh cement paste and hardened state.

2 Materials and Methods

2.1 Material

2.1.1 Cement

The type of cement used in this work is CMI-42.5 from the plant Amran in Yemen. The chemical and mineralogical compositions of clinker, gypsum, and cement used determined by XF and XRD are presented in Tables 1 and 2 and Fig. 1.

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

Names	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	61.29	19.99	5.57	2.85	1.89	3.22	1.15	0.2	0.02

Table 2 Mineralogical composition of clinker

Chemical name	Mineral name	Chemical formula	Cement nomenclature	Content
Tricalcium silicate	Alite	CaO_3SiO_5	C_3S	47.70
Dicalcium silicate	Balite	CaO_2SiO_4	C_2S	25.10
Aluminate tricalcium	Aluminate	$CaO_3Al_2O_2$	C_3A	10.40
Tetracalcium aluminoferrite	Ferrite	$CaO_4Al_2O_3Fe_2O_3$	C_4AF	9.10

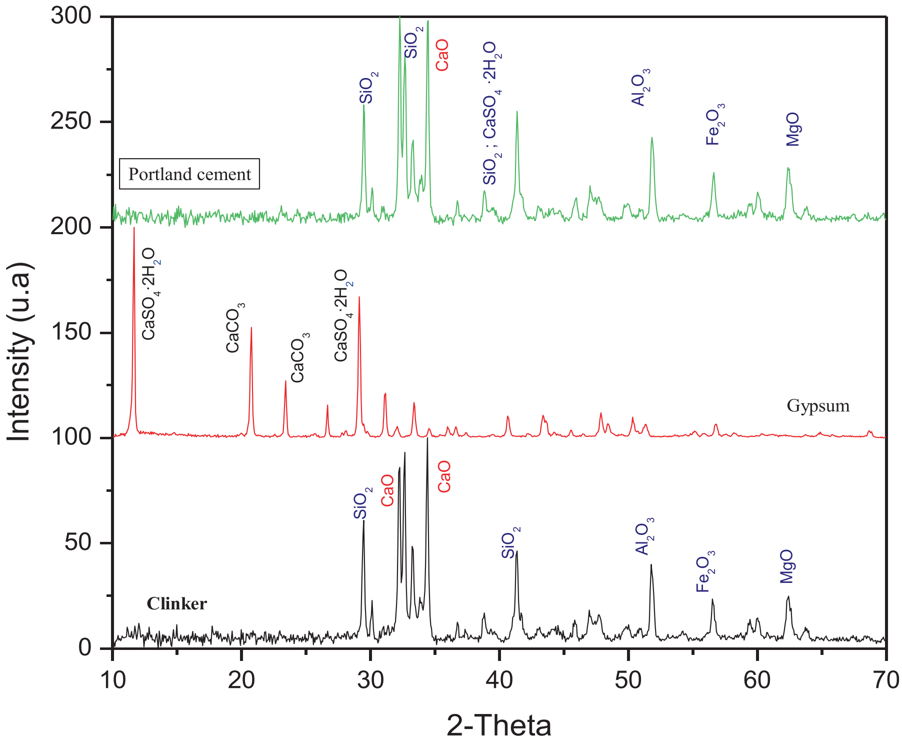

Fig. 1 Spectrum of XRD analysis of clinker, gypsum, and cement

2.1.2 Natural Pozzolan

This is a material of a volcanic origin, extracted from Amran of Yemen deposit. The analysis results by X fluorescence of PN are represented in Table 3. The PN used in this work is a local available material in our country with very high quantity.

From the results shown in Table 3, we observed that PN contained 8.8% of lime (CaO), 41.43% of silica (SiO_2), 16.16% of alumina (Al_2O_3), 9.41% iron of (Fe_2O_3), and 4.79% of magnesia (MgO). These pozzolans have a black color, a specific surface Blaine 4576 $cm^2\ g^{-1}$, a density 2.81, and size of particles lower than 50 µm.

The results of mineralogical analysis by X-ray diffraction of natural pozzolan of Amran, Yemen, are represented in Fig. 2.

From Fig. 2, we have noticed that the natural pozzolan reveals the strong presence of feldspar, plagioclase (anorthite, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$), followed by the pyroxene (augite, $(Mg,Fe)_2{\cdot}2SiO_6$), then volcanic glass of analcime (zeolite) chlorite ($6Mg_5{\cdot}AlSi_3{\cdot}O_{10}$) (OH), and some traces of hematite—Fe_2O_3 also as the magnetite, Fe_2O_3 OTF as well as the biotite, $2K(Fe,Mg)_3AlSiO_{10}(OH)$ and traces of minerals: basalts, dolomites, calcite, clays, etc.

Table 3 Elementary chemical compositions and physical properties of natural pozzolan in weight of atomic

Names	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Cl^-	LOI	Color	Particles size (μm)	Specific surface ($cm^2\ g^{-1}$)	ρ
Content	8.8	41.43	16.16	9.41	4.79	0.13	0.9	3.47	0.04	14.87	Black	50 μm	4576	2.81

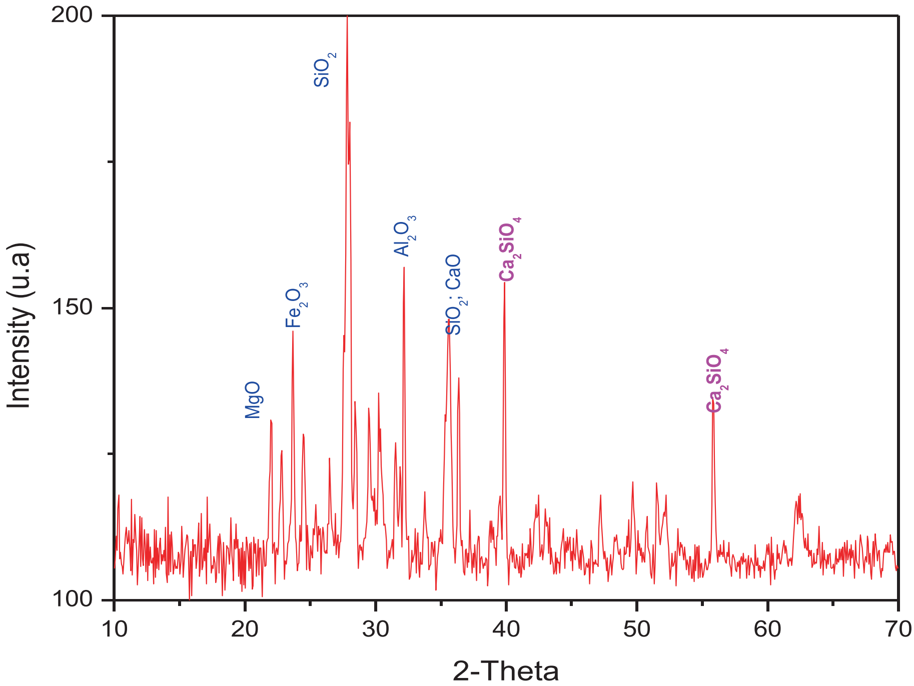

Fig. 2 Spectrum of XRD analysis of PN

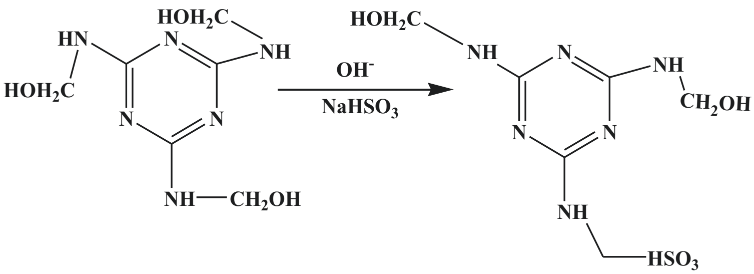

Fig. 3 Chemical structure of sulfone-poly-melamine

2.1.3 Polymeric Admixtures

The polymeric admixtures used are polymers in liquid form, prepared especially for cement industry and concrete. They are based on sodium or sulfonated naphthalene-formaldehyde, Fig. 3, or sulfonated melamine formaldehyde, Fig. 4.

The physical properties of polymeric admixtures are collected in Table 4.

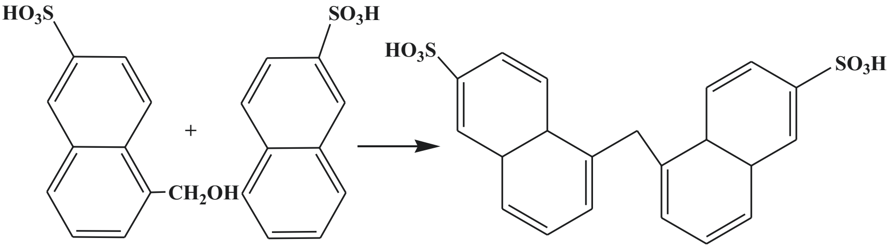

Fig. 4 Chemical structure of sulfone-poly-naphthalene

Table 4 Physical properties of PAS

Name	Nature	Color	Density	Area training (%)	Chloride content
Polymeric admixtures	Liquid	Brown	1.23	0.50–1.00	Nil

2.1.4 Mixing Water

To mix our mixture, we used a tap water (wells).

2.1.5 Sand

To prepare our mortar, we have used standard sand delivered by the new French company of Littoral, conferring to the norm EN 196-1.

2.2 Methods

To achieve the objective of our study, we have prepared a reference mortar without additions whose composition is 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 another mortar with mineral additions and superplasticizers, always keeping the standardized consistency, was fixed. For each mortar having acquired this consistency, we have prepared prismatic specimens with dimensions $40 \times 40 \times 160$ mm^3. 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 of 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 (six halves).

The formulations of different tests prepared for elaboration of new ecological cementitious material, while still maintaining the content of gypsum to 5% of total weight of cement with addition of PN, are presented in Table 5.

Table 5 Formulation matrix of cement at base of PN

Content %	0	5	10	15	20	25	30	35	40
Cement (%)	100	95	90	85	80	75	70	65	60
PN (%)	0	5	10	15	20	25	30	35	40

2.2.1 Porosity Methods

The concrete is a porous material; this porosity plays an important role in the mechanisms of concrete damage; it is complex since it spreads on different scales and results from different phenomena. However, the porous nature of concrete is very important since the resistance of the latter is related to its porosity. In general, it can be seen that the more porous the concrete, the higher its permeability and the lower its compressive strength. This is the simplest method for measuring the porosity. It measures the amount of water that can circulate in the network of interconnected pores of the material. The procedure is that recommended by Ollivier [14]. It requires three weighings:

- The mass of the saturated sample M_{sat} when the sample is out of water.
- The hydrostatic mass M_{hyd} corresponding to the mass of the sample in water.
- The dry mass M_{sec} of the sample after stabilization of its mass in an oven.

The weighing must be carried out on a sample which has not undergone a prior saturation/desaturation cycle, in order to avoid the influence of a removal of cement matrix following this preliminary cycle. The apparent volume V_{app} (in m^3) of the sample is calculated from the saturated masses M_{sat} (in kg) and hydrostatic masses M_{hyd} (in kg) thanks to the buoyancy of Archimedes according to the Eq. (1)

$$M_{hyd} = M_{sat} - \rho_{water} \times V_{app} \tag{1}$$

where ρ_{water} is the density of water (1000 kg m^{-3}).

Assuming then that the interconnected pores are saturated with water, the porosity η is calculated of sample by Eq. (2).

$$\eta = \frac{V_{vides}}{V_{app}} = \frac{M_{sat} - M_{sec}}{M_{sat} - M_{hyd}} \tag{2}$$

2.2.2 Capillary Absorption Methods

The water absorption test consists following by weighing the quantity of water absorbed by a previously dried specimen and allows the indirect characterization of capillary porosity. There is no standard for this test, and several procedures are proposed in the literature. We followed a variant of the procedure proposed by the AFREM [15] after having optimized the preconditioning of the specimens.

2.2.3 Compressive Strength Methods

The compressive strengths were evaluated at a young age (2 days), at middle age (7 days), and at long term (28 days) using a compression testing machine. The value of the resistance considered is the average of crushing stress of three test pieces (six halves of the test pieces).

3 Results and Discussion

3.1 Physicochemical Properties of Hydraulic Binders at Base of PN Add

3.1.1 Chemical Compositions

Table 6 presents the results of new ecological cementitious material made from PN at different percentages ranging from 0% to 40% with a step of 5% by weight of clinker, in fixing the content of gypsum at 5% by weight of cement which are determined using XRF.

From the results presented in Table 6, we found that the partial substitution of clinker by PN influences the physicochemical properties such as the increase in content of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), and magnesium oxide (MgO) as a function of increase in mass fraction of PN. However, calcium oxide (CaO) was decreased as a function of increase in mass fraction of PN in formulation matrix. This will subsequently influence the physical properties and mechanical performance.

3.1.2 Physical–Chemical Properties

Table 7 shows the physical–chemical properties of cement paste formulated by different percentages of natural pozzolan.

Table 6 Chemical compositions of hydraulic binders formulated by different percentages of PN add

Content (%)	0	5	10	15	20	25	30	35	40
SiO_2	19.32	20.00	21.16	22.85	23.15	24.10	25.79	26.46	27.98
Al_2O_3	5.87	6.12	6.68	7.00	7.54	7.90	8.57	8.83	9.34
Fe_2O_3	2.97	3.59	4.51	5.20	6.24	7.80	8.21	9.08	10.58
CaO	61.35	59.23	56.47	53.36	50.61	47.00	44.35	40.87	37.64
MgO	2.01	2.23	2.29	2.52	2.68	2.84	3.05	3.16	3.30
SO_3	2.37	2.22	2.20	2.10	1.95	1.80	1.79	1.78	1.71
K_2O	1.17	1.12	1.08	1.04	0.97	0.92	0.88	0.86	0.81
Na_2O	0.14	0.25	0.29	0.33	0.43	0.50	0.63	0.68	1.05
Cl^-	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03

Table 7 Physical and chemical properties of the cement

Content	Loss on ignition	Free lime	Fineness		Surface specific Blaine	Density	*W/C*	Setting time	
			45 μm	90 μm				Initial	Final
0	1.59	0.5	12.5	1.5	3240	3.14	0.5	60	90
5	1.62	0.55	13.7	1.7	3250	3.13	0.49	60	90
10	1.88	0.58	14.5	1.8	3260	3.12	0.48	70	100
15	2.00	0.6	15.3	1.9	3290	3.11	0.47	75	110
20	2.04	0.63	18	2	3340	3.09	0.45	80	120
25	2.25	0.65	19.5	2.1	3420	3.06	0.44	90	130
30	2.28	0.68	22	2.2	3510	3.04	0.42	120	160
35	2.42	0.71	24	2.3	3600	3.02	0.4	120	170
40	2.54	0.74	27	2.4	3630	3.00	0.4	130	180

From the results shown in Table 7, we observed that the loss on ignition value is increased as function of percentage of PN. This increase is mainly due to the expelled water and oxidizable elements present including our addition. In addition, we noticed that the insoluble residue rate of cement is increased as function of percentage of PN. This increase is essentially due to the residues present in pozzolan. Moreover, we detected that the fineness by saving sizes methods (45 and 90 μm) of cement increases with addition of PN; this increase is usually due to the fineness of PN, which facilitates the hydration of mixture during mixing. In addition, we observed that the fineness of cement increase with addition of PN. This increase is habitually due to the fineness of PN, which facilitates the hydration of mixture during mixing and filling the void between the particles of cement and that of aggregate on one hand and on the other hand is to improve the physical and mechanical properties thereafter. However, we illustrate that there is a decrease in density of cement with PN by cement witness report. This decrease is logically explained by the fact that adding of PN that replaces clinker has a lower real density, which enabled us to manufacture a cementitious material which is very light and durable. Similarly, we have realized that the *W/C* ratio decreases with increasing the percentages of PN. This decrease is normally due to the chemical and mineralogical compositions of PN, which is poor in CaO; the presence of a low fraction of CaO influencing on the phenomenon of pozzolan hydration in this mineral phase to a tendency to have a water demand decreased and, on the other hand, related to the fineness of the addition of PN. However, we remark that setting time (initial and final) increases in function the quantity of PN in the cement matrix; this increase is usually due to the chemical/mineralogical compositions and physical properties of PN and also the slow pozzolanic reaction of the mixture.

3.1.3 Mechanical Properties

Figure 5 explains the compressive strength of mortar based on different percentages of addition of PN add as a function of age in days.

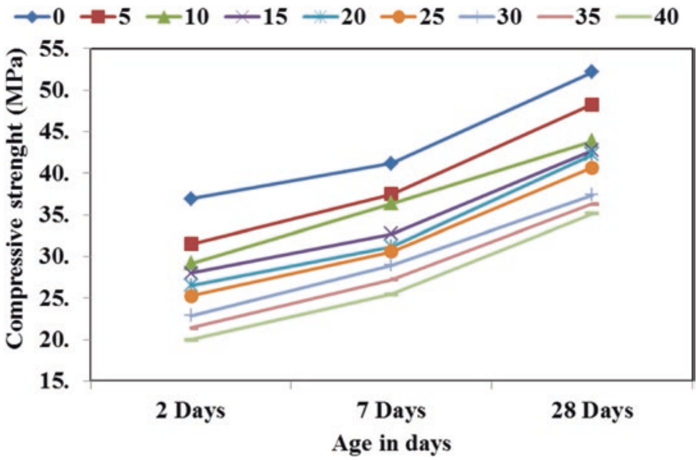

Fig. 5 Compressive strength of cement mortar formulated by different percentages PN add

According to Fig. 5, we identified that the compressive strength of all mortars at a base of PN is progressively increasing with age and does not fall. But it decreases with the increase in the percentage of PN.

In order to improve the physical properties and mechanical performance of mortar or concrete formulated by natural pozzolan, we have incorporated into the different formulation matrix 3.5% of polymeric admixture of polycarboxylate (PAP).

3.2 Mechanical Properties of Mortar and/or Concrete in Hardened State

3.2.1 Porosity

Figure 6 illustrates the porosity of cement mortar as a function of mass fraction of natural pozzolan with 3.5% of polymeric admixture of polycarboxylate.

From Fig. 6, we have established that the porosity of cement mortar formulated by different percentage of PN add with and without of 3.5% of polymeric admixture of polycarboxylate increases. This increase is explained by the fact that the addition of natural pozzolan (very fine materials) fills the voids between the cement and the aggregate particles (PN case). In the second case (PN + PAP), we noticed an increase in the compactness. These increases are due to the effect of the combination between the admixture and pozzolan that is to disperse the cement grains and fill the interstitial voids.

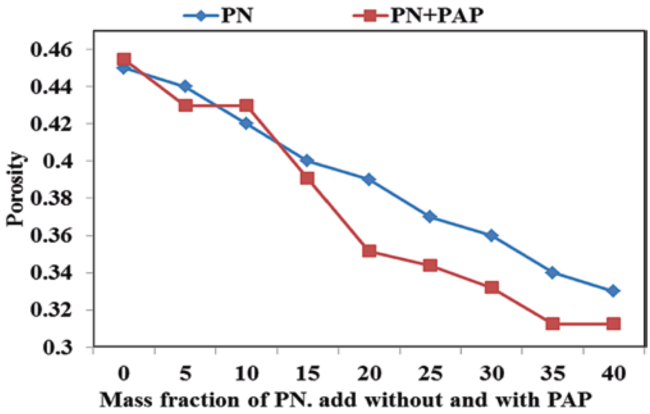

Fig. 6 Porosity of cement mortar formulated by different percentage of PN add with and without PAP

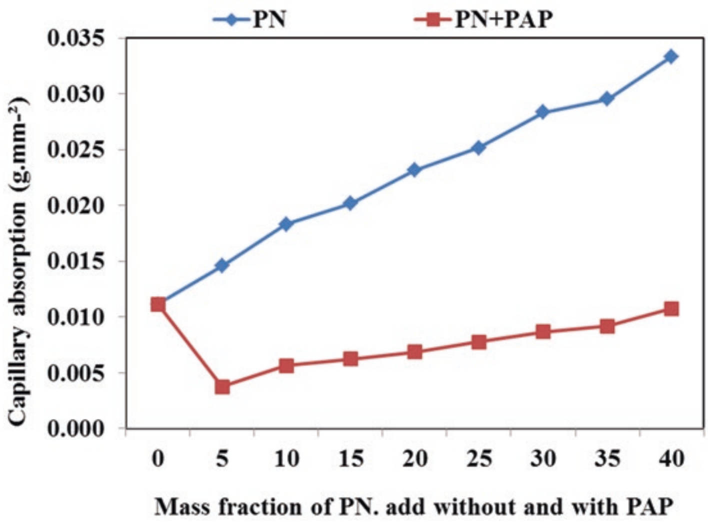

Fig. 7 Capillary absorption of cement mortar formulated by different percentage of PN add with and without PAP

3.2.2 Capillary Absorption

Figure 7 shows the capillary absorption of cement mortar as a function of mass fraction of natural pozzolan with 3.5% of polymeric admixture of polycarboxylate.

From the results presented in Fig. 7, we observed that the capillary absorption of cement mortar formulated by PN increases compared to the control mortar. On the other hand, we have noticed that the incorporation of 3.5% of polymeric admixture of polycarboxylate reduces the capillary absorption. This decrease can be explained on one hand by the initial role of superplasticizers which disperses the cement grains from each other. On the other hand, it relates to the fineness of mineral addition which fills the voids between the particles and contributes to reduce of capillary absorption of concrete in hardened state.

3.2.3 Compressive Strength

Figure 8 explains the compressive strength of mortar based on different percentages of addition of PN add in presence of 3.5% of polymeric admixture of polycarboxylate.

From Fig. 8 we have observed that the compressive strengths of all mortars formulated by natural pozzolan in combination with 3.5% of polymeric admixture of polycarboxylate increase steadily and show no drop. These increases are related to the role of polymeric admixture of polycarboxylate, which disperses the cement grains from each other (physical–chemical effects).

3.2.4 Gain of Compressive Strength

Figure 9 displays the gain compressive strength at 28 days of mortar based on different percentages of addition of PN add in the presence of 3.5% of polymeric admixture of polycarboxylate.

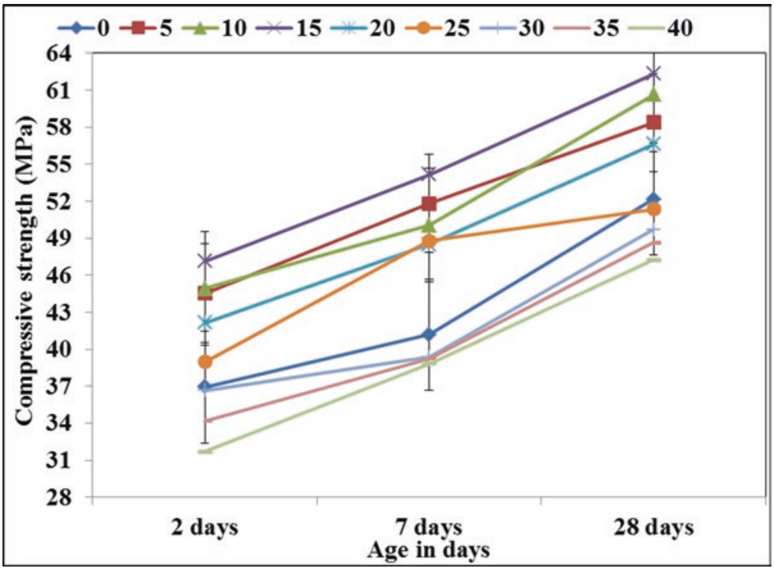

Fig. 8 Compressive strength of cement mortar formulated by different percentages of PN add with and without PAP

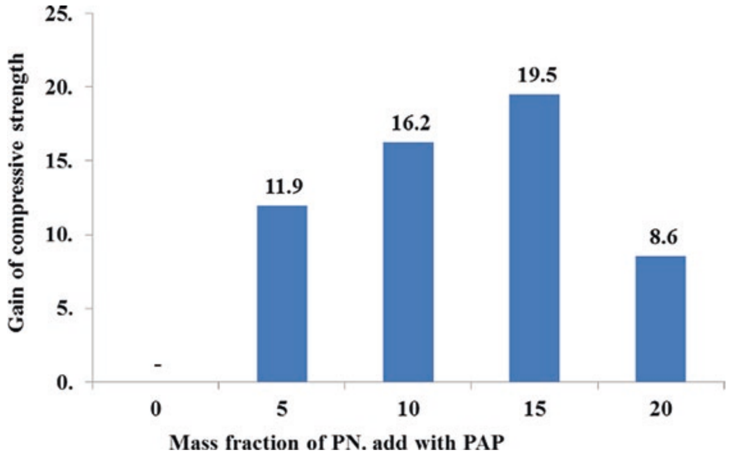

Fig. 9 Gain of compressive strength at 28 days of mortar formulated by different percentages PN add with PAP

According to Fig. 9, we detected that the gain of compressive strength increases with the mass fraction of PN increased in the presence of 3.5% of polymeric admixture of polycarboxylate. These increases are related to the role of polymeric admixture of polycarboxylate, which disperses the cement grains from each other.

4 Conclusion

In this work, we studied the influence of partially substitution of clinker by natural pozzolan at various percentages ranging from 5% to 40% by weight of cement with a step of 5% in the presence of 3.5% of the polymeric admixture of polycarboxylate. The influences of the incorporation of these additions on physical properties of fresh cement paste and mechanical performances in the hardened state have been studied.

The obtained results from the various formulations elaborated show that the granular, physical–chemical, and microstructural effects have been observed. These effects influence the physical–chemical and mechanical properties, namely, the reduction of the quantity of water used. Similarly, the density decreases. In addition, the fineness of the specific surface and the setting time were increased with the increase in the percentages of pozzolan with the superplasticizers. We found that the capillary absorption decreased. However, the compactness increases with increasing the mass fraction of natural pozzolan with superplasticizers (granular and microstructural effects). We have also observed that the mechanical of compressive strengths at a young age (2 days), median age (7 days) and long-term (28 days) have been improved as a function of the increase in the percentage of pozzolan in presence of 3.5% of the polymeric admixture of polycarboxylate in the mix, that is main that Physical-chemical and mechanical effects of the pozzolan i t was effective.

Our study contributes to valorize an abundant mineral resource in combination with the superplasticizers in cement manufacturing, allowing us to develop a new durable concrete with improved physical and mechanical properties and thus represents a great economic and environmental interest:

- Reduction in cost of the cement production.
- Minimization the emissions of CO_2 into the atmosphere.
- Decrease the use of mixing water.

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