



Mechanical behaviour of various mortars made by combined fly ash and limestone in Moroccan Portland cement

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Received 15 October 2001; accepted 24 April 2002

Abstract

Physico-chemical properties and mechanical behaviour of ternary cements made by Portland cement, fly ash and limestone are studied. The mixtures at various compositions of clinker, gypsum fly ash and limestone are intimately ground and compared to other compositions without fly ash. Blended fly ash cements are also studied. The results show that fly ash acts as grinding agent by reducing the required time to obtain the same percentage of particles retained on a 80- μm sieve as the standard cement. Fly ash cements lead to an important extension of setting time than limestone cements. The replacement of clinker by limestone gives better mechanical strengths than the mixtures containing fly ash at early days; after 28 days, the cements prepared by incorporation of fly ash gain an important strength. From mechanical point of view, an optima dosage was obtained at 77% clinker, 2% gypsum, 7.5% fly ash and 13% limestone composition.

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Keywords: Fly ash; Limestone; Mortars; Mechanical behaviour; Grinding

1. Introduction

The use of limestone and fly ash to produce different types of cement is a common practice in developed countries. The European standards (UNE-EN 197-1) [1] permits the incorporation of up to 65% and 35% for fly ash and limestone, respectively.

The effect of limestone on the hydration of cement is discussed in many investigations [2–5]. It is known that its major constituent, calcium carbonate (CaCO_3), modifies the vigorous initial reaction of C_3A , accelerates the C_3S hydration and improve the lubricating effects between the grains of clinker [6,7].

Many investigations have studied the use of fly ash in the cement production. In general, this requires the use of fly ash of fine particle size, low carbon content and effective pozzolanic reactivity with clinker. Fly ash with such characteristics

is usually found to improve workability and contribute to strength development at a sufficiently early age to be an effective cementitious component of concrete.

The objective of this paper is to study the combined effect of limestone and fly ash on Moroccan Portland cement. Physico-chemical properties of ternary cements made by Portland cement, fly ash and limestone are determined using laser granulometer, Vicat probe and needle, scanning electronic microscopy, X-ray fluorescence and diffraction. The compressive and flexion strength are measured on the corresponding mortars.

2. Experimental

2.1. Materials

The chemical composition of the materials was carried out by X-ray fluorescence spectrometer. The mineralogical composition was determined by X-ray diffraction. The chemical composition of used materials, clinker, limestone

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Table 1
Chemical compositions of used materials (wt.%)

Oxide	Clinker	Limestone	Fly ash
SiO ₂	21.14	19.96	47.26
Al ₂ O ₃	4.98	1.97	27.63
Fe ₂ O 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 ₂ O	0.53	0.34	0.83
TiO ₂	0.47	1.02	1.45
MnO	0.09	0.04	0.14
Na ₂ O	0.01	0.02	0.01
P ₂ O ₅	0.6	0.72	0.93
CaO _{free}	0.48	—	0.00
CaCO ₃	—	70.31	—
LOI	0.71	31.78	4.58

and fly ash, are listed in Table 1. All these materials are from Morocco. The mineralogical composition of clinker calculated by Bogue's formula is listed in Table 2.

From Table 1, it can be seen that fly ash contains a large amount of SiO₂, Al₂O₃, Fe₂O₃ and a low content of CaO. It allows classifying it into F class according to ASTM specification [8]. The purity of used gypsum is around 84.52% with 39.31% SO₃ consistence and 0.075% chlorine traces.

The X-ray diffractogram of limestone (Fig. 1) shows that the major crystalline components of limestone are calcite (CaCO₃) and quartz (SiO₂). The fly ash diffractogram (Fig. 2) shows that the crystalline phases present are quartz (SiO₂), mullite (Al₆Si₂O₁₃), magnetite (Fe₃O₄) and hematite (Fe₂O₃).

2.2. Samples preparation

A ball mill is used to produce different types of cements. All materials in each type of cements were ground together, up to 2.5% retained at 80 μm. The standard specimens used are as follows:

Ordinary Portland cement (OPC) obtained by intergrinding clinker and gypsum, respectively, in the proportion of 97 and 3 wt.%.

Two limestone cements CL and CL₁ prepared by intergrinding clinker, gypsum and limestone, respectively, in the proportions of 85, 2, 13 wt.% (CL) and 80, 2, 18 wt.% (CL₁).

The first series of samples were prepared by replacing the clinker by fly ash before grinding stage. Six blended cements were selected and noted KF_x in the case of

Table 2
Mineralogical composition of used clinker (Bogue calculation) (wt.%)

Phase	C ₂ S	C ₃ S	C ₃ A	C ₄ AF
	19.71	54.2	7	11.16

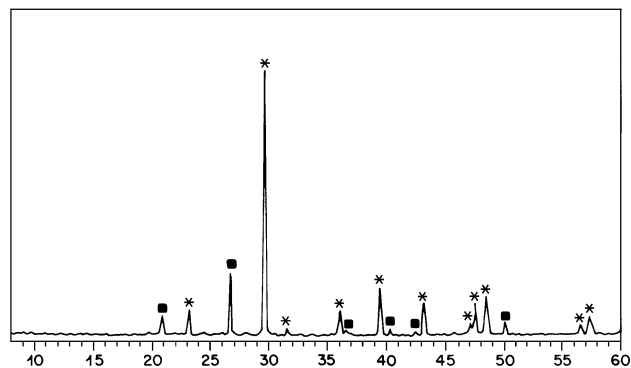


Fig. 1. X-ray diffraction of limestone. *: Calcium carbonate (CaCO₃), ■: quartz (SiO₂).

clinker–fly ash–gypsum mixtures, and KLF_x in the case of clinker–fly ash–gypsum–limestone mixtures. These samples were tested and compared to standard cements OPC, CL and CL₁.

The second series of samples were made by substitution of standard cements by fly ash. The used designations of these blended cements were CF_x in the case of OPC–fly ash mixtures, and CLF_x in the case of CL–fly ash mixtures. Table 3 gives all names and compositions of prepared samples.

2.3. Test carried out

The analysis of individual particle shape and morphology of fly ash are carried out by a scanning electron microscope (SEM). The particle size distribution data are obtained by a laser granulometer and by sieving.

The pozzolanicity test is determined according to European standard EN196-5 [9]. The physical properties as water requirement and setting time are determined on the fresh paste of prepared cements. The normal consistency and setting time are determined by Vicat probe and Vicat needle apparatus, respectively.

The mortars are made by the mixing of cement, sand and water in the proportions 1/3/0.5. The water and binder are introduced into the mixture and mixed for

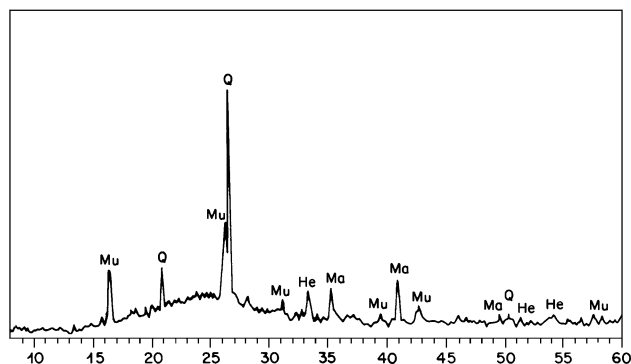


Fig. 2. X-ray diffraction of fly ash. Mu: Mullite (Al₆Si₂O₁₃), Q: quartz (SiO₂), He: hematite (Fe₂O₃), Ma: magnetite (Fe₃O₄).

Table 3
Compositions of cement mixtures samples (wt.%)

Standard cement samples					
Mixtures	Clinker	Gypsum	Fly ash	Limestone	Above 80 μm sieve
OPC	97	3	0	0	2.5
CL	85	2	0	13	2.5
CL ₁	80	2	0	18	2.5
Substitution clinker–fly ash in OPC					
KF ₁₀	87	3	10	0	2.5
KF ₂₀	77	3	20	0	2.5
KF ₃₀	67	3	30	0	2.5
Substitution clinker–fly ash in CL					
KLF ₅	80	2	5	13	2.5
KLF _{7.5}	77.5	2	7.5	13	2.5
KLF ₁₀	75	2	10	13	2.5
Substitution OPC–fly ash					
	Cement OPC		Fly ash		
OPC	100		0		2.5
CF ₁₀	90		10		3.2
CF ₂₀	80		20		4.1
CF ₃₀	70		30		5.5
Substitution CL–Fly ash					
CL	100		0		2.5
CLF ₅	95		5		3.3
CLF _{7.5}	92.5		7.5		3.6
CLF ₁₀	90		10		3.7

few seconds for having a good homogeneity; afterwards, the quartz standard sand is incorporated to the mixing and all the constituents are mixed for 3 min with a slow speed (140 rd/min) and 2 min with fast speed (280 rd/min). At the end of mixing period, each mortar mixture is cast in the oiled moulds (40 × 40 × 160 mm) and packed with the shock apparatus. On the completion of casting, 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 compressive and flexion strengths are performed at those times.

3. Results

3.1. Morphology and particle distribution of fly ash

Fly ash particles are generally spherical in shape and very small in size (from <1 to 20 μm). Fig. 3 shows SEM images of this fly ash. It seems that most of these particles are solid glass spheres, with the existence of some angular particles. Table 4 indicates the particle size distribution data, expressed as weight fraction in the range >45 to >100 μm . Fig. 4 shows the cumulative

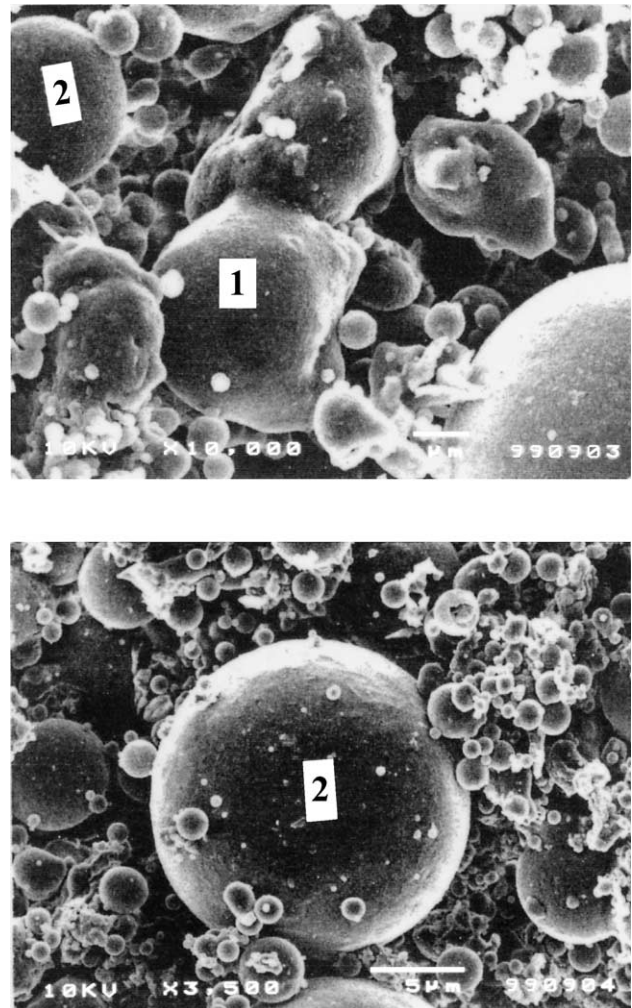


Fig. 3. Morphology of fly ash. 1: Irregular form, 2: spherical form.

data of particle size distribution of fly ash obtained by Laser granulometry.

3.2. Pozzolanic test

Fig. 5 exhibits the result of Frattini pozzolanic test, which explains the reaction between $\text{Ca}(\text{OH})_2$ liberated from clinker hydration and glassy phases of fly ash. It can be seen that, when we added fly ash to cement, the concentration of OH^- ions in the aqueous solution in contact with hydrated cement decreased and became under the concentration curve of those ions in the saturated solution at 40 °C after 8 days. This result means that the used fly ash has a pozzolanic activity.

Table 4
Particle size distribution of fly ash (wt.%)

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

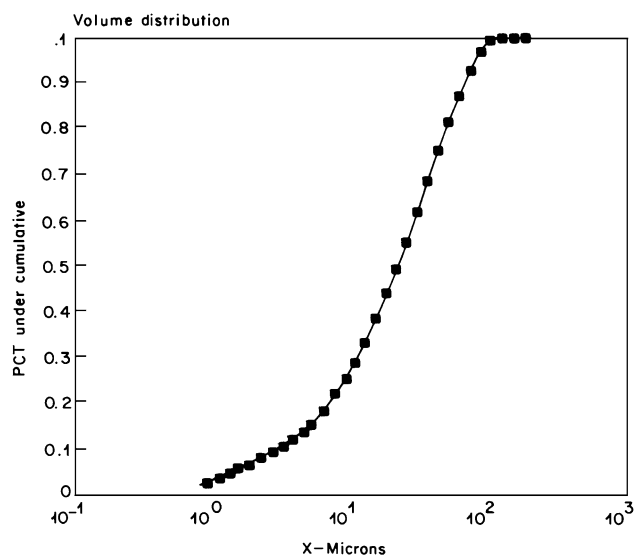


Fig. 4. The cumulative data of particle size distribution of fly ash.

3.3. Grinding time

Fig. 6 shows the evolution of grinding time as a function of added fly ash percentage. It appears clearly that the introduction of fly ash in the preparation of the composite cements, KF₁₀, KF₂₀, KF₃₀, KLF₅, KLF_{7.5} and KLF₁₀, reduces considerably the grinding time for the same retained sieve at 80 μ m.

3.4. Water requirement and setting time

The water requirement and setting time, determined by Vicat probe and Vicat needle apparatus, are reported in Table 5. It indicates the initial and final setting times of the cements obtained after clinker–fly ash substitutions. The obtained values show that the incorporation of fly ash in the OPC or in the cement containing limestone has a low effect

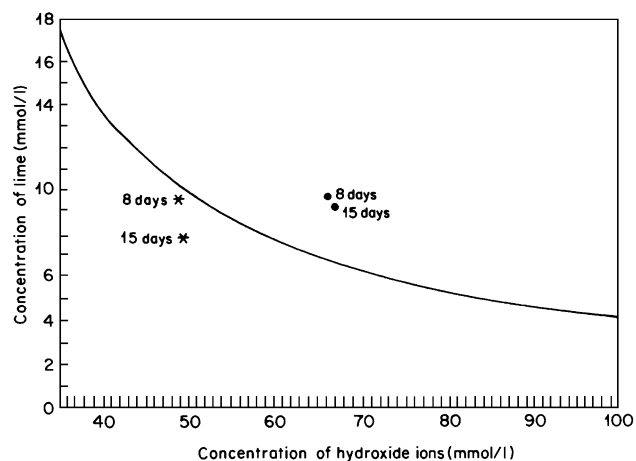


Fig. 5. Curve of pozzolanicity test. ●: Before adding fly ash, *: after adding fly ash.

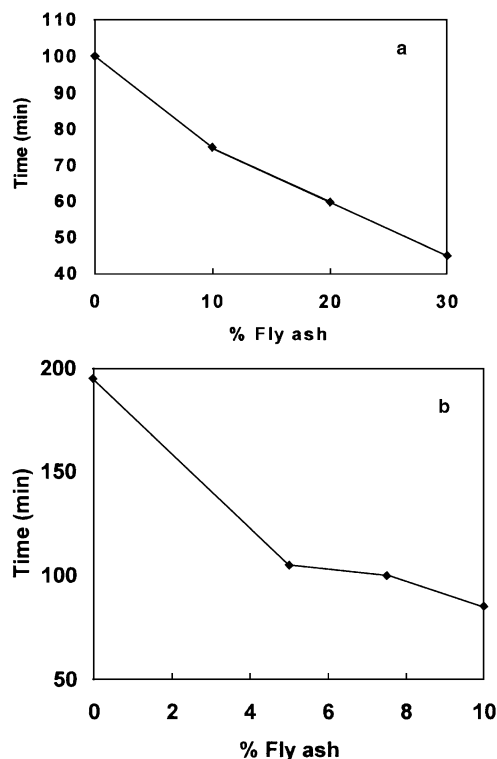


Fig. 6. Effect of fly ash on grinding time. (a) Replacement of clinker by fly ash in CL, (b) replacement of clinker by fly ash in OPC.

on water content for standard consistency, but the setting time is generally prolonged with increased fly ash content.

3.5. Mechanical measurements

The mortars of studied samples are tested at compressive and flexural strengths after 2, 7, 28 and 90 days of curing. The obtained results are reported in Table 6.

The mortars containing cements with fly ash (KF₁₀, KF₂₀, KF₃₀, CF₁₀, CF₂₀ and CF₃₀) show a decrease of the mechanical strengths at all ages. There is no difference between the value of compressive and flexural strength for

Table 5
Water requirement and setting times of substituted clinker–fly ash cements

Samples	Water (wt.%)	Setting time (h:min)	
		Initial	Final
<i>Substitution clinker–fly ash in OPC</i>			
OPC	24	2:40	6:40
KF ₁₀	25	3:15	7:20
KF ₂₀	25.5	4:00	8:15
KF ₃₀	26	4:40	9:15
<i>Substitution clinker–fly ash in CL</i>			
CL	24	3:50	5:55
CL ₁	24	4:00	6:10
KLF ₅	24	3:15	5:45
KLF _{7.5}	25	4:10	6:55
KLF ₁₀	25.5	4:25	7:30

Table 6
Compressive and flexion strengths (MPa) of tested composite cements

Samples	Compressive strength (MPa)				Flexion strength (MPa)			
	2 days	7 days	28 days	90 days	2 days	7 days	28 days	90 days
<i>Standard cement samples</i>								
OPC	24	38.3	53.8	61.2	4.9	6.4	9.2	9.8
CL	24.1	37	50	59	4.8	6.8	7.7	8.6
CL ₁	19.6	33.1	45.5	55.7	4.3	6.1	7.4	8
<i>Substitution clinker–fly ash in OPC</i>								
OPC	24	38.3	53.8	61.2	4.9	6.4	9.2	9.8
KF ₁₀	14.4	30.8	43.2	58	3	5.6	7.8	9.3
KF ₂₀	11	23.1	36.5	53	2.5	4.1	6.2	8.8
KF ₃₀	7.2	17	30.7	48	1.5	3.1	6	8.2
<i>Substitution clinker–fly ash in CL</i>								
CL	24.1	37	50	59	4.8	6.8	7.7	8.6
KLF ₅	21.4	35.5	50.4	61	4.8	7.2	8.2	9.2
KLF _{7.5}	20.6	34.9	53.5	63	4.3	7	8.5	9.3
KLF ₁₀	17.8	31.6	45.9	59	3.9	6.5	8.1	8.7
<i>Substitution OPC–fly ash</i>								
OPC	24	38.3	53.8	61.2	4.9	6.4	9.2	9.8
CF ₁₀	19.9	33.6	46.55	57	3.7	5.9	7.9	9.4
CF ₂₀	16.4	26.2	38.2	52	3.4	5.3	7.5	9.2
CF ₃₀	12.7	21.5	33.4	47	2.6	4	6.3	8.7
<i>Substitution CL–fly ash</i>								
CL	24.1	37	50	59	4.8	6.8	7.7	8.6
CLF ₅	22.8	36.8	50	58.8	4.6	7.1	7.5	8.2
CLF _{7.5}	22.2	36.4	49.5	58	4.4	7.1	7.2	8
CLF ₁₀	21.4	35.9	48	57	4.2	6.2	6.8	7.9

the cements prepared by intergrinding clinker, gypsum and fly ash together and those obtained by the substitution of OPC by unground fly ash.

The tested mortars made by substitution of clinker in cement containing limestone (samples KLF₅, KLF_{7.5} and KLF₁₀) show that the compressive and flexural strength passes through maximum values for KLF_{7.5} composition. The compressive strength values of this sample reach 63 MPa at 90 days.

In the case of mortars composed by limestone cement and unground fly ash (CLF₅, CLF_{7.5} and CLF₁₀), the compressive and flexural strength values are preserved in spite of added fly ash, compared to cement obtained by intergrinding clinker, limestone and fly ash.

4. Discussion

In this study, the effects of added fly ash in OPC cement and in composite limestone cement CL, at grinding stage and at cement mixing stage, will be discuss.

In the grinding stage, the results show that increasing the amount of added fly ash in the blended cement significantly reduces the grinding time. This result is available in two types of studied cements, OPC and CL (Fig. 6). This indicates that fly ash acts as grinding agent. So, intergrind-

ing clinker and fly ash yields an even faster increase in fineness and a less grinding energy is consumed, consequently, an energy saving is obtained. Many authors [10,11] have indicated that, for the blended cements when the fly ashes were ground together with the clinker, the time required to obtain the same Blaine fineness as the laboratory produced Portland cement was reduced. This reduction of grinding time is probably due to the high content of SiO₂ in the fly ash, and this suggestion was also proposed by Bombléd [12].

The water requirement is an important factor, which is directly linked to setting stage. From Table 5, it seems that the introduction of limestone has no effect on water requirement (cements CL and CL₁) compared to OPC. However, the two types of cements obtained by intergrinding clinker, gypsum and fly ash with or without presence of limestone (KF₁₀, KF₂₀, KF₃₀, KLF₅, KLF_{7.5} and KLF₁₀), show a low increase of water content required to achieve standard consistence. This effect is due to the high specific surface area of fly ash particles. Also, the intergrinding of fly ash with clinker separates the agglomerates of spheres and increase broken coarse ashes. Consequently, the level of fine particles increases to higher specific surface area, which requires much water according to the results mentioned by Barker [13]. However, the low increase of water requirement can be attributed to the effects of loss on ignition of fly ash (adsorption of water by porous carbon particles) [14,15].

The cements obtained by mixing clinker, gypsum and fly ash (mixtures noted KF₁₀, KF₂₀ and KF₃₀) present more important extension of setting time than the cement containing only limestone (CL and CL₁) or the joint addition of fly ash and limestone (KLF₅, KLF_{7.5} and KLF₁₀) (Table 5). The delay in the time of setting can be attributed to the dilution effects resulting from clinker replacement, or to the change of the paste rheology, which can be affected by the existence of elementary carbon. Many investigations have been shown that aluminosilicate fly ashes retard the setting of cement for several reasons. Skalny and Young [16] and Plowman and Cabrera [17] have reported that fly ash retards the hydration of C₃A, and the degree of this retardation mainly depends on the amount of dissolved alkalis and to the sulphate from fly ash, which retards the hydration more than the equivalent amount of added gypsum. But other studies reported the extension of setting time to the fineness of fly ash [18,19]: the particles of fly ash fill between the clinker grain and act as nuclei for crystallisation of cement hydration products like C–S–H. If we take into account the time between the initial and final setting times (Table 5), we can classify the duration of setting as follows: KF_x>OPC>KLF_x>(CL, CL₁).

From the examination of mechanical behaviour of the mortars (Table 6), we can see that, in the first 28 days, the mortars prepared with the cement obtained by the replacement of clinker by limestone (cement CL and CL₁) decrease the mechanical strengths than the replacement of clinker by

fly ash (cement KF₁₀, KF₂₀ and KF₃₀) in the same period. This result is probably due to the hydration enhancement of C₃A and C₃S by the presence of CaCO₃ leading to the formation of hydration products such as monocarboaluminate, monosulfoaluminate and carbosilicate hydrates [20–23].

The cement mortars prepared by substitution clinker by fly ash (samples KF_x) show a low rate of strength development at early ages compared to standard mortars. After 28 days, the compressive strength values increase rapidly. The strength gain between 28 and 90 days reaches 14.8, 16.5 and 17.3 MPa, respectively, for KF₁₀, KF₂₀ and KF₃₀. Whereas this evolution do not succeed 7.4, 9 and 10 MPa, respectively, for standard samples OPC, CL and CL₁. This result predicts a good evolution of compressive strength, at long-term, in cements composed by substitution of clinker by fly ash at grinding stage. The accelerating effect of mechanical properties, observed in KF_x samples, may be attributed to an evident acceleration of pozzolanic activity between the glassy phases of fly ash and Ca(OH)₂ liberated by C₃S hydration, consequently, the size of pores becomes smaller and the strength increases.

Another important specific result of this study is observed in mortars prepared by intergrinding clinker, fly ash and limestone (cements KLF_x). The compressive and flexural strength on hardened moulds, at 28 and 90 days, passes through a maximum value in the region of KLF_{7.5} composition (Table 6) and they reach 53.5 and 63 MPa, respectively. The explanation of this result is difficult, but we can attribute this evolution to the porosity effect. When intergrinding of clinker, gypsum, limestone and fly ash in initial mixtures, there is a mutual interaction of individual components and the influence of the harder to grind (clinker) is reduced and the mixture becomes rich in small clinker fractions, also in the same time the morphology of fly ash is affected by mechanical treatment. The glassy fly ash particles are broken down and increase the homogeneity of the mixture [24–26]. During hydration, the particles of CaCO₃, from limestone react with C₃A and C₃S liberating Ca(OH)₂. The basicity of the system increases and glassy fly ash broken particles are easily combined to the Ca(OH)₂ giving more C–S–H gel. Consequently, the porosity becomes smaller leading higher mechanical strength. After the optimum mix KLF_{7.5}, the compressive and flexural strength decreases. This may be due to the diminution of clinker amount in the cement. A supplementary grinding is suitable to preserve strengths.

In the case of samples made by replacement of cements by fly ash, the CF_x series has shown a remarkable decrease of strengths when the amount of fly ash increases in the mixture. In cements containing limestone, the additions of fly ash do not give important changes (series CLF_x). But the latter, compared to KLF_x series, remains with low mechanical properties.

In sum, it seems that the intergrinding clinker and additives give higher compressive and flexural strengths than the cements obtained by the replacement of cement with unground fly ash, this observation agrees with many investigations [9,12,26,27], which have mentioned that the intergrinding of clinker, gypsum and fly ash yields the separation of fly ash agglomerates and promotes the formation of wider particle, and consequently the blended product becomes more homogeneous.

5. Conclusion

The investigation on ternary cements based on clinker, fly ash and limestone showed the following observations:

- The fly ash act as grinding agent because it reduces the time required to obtain the same percentage of particles retained on a 80-μm sieve as the standard cement.
- The use of fly ash like additive in the cement field leads to an important extension of setting time than the limestone.
- The replacement of clinker by limestone gives a good behaviour than the mixtures containing fly ash at early days, but after 28 days, the cements prepared by incorporation of fly ash gain an important strength.
- The intergrinding of clinker by fly ash and limestone shows that there is an optimal dosage around (77% clinker, 2% gypsum, 7.5 fly ash, 13% limestone), which gives a packing structure to mixtures and a good mechanical properties.

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