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PROPERTIES OF BLENDED CEMENTS WITH LIMESTONE FILLER AND FLY ASH CONTENT

Maria GEORGESCU[1], Nastasia SACA[2]

Lucrarea aduce informații cu privire la evoluția proprietăților fizico-mecanice ale unor lianți micşti, cu conținut de calcar, cenuşă şi cimenturi portland compozite (cu calcar şi cenuşă). Au fost efectuate determinări privind timpul de priză, rezistențele mecanice şi comportarea în diferite medii acide.

This paper brings information regarding the evolution of physical mechanical properties of some blended cements with limestone content, fly ash content and of some composite Portland cements (with limestone and fly ash). Determinations concerning setting time, mechanical strengths and behavior in different acid solutions were performed.

Keywords: composite cement, limestone filler, fly ash, mechanical properties

1. Introduction

The manufacture of composite cements, Portland cement - limestone – fly ash type, Ternary Blended Cements (TBC) implies especially the following advantages:

- ecological - the reduction of toxic gases emissions, as a result of the diminution of the “clinker factor” and of the recovery of the fly ash;
- economical - the reduction of the cements production and sales cost;
- technical - the improvement of some properties of pastes, mortars and concretes.

Due to the complex action – physical and chemical, the limestone filler and the fly ash, added separately or altogether, induce changes of the hydration - hydrolysis processes, of the physical-mechanical properties and of the concretes durability [1-15]. The limestone presence in the binding system determines the acceleration of the cement initial hydration, especially of the tricalcium silicate. in

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[1] Prof., Dept. of Engineering and Science of Oxide Materials and Nanocompounds, University POLITEHNICA of Bucharest, Romania

[2] Eng., Dept. of Chemistry and Building Materials, Technical University of Civil Engineering of Bucharest, Romania

In the initial stages of the process, the increasing of the hydration degree compensates the dilution effect of the binding material by the limestone filler, as a consequence of the formation of a higher volume of hydrates. Therefore, pastes, mortars and concretes can develop higher initial strengths, but diminished after a long time, compared to ordinary Portland cement, because the binding dilution effect becomes important. Fly ash can develop some mechanical strength, due to slowly pozzolanic reaction, strength which grows after longer periods of time. The simultaneous presence of the limestone filler and fly ash in cement cumulates the effects determined by every addition separately, prevailing the effects of the addition present in a bigger proportion.

The present paper brings data regarding the influence of the fly ash and limestone filler additions single or altogether on the properties of some blended cements – composite cements type - with up to 30% addition.

2. Experimental

The following materials were used: Portland cement CEM I 52.5R, fly ash (Mintia) with Blaine specific surface area of 2108 cm^2/g, limestone filler with $CaCO_3$ content higher than 75%, according to SR EN 197-1 [16] and Blaine specific surface area of 4700 cm^2/g. The Portland cement had the compositional characteristics shown in Table 1. The Mintia ash contains as crystalline compounds: mullite, quartz, C_2S, calcium aluminates, calcium oxide, magnesium oxide (periclase), identified by X-rays diffraction analysis. The binding compositions shown in Table 2 were obtained by the homogenization of the Portland cement, limestone filler and fly ash into a rolling ball mill.

Table 1

Chemical and mineralogical composition of Portland cement

Chemical composition (%)		Mineralogical composition (%)	
SiO_2	18.46	$C_3S^{*)}$	72.63
Al_2O_3	5.85	C_2S	1.02
Fe_2O_3	3.40	C_3A	9.76
CaO	63.16	C_4AF	10.34
MgO	0.41		
SO_3	1.65	LFS	1
PC	6.48	M_S	1.99
		M_A	1.72

*) C = CaO; S = SiO_2; A = Al_2O_3; F = Fe_2O_3.

Table 2

Compositions and fineness of the blended cements

Code of the binder	Composition (%)			Specific surface area (cm^2/g)
	Portland cement	Fly ash	Limestone	
C3	100	-	-	4189
C3-FA10	90	10	-	3685
C3-FA20	80	20	-	3626
C3-FA30	70	30	-	3634
C3-L10	90	-	10	4485
C3-L20	90	-	20	4646
C3-FA10-L10	80	10	10	4361
C3-FA20-L10	70	20	10	4333
C3-FA10-L20	70	10	20	4594

The binding properties were estimated by compressive strengths determinations using cubic micro samples of 20mm x 20mm x 20mm prepared from mortar with 1/3 binder/sand ratio and 0.5 w/b ratio by vibration. The samples were demoulded after 1 day and kept for hardening in water until the days of mechanical determinations (2, 28, 60, 90, 360 days). There were also determined the initial and final setting time of blended cements, including the quantity of water needed for preparing the paste with standard consistency, as well as the behavior of mortars based on binders with limestone filler and fly ash content in acid solutions. The aggressive solutions were hydrochloric acid and acetic acid of 0.5 M concentration. The samples were kept for hardening in water 28 days and then were introduced in the corrosive acid solutions. Aggressive solutions were changed every 3 months.

3. Results and discussions

Setting time of the blended cements

The determinations made in order to assess the quantity of water needed to prepare the paste with standard consistency, led to the results presented in Table 3. The setting time of the blended cements was determined on the paste of standard consistency. The results are presented in the table 3.

It can be noticed that, for the cements with limestone filler content, it is necessary a smaller quantity of water to obtain a paste with standard consistency in comparison with the ordinary Portland cement. This fact could be explained by the wider dimensional distribution of limestone cements in comparison with Portland cement.

Table 3

Water of standard consistency and the setting time for the blended cements

Code of binder	**(H_2O)s.c cm^3/100g cem.**	**Setting time (minutes)**	
		Initial	**Final**
C3	30.2	105	195
C3-FA10	30.0	100	195
C3-FA20	29.2	115	120
C3-FA30	28.0	120	230
C3-L10	29.8	90	195
C3-L20	29.4	80	160
C3-FA10-L10	29.2	75	180
C3-FA20-L10	28.6	85	190
C3-FA10-L20	28.8	95	200

The partial substitution of cement with fly ash causes the decrease of the quantity of water needed to obtain the paste with standard consistency. This result is mainly due to the following actions [17]:

- the particles of ash are kept on the surface of the cement particles charged with electrical charge of opposite sign, favoring their high dispersion and avoiding flocculation which could cause detention of water in the agglomerations formed;
- the sphericity and the smooth surface of the fly ash particles reduce the friction between particles and, therefore, favor their mobility in pastes and, by default, a higher fluidity;
- the “packaging” effect of particles leads also to the decrease of amount of water needed for a good workability of the system.

The setting time is longer for the blended cements in comparison with Portland cement. An emphatic delay seems to be caused by the addition of fly ash (10-30%). The addition of limestone filler (10-20%) delays the initial setting time but the final setting time is just a little increased (C3-L10), or is not modified as compared to the reference. The complex additions of fly ash and limestone filler cause the delay of the initial setting time, but do not visibly modify the final setting time.

Mechanical strengths of the binding systems Portland cement–limestone-fly ash - water

The compressive strengths determined on cubes with the side of 20 mm, prepared from mortar and kept for hardening in water at 20°C until the days of mechanical strengths determinations, are presented in Table 4.

Table 4

Compressive strengths of mortars containing binders with limestone filler and/or fly ash addition

Code of binder	Compressive strengths (MPa) after:				
	2 days	28 days	60 days	90 days	360 days
C3	14.5	49.7	49.8	50.2	52.0
C3-FA10	15.2	44.3	48.5	48.8	50.1
C3-FA20	13.8	37.8	43.8	44.5	47.8
C3-FA30	8.7	33.1	34.4	38.6	40.4
C3-L10	20.6	40.5	41.0	42.9	45.1
C3-L20	12.9	35.2	38.6	39.3	40.0
C3-FA10-L10	12.9	28.9	37.7	38.0	39.1
C3-FA20-L10	9.5	27.8	34.6	35.0	36.8
C3-FA10-L20	9.5	30.4	30.8	31.5	34.8

In Figs. 1 and 2 the relative mechanical strengths of the blended cements are represented, calculated with relation:

$$C_{s,rel.} = \frac{C_{s,t}}{C_{s,r}} \times 100$$

in which: $C_{s,t}$ is the compressive strength of blended cements, after a certain period of hardening t;

$C_{s,\,r}$ – the compressive strength of Portland cement (reference) after the same hardening time.

The addition of fly ash generally causes the decreases of the mechanical strengths of blended cements in comparison with the reference. The decreases are important up to 28 hardening days, and they attenuate for longer periods of time. This can be the effect of dilution of active component from the binder (Portland cement) – especially for a short hardening time, and the relative coarse character of fly ash (the specific Blaine surface area 2108 cm^2/g), which causes a very slow evolution of pozzolanic reaction.

At 60 days of hardening, the binder with 10% fly ash develops a compressive strength of about 97% from the mechanical strength of the reference, without modifications until 360 days. At this term, the compressive strengths of mortars with 20% and 30% fly ash content represent 92% and, respectively, 78%

from the value corresponding to the reference. At 60 days of hardening, the compressive strengths of the same compositions represent about 88% and, respectively, 70% from the value corresponding to the reference (Fig. 1). These values confirm the role of pozzolanic reaction in the development of mechanical strengths of the cements with fly ash content for longer hardening periods.

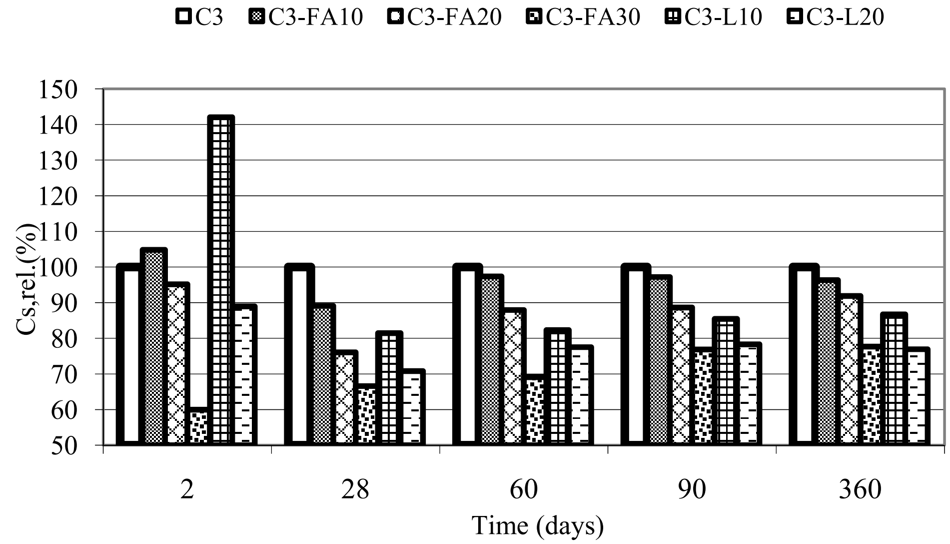

Fig.1. Relative strengths for the binders with limestone filler or fly ash additions

The additions of the limestone filler in cement cause significant decreases of the compressive strengths, in comparison with the reference, especially after 28 days of hardening. Initially (after 2 days), the negative effect of the addition of 20% limestone is small, and the addition of 10% limestone has even a positive influence on mechanical strengths, due to its filler effect and of a better dispersion in water of the cement particles, which favors the hydration processes.

After 28 days of hardening, the dilution effect of the active component in binder is uppermost. The decrease of mechanical strength due to the presence of 20% limestone addition in cement is almost the same with the value corresponding to cement with 30% fly ash content after 360 days.

The mechanical strengths developed by the composite cements with complex additions of limestone filler and fly ash are smaller in comparison with those of the cements with similar contents of fly ash or limestone and implicitly, in comparison with the values corresponding to the reference (Table 4 and Fig. 2).

The binding behavior of the cements with 30% addition of limestone filler and fly ash is very similar, regardless of the preponderance of one of additions.

The binder with 20% complex addition (C3-FA10-L10) is distinguishable by a better mechanical strength just for an initial period of time (2 days).

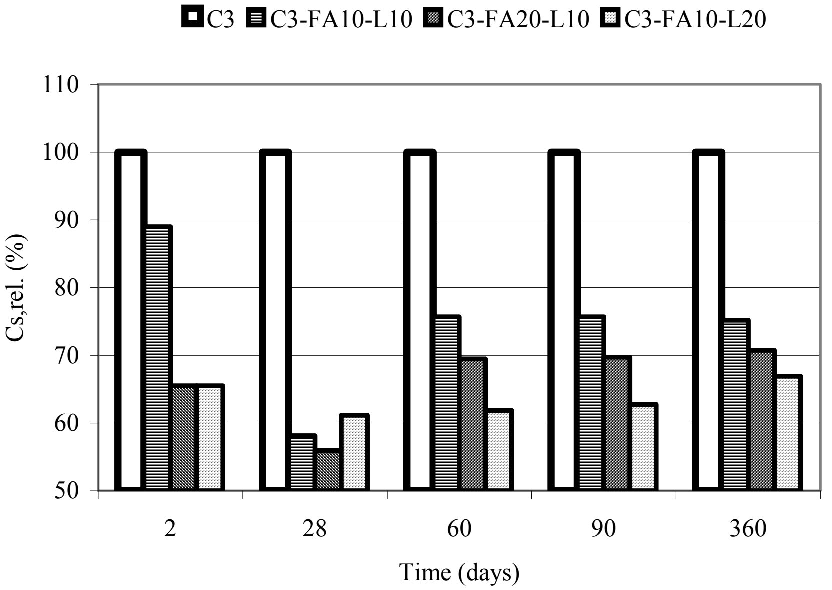

Fig. 2. Relative strengths for the binders with limestone filler and fly ash additions

The behavior of the blended cements with limestone filler and fly ash content in the acid solutions

The fly ash utilization as addition in cement has to provide a good resistance of the composite materials realized with such kind of binders in different corrosive solutions. This is the result of the capacity of fly ash to bind progressively calcium hydroxide produced by the hydrolysis of Portland cement.

The acid solutions can also react with other hydrates than $Ca(OH)_2$ from the hardened cement: calcium silicate (aluminate) hydrates [18-20], which amplifies the corrosive effect.

The data presented in Table 5, Figs. 3 and 4 demonstrate the stability in acid solutions of the blended cements which is comparable, or sometimes reduced, in comparison with the reference. The relative compressive strengths presented in Figs. 3 and 4 were calculated using the formula:

$$C_{s,rel.} = \frac{C_{s,a}}{C_{s,r}} \times 100$$

in which: $C_{s,a}$ represents the compressive strengths of the samples kept into acid solutions for a certain time period, t;

$C_{s,r}$ - the compressive strengths of the samples kept in water for the same period of time, t.

The potential positive effect of the fly ash on corrosion resistance was not enough revaluated due to a low grinding fineness of the material used. Otherwise, the data presented in other work, [21], have evidenced a low capacity of this fly ash to bind calcium hydroxide in the hydration process of the blended cements.

By thermal analysis (TG&DTA), in the cement pastes with fly ash content, hardened for 28 days there was identified the presence of bigger quantities of $Ca(OH)_2$ in comparison with the reference. These data corroborated with the information provided by X-ray diffraction analysis suggest an increase of the Portland cement hydration rate in the blended cements with fly ash addition. The effect of diminution of the active component – Portland cement, by the substitution with the fly ash, it is also felt in the resistance of the blended cement in corrosive solutions. It decreases the volume of CSH hydrates (with low basicity), therefore the gel/space ratio, and as a consequence, the volume of the pores is bigger and favors the diffusion of corrosive agent.

The binders with limestone filler content – separately (C3-L10, C3-L20) or altogether with fly ash (C3-FA10-L10, C3-FA10-L20) have a good stability in both corrosive solutions – hydrochloric acid and acetic acid, after 60-90 days of curing. Their behavior is supposed to be caused by the filler effect of the limestone, as well as by the increase of the rate of Portland cement hydration process, as a consequence of the role of nucleation centers of the fine limestone particles.

After 60 days of curing, a favorable contribution of the fly ash in the binders by the pozzolanic reaction is expected.

For all binders, the mechanical strength decreases when immersed in corrosive solutions are amplified at longer periods of attack, therefore, at 360 days, when the strengths decreases are generally bigger than 60%.

Table 5

Mechanical strengths of samples kept in corrosive solutions (the terms include 28 days for hardening in water).

Code of binder	**Corrosive solutions**	**Compresive strengths (MPa) after:**		
		60 days	**90 days**	**360 days**
C3	HCl	32.9	37.8	19.6
C3-FA10		29.1	29.9	15.1
C3-FA20		27.1	31.4	13.0
C3-FA30		22.3	25.2	16.5

C3-L10		28.0	30.6	14.1
C3-L20		25.4	25.4	13.4
C3-FA10-L10		28.6	28.1	14.4
C3-FA20-L10		21.9	24.3	11.6
C3-FA10-L20		22.2	16.9	9.5
C3	CH_3COOH	32.3	34.5	19,5
C3-FA10		33.6	28.1	14.9
C3-FA20		33.0	42.3	14.8
C3-FA30		24.6	27.7	11.8
C3-L10		30.6	35.7	13.8
C3-L20		24.5	24.0	10.9
C3-FA10-L10		29.1	30.1	14.1
C3-FA20-L10		22.8	25.6	7.6
C3-FA10-L20		19.0	23.5	7.4

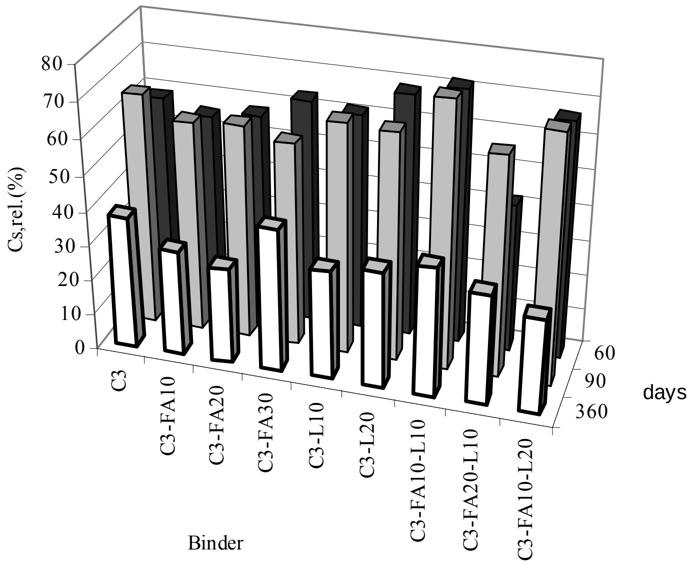

Fig. 3. Relative strengths for mortar samples kept in hydrochloric acid

Comparing the values of the relative strengths of blended cements samples cured in two acid solutions, it could be generally considered that acetic acid solution was more corrosive than hydrochloride acid solution (Figs. 3 and 4).

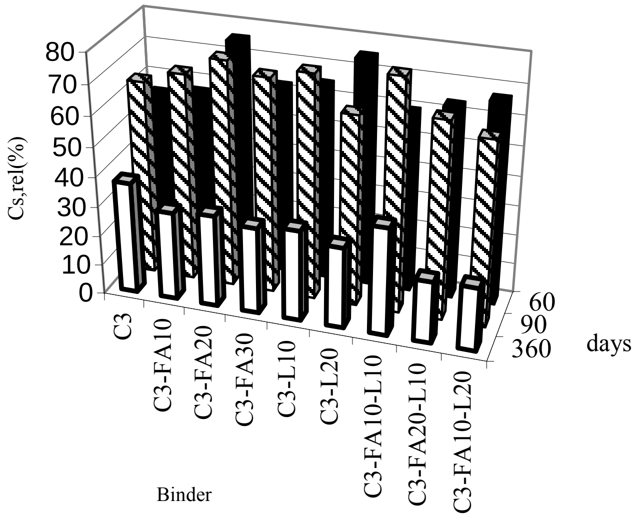

Fig. 4. Relative strengths for mortar samples kept in acetic acid

4. Conclusions

- The additions of limestone filler or fly ash – taken separately or altogether, determine a decrease of the setting time for the blended cements in comparison with Portland cement, the effect being stronger in the case of cements with greater addition of fly ash (20-30%);

- The addition of fly ash in cement generally causes decreases of the mechanical strengths of the binders in comparison with the reference. The decreases of the mechanical strengths are enough accentuated even at 28 days of hardening and attenuate for bigger periods of time. Therefore, after 360 days, the mechanical strengths of the blended cements with 20% and 30% fly ash content represent 92% and, respectively, 78% from the values corresponding to the reference. After 360 days of hardening, the mechanical strengths of the same compositions represent 88% and, respectively, 70% from the value corresponding to the reference. These data confirm the participation of the fly ash to the development of the mechanical strengths by pozzolanic reaction, at longer hardening period.

- The presence of the limestone filler in the cement determines significant decreases of the compressive strengths, in comparison with the reference, especially after longer periods of time (28-360 days), as a consequence of the dilution effect of the active component in the binder. The decrease of the mechanical strength associated with the limestone filler presence in cement is, after 360 days, similarly to that corresponding to 20-30% fly ash additions.

- The mechanical strengths developed by the composite cements, with complex addition of limestone filler and fly ash, were also smaller in comparison with the one of unitary Portland cement and even in comparison with the values corresponding to the cements with the same proportions of fly ash/limestone filler.
- The stability of the blended cements containing up to 30% fly ash/limestone filler additions in acids solutions was not much different from the reference. The cements with fly ash additions suffered more accentuated decreases of the mechanical strengths in corrosive solutions in comparison with the reference. This behavior could be explained by a small pozzolanic activity of the fly ash with a low grinding fineness. A better stability in contact with the acid solutions manifested at the binders with limestone content – separately or associated to fly ash. This may be due to a smaller porosity of these binders.

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