INFLUENȚA UNOR ADAOSURI VARIABILE DE CENUŞĂ DE TERMOCENTRALĂ, ASOCIATĂ CU UN SUPERPLASTIFIANT POLICARBOXILIC, ASUPRA PRINCIPALELOR PROPRIETĂȚI ALE PASTELOR ŞI MORTARELOR PE BAZĂ DE CIMENT PORTLAND▲

THE INFLUENCE OF FLY ASH ADDITIONS ASSOCIATED WITH POLYCARBOXYLATE SUPERPASTICIZER ON THE MAIN PROPERTIES OF PORTLAND CEMENT PASTES AND MORTARS

CARMEN MUNTEANU*, MARIA GEORGESCU, ANDREEA MONCEA
Universitatea Politehnica Bucureşti, Str. G. Polizu nr.1, 011061, Bucureşti, România

The paper provides information regarding the influence of fly ash additions - alone or associated with a polycarboxylate type superplasticizer – on the main physical and mechanical properties of pastes and mortars containing Portland cement CEM I 52.5 R.

Fly-ash, from Govora plant, was used as addition in blended cements, in quantities of 10% up to 50%. The superplasticizer was of polycarboxylate type - CHRYSO Fluid Premia 180 (solution containing 21.5±1.0% active substance). The superplasticizer was dosed at a ratio of 0.9% (with reference to cement).

Information of the influence of the fly ash addition, associated with superplasticizer, on the physical properties of cement pastes were obtained by the assesment of water for normal consistency and setting time. The hardening processes of cement mixed with different amounts of fly ash associated with polycarboxylate type superplasticizer, were evaluated by the assessment of mechanical strength, on the mortar specimens with binder/sand = 1/3 and water to binder ratios in order to ensure a similar workability for mortars without and with superplasticizer.

The increase of fly-ash addition determines a continous increase of water for standard consistency (32.2%-37.6%). Polycarboxylate superplasticizer addition (0.9%) significantly reduced the values of the water for standard consistency, at levels between 22% and 28%, for cement containing 10 - 50% fly ash. The increase of fly ash amount increases the setting time, but for the pastes with 0.9% polycarboxylate additive this retarding effect is dimished.

Mechanical strengths of the mortars based on cements with fly ash decreased, while the content of fly ash increased. The decrease of mechanical strengths was less important for the cements containing fly ash and 0.9% polycarboxylate superplasticizer, in correlation with the smaller water/binder ratio. Thus, for the binder with 30% fly ash and 0.9% superplasticizer, the compressive strengths were higher as compared with the ordinary Portland cement.

Lucrarea prezentă aduce informații privind influența unor adaosuri variabile de cenuşă de termocentrală – singură sau asociată cu un aditiv superplastifiant de tip policarboxilic – asupra proprietăților fizico-mecanice ale unor paste şi mortare pe bază de ciment portland CEM I 52,5 R. Cenuşa de termocentrală, de proveniență Govora, a fost considerată ca adaos de ciment, în cantități cuprinse între 10% şi 50%. Superplastifiantul utilizat a fost de tip policarboxilat – CHRYSO Fluid Premia 180, utilizat ca soluție, cu un conținut de substanță activă de 21,5±1,0%. Pe baza rezultatelor unor cercetări anterioare, aditivul s-a dozat în proporție de 0,9% față de ciment.

Informații privind influența adaosului de cenuşă, asociată eventual cu superplastifiant, asupra proprietăților fizice ale pastelor liante, s-au obținut prin determinări ale apei necesare obținerii pastelor de consistență standard şi determinări ale timpului de priză. Comportarea liantă a cimenturilor mixte, cu conținut diferit de cenuşă, asociată cu aditiv superplastifiant, a fost apreciată prin rezistențele mecanice dezvoltate în timp, de probe din mortar cu raport liant/nisip = 1/3 şi raport apă/liant variabil, astfel încât să se asigure o lucrabilitate similară a mortarelor fără şi cu superplastifiant. Adaosurile crescânde de cenuşă au determinat creşteri continue ale apei pentru pasta de consistență standard (în limitele 32,2%-37,6%). Asocierea superplastifiantului policarboxilic (0,9%) a diminuat sensibil apa pentru pastele de consistență standard, la valori cuprinse între 22% şi 28%, pentru cimenturile cu conținut de 10%, respectiv 50% cenuşă. În corelare cu aceasta, timpul de priză a fost mai lent pentru cimenturile cu cenuşă, dar, efectul întârzietor al acesteia a fost atenuat în prezența superplastifiantului. Rezistențele mecanice ale mortarelor preparate din cimenturi cu cenuşă au diminuat, paralel cu creşterea proporției de cenuşă. Scăderile de rezistență au fost mult atenuate pentru compozițiile conținând cimenturi cu cenuşă şi 0,9% superplastifiant policarboxilic, în corelare cu reducerea raportului apă/liant, pe care aditivul o determină. Astfel, pentru compoziția liantă cu 30% cenuşă şi 0,9% superplastifiant, s-au obținut rezistențe la compresiune mai bune chiar decât pentru cimentul unitar, fără superplastifiant.

Keywords: *fly ash, polycarboxilate superplasticizer, physical and mechanical properties*

1. Introduction

It is known that Portland cement clinker production requires a high energy-intensive technology, accompanied by a significant release of CO_2, with negative consequences on the environment; in consequence, it is of great interest to reduce these negative impacts, in different ways

* Autor corespondent/Corresponding author,
Tel.: +4 0744378029, e-mail: carmen.munteanu99@yahoo.com

▲ Lucrare prezentată la / *Paper presented at:* Consilox XI

[1-6]. One of the most important is the reduction of "clinker" factor in cement clinker, by partial substitution with different siliceous materials, reactive or of filler type. Fly ash is such a siliceous material accessible, but rarely used in our country, although worldwide use of this material is common, even for obtaining concrete composite type, with performance characteristics, in conditions of optimization of the composition and processing factors.

This material, as well as blast furnace slag or silica fume, can improve the durability of concrete by controlling thermal gradients developed in massive concretes during the cement hardening, as well as by the consumption of Ca $(OH)_2$ in pozzolanic reaction, which takes place slowly in time. At these technical favourable effects, environmental and economic implications are added. Partially replacement of cement by fly ash in concrete reduces its cost, making in the same time, the concrete an "environment friendly" material, by reducing of CO_2 emission and in the same time reducing the area occupied by fly ash deposit. Composition and dispersion characteristics of the two main components of the binder - Portland cement and fly ash, together with water/binder ratio, determine the development of high mechanical strength of the concrete. If the initial development of strength is conditioned mainly by the reactivity of the cement, after long time, the development of strength is directly dependent, in particular, on the fly ash reactivity [7-9].

Although, according to some literature data [10 - 13], fly ash additions reduces the necessary water for normal consistency preparing, this influence must be considered in correlation with grinding fineness of the ash. A high fly ash fineness negatively affects rheological properties of concrete, for a given water/binder ratio. Therefore, it is required the association of the fly ash addition with a superplasticizer additive, in order to prepare concretes with good workability and in which the hydration-hydrolysis reactions of cement and pozzolanic reaction of fly ash, take place with convenient speed.

The influence of varying additions of fly ash (10-50%) - alone or associated with a superplasticizer of polycarboxylic type additive, on the main physical-mechanical properties of Portland cement pastes and mortars is presented in this study.

2. Experimental

Portland cement CEM I 52.5 R and a type fly ash (Govora origin), characterized by a specific surface area of 2.642 m^2/g (BET surface area) were used. As superplasticizer, a polycarboxylic solution with concentration 21.5 ± 1% was used.

Standard consistency pastes were made, from cement with variable fly ash additions -10 to 50% - with and without addition of 0.9% polycarboxylic type superplasticizer; this value of superplasticizer additive was considered optimal based on previous research [14]. For each binder, the amount of water required to obtain standard consistency paste was determined, and for such pastes the initial and final setting time were determined, according to SR EN 196-3:2006 [15].

The influence of variable fly ash additions on the mechanical strength developed by mortars based on Portland cement CEM I 52.5 R, was estimated by determinations of the compression and flexural strengths, on samples with sizes of 40 mm x 40 mm x160 mm, made and kept for curing, 2-28 days, according to SR EN 196-1:2006 [16].

In order to assess the influence of fly ash amount - alone or associated with polycarboxylic type superplasticizer additive - influence the mechanical strengths of the mortars based on Portland cement, the binding compositions presented in Table 1 were considered.

At the mortars' preparation, obtaining of similar consistency was taken into consideration by taking into account the results obtained at determination of the water for standard consistency pastes.

The superplasticizer was dosed in relation to the amount of binder (portland cement+fly ash).

Table 1

Mortars compositions / *Compoziții mortare*

Nr. sample *Indicativ probă*	Content mortars / *Conținut mortare*				w/b ratio *Raport apă/liant*
	Binder *Liant* (g)	Water *Apă* (cm^3)	Sand *Nisip poligranular* (g)	Superplasticizer (solution) *Superplastifiant* (g)	
C0	450	225	1350	-	0.5
C1	450	225	1350	-	0.5
C2	450	240	1350	-	0.53
C3	450	250	1350	-	0.56
C4	450	255	1350	-	0.57
C0 – 0.9	450	158	1350	4.05	0.35
C1 – 0.9	450	166	1350	4.05	0.37
C2 – 0.9	450	170	1350	4.05	0.38
C3 – 0.9	450	175	1350	4.05	0.39
C4 – 0.9	450	180	1350	4.05	0.40

3. Experimental results

3.1. The influence of variable fly ash additions - alone or associated with the polycarboxylic type superplasticizer on physical properties of Portland cement CEM I 52.5 R pastes

The assessment of the water necessary to obtain standard consistency pastes showed an increase of the volume of water parallel with the increase of fly ash content, both for pastes without superplasticizer and for those with superplasticizer (Table 1).

In the case of pastes without superplasticizer - C0, C1, C2, C3 and C4 - it is highlighted the increase of the volume of water for standard consistency, from 31.4% - for Portland cement paste, up to 37.6% - for cement paste with 50% fly ash (Figure 1). The additions of fly ash with high specific surface area BET (surface area = 2.6421 m^2/g) affect the pastes workability and in order to bring it within limits related to the standard paste, the increase of water volume was necessary (Figure 1).

The presence of superplasticizer in the cement paste, determined significant reductions of the volume of water for standard consistency pastes (29.9-25.5%) (Table 2 and Figure 1).

The setting time, determined on the standard consistency pastes with variable content of fly ash, without superplasticizer, presented a continuously increase, parallel with the fly ash content increase, as outlined in Figure 2. As it can be seen, the initial setting time for the cement with fly ash varied between 93 min. and 225 min., and the final setting time - between 168 min. and 315 min.

In the case of the pastes prepared with superplasticizer, fly ash content causes the delay of the setting. The initial setting time increase from

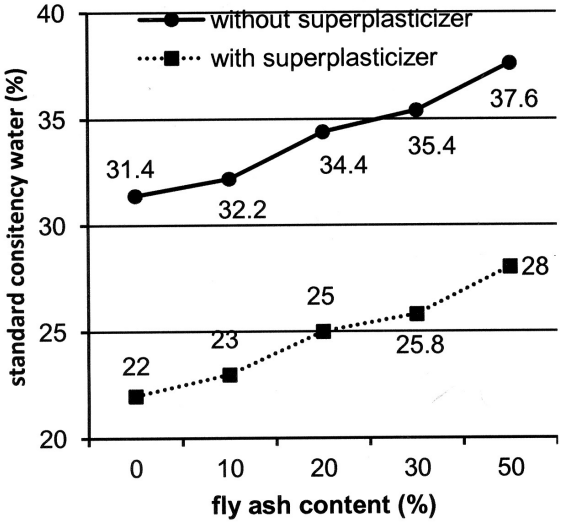

Fig. 1 - The variation of standard consistency water for binder pastes, with and without superplasticizer, depending on the fly ash content / *Variația apei pentru pasta de consistență standard, cu şi fără superplastifiant, în funcție de conținutul de cenuşă.*

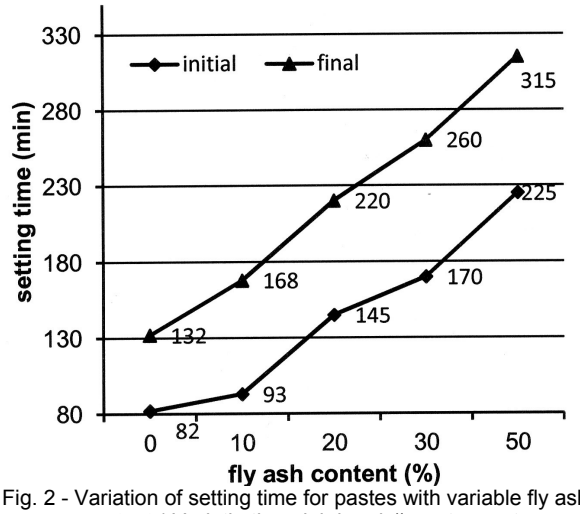

Fig. 2 - Variation of setting time for pastes with variable fly ash content / *Variația timpului de priză pentru paste cu conținut variabil de cenuşă.*

Table 2

Water for standard consistency of cement pastes containing fly ash - without and with superplasticizer.
Apa de consistență standard pentru pastele cu conținut de cenuşă – cu sau fără aditiv superplastifiant

Nr. sample *Indicativ probă*	Binder composition *Compoziție liant* (%)		Super-plasticizer *Super-plastifiant* (%)	H_2O (cm^3 /100g binder/*liant*)	w/b ratio *raport apă/liant*	Water volume changes Volum de apă (%)	
	Cement *Ciment*	F.A.				Increase *Creştere**	Reduction *Reducere●*
C_0	100	-	-	31.4	0.31	-	-
C_1	90	10	-	32.2	0.32	2.5	-
C_2	80	20	-	34.4	0.34	9.6	-
C_3	70	30	-	35.4	0.35	12.7	-
C_4	50	50	-	37.6	0.38	19.7	-
C_0-0.9	100	-	0.9	22	0.22	-	29.9
C_1-0.9	90	10	0.9	23	0.23	-	27.9
C_2-0.9	80	20	0.9	25	0.25	-	27.3
C_3-0.9	70	30	0.9	25.8	0.26	-	27.1
C_4-0.9	50	50	0.9	28	0.28	-	25.5

*Water increase for samples C1, C2, C3, C4, relative to sample C0 / *Creşterea de apă pentru probele C1, C2, C3, C4 raportat la proba C0.*

●Reduction of water for samples C0-0.9, C1 0.9, C2 0.9, C3-0.9, C4-0.9, as compared with samples C0, C1, C2, C3, C4.

●*Reducerea de apă pentru probele C0-0.9, C1 0.9, C2 0.9, C3-0.9, C4-0.9 în comparație cu probele C0, C1, C2, C3, C4.*

48 minutes - for standard paste, to 195 minutes - for paste with 50% fly ash. The final setting time increased from 90 minutes to 310 minutes as shown in Figure 3.

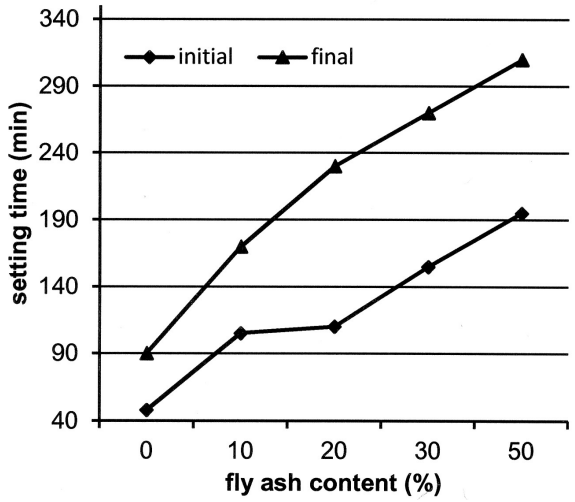

Fig. 3 - Setting time for pastes with variable fly ash content and superplasticizer admixture / *Variația timpului de început de priză în funcție de conținutul de cenuşă.*

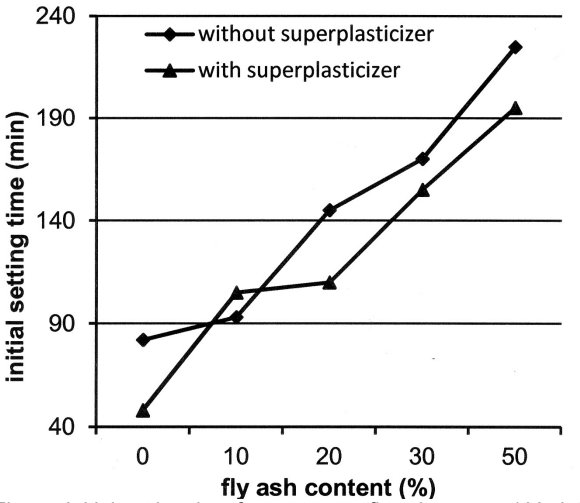

Fig. 4 - Initial setting time for pastes vs. fly ash content / *Variația timpului de priză pentru paste cu conținut variabil de cenuşă şi aditiv superplatifiant.*

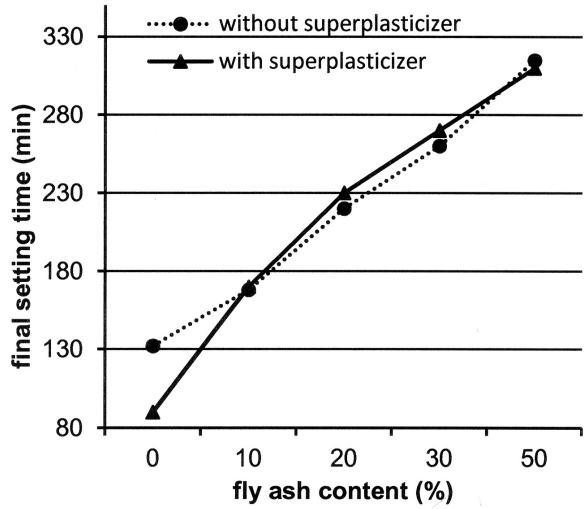

Fig. 5 - Final setting time for pastes vs. fly ash content / *Variația timpului de sfârşit de priză în funcție de conținutul de cenuşă.*

Figures 4 and 5 show the initial and final setting time vs. fly ash content for pastes with and without superplasticizer.

Considerable differences are observed between the initial setting time for pastes with superplasticizer, compared with pastes without superplasticizer the values range from 48 to 82 minutes for fly ash-free pastes, and from 195 to 225 minutes for pastes with 50% fly ash.

The lower value of initial setting time for pastes with superplasticizer additive is correlated with the lower volume of water for standard consistency pastes.

For the final setting time, no significant differences between pastes with and without additives, prepared with binders of similar composition, were noticed. The influence of water/binder ratio seems to diminish for hydration periods longer than 2 hours.

3.2. The influence of variable fly ash additions - alone or associated with the polycarboxylic type superplasticizer additive on mechanical properties of mortars based on portland cement

The data presented in Table 2, shows that in order to obtain similar consistencies for the mortars, the water volume should grow in parallel with the increasing of the fly ash content in the binders, similar cariation was recorded for both series of mortars without or with superplasticizer polycarboxylic additive.

The superplasticizer's presence determines reductions of the water/binder ratio, which varies between 0.13 and 0.17, as is showed in Figure 6.

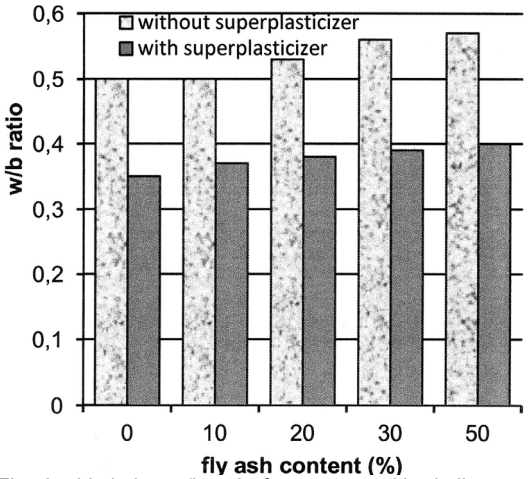

Fig. 6 - Variation w/b ratio for mortars with similar workability, prepared with/without superplasticizer/*Variația raportului apă/liant pentru mortare cu lucrabilitate comparabilă, fără şi cu aditiv superplastifiant.*

The mechanical strengths, determined in standard conditions, show the influence of fly ash and superplasticizer content in the binder.

Figures 7 and 8 show the continuous decrease of compressive strengths when the fly ash content

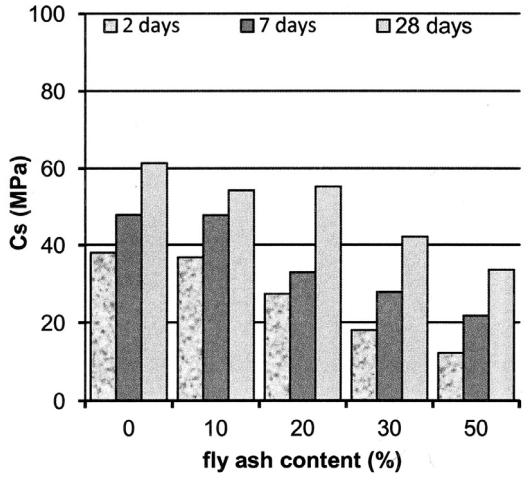

Fig. 7 - The evolution of compressive strengths, 2, 7 and 28 days for mortars prepared without superplasticizer additive/*Evoluția rezistențelor la compresiune la 2, 7 şi 28 zile pentru mortare fără aditiv superplastifiant.*

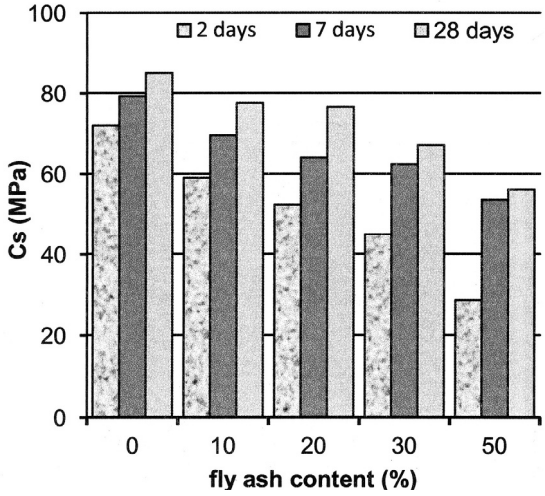

Fig. 8 - The evolution of compressive strengths, 2, 7 and 28 days for mortars prepared with superplasticizer additive/ *Evoluția rezistențelor la compresiune la 2, 7 şi 28 zile pentru mortare cu aditiv superplastifiant.*

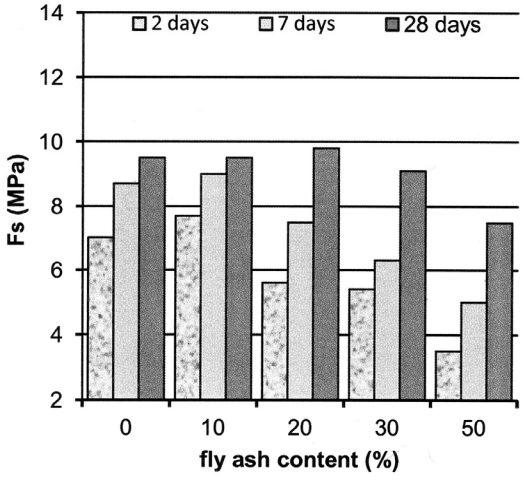

Fig. 9 – The evolution of flexural strengths, 2, 7 and 28 days for mortars without superplasticizer additive/ *Evoluția rezistențelor la încovoiere la 2, 7 şi 28 zile pentru mortare fără aditiv superplastifiant.*

increase. Compressive strength values decreases (with reference to the mortar without fly ash) due to the presence of fly ash in binders 67.9% for 2 days of curing, to 45.2% for 28 days of curing. The decrease of the compressive strengths differences over time (28 days compared to 2 days), is due to the pozzolanic reaction of fly ash which, generally, occurs with low speed. The calcium silicate hydrates formed by pozzolanic reaction, contribute to the development of a high strength hardening structure.

The reduction of the mechanical strengths values, due to fly ash presence, for mortars with superplasticizer additive is smaller as compared with the specimens without additive (Figure 8), in correlation with the lower values of the water/binder ratio for these mortars.

Figures 9 and 10, show the values of flexural strengths recorded on mortars, prepared with binders with fly ash admixture – with and without superplasticizer additive.

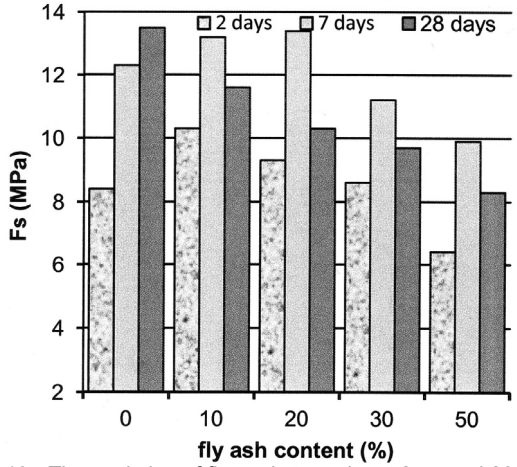

Fig. 10 - The evolution of flexural strengths at 2, 7, and 28 days for mortars with superplasticizer additive/ *Evoluția rezistențelor la încovoiere la 2, 7 şi 28 zile pentru mortare cu aditiv superplastifiant.*

As it can be seen, the mortars with small amount of fly ash (10%) have higher values of flexure strengths, or close to the values recorded for reference mortar, even after 2 days. For mortars without superplasticizer, after 28 days of hardening, the addition of 10-20% fly ash has a neglijable influence on the flexural strengths values (Figure 9).

For mortars with superplasticizer additive, the flexural strengths have higher values than those for mortars without additive, regardless of the binder composition (Figure 10 compared with Figure 9).

The specimens with 10-20% fly ash have superior values of the flexural strength (as compared with reference mortar), for the terms of 2 and 7 days. An unexpected trend was recorded for the 28 days strengths fro the mortars with superplasticizer additive; the flexural strengths are

lower as compared with those recorder after 7 days. A possible explanation for this strength decrease can be due to air entrainment together superplasticizer additive [15] in mortars which contain fly ash; the flexural strengths could be more sensitive to this class of pores.

4. Conclusions

- Admixtures of fly ash with specific surface area of 2.6421 m^2/g (BET), ranging between 10-50% affect the workability of the pastes. For their bringing into the limit values correlated with that of the reference paste, the increase of water volume was necessary, from approximately 31% to approximately 34%.
- The superplasticizer of polycarboxilic type additive into the paste the differences between water/binder ratios of the pastes having different compositions.
- Setting times - initial and final - for the pastes with fly ash increase constantly parallel with the fly ash content. Considering the paste with 50% fly ash, compared with standard paste, the setting time increase was from 82 to 225 min. - for initial setting time, respectively, from 132 to 315 min. - for final setting time. The duration of the setting times was reduced by the superplasticizer additive presence in pastes, at values 48 - 195 min. - for the initial setting time and 90 - 310 min. – for final setting time, respectively. In addition to the reduction of the water amount required for standard consistency pastes, the superplasticizer contributes to the increase of pastes workability.
- The presence of fly ash in high proportions (up to 50%) determines an important decrease of the compressive strengths values this decrease is more important for a higher fly ash content (over 20%).
- The polycarboxylic superplasticizer addition (0.9%) determined the development of higher strengths for mortars with similar compositions as those without additive; this behaviour was observed for all the test periods i.e. 2-28 days. It is noteworthy for example, the mortar containing 30% fly ash and 0.9% polycarboxylic additive developed a compressive strength of 67 MPa, after 28 days of hardening, compared with 61.3 MPa, for reference mortar without additive.
- Flexural strengths are less affected by fly ash's presence, especially when used in combination with the polycarboxilic superplasticizer additive.

Acknowledgements

This work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/60203.

REFERENCES

1. C.D. Lawrence – The production of Low-Energy Cements, in Lea's Chemistry of Cement and Concrete, St. Edmundsbury Press LTD, St. Edmunds, 1998.
2. J.P. Merik – Low Energy Clinker Formation, Proc. 8th Intern. Congr. Chem. Cem., Rio de Janeiro 1986, 1, 52.
3. F.W. Locher - Low-Energy Clinker, Proc. 8th Intern. Congr. Chem. Cem., Rio de Janeiro, principal paper, 1986, **1**, 57.
4. P.K. Mehta – Investigation on Energy-Saving Cements World Cement Technology, 1980, (5), 166.
5. G.K. Moir, F.P. Glasser – Mineralisers, Modifiers and Activators in the Clinkering Process, Proc 9th Intern Congr. Chem. Cem. New Delhi 1992, **1**, 125.
6. J. Harder – Development of Clinker Substitutes in the Cement Industry, ZKG International 2006, **59** (2), 58.
7. R.N. Swamy – Design for durability and strength through the use of fly ash abd slag in concrete, Mario Collepardi Symposium on advances in Concrete Science and Technology, Fifth CANMET/ACI, 1997,127.
8. V. Costa, and F. Massazza, Some Properties of Pozzolanic Cements Containing Fly Ashes, ACI Publ. SP-79, ed. V.M. Malhotra, 1983, **2**, 235.
9. N.P. Mailvaganam, R.S. Bhagrath, and K.L. Shaw, Effects of Admixtures on Portland Cement Concretes Incorporating Blast Furnace Slag and Fly Ash ACI Publ. SP-79, ed. V.M. Malhotra, 1983, **1**, 579.
10. R.N. Swamy, and J.C. Laiw, Effectiveness of Supplementary Cementing Materials in Controlling Chloride Penetration into Concrete, Fly Ash, Silica Fume, Slag and Natural Pozzolane in Concretes, ACI Publ. SP-153, ed. V.M. Malhotra, 1995, **2**, 657.
11. R.A. Helmulth, Water-reducing Properties of Fly Ash in Cement Pastes, Mortars and Concretes: Causes and Test Methodes, ACI Publication SP-91, ed. V.M. Malhotra, 1986, **1**, 171.
12. I. Papayianni, and E. Anastasiou, Self compacted concrete with fly ash adition, Romanian Journals of Materials, 2011, **41** (3), 181.
13. M. Gheorghe, N. Saca, C. Ghecef, and R. Pintoi, Development of low-cost concrete for road pavements, Romanian Journals of Materials, 2012, **42** (1), 11.
14. C. Munteanu, and M. Georgescu – The influence of carboxylate type polymer as superplasticizer additive type in the water-cement system, Romanian Journal of Materials,2012, **42** (2), 122.
15. xxx, Romanian Asociation of Standardization. SR EN 196-3:2006 Cements testing methods. 3rd Part: Determination of setting time and stability.
16. xxx, Romanian Asociation of Standardization. SR EN 196-1:2006 Cements testing methods. 1st Part: Determination of mechanical strength.

****