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Morrocan composite cement with minor addition of fly ash

I. ELKHADIRI*
Instituto de Ciencias de la Construcción Eduardo Torroja-CSIC,Dpt. Síntesis, Caracterización y Estabilización de Materiales, Serrano Galvache, s/n., 28033 Madrid, Spain
E-mail: ielkhadiri@ietcc.csic.es; elkimad@yahoo.fr

A. DIOURI, A. BOUKHARI
Laboratoire de Chimie du Solide Appliquée,Laboratoire Associe Francophone 501, Faculté des Sciences, Université Mohammed V-Agdal, BP. 1014, Avenue Ibn Battouta, 10000 Rabat, Morocco

MY. Y. BENARCHID
Laboratoire TECSEN,UMR6122-CNRS, Case 251, Faculté des Sciences et Techniques de St Jérôme, Université Aix-Marseille III, Avenue Escardille Normandie Niémen, 13397 Marseille, France

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In order to lower the consumption of natural raw materials, to save fuel energy for clinker production and to make appreciable reduction of CO_2 emission, the Morrocan plants cements become to produce some composite cements types by adding some components. This paper describes the production of composite cements by intergrinding clinker, gypsum and limestone with a minor addition of fly ash up to 10%. Physical and mechanical properties are discussed, and the main result is that the addition of fly ash with low quantity acts as grinding agent by reducing the required time to obtain the same percentage of particles retained on an 80 μm sieve compared to the cement without addition of fly ash. From 28 days to 90 days, the compressive strength increases rapidly in the case of cement with a minor addition of fly ash.

1. Introduction

The addition of limestone during the grinding of Portland clinker has become generally a common procedure in all Morrocan cement manufactures cements. The Limestone improves several properties such as compressive strength, durability, and workability and favours a wider size distribution [1–5]. Many investigations about the effect of limestone on the hydration of different phases of Portland clinker especially C_3S and C_3A have indicated that, the limestone accelerates the rate hydration of C_3S producing calcium hydroxide and modifies the Ca/Si ratio of C-S-H, in addition the limestone causes formation of calcium carboaluminates as results of the reaction with C_3A [6–10].

The Morrocan standard NM1001F004 [11] currently applied defines different categories of cement, a category being characterised by its composition and different classes. Each class is characterised by the corresponding compressive strength. There are two categories of cement depending on the properties of clinker contained (excluding gypsum): pure Portland cement contain at least 97% of clinker (CPA), and compound cements (CPJ) contain at least 65% of clinker, which means less than 35% secondary which is currently limestone.

During the last years, the use of fly ash like secondary constituent attracts the attention of some Morrocan manufactures cement. The cost of this waste industrial product and its transport prevent its utilisation and the producers prefer to use it like minor addition in the presence of limestone, for producing composite cement in accordance with the Morrocan standard.

This paper, therefore, describes an experimental program on the composite cements obtained by adding fly ash like minor constituent to the mixture of clinker, gypsum and limestone, and to study there physical and mechanical behaviour.

2. Experimental and results

The chemical composition of used materials (clinker, limestone and fly ash), carried out by fluorescence X-ray analysis is listed in Table I. The purity of used gypsum is around 84.52%, with 39.31% SO_3 consistence and 0.0075% Chloride.

*Author to whom all correspondence should be addressed.

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TABLE I Chemical compositions of used materials (% by weight)

Oxide	Clinker	Limestone	Fly ash
SiO_2	21.14	19.96	47.26
Al_2O_3	4.98	1.97	27.63
Fe_2O_3	3.67	3.64	4.35
CaO	64.52	39.37	8.11
MgO	1.22	0.61	2.19
SO_3	1.86	0.31	–
K_2O	0.53	0.34	0.83
TiO_2	0.47	1.02	1.45
MnO	0.09	0.04	0.14
Na_2O	0.01	0.02	0.01
P_2O_5	0.6	0.72	0.93
CaO_{free}	0.48	–	0.00
LOI	0.71	31.78	4.58

The mineralogical composition of clinker calculated by the Bogue formula is listed in Table II. The X-ray diffractogram of limestone (Fig. 1) shows that the major crystalline components of limestone are calcite ($CaCO_3$) and quartz (SiO_2). The fly ash difractogram (Fig. 2) shows that the crystalline phases present are quartz (SiO_2), mullite ($Al_6Si_2O_3$), magnetite (Fe_3O_4) and hematite (Fe_2O_3).

TABLE II Mineralogical composition of used clinker (Bogue calculation)

Phase	C_2S	C_3S	C_3A	C_4AF
% by weight	19.71	54.2	7	11.16

TABLE III Particle size distribution of fly ash (% by weight)

Range dimention	>45 μm	>63 μm	>80 μm	>100 μm
Observed%	38.29	20.35	13.35	8.45

The size distribution expressed as weight fraction in the range 45–100 μm, obtained with Alpine zigzag classifier, is showed in Table III. The pozzolanic test for fly ash was determined according to European standard EN-196-5 [12]. Fig. 3 explains the reaction between $Ca(OH)_2$ liberated from clinker hydration and glassy phases of fly ash. It can be see that when fly ash is added to cement, the concentration of OH^- ions in the aqueous solution in contact with hydrated cement decreases and becomes under the concentration curve of those ions in the saturated solution at 40°C after 8

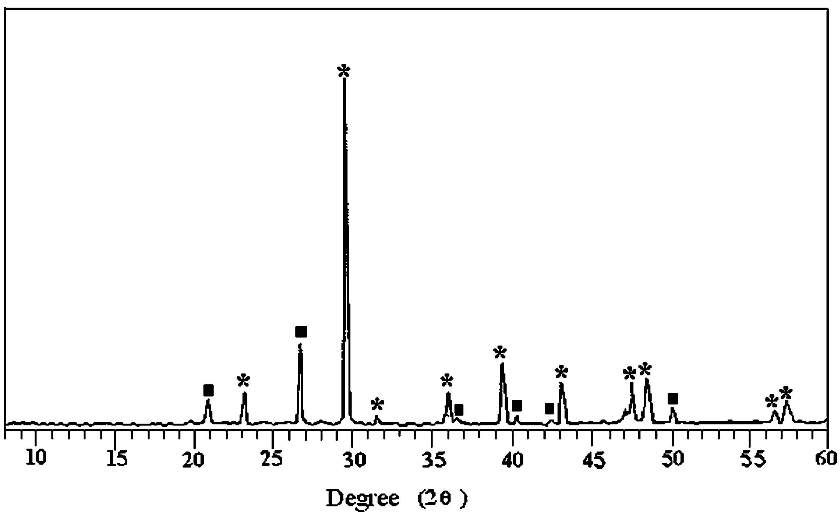

Figure 1

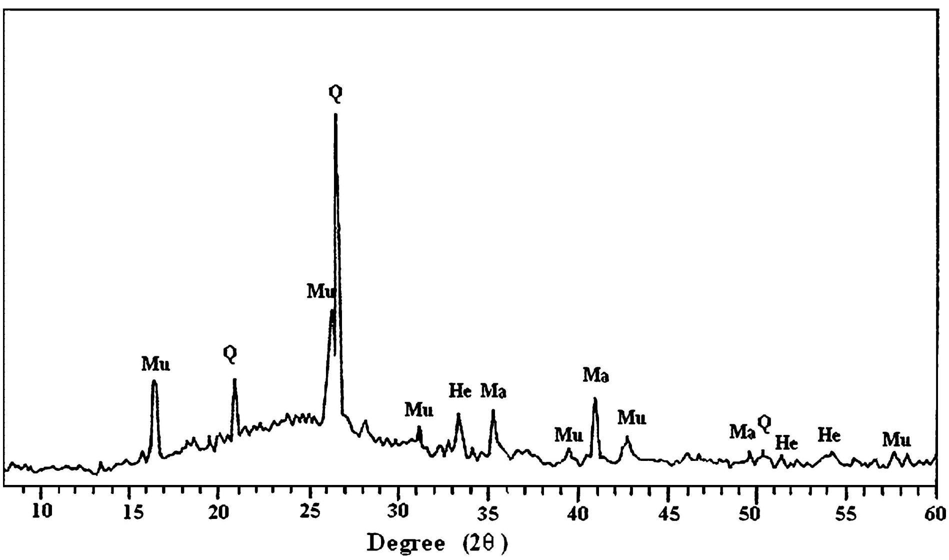

Figure 2 X-Ray diffraction of fly ash. Mu: Mullite ($Al_6Si_2O_{13}$), Q: Quartz (SiO_2), He: Hematite (Fe_2O_3), Ma: Magnetite (Fe_3O_4).

TABLE IV Compositions of cement mixtures samples (% by weight)

Mixtures	Clinker	Gypsum	Fly ash	Limestone	Above 80 μm	Grinding time (h:min)
A_0	70	3	0	27	5.5	2:50
A_1	70	3	5	22	5.5	1:20
A_2	70	3	10	17	5.5	1:00

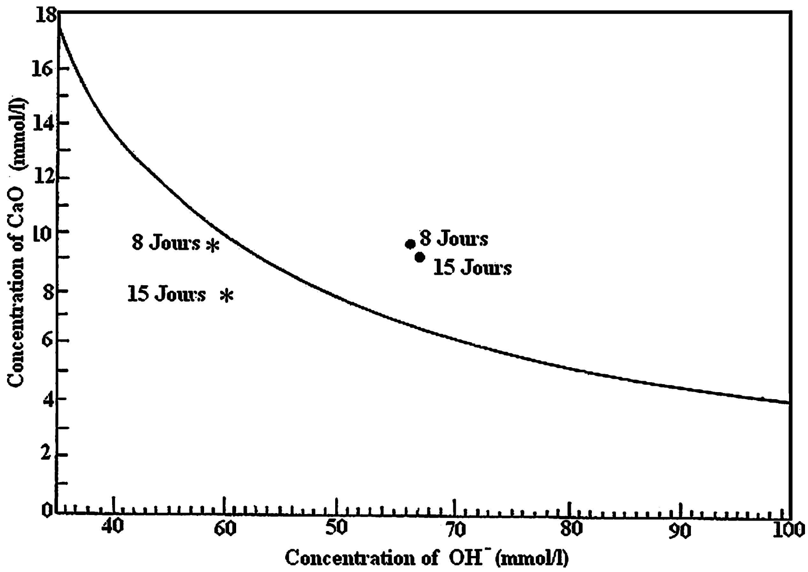

Figure 3 Curve of pozzolanicity test. •: before adding fly ash, ∗: after adding fly ash.

days. This result means that the fly ash used has a good pozzolanic activity.

A ball mill is used for producing different composite cements. All materials in each type of cement were interground together from the beginning until 5.5% retained at 80 μm. Table IV gives summarised all prepared samples and grinding time required to obtain the same retained at 80 μm.

Vicat probe and Vicat needle apparatus, determine respectively the physical properties for the fresh paste of prepared cement as water requirement and setting time. Table V gives a water requirement and setting times of studied samples. The mortars bars ($4 \times 4 \times 16$ cm^3) were made by mixing of each composite cement with sand and water in proportion (1/3/0.5) respectively. The specimens are transferred to the moisture room (20±1° C, and 96% relative humidity), after 24 h the mortar specimens are demoulded and then cured for 2, 7, 28 and 90 days under water. The mechanical properties (compressive and flexion strengths) are performed at those times, and the results are showed in Table VI and plotted in Figs 4 and 5.

TABLE V Water requirement and setting times of substituted Clinker-Fly ash cements

		Setting time (h:min)	
Samples	Water demand (wt%)	Initial	Final
A_0	24	3:40	5:15
A_1	25	3:50	6:40
A_2	27	4:25	7:30

TABLE VI Compressive and flexion strengths of tested composite cements (MPa)

	Compressive strength (MPa)				Flexion strength (MPa)			
Samples	2d	7d	28d	90d	2d	7d	28d	90d
A_0	16	27.5	39	46	3.7	6	8	8.8
A_1	15.7	25.8	38.7	48	3.4	6	7.8	8.6
A_2	12.5	25	38.5	52	2.6	5	7.8	9

3. Discussion

During the preparation of different types of composite cements by intergrinding clinker, limestone, gypsum and fly ash together, the grinding time is significantly reduced by adding fly ash in mixtures for the same retained sieve at 80 μm (Table VI). This result indicates that the fly ash act as grinding agent. The incorporation of fly ash yield rapidly to the desired fineness and consequently an energy saving is obtained.

This result is agree with the investigation carried out by Bouzzoubaâ *et al*. [13], who have indicated that for the blended cements, when the fly ash were ground together with clinker and gypsum, the time required to obtain the same Blaine fineness as the laboratory-produced Portland cement was reduced. Opoczky [14] has studied a series of composite cements, which contain at least two further components in addition to clinker and gypsum. That, the grindabilities of the composite cements are governed by the grindabilities of the individual components, but in ever case turned out to be better than the individual grindibility of the clinker, and the presence of fly ash had a more favourable effect on the grindibility of the composite cement. Also Alsted *et al*. [15] have mentioned that the combined grinding

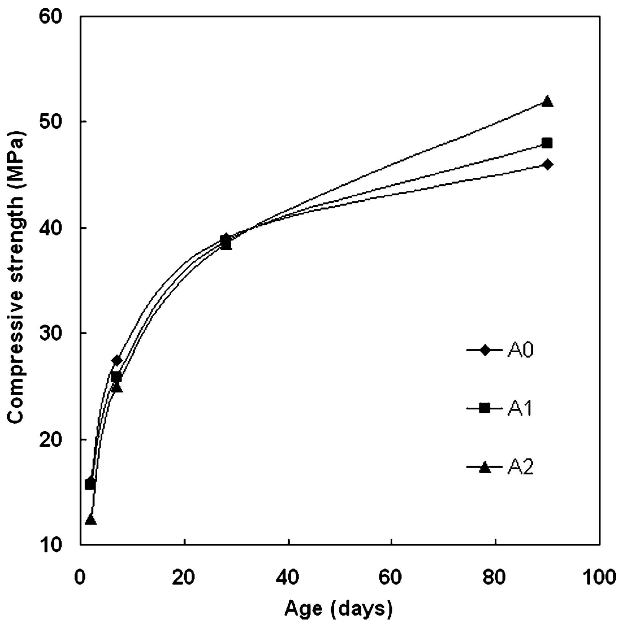

Figure 4 Compressive strength of different composite cements (MPa).

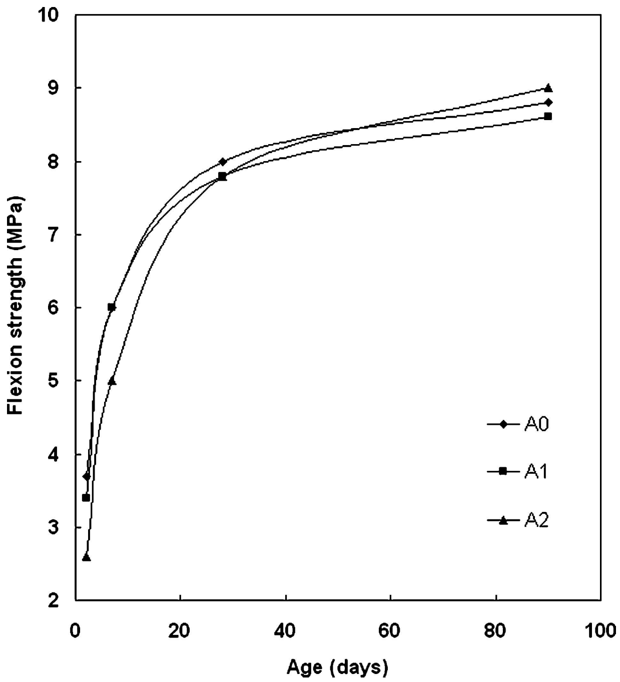

Figure 5 Flexion strength of different composite cements (MPa).

appears to be the optimum solution, possibly owing to the mutual abrasion of fly ash and clinker than the separate grinding, and the reason for this is that generally, when grinding materials of different hardness or toughness, a saving in energy is obtained.

From Table V, the incorporation of fly ash like minor addition in Morrocan composite cements has no effect on the water requirement for attain a paste of normal consistency, but the setting times are generally prolonged in the case of composite cement with fly ash. This extension of setting time is due generally to the decrease in the amount of $CaCO_3$ which is the major crystalline compound in limestone: the $CaCO_3$ accelerates the hydration of C_3A and C_3S yielding to the formation of carboaluminate hydrate and C-S-H [1], which improve the setting time. Therefore, the replacement of limestone by fly ash decreases the amount of those hydrate compounds. In addition, according to the ASTM specification [16], and the composition of fly ash used in this work, we can classified it into F class, and it's well recognised that low-calcium fly ash has an effect on cement hydration and reduces the heat evolution and retards the setting time [17–20].

The mechanical properties, compressive and flexion strengths, of the composite cements, which contain 70% of clinker (A_0, A_1 and A_2), show that in the first 28 days, the composite cement without fly ash has a better performance than the composite cements with fly ash (A_1 and A_2). This result is due to the amount of limestone in A_0: the particles of limestone file between the grains of clinker and the $CaCO_3$ accelerates the hydration of C_3A and C_3S occurring ettringite, carboaluminate hydrate, monosulfoaluminate and C-S-H, which contribute to the improvement of the mechanical properties. From 28 days on ward up to 90 days the compressive strength increases rapidly in the case of A_1 and A_2, due to the acceleration of pozzolanic activity. However, if we calculate the rate of compressive and flexion strength gains ($\frac{R_c^{Ai}}{R_f^{A0}}$ and $\frac{R_f^{Ai}}{R_f^{A0}}$) (with i = 1 and 2) at 90 days, we find that the composite cement A_1 and A_2 gave higher mechanical strength ($\frac{R_c^{Ai}}{R_f^{A0}}$ and $\frac{R_f^{Ai}}{R_f^{A0}}$ are ≥ 1). This implies that the pozzolanic activity begins after 28 days and contributes to strength development, and compensates the partial substitution of filler calcaire in composite cement containing low percentage of fly ashes. The explanation of this result is difficult, but we can attribute this evolution to the porosity effect, when intergrinding clinker, gypsum, limestone and fly ash, there is a mutual interaction of individual components. The influence of harder, to grind (clinker) is reduced and the mixture becomes rich of the small clinker fraction in the same time the shape morphology of fly ash particles is affected, because the mechanical treatment of fly ash breaks down the glass phase, and the particle size distribution becomes widest and increases the homogeneity of the mixture. During the hydration the particles of $CaCO_3$ react with C_3A and C_3S leading to the liberation of more $Ca(OH)_2$ and the alkalinity of the system increase. The fine particles of fly ash provide additional nucleation sites, and the breaking down of the glass phases corrode easily by the presence of $Ca(OH)_2$ leading to the crystallisation of C-S-H gel on those sites. Therefore, the porosity becomes smaller than that of the composite cement without fly ash A_0 and obviously the mechanical strength increases.

4. Conclusion

The use of fly ash like minor addition up to 10%, in the integrinding stage gives an important energy saving during grinding and the extension of the setting time. The investigation on ternary cements based on clinker, limestone and minor addition of fly ash, showed a substantially strength gains in the period between 28 and 90 days, due to the acceleration of pozzolanic reaction by the mechanical treatment of fly ash in the grinding stage, which increases the number of precipitation sites for deposition of C-S-H gel.

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References

1 J. ZELIČ, R. KRSTWLOIČ, E. TKALČEC and P. KROLOM, *Cem. Conc. Res.* **29** (1999) 819.
2 T. VULK, V. TINTA, R. GABROVSĚK and V. KAUČIČ, *ibid.* **31** (2001)135.
3 J. PERA, S. HUSSON and B. GUILHOT, *ibid.* **21** (1999) 99.
4 L. OPOCEZKY, *Int. J. Iner. Proc.* **44** (1996) 99.
5 H. G. ELLERBROCK, S. SPUNG and K. KUHLMANN, *Zem. Kalk Gips* **43**(1) (1990) 13.
6 A. BACHIORRINI, A. FOURNIER, B. GUILHOT, A. MURAT, A. NEGRO and M. M. SOUSTELLE, in Proceedings of the 8th International Congress on the Chemistry of Cement, edited by FINEP, Rio de Janeiro, Sept. 1986, p. 376.
7 V. S. RAMANCHANDRAN, in Proceedings of the 8th International Congress on the Chemistry of Cement, edited by FINEP, Rio de Janeiro, Sept. 1986, p. 109.
8 *Idem.*, *Cemento* **83**(1) (1986) 13.
9 S. HUSSON, B. GUILHOT and J. PERA, in Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, 1992, p. 83.
10 C. VERNET and G. NOWORYT, in Proceedings of the 9th International Congress on the Chemistry of Cement, New Delhi, 1992, p. 430.
11 Norme Marocaine, Liants Hydrauliques, NM1001F004, 1986.
12 European Standard, Methods of testing cement; pozzolanicity test for pozzolanic cements EN 196-5, 1987.
13 N. BOUZZOUBAÂ, M. H. ZHANG, A. BILOUDEAU and V. M. MALHOTRA, *Cem. Concr. Res.* **28**(11) (1998) 1555.
14 L. OPOCZKY, *Zem. Kalk Gips* **3** (1993) 136.
15 H. C. ALSTED and F. L. SMIDTH, in Proceedings of the 7th International Congress on the Chemistry of Cement, edited by Septima (Paris, Sept. 1980) p. 72.
16 American Society for Testing and Materials, Specification of fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. ASTM C 618–78, 1978.
17 C. PLOWMAM and J. C. CABRERA, Mechanism and kinetics of hydration of C_3A and C_4AF Extracted from cement. *Cem. Conc. Res.* **14** (1984) 238.
18 D. G. MONTGOMRY, D. C. HUGHS and R. T. Z. WILLIAMS, *ibid.* **11** (1981) 591.
19 R. O. LAND and J. F. BEST, *Conc. Int.* **4**(7) (1986) 81.
20 G. G. CARETTE and V. M. MALHOTRA, in "CANMET Report 86-6E," edited by V. M. Malhotra, 1986.

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