International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.06 pp 392-399, 2016

The Effect of Pozzolanic Addition on Expansive Portland Cement

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Abstract : Laboratory experiments were conducted to investigate the effects of local natural pozzolan in Nador (North of Morocco) on certain expansive cements containing a great content of f-CaO. The expansion was caused by high rate of free lime in cements. The reaction of natural pozzolan with f-CaO already existing in cement or liberated during the hydration process modifies some properties of these blended cements. In this study a portion of expansive cements was replaced by natural pozzolan, with three different dosages (15%, 25% and 35%). The results obtained of natural pozzolan on expansive cements exhibited much less expansion, and great reduction ofheat of hydration. Moreover, we obtain satisfactory compressive strength values.
Keywords : natural pozzolan, expansive cements, free lime, blended cements.

Introduction and Experimental:

The use of mineral admixtures as partial replacement for Portland cement in blended cements and concrete has become almost unavoidable due to energy-saving concerns and other environmental considerations[1,2,44]. So more than 3,8 billion tonnes of cement is produced annually worldwide. One tonne of cement results in approximately one tonne of CO_2 and requires about 4 GJ of energy[3,4]. Moreover, around 5-8 % of global CO_2 emissions is due to cement manufacture and makes it the third most polluting activity of mankind[5].The energy consumption is hence more than 2500 TWh/year[6,45]. Recently to compensate for high energy consumption and CO_2 emissions, the use of additives as partial substitutesfor cement, like pozzolan(PZ), silica fume (SF), fly ash (FA), palm oil fuel ash (POFA), metakaolin (MK) , rice husk ash (RHA) or geo-polymer is necessary to decrease the CO_2 emissions and increase the durability of mortar and concrete[7,8,39,41,42,43].

Natural pozzolans, owing to their abundance and relatively low costs, present considerable potential for employment in the construction industry[9].

The objective of this investigation is to study the influence of natural pozzolans on the properties of cements containing high content of f-CaO.

Adding natural pozzolans is one of the methods to reduce, eliminate or transform f-CaO, which is responsible for the loss of mechanical strengths and the expansion of cement and concrete[10,11].

This present paper focuses on the hydration evolution of binary blended Portland cements containing a high rate of f-CaO and natural pozzolan. Six different cements mixtures were prepared by adding pozzolan up to 35%. The produced binder cements were tested by determining their initial and final setting times, water demand, expansion, heat of hydration and compressive strength at 2, 7, 28 and 90 days.

The clinkers and gypsum obtained from the cement manufacturer of Lafarge-Holcim Oujda-Morocco. We prepared two reference cements designed by PC_1 and PC_2 containing 4,2 and 5,24% of f-CaO respectively.Their expansions measured according to the Le Chatelier process, were well above the maximum accepted value of 10mm. the expansion values were 18 and 34,9mm respectively.

For all cementsprepared, the clinker and gypsum were ground together at the same fineness(around365±5 m^2/kg)with the proportions 95:5 by weight respectively.

Three cements were prepared in the laboratory of the manufacturer by adding to the Portland cement PC_1 a pozzolan with three dosages 15, 25 and 35%. These cements were designated by $BC_1$15, $BC_1$25 and $BC_1$35 according to the pozzolan content present in blended cements.

$BC_2$15, $BC_2$25and $BC_2$35 were three blended cements, designated according to the amount of pozzolan present in the reference Portland cement PC_2.Fineness level of all blended cements was similar (around 450 ±5 m^2/kg).

The uncombined lime in the clinker was determined by acidimetric method using $(CH_2OH)_2$[12].

Standard consistency and setting times of cements were determined using aVicat apparatus according to the European standard EN 196-3[13]. The expansion was measured according to the LeChateliermethod[13]. Compressive strength measurements were conducted at the ages of 2, 7, 28, and 90 days on mortar specimens (dimensions 40× 40 ×160) prepared and tested in accordance with the European standard EN 196-1[14].

The heat of hydration measurements were conducted- according to the European standard EN 196-9-by semi-adiabatic calorimetry, also known as the Langavantcalorimeter[15].

The reactive silica (RS) of pozzolan was determined according to the established procedure of chemical treatment of the samples with concentrated HCl(36-37%w/w) and KOH in accordance with the European standard EN 196-2[16].

According to the standard specifications of ASTM C618[17], the strength activity index is defined as the ratio of the compressive strength for a mortar with 20% pozzolan replacement for cement by mass to the compressive strength of a control mortar. For the control mortar, the water-to-binder ratio by mass (w/b) equals 0,485, and water in the test mortar is regulated to give the same consistency (flow) as the control mortar.

Results and Discussion:

The chemical compositions of clinkers K_1 and K_2 obtained from the cement manufacturer of Lafarge-Holcim, Oujda-Morocco are shown in table1, andtheir potential compositions are given in table2, according to Bogue. These clinkers K_1 and K_2were used to preparetwo reference cements designed by PC_1 and PC_2 respectively.

Table1: chemical compositions of clinkers K_1 and K_2

clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	f -CaO
K_1	20,41	5,67	2,61	64,89	2,74	1,39	1,33	4,2
K_2	19,91	5,72	2,64	64,94	2,65	1,31	1,32	5,24

Table2: Bogue potential compositions of clinkers K_1 and K_2

clinker	C_3S	C_2S	C_3A	C_4AF
K_1	50	21	11	8
K_2	49	21	11	8

Table 3: Chemical and Physical properties of natural pozzolan

Requirements	Natural pozzolan PZ
$(SiO_2+ Al_2O_3+ Fe_2O_3)\%$	49,17 + 13,56 + 6,88
$SO_3\%$	0,07
CaO%	8,30
MgO%	2,96
$K_2O\%$	2,45
$Na_2O\%$	1,03
$TiO_2\%$	2,52
$P_2O_5\%$	0,46
$Mn_2O_5\%$	0,15
Moisture content %	2,80
Loss on ignition LOI %	8,38
Strength activity index, at 28days	94,7
Reactivesilica RS %	33,32

Table 4: mineralogical identification of natural pozzolan

Minerals	Content %
Amorphous phase	25
calcite	11
dolomite	14
feldspar	19
hematite	0,5
magnetite	1
mica	3
pyroxene	18
quartz	6
total	**97,5**

The chemical compositions of clinkers and the natural pozzolan were conducted by X-ray fluorescence.

The chemical and physical properties of natural pozzolan used in the cement manufacturer of Lafarge-Holcim Oujda-Morocco are presented in table 3, and the mineralogical analyses obtained from X-ray diffraction (XRD) technique are determined in table 4.

1. Normal consistency

The test results given in table5showed that the water-to- cement ratio required for normal consistency of reference Portland cements increased with the increase of free lime. This could be an indication to the increase of water consumption caused by the transformation of f-CaO into calcium hydroxide. So, when the water reacts with the free lime, it will be absorbed rapidly to form the hydroxide of lime[18] of this fact the demand in water increased to realize the normal consistency of the cement paste.

Table 5: water demand of the blended cements and reference Portland cements

Cement	Water Demand
PC_1	0.26
PC_2	0.27
BC_115	0.29
BC_125	0.31
BC_135	0.32
BC_215	0.30
BC_225	0.33
BC_235	0.34

Compared to the PC_1 and PC_2, the corresponding blended cements showed higher water demand to develop their standard consistency. On the other hand, for all blended cements, the water consistencyincreasedwith the percentages of replacement of pozzolan, it could attributedto thehigh specific area of blended cements and the very small pozzolan particles[19],which when mixed with water may form agglomerations and are soon covered with a gel like layer. Water may become enclosed in this layer[20], which has been suggested as the cause of the increase of water consumption.

2. Setting times

We notice, as presented in table 6 that for the reference cements, the initial and the final setting times increased with the increase of the percentage of the free lime, but they were lower with the pozzolan addition in blended cements compared to their reference cements.

Table 6: Setting times of the blended cements and reference Portland cements

Cement	Initial setting times (mn)	Final setting times (mn)
PC_1	160	250
PC_2	170	260
BC_115	154	242
BC_125	130	222
BC_135	110	196
BC_215	160	250
BC_225	137	226
BC_235	120	208

This phenomenon could be explained by the following mechanism:

In contact with water, the accelerating effect of C_3A begins earlier[21-22], but the action of the hydroxide of calcium involves the transformation ofC_3A into C_4AH_{13}. The formation of C_4AH_{13} as a gel retards hydration of cement[23,24,36]. So the role played by $Ca(OH)_2$ is to prolong the cement setting, which it is liberated during the hydration process of f-CaO,C_3S and C_2S. However, the pozzolan addition in blended cements reduces the hydroxide of lime and contributes to the accelerated hydration of these cements.

3. Le Chatelier expansion

In fig.1 and fig.2, the expansion increased with the increase of f-CaO content and decreased with the increase of pozzolan replacement.

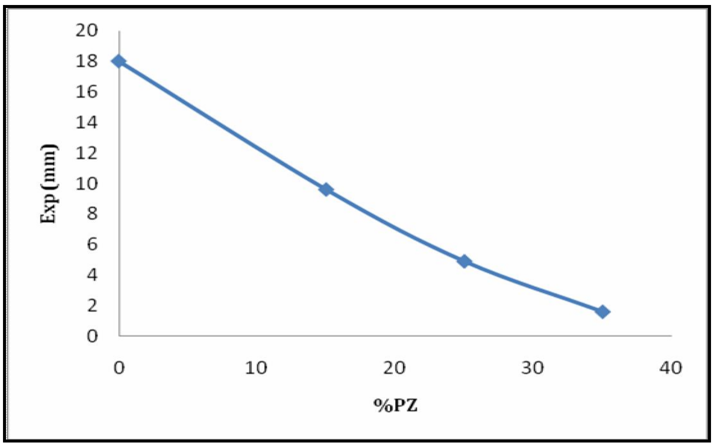

Fig.1: Effect of pozzolan content on expansion of blended versions BC_1

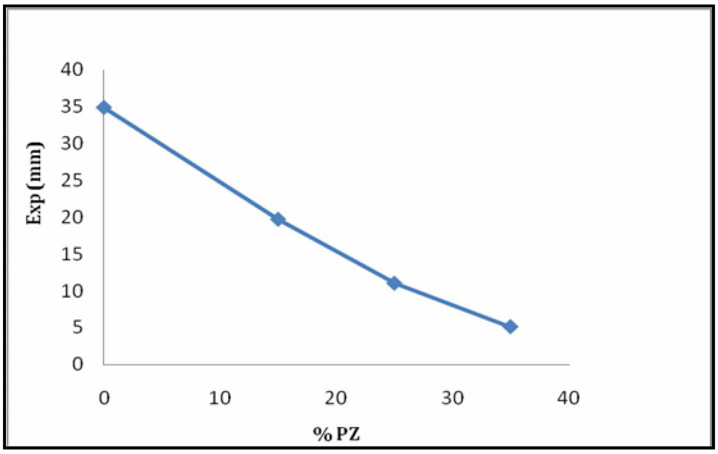

Fig.2: Effect of pozzolan content on expansion of blended versions BC_2

f-CaOreacts with water so speedily, and releases a rapid increase of volume(about 1,8 times) due to the formation of $Ca(OH)_2$which is accompanied with an effective expansion[18-25].Loss in expansion of all blended cements increased with pozzolan addition due to lime fixation as a result of pozzolanic reactivity of these cements[26]. The reactive silica in pozzolan is adominant parameter to mitigate oreven eliminate expansion, by consuming more portlandite at early ages of testing.

4. Compressive strengths

The results of compressive strength determined by mechanical tests are given in table 7.Concerning the reference cements PC_1 and PC_2, the decrease of the compressive strength when the free lime increased could be explain by the high undesired expansion of these cements, which would result the creation of the fissuring in low stress[18-37].

Table 7: compressive strength of the blended cements and reference Portland cements

Cement	Compressive Strength (MPa)				Compressive Strength (MPa; normalized to PC content)			
	2days	7days	28days	90days	2days	7days	28days	90days
PC_1	16,7	31,60	40,40	46,70	16,7	31,60	40,40	46,70
PC_2	15,46	27,10	32,10	41,10	15,46	27,10	32,10	41,10
$BC_1$15	14,83	28,75	38,98	47,08	17,44	33,82	45,85	55,38
$BC_1$25	20,45	32,63	39,73	48,28	27,26	43,50	52,97	64,37
$BC_1$35	16,63	25,48	34,90	46,60	25,58	39,2	53,69	71,69
$BC_2$15	14,10	26,20	32,43	44,95	16,58	30,82	38,15	52,88
$BC_2$25	15,04	26,80	33,19	46,28	20,05	35,73	44,25	61,70
$BC_2$35	15,30	25,43	31,90	44,65	23,53	39,12	49,07	68,69

On the other hand, the natural pozzolan especially its reactive silica is effective in reducing the concentration of calcium hydroxide[27], and because of R-Silica activation, the microstructure of cement paste has been modified. The hydration products, especially CSH together with C_2ASH_8 are distributed more homogeneously filling the pores[28-29], thus contributes to a greater extent to the development of the mechanical resistance of these blended cements[30,31-39]; some what the strengths could be improved by their highfinenesses[32,33-38,40].

5. Heat of hydration

Results as illustrated in fig.3and fig.4, showed that the higher the replacement of pozzolan, the lower the hydrationheat of the blended cements and the higher the rate of f-CaO, the greater the heat of hydration.

f-CaO reacts with water so speedily and so exothermally to form the calcium hydroxide[18-34], which is responsible of the increase of hydration heat, however, when natural pozzolan is present in aqueous solution, the SiO_2 will react with water to form a saturated solution of monosilicic acid and releases an endothermic reaction[35], which alters the heat evolution and reduces the heat of hydration in any ages.

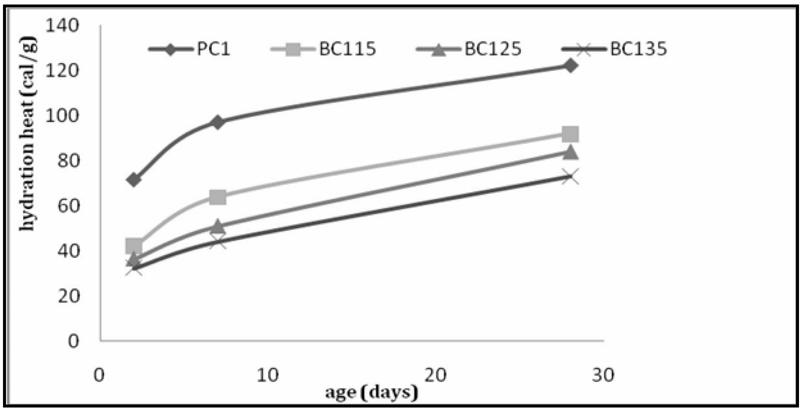

Fig. 3: Head of hydration of reference Portland cement $PC_1$and blended versions BC_1

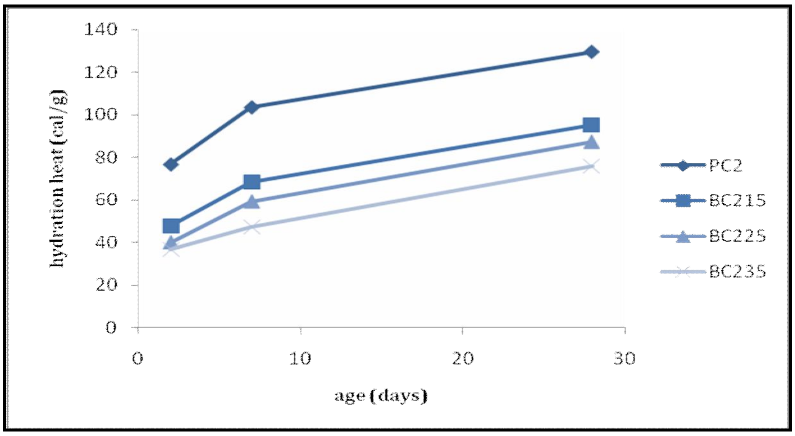

Fig.4: Head of hydration of reference Portland cement $PC_2$and blended versions BC_2

Conclusion:

Based on the test results of this study, the following conclusions can be drawn:

- The expansive cements containing high amount of f-CaO causes a great expansion, and give rise to water demand and setting times when the rate of free limeis increased. Besides, the high content of f-CaO hampers the development of mechanical strengths of these cements and because of the exothermic reaction of f-CaO with water; the rapid growth of their hydration heat is well concretized at earlier ages.
- The use of pozzolanic additives in partial substitution of expansive cements may be an efficient way to prevent these cements from an excessive expansion, and raise their mechanical performances. Moreover, the pozzolans when added to expansive cements reduce neatly the heat of hydration.

Acknowledgements:

The authors would like to thank the personnel of quality control department of Lafarge-Holcim Oujda-Morocco for the technical assistance, especially Mr. J.ALLA.

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