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Inorganic additions effect on the mechanical performance of cement and concrete

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Abstract
In the last few decades, considerable research effort has been spent on the utilization of natural resources (pozzolan and limestone) as partial replacement of the Ordinary Portland cement. The benefits of addition of supplementary materials to Ordinary Portland cement are well documented. Limestone powder substitution for cement makes perfect sense in these lower w/c concretes, saving money and energy and reducing carbon dioxide emissions. The use of pozzolan powder as organic addition for mortars and concretes provided maximum compressive strength at the same workability level, comparable to that of the reference mixture after 28 days of curing. This paper describes about the properties, the mechanical strength of cement and the abrasion resistance of the concrete incorporated with limestone powder and pozzolan powder to the penetration of chloride ions. Limestone Powder and Pozzolan Powder are partially replaced with Ordinary Portland Cement for certain Percentages. Limestone powder (LMSP) and pozzolan Powder (PZNP) was used as compensating materials with different ratio of cement include 0, 5, 10, 15, 20, 30 and 40 %.

Keywords: Pozzolan Powder, Limestone Powder, Portland cement, abrasion resistance

Introduction
Most cement plants consume much energy and produce a large amount of undesirable products, which affect the environment. In order to reduce energy consumption and CO_2 emission and increase production, cement manufacturers are blending mineral additions such as slag, natural pozzolan, sand and limestone [1- 4], limestone has been used in concrete production for the last 25 years, not only for the main purposes of lowering the costs and environmental load of cement production, but also to increase the concrete durability, more recently limestone is also used as a filler material to improve the workability and stability of fresh concrete and for a high flowable concrete. The presence of limestone [5] in hardened cement paste has a filler effect. Limestone is an inert or quasi-inert material being non-cementitious from hydraulic points of view.
The effects of limestone on cement properties are not only physical corresponding to reduction in paste porosity but also chemical [6 - 9]. The chemical interactions take place between calcite and Portland cement paste leading to calcium carboaluminates formed by a reaction between hydrated calcium aluminates and carbonate ions [10].
Calcareous filler has an important binding property that is developed by hydration of calcite and C_3A [11]. Another partial replacement material used in this study is pozzolan which are used as supplementary cementitious materials [12].
In recent times, pozzolan powder has found some use in the construction industry and research has been conducted to examine their applications. Extensive studies were carried out and the hardened properties of bituminous concrete with pozzolan. The behaviour of bituminous concrete with pozzolan dust compared very well with bituminous concrete with lime and stone dust [13, 14]. More research is still needed to see its wider application in concrete, especially as partial replacement of cement. If this is successful there will be less demand on cement, thus providing possible solutions to environmental concerns of CO_2 pollution and waste

production [15-18]. Therefore, the utilization of Pozzolan Powder in the production of new materials will help to protect environment [19]. Recently the use of pozzolana powder as replacement materials has been investigated. So, this study consists to analyze the influence of the incorporation of these mineral additions on the properties and the mechanical strength of cement and the abrasion resistance of the concrete to the chloride ion penetration.

2. Materials and methods

2.1. Materials

- Raw materials: clinker, sand, gypsum, limestone, pozzolan and aggregate are supplied from the cement plant "Asment Temara".
- Mixing Water: Drinking Water

For each matter an average sample of CPA cement was prepared by the quartering method [20] and characterized by X-ray fluorescence Bruker type for determining the chemical composition. For all samples of clinker a chemical analysis of free lime CaO_l was affected in addition to the chemical composition. All analyzes were performed according to the standard Moroccan NM.10.1.004 [21].
The chemical composition of the clinker and various additives which is used, are shown in Table 1.

Table 1: Chemical composition of the clinker and various additives

Material	Elements in % weight										
	SiO_2	$A1_2O_3$	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Cl^-	In[1]	LOI[2]
Clinker	21.27	5.05	2.79	65.79	1.75	0.70	0.16	1.44	0.017	0.05	0.25
Gypsum	1.95	0.29	0.30	34.82	0.73	0.07	0.01	40.36	0.010	-	20.33
Limestone	1.92	0.66	0.98	52.81	0.62	0.11	0.02	0.92	0.010	-	41.91
Pozzolan	47.22	18.07	9.0	11.23	5.8	1.0	2.0	0.9	0.04	-	1.2
Sand	44.87	8.43	0.89	44.02	2.91	0.6	0.1	0.65	0.001	-	4.66

[1]In: insoluble
[2]LOI: loss on ignition

2. 2. Methods

The cements with additions are trained in the following combinations:

- Mortar witness : CPA
- Limestone: 5% - 10% - 15% - 20%
- Natural Pozzolan: 10% - 20% - 30% - 40%

The concretes are formulated according to the following compositions:

- Concrete 1: CPA + limestone (0 - 15 to 30%) + aggregates + sand + water
- Concrete 2 CPA + pozzolan (0 - 15 to 30%) + aggregates + sand + water

2. 2.1. Preparation of cement CPA

The portland cement without additions CPA are prepared from 97% clinker and 3% gypsum. Everything is grounded up to a fineness of 1 ± 0.2µm in a ball mill. The CPA is ready to physicochemical and mechanical tests according to standard NM 10.1.004.

2.2.3. Preparation of mortars:

The mortars were prepared using quartz sand, crushed continuously with the size varied between 0-315µm, mixed with the binder and water in the weight ratios: 3: 1: 0.5 (1350g of sand, 450g of binder and 225ml of water to fill three specimens 4*4*16cm) according to standard methods NM 10.1.005 [22]. These components mechanically kneaded for 10 minutes, were introduced by vibration in the tubes. The latter, after 24 hours of storage at 100% humidity, were unmolded and placed in water at 20°C in a humidity cabinet. They broke down after aging 2, 7, 28 and 90 days, first by bending under constant moment, the tips obtained in this test are then subjected to a simple compression test. The Compressive strength is determined by the NM10.1.005 standard.

2.2.4. Formulation of the concrete cylindrical :

The composition of the normal concrete is as follows:

The 450g of the mixture (additions are always introduced in substitution of cement) is added to 1125g of standard sand and 1575g of gravel. The mixing water rate (W/C=0.5) was kept constant for all the preparations.

To characterize the chemical resistance of the concrete, we are preparing the specimens in a mole which has a diameter=9cm and height=15cm. These specimens were unmolded after 24 hours of curing and they were keeped in water at 20°C ± 2°C for 28 days.

After 28 days of curing under water, the samples are weighed to determine Minitial, then they are immersed in 5% of hydrochloric acid (HCl) (which presents the most harsh and aggressive conditions that the concrete can suffer). The abrasion resistance of concrete in the hydrochloric acid solution is measured according to ASTM C 267-96 standard. The specimens are cleaned 3 times with fresh water to remove the concrete altered and they are allowed to dry for ½ hour. Then we proceed again to the measure the weight of these samples (M_{final}). This operation is performed after 1, 7, 14 and 28 days of immersion in HCl (pH=2). The HCl solution is renewed every seven days (depending on the pH). The extent of the attack is evaluated by the mass loss.

2.2.5. Mass loss of concrete

To assess the degree of degradation by calculating the mass loss of the specimens immersed in HCl solution according to time, we adopted the procedure below:

After 1, 7, 14 and 28 days of attack, the samples are cleaned with fresh water to remove the mortar removed altered, dried and stewed until the total elimination of absorbed moisture (the mass becomes constant) at a temperature of 105°C. The degree of degradation is evaluated by the following formula loss weight:

$$\textbf{Mass loss (\%)} = [(M_1 - M_2) / M_1)] \times 100$$

With: M_1: dry mass of the specimens before immersion

M_2: dry mass of the specimens after immersion

2.2.6. Fixing rates of chloride ions in concrete

Determined by complexometric after 28 days of immersion the concrete in a NaCl solution with a variation of the concentration between 0 and 100g/l.

3. Results and discussion

3.3. Effect of the pozzolan on CPA cement according to the time and the percentage of the pozzolan:

The following figure shows the effect of substitutions additions rate used on the compressive strengths of mortars at 2, 7, 28 and 90 days.

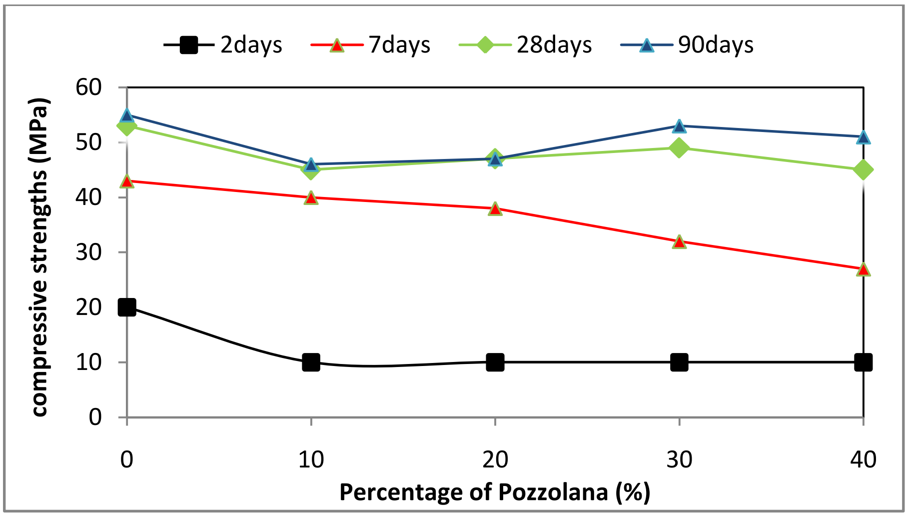

Figure 1: Effect of the pozzolan on the CPA compressive strength

There is an increasing trend in the strength of CPA cement as the days of curing increases and whatever the added pozzolan rates. In young age (2 days of curing), the strength of CPA cement reduces as the percentage

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replacement of cement with CPA increases. This strength improvement is believed to continue as long as the curing period is prolonged to allow completion of hydration.
The compressive strength of CPA with the pozzolan (from 10 to 30%) compared to CPA reference, at 2 days and 7 days passes from a gap of 45% to 48% and from 6% to 27%, respectively. At 90 days and for the same substitution rates, the gap of the compressive strength of CPA cement tends to decrease from 17% to 11% at 28 days and from 18% to 10% at 90 days. This shows that the pozzalan has a positive effect in long-term. The optimum substitution percentage of the CPA cement by the pozzolan is 30%.

3.4. Limestone effect on the compressive strength of CPA cement
Limestone is a non-reactive and inert additive which means that its chemical elements don't react with those of the clinker. Therefore, we used the limestone with a percentage which varies between 0 and 20%. The results of experiments are shown in the following figure:

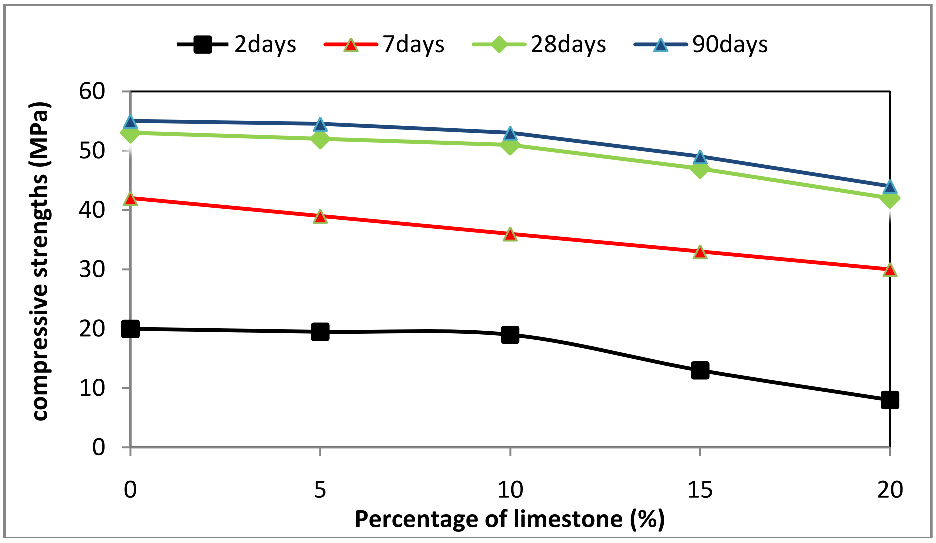
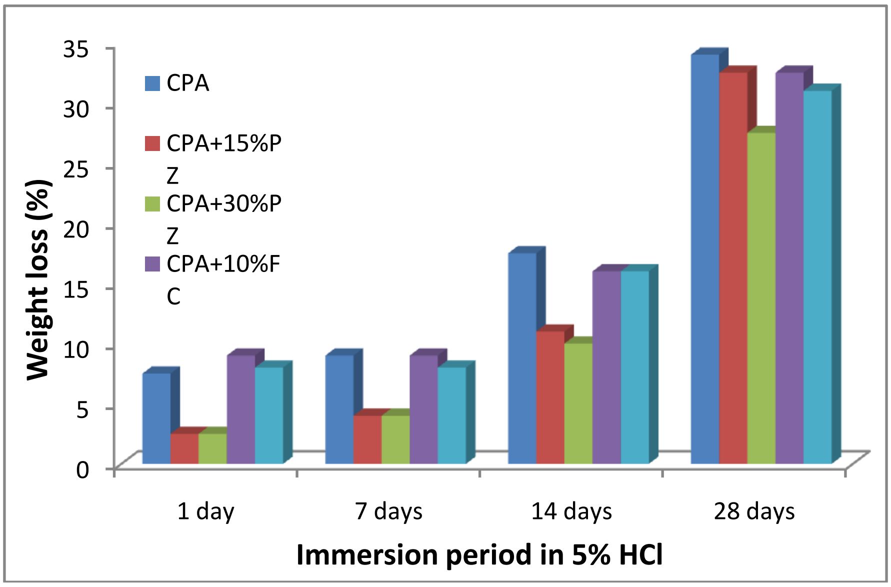


Figure 2: Limestone effect on the compressive strength of the CPA cement

Test results show that the presence of limestone in CPA cement accelerates its strength development (figure 2). Substitution CPA cement by 10% of limestone, gives a better result than the 20%. At 2 day age the CPA cement+10% of limestone reduces the loss of compressive strength from 50% to 8%. At 7 day age the loss of compressive strength is reduced by about 10 to 20. At 28 day age the limestone decreases the loss of compressive strength from 16% to 3%. At 90 day age the loss of compressive strength decreases from 16% to 3%. So, Beyond 10%, limestone has a negative effect on the development of the compressive strength of the CPA cement.

3.5. Effect of hydrochloric acid (HCl) on the concrete:
The effect of the acid HCl on the durability of the concrete is shown by measuring the mass loss of this concrete which have been emerged in a HCl solution.
The Figure below shows that there is an evolution of the mass loss of the four mortars of CPA: CPA + 15% pozzolan, CPA + 30% pozzolan, CPA + 10% limestone and CPA + 15% limestone according to the period of the immersion in an acid solution of 5% HCl. After 24 hours to 28 days, it is clear that the mortars of CPA + 15% pozzolan and CPA + 30% pozzolan increase their abrasion resistance of concrete in hydrochloric acid solution.
The mortar of CPA reference and the CPA + limestone are the most attacked by the HCl acid. Those mortars presented a mass loss of 8%, while the mortars of CPA + pozzolan are developed some abrasion resistance because its mass loss was 2.8%. The Pozzolan mortars develop a greater ability of abrasion resistance of concrete to acid attacks (HCl). Compared to the reference, we record a reduction of mass loss of 5.2, 3.5, 7.5 and 6% after 1, 7, 14 and 28 days of immersion in HCl solution, respectively.



PZ: Pozzolan
FC: limestone

Figure 3: Mass loss of concrete mortars in function of the type of addition and time of immersion in HCl.

3.6. Effect of the concentration of chloride ions on the concrete with 15% limestone and 30% pozzolan

The nature of the cement additives has an important role in setting the percentage of the chloride ions fixed in the concrete matrix. Indeed, the chloride ions are either absorbed by the CSH or set by aluminate (C_3A), which they depend on the composition of the cement and the additives.

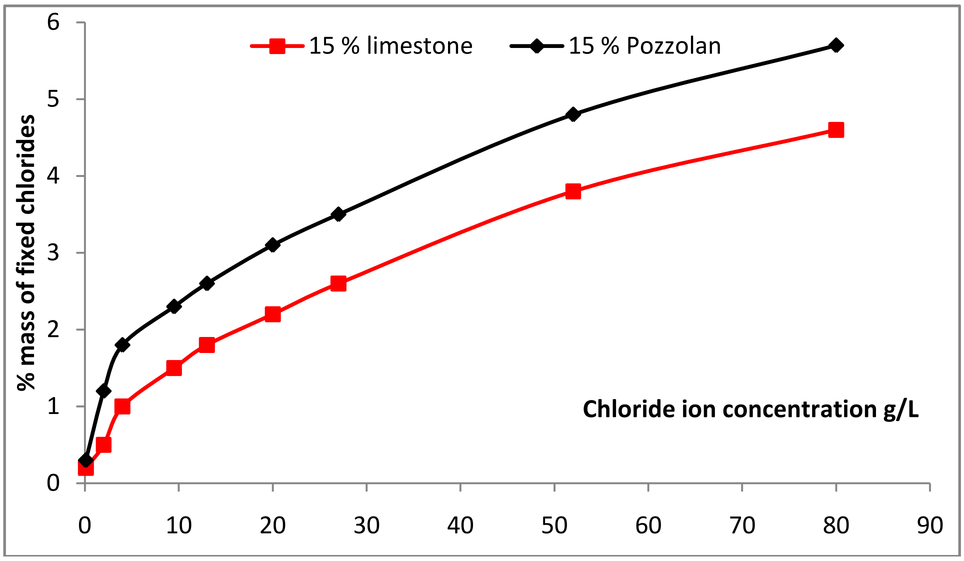


Figure 4: Percentage mass of fixed chloride on concrete matrix with 15% limestone and 30% pozzolan in function the concentration of Cl^-

The results shown in figure 4 indicate that whatever the additives concrete the chloride ion concentration increases and the rate of their attachment in concrete matrix increases also. For the same concentration of the NaCl solution, the limestone mortar is more easily attacked by the chloride ions than the pozzolan mortar and which present a decrease in mass of concrete. So, the pozzolan resistant more to the attack of chloride ions. This is because the pozzolanic additions react with water to form hydrated compounds similar to those of the clinker, improving resistance of the concrete against the penetration of chloride ions. In contrary, the limestone is an inert material which doesn't react with water to develop the concrete strength.

Conclusion

The study undertaken in this paper indicates that it is possible to exploit deposits of natural resources such as pozzolana and limestone to produce cements composite in our country. These have compelling interests of technical, economic, environmental and sustainability point of view towards different chemical attacks. The experimental results conducted through this study allow drawing the following general conclusions:

- The incorporation of inert mineral additives (limestone) at 10% and active (Pouzzolana) at 30% on CPA cement, improved the mechanical strength of this cement.
- This study adds value by replacing the addition of a portion of clinker.
- Limestone presents a protection against the attack of chloride ions less than the pozzolan
- The pozzolan reduce the capillary absorption of chloride ions by reducing the porosity of the concrete which increases the resistance of the latter against the attacks of the acid medium.
- -This substitution can save 10% to 30% of clinker used to manufacture cement; this will have a beneficial effect for cement economic (less energy spent for the clinker burning).
- This study contributes to the protection of the environment as to produce 1ton of clinker generates about 1ton of CO_2 is harmful to the atmosphere. Based on our findings we will reduce from 10% to 30% CO_2 gas responsible for the greenhouse effect.

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