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PERFORMANCE STUDY OF LOW ENVIRONMENTAL IMPACT MORTARS BASED ON MINERAL ADDITIONS AND CEMENT RESISTANT TO SULFATE (CRS)

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Abstract: The use of cement resistance to sulphate in aggressive environments showed a lot of benefits such us good mechanical development and therefore better durability; however, the consumption for great amount of clinker lead to random hazardous deposits, shortage of natural resources, gas and dust emissions mainly (CO_2) causing negative impact on the environment. Recently, technical, economic and environmental benefits by the use of blended cements have been reported and being considered as a research area of great interest in cement production industry.

The present research aim is to evaluate the effect of partial replacements of cement resistant to sulfate (CRS) by a pozzolanic addition, on the physical-chemical properties, as an alternative novel composition binder. Furthermore, the behaviour of the mortars based on this new combined blends was investigated in the study program, including chemical composition, density and fineness, consistency, setting time, swelling, shrinkage, absorption and mechanical behaviour.

The results obtained showed that the substitution of pozzolan at the optimal ratio of 5% had a positive effect on the resulting cement properties, namely: greater specific surface area, reduced water demand, accelerated process of hydration, better mechanical behaviour and decreased water absorption. Therefore, economic and ecological cement based on mineral addition like pozzolan could be possible as well as advantageous to the formulation of environmental performance mortars.

***Keywords**: Cement Resistant to Sulphate (CRS), pozzolan, environmental performance mortars, mechanical development, physical-chemical properties.*

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INTRODUCTION

Portland cement is based on one principal constituent; the clinker, for which is added a quantity of gypsum to regulate the setting time. The impact of the production of Portland cement on CO_2 gas and dust emissions are well known as a current polluting source of the worldwide environment. This, represents about 7-8% of global CO_2 emissions. Both non-combustion and combustion emissions from cement manufacturing plants occur during the clinker production process (Olivier G.J et al, 2015).

Hence, recent research studies are being undertaken to formulate new binders with reduced environmental impact, either by replacement of substantial amount of the clinker with mineral industrial additions (e.g. blast furnace slag or fly ash) or natural additives like pozzolana .These added constituents could contribute to improve the long-term performance of concrete based on these binders (Cassagnabère F et al, 2011; Imbabi M. S et al, 2012). To modify the properties of the cement other consituentes could be added. These additions, influence in a significant manner the chemical or physical properties of the resulting cement as well as the mortar and concrete based on alike binder. The substitution of a part of the cement weight in the form of an addition is aiming to improve the performances of based materials and to reduce the cost of the final product (Deboucha et al., 2012; Kerbouche et al.,2009).

Pozzolans are material that when combined with lime in the presence of water at a normal temperature results a product that is stable and insoluble component with specific properties (Caijun, 2003). Pozzolan incorporation leads to improve the workability, water retention and good particle homogeneity, together with a reduction in bleeding tendency at fresh state (Macleod, 2005). It reduces the heat of hydration; this effect will result in a significant reduction of shrinkage and limiting cracking (Baron et al., 1997; Macleod, 2005). Pozzolan also enhances internal cohesion by increasing the compactness of the cement paste and improves the strength and the durability of mortars in general at hard state (Macleod, 2005).

The purpose of the present research study is to evaluate the influence of the partial replacement of cement by natural pozzolans on the physical-chemical properties of the new formulated binder and the mechanical behaviour of mortars produced with this binary cement. Hence, the cement resistant to sulfate (CRS) is replaced by pozzolan at different proportions (0%, 2.5%, 5%, 7.5% and 10%). A control mixture (CT) based on CRS cement only and normalized sand was prepared for comparison purposes.

EXPERIMENTAL PROGRAM

MATERIALS

This research work involves the preparation of various compositions by replacing CRS with a pozzolanic addition with percentages of 0%, 2.5%, 5%, 7.5%, and 10%. The base clinker is delivered from Ain Kebira (Setif region east of Algiers), natural pozzolan was extracted from the Bouhamedi deposit quarry located south of Beni Saf (Wilaya of Ain Temouchent the western region of Algeria) and the gypsum is obtained from the deposit of Ain Kebira from Setif region. The gypsum is used as a setting regulator. The sand used for mortar mixtures is in compliance with EN 933-1 standard. Distilled water was used for this research project. The physical, chemical and mineralogical compositions of clinker, gypsum and pozzolan studied are summarized in Tables 1, 2 and 3.

Table 1. Physical Properties of the Pozzolan and Gypsum

	γ (g/cm^3)^a	ρ (g/cm^3)^b	SSB (cm^2/g)
Pozzolan	1.311	2.795	3600
Gypsum	2.204	2.747	5149

Table 2. Chemical composition of Clinker

Chemical compound	Percentage (%)
C_3S	53.19
C_2S	23.22
C_3A	03.55
C_4AF	15.84

Table 3. Cement blends mix proportions

Sample name	Pozzolan (%)	Clinker (%)	Gypsum (%)
CT	0	97	3
$CPZ_{2.5}$	2.5	94.5	3
CPZ_5	5	92	3
$CPZ_{7.5}$	7.5	89.5	3
CPZ_{10}	10	87	3

MIX DESIGN

To complete the experimental program, several tests were conducted on mortar specimens in order to evaluate the effect on the physical-chemical and mechanical properties of CRS cement blended with pozzolan. Five mortars were prepared according to the increasing dosages of pozzolan substitutions by the cement weight (0, 2.5%, 5%, 7.5% and 10%) (Table 4). Prismatic specimens (40×40×160) mm^3 were prepared according to EN 12350-2 standard. The samples were stored under the following curing conditions: the ambient temperature T equal to 20 ± 2 °C and a relative humidity (RH) of 50% ± 5 (see Table 5).

Table 4. Chemical oxide composition of clinker, pozzolan and gypsum

Element	Clinker (%)	Pozzolan (%)	Gypsum (%)
SiO_2	22.30	45.56	19.84
Al_2O_3	04.66	15.57	06.98
Fe_2O_3	05.20	08.60	03.21
CaO	65.26	14.41	27.82
MgO	01.32	04.34	08.46
SO_3	00.60	00.18	28.45
LOI	00.30	09.80	01.02
Na_2O	00.17	/	00.15
K_2O	00.13	/	01.13
Cl	/	/	00.04
CaO free	01.13	/	/
R.ins	00.18	/	/

Table 5. Physical and mechanical properties of studied cement blends

Properties		CT	$CPZ_{2.5}$	CPZ_5	$CPZ_{7.5}$	CPZ_{10}
ρ (g/cm^3)		3.20	3.19	3.17	3.16	3.14
SSB (cm^2/g)		3427	3478	3503	3553	3578
Normal consistency (%)		24.80	24.70	24.4	24.2	24.00
Initial setting time (min)		200	185	180	175	170
Final setting (min)		270	250	245	245	240
Shrinkage (µm/m)		793	775	768	766	750
Swelling (µm/m)		268	256	250	218	216
Heat Expansion (mm)		0.50	0.50	0.5	1.00	1.00
Absorption (%)		6.15	6.10	6.00	6.00	5.84
Flexural strength (MPa)	2 days	4.55	4.00	4.00	3.90	3.90
	7 days	6.55	6.60	6.65	6.50	6.50
	28 days	8.00	7.9	8.40	7.75	7.75
Compressive strength (MPa)	2 days	20.88	17.35	19.03	17.40	16.15
	7 days	41.38	38.95	41.90	37.88	36.93
	28 days	62.18	58.10	60.55	57.20	56.45

RESULTS AND DISCUSSION

THE DENSITY

Fig. 1 shows the effect of the pozzolan addition on the physical properties of the mortars such as the density. It could be noted that the different types of mortars studied were lower in density compared to the control one (CT). The mix sample CPZ10 shows a slightly lower density (3.14 g/cm^3) than the control cement CT (3.20 g/cm^3); the reduction is about 1.8 %.

Noting also, that the variation of the content of pozzolan in the mixtures has a striking effect on the bulk density of the binder, where there is a reverse relation, as this decreases while increasing the dosages of addition of mineral pozzolan for the two parameters, as mentioned in previous studies (Bouglada, 2008). This decrease can be attributed to the low density of the pozzolan because of its porous structure compared to the cement.

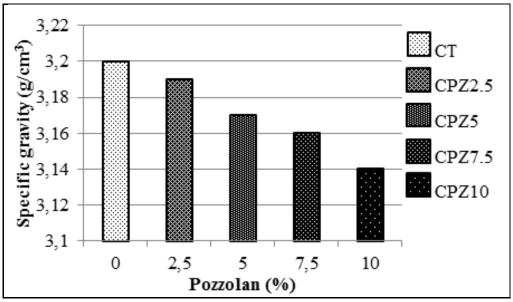

Fig. 1**.** Change in the specific gravity of CRS cement with pozzolan content

BLAINE SPECIFIC SURFACE AREA (S.S.B)

Fig. 2 shows the effect of adding pozzolan on the fineness (SSB) of blended cements studied. One can note that the S.S.B is proportional to the percentage of cement substitution by pozzolan; the cements studied with added pozzolan give greater values of fineness than the control cement mixture (CT). Sample CPZ10 has the higher value of SSB (3578 cm²/g), corresponding of an increase around 4.22% compared to cement (CT) with a SBB value of 3427 (cm²/g).

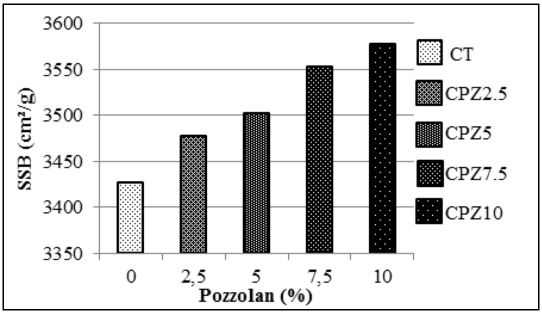

Fig. 2. Change of the Blaine specific surface area (SSB) of cements CRS with pozzolan content.

CONSISTENCY

The compositions of sole cement paste and cement blended with pozzolan show that the standard consistency varies inversely with the dosage of pozzolan; the higher the percentage of the addition, the lower the water requirement necessary to have a standard consistency.

The lowest consistency value was found for CPZ10 sample mix of around 24 % compared to the control one (CT) with 24.8 %. The reduction is probably caused by the decrease in the Ca/Si ratio; this ratio is lower by increasing the percentage of pozzolan (rich in silicon dioxide). The content of (CaO) with respect to that of (SiO_2) must therefore be the determining factor affecting the amount of water demand to achieve a normal consistency. The control cement (CT) without the addition has a ratio (Ca/Si) of more than the unity compared to the different cement mixtures with pozzolan (CPZ) tested; this results is in accordance the explanation given above.

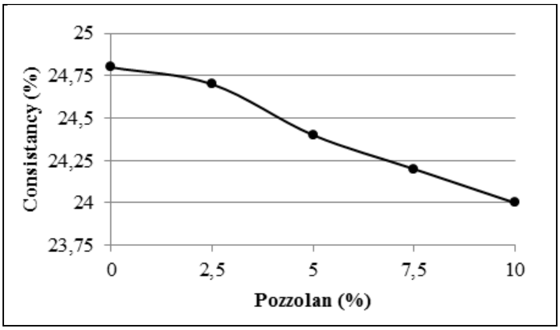

Fig. 3. Changes in the consistency of the cements studied versus the pozzolan content

SETTING TIME

From figure 4, it can be observed that the amount of pozzolan addition over a percentage of 5% has no significant influence on the setting time. It can be concluded that the increase of the fineness of the pozzolan reduces the final setting time for all the cement blends studied. This reduction is due to the accelerating process of the reactions of cement hydration; once the pozzolan is believed to provoke a physical-chemical effect on the hydrates products. For pozzolan contents over 5 % the improved setting time could be attributed to the higher dosage of pozzolan substitution that is promoting pozzolaninteracts with the hydration phases. This leads to the formation of mono or hemicarboaluminate hydrates enhancing the process of hardening of cement blends mixtures and strength development at early ages.

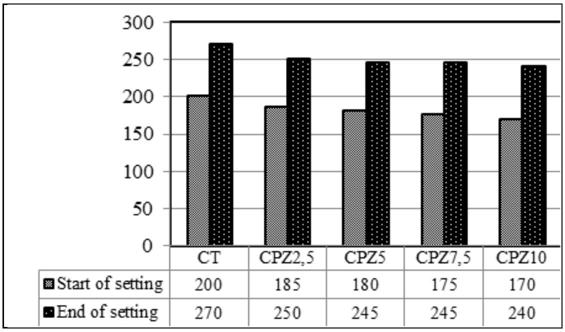

Fig. 4. The setting time versus pozzolan content
for the different blended cements (CRS and pozzolan)

SHRINKAGE AND SWELLING

It can be noted from Fig. 5, that the mortars made with different types of cement studied present a lower shrinkage than those of the control cement (CT). Indeed, the lower value is recorded for the mortars with 10 % pozzolan CPZ10 cement, this was of the order of 750 µm/m, 5.42 % lower than that of the control cement CT (793µm/m); The same trend is noticed regarding the swelling, hence there is a difference of about 19.4 % between the based pozzolan cement mortars CPZ10 (216 µm/m) and the control cement (268 µm/m). There is an inverse relationship between the ratio of pozzolan and shrinkage as well as for swelling (Fig. 5 and 6). The drying shrinkage and the swelling of the water are linked essentially to the mineralogical composition of the clinker and mainly due to the amount of C_2S in the cement matrix. The amount of C_2S in the cement depends on the percentages of additions incorporated; the higher is the percentage of addition, the greater is the amount of C_2S and therefore leads to the reduction of swelling and limited shrinkage.

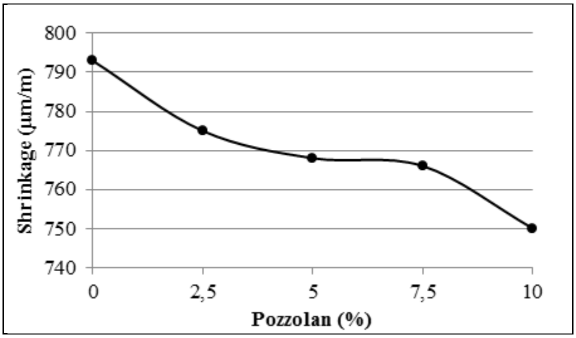

Fig. 5 Influence of pozzolan contents on the shrinkage for the different studied cements (CRS and pozzolan)

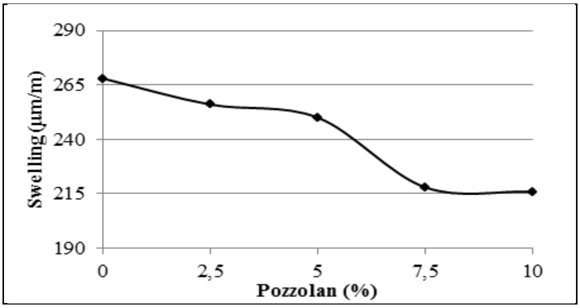

Fig. 6. Influence of pozzolan contents on the swelling for the different studied cements (CRS and pozzolan)

ABSORPTION

Fig. 7, shows the changes in water absorption property as a function of pozzolan content. The results obtained from the cement-based mortars with pozzolanic addition are comparable with those based on the control cement (CT). But, there is a reduction in the rate of water absorption due to the presence of pozzolan. The lowest absorption value was registered for the mixture (CPZ10) resulting in a reduction of approximately 5% compared to the results obtained by the mortars produced with the control cement (CT). There is an inverse proportion between the absorption and the pozzolan content; this result can be explained by the decrease in size of the capillary pores through the presence of pozzolan in the cementitious matrix, which means that the pozzolan ensures a very good seal making more compact and impermeable cement matrix.

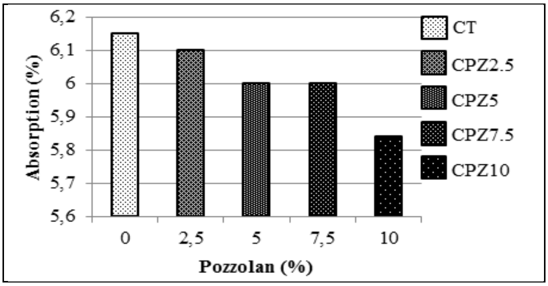

Fig. 7. Change in absorption for the different mortars studied (CRS and pozzolan)

FLEXURAL STRENGTH

Fig. 8, illustrates the effects of the pozzolan content on the flexural strength for mortars at 2, 7 and 28 days.

At the very early age (2 days), it can be noticed that the reference mortars gave higher flexural strengths than those with pozzolan mortars. At seven days of age, all mortars have very similar flexural strength. Indeed, at 28 days of age, the pozzolan mortars loss of the flexural strength is appreciated; except for mortars (CPZ5) with 5 % pozzolan, where an increase of resistance of around 5 % compared to control mortars is obtained. So, the percentage of 5 % pozzolan addition is the optimal dosage to be considered in cement composition for pozzolan based cement in this case.

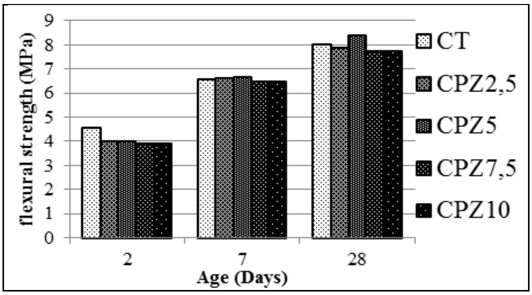

Fig. 8. Change of the flexural strength of the mixtures studied

COMPRESSIVE STRENGTH

Fig. 9 shows the change of the compressive strength with pozzolan contents at 2, 7 and 28 days.

In general, a normal development of mechanical compressive strength is noticed with the age of hardening at 2, 7 and 28 days. This may be due to the change in the hydration kinetics of mineral C_3S and C_2S. These are the two main minerals that ensure the development of mechanical resistance in the short and medium term (Baron et al., 1997).

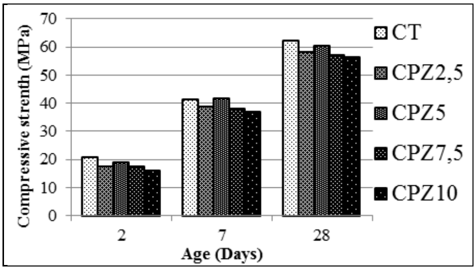

Fig. 9. Change of the compressive strength of the mixtures studied

The analysis of the evolution of the mechanical compressive strength shows that pozzolan mixtures have slightly lower strengths than those of the control mortar (CT). This occurs because pozzolan has slower kinetics hydration process by reacting with portlandite ($Ca(OH)_2$) at all ages 2, 7 and 28 days. The results obtained so far can lead us to believe that the benefit effect of pozzolan addition could be attended at a longer hardening state 90 days or beyond. For the case of pozzolan based mortars at a dosage of 5 % (CPZ5) the values of resistances obtained are nearly similar to reference mortar strengths (CT), 60.55 and 62.18 MPa, respectively. Again, it can be noticed that the lowest value of strength for pozzolan mortars is given for high dosage of 10 % pozzolan addition among all the mortars studied.

CORRELATION BETWEEN THE FLEXURAL AND COMPRESSIVE STRENGTH

In the literature, several empirical formulas have been proposed to link these strengths, most of the following forms:

$$R_f = kRc^a \tag{1}$$

where: R_f – flexural strength, Rc – compressive strength, K and a – coefficients.

Kerbouche et al., (2009) proposed in their study on the influence of mineral additions on the mechanical strength of mortars, nonlinear correlations connecting the flexural and compressive strength, these correlations are considered for binary and ternary mortars where:

Binary mortars:

$$R_f = 0.61(Rc)^{0.73} \tag{2}$$

Ternary mortars containing CPA / PZN / CF

$$R_f = 0.48(Rc)^{0.73} \tag{3}$$

Ternary mortars containing CPA / PZN / FS

$$R_f = 0.55(Rc)^{0.63} \tag{4}$$

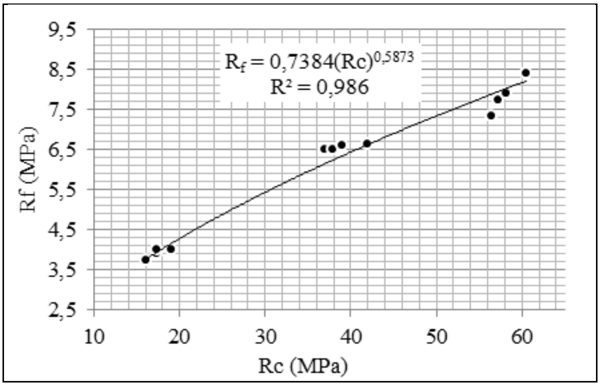

Fig. 8. Correlation between the flexural strength
and the compressive strength for binary mortars

For our case study, we obtain a good correlation of nonlinear type in the case of binary mortars (Fig. 10), the correlation is in good agreement with those proposed by other researchers (Kerbouche et al., 2009) and it is proposed as follows:

$$R_f = 0.7384(R_c)^{0.5873} \qquad (5)$$

$R^2 = 0.986$

CONCLUSION

In the light of the results obtained in the present research study to see the effect of natural pozzolana on the behaviour of mortars based on the this addition and CRS cement, the following conclusions could be drawn;

The percentage of natural pozzolan used as an addition, has a significant effect on the surface area for the cement composition obtained.

The good physical and mechanical properties are obtained for an optimal dosage of 5% natural pozzolan, with a specific surface area (SSB) well defined; mainly, limited shrinkage, acceptable flexural and compressive strengths.

A nonlinear correlation formula could be proposed in the present study for binary cement relating the flexural and the compressive strength.

In general, the effect of pozzolan substitution on the properties of cement binder compositions is beneficial and promising venture for the cement industry to limit emissions as for environment preservation, further, to the economic energy purposes gained in the reduction of clinker consumption.

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