ROLE OF SUPERPLASTICIZER ADDITIVES UPON HYDRATION PROCESS OF CEMENT PASTES

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Abstract. *The article presents a comparative analysis on the hydration of cement paste without superplasticizer and water/cement ratio of 0.35 and a cement paste with the same water /cement ratio but has in its composition 2% superplasticizer additive Glenium Sky 526. For characterizing the hydration process of cement paste, both mixtures were subjected to X-ray diffraction and thermogravimetry analysis, at 3, 7, and 28 days passed since the initiation of hydration process.*

Keywords: *portland cement, superplasticizer additive, X-ray difraction, termogravimetry*

1. INTRODUCTION

Coagulation structures that occur in the curing / hydration process of Portland cement binders, are of great importance in implementing technologies in the work of Portland cement based products. Based on coagulation structures develop crystallization structures and condensation-crystallization structures with different properties, their occurrence as a consequence of hydration-hydrolysis processes of mineralogical constituents passing into stable hydration systems.

The present of superplasticizers additives can alter the kinetics of hydration than by changing curing time and the occurrence of specific hydration products at different time intervals [1].

2. MATERIALS USED AND EXPERIMENTAL WORKS

2.1. Superplasticizers

In present study are *used* two types of polycarboxylate based superplasticizer, more exactly polycarboxylate ether admixtures/additives. First used is the superplasticizer known as Glenium Sky 526. For this superplasticizer additive the technical data and the chemistry are presented also in table 1 [2].

2.2. The cement

Cement paste mixtures were prepared with a CEM I 42.5R type cement with Blaine specific surface area of 380 m2/kg and specific gravity of 3.12. The same cement was also used in concrete mixtures. Oxide compsition of the cement is shown in Table 2.

Table 1 Technical data and chemistry for Glenium Sky 526

Superplasticizer type	Glenium Sky 526
Relativ density (20ºC):	1,07 ± 0,02 g/cm3
Viscosity (20ºC):	< 100 cps
Alkali content	≤ 2.5 % (EN 934-1 / 2008)

Table 2: The chemical properties of cement (CEM I 42.5 R)

Oxide (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Cl	L.O.I.
Cement	19.30	5.57	3.46	63.56	0.86	0.13	0.80	2.91	0.013	2.78

3 . RESULTS AND INTERPRETATION OF EXPERIMENTAL WORKS

3 3.1. Analysis by X-ray diffraction

There were determined the mineralogical compounds of portland cement (cement paste prepared with a water/cement ratio of 0.35 and without superplasticizer), such as alite, belite and celite, and CaO, the compounds of the blast-furnace slag, admixture of cement (SiO_2, $Al_3Fe_5O_{12}$, Al_3FeSi, $Ca_3Al_2Si_3O_{12}$), and hydration products $Ca_6Si_2O_7SiO_4\ (OH)_2$, which is a type CSH and portlandite $Ca(OH)_2$ (Fig. 1). Following roentgenografic spectrum in Fig. 1 a, b and c, it can be seen that with increasing hydration period from 3, 7 and then at 28 days, the alite spectral lines decrease in intensity. This phenomenon proves that the alite after hydration turns into CSH, even if they are not very well highlighted in Fig. 1 b and c. CSH can be seen only by X-ray diffraction analysis in simple cement paste at 3 days of hydration. The difficulties of highlighting the CSH hydration product in simple cement paste at periods of 7 and 28 days, is because this product is not well crystallized, being in the form of gel, which makes hard to identify it, in the X-ray spectrum [1, 3 - 5].

X-ray diffraction analysis carried out on a sample of cement paste with 2% additive Glenium Sky 526, at 3, 7 and 28 days highlighted the presence of mineralogical and hydration products - also determined on simple cement paste, supplementary one more compound, $CaFe+2SiO_4$, originated probably from the addition of blast-furnace slag used in the preparation of portland cement (Fig 2).

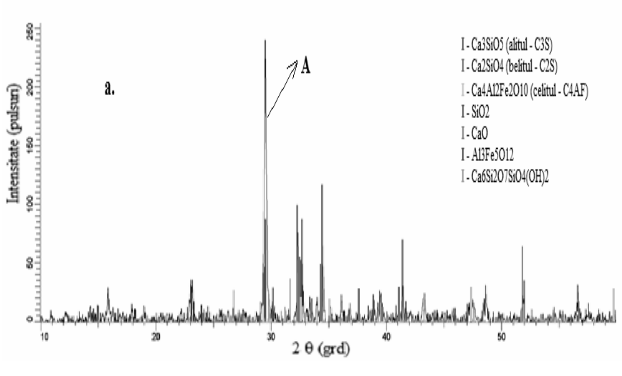
Following the results of X-ray diffraction analysis for both normal and additivated cement pastes, it can be seen that the spectral intensities reveals that alite hydration process occurs similarly from 3 to 7 days in both mixtures and from 7 to 28 days, more intense hydration process occurs in the mixture with 2% additive Glenium Sky 526, as evidenced by the reduced spectral intensities of alite (Fig. 2 c), in comparison with the simple cement paste (Fig. 1 c) [3 - 5].

3.2. Thermogravimetric analysis of cement pastes

For the samples without superplasticizers additive there were 3 temperature intervals where there were mass losses. Interval I (50° - 200° C), the maximum effect of this mass loss occurs at the minimum of the DTG curve at 127.2° C, denoted by A on the curve, this loss being 6.07% (point 1 – Fig. 3 a) at 3 days of hydration. At 7 days the mass loss was 7.31% (1) at a temperature of 125.1° C (point A, Fig. 3 b), and at 28 days (Fig. 3 c) a loss of mass was 10.89% with a maximum at 145.5° C. In this temperature interval the mass loss was due to the elimination of free water.

On the interval II (420^o – 520^o C) the mass loss was recorded only at 28 days, 3.15% (point 2) with a maximum temperature of 486.5° C, mass loss due to dehydration of calcium hidrosilicates and, possible, hydrosulphite aluminate phases.

The third interval (700^o- 800^{o}C) had a mass losses of 14.27% (2) with a temperature maximum at 822.9 ° C (B) at 3 days. At 7 days the mass losses was 16.26% at 825.2^o C and after 28 days the mass losses were 9.65% (3) at a temperature of 836.5 ° C. The mass loss on interval III are due to the elimination of the chemically bound water of hydration products of the cement, such as calcium hidrosilicates CSH (type II) in crystalline form [6 - 10].



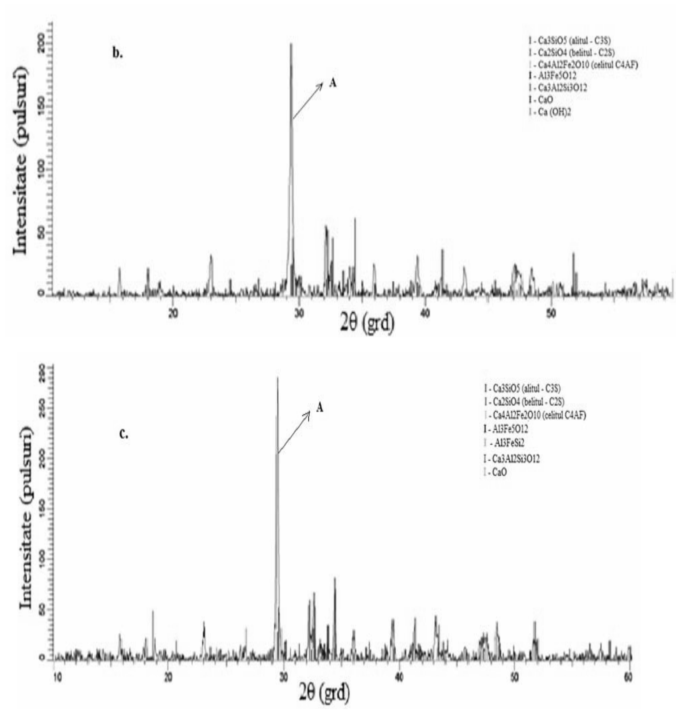


Fig. 1. X-ray diffraction spector of simple cement paste, without superplasticizer additive: a. at 3 days of hydration, b. 7 days of hydration; c. 28 days of hydration

In the case of cement paste with 2% superplasticizer additive Glenium Sky 526, the mass losses interval I (50^o – 200^{o}C), at 3 days was 9.31% with a maximum at 134.9^o C. At 7 days there was a mass loss of 8.98% with a maximum at 136.5° C and at 28 days there was a mass loss of 10.56% with a maximum at 134.7^o C (Fig. 4).

In second interval II (420^o – 520^{O}C) were recorded at 3 days a mass losses of 1.76%, with a maximum at 475.8° C (Fig. 4 a), at 7 days the mass losses was 1.65 % at a temperature of 479.3 ° C (Fig. 4 b), and at 28 days the mass losses was 2.56% with a maximum at 479.3 ° C (Fig, 4 c).

On interval III (700^o – 800^o C), mass losses were 11.09% with a maximum at 833.4° C, at 3 days, at 7 days were recorded mass losses of 14.45% within at 838^o C and at 28 days the mass losses were of 11.07% with a maximum at 839.1° C [6 - 10].

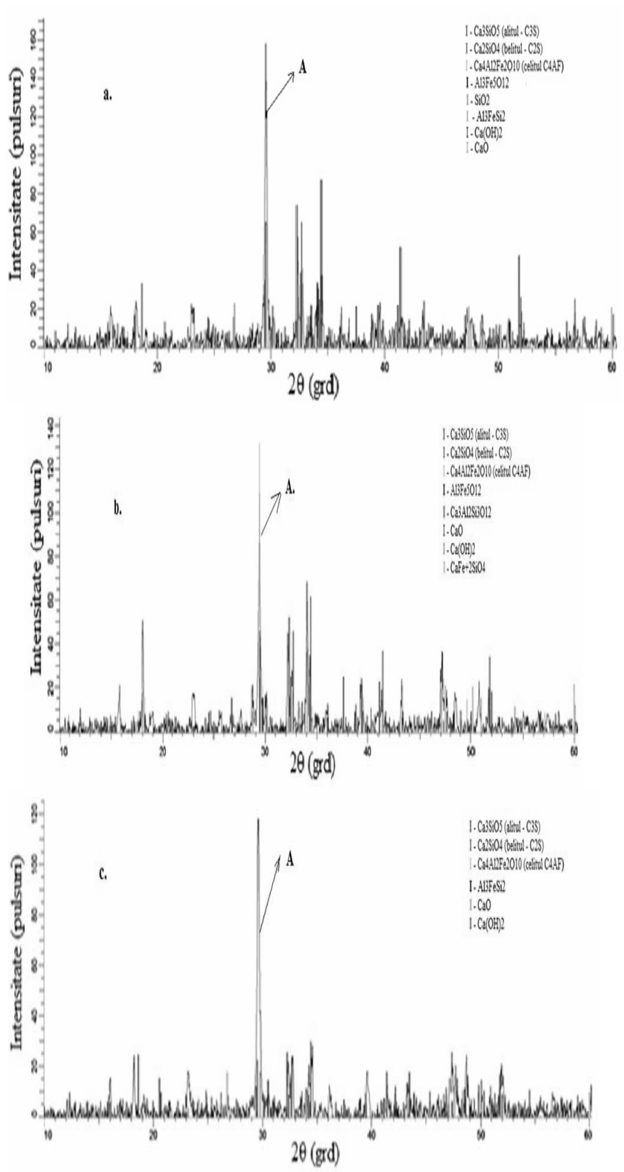


Fig. 2. X-ray diffraction spector of cement paste with 2% superplasticizer additive Glenium Sky 526: a. at 3 days of hydration, b. 7 days of hydration; c. 28 days of hydration

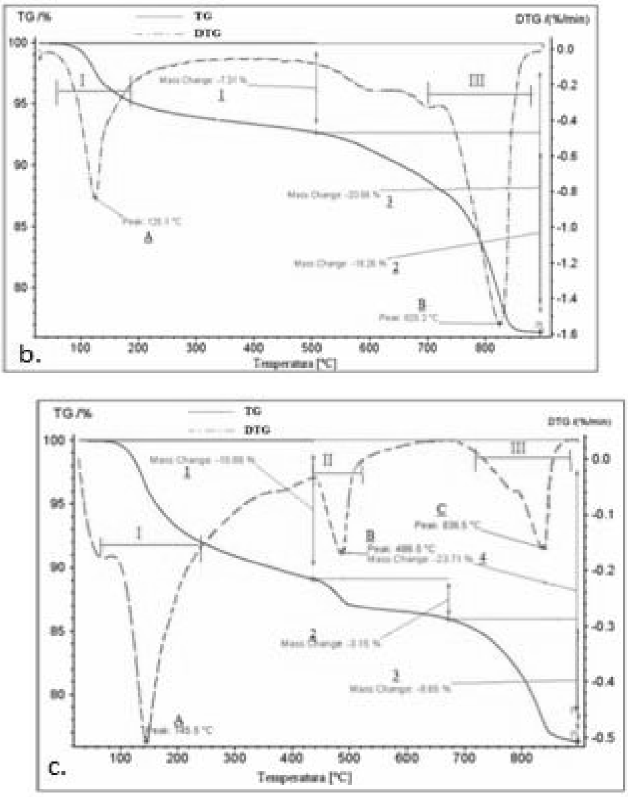
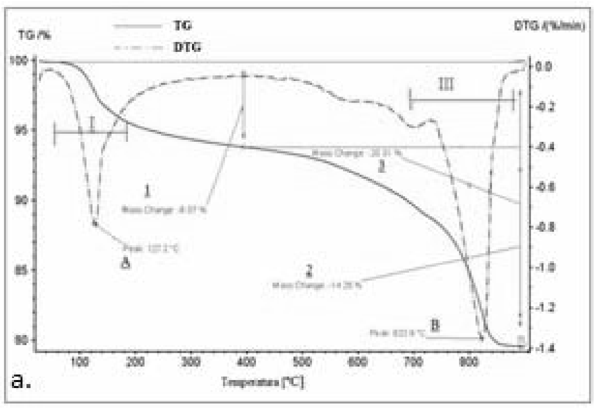
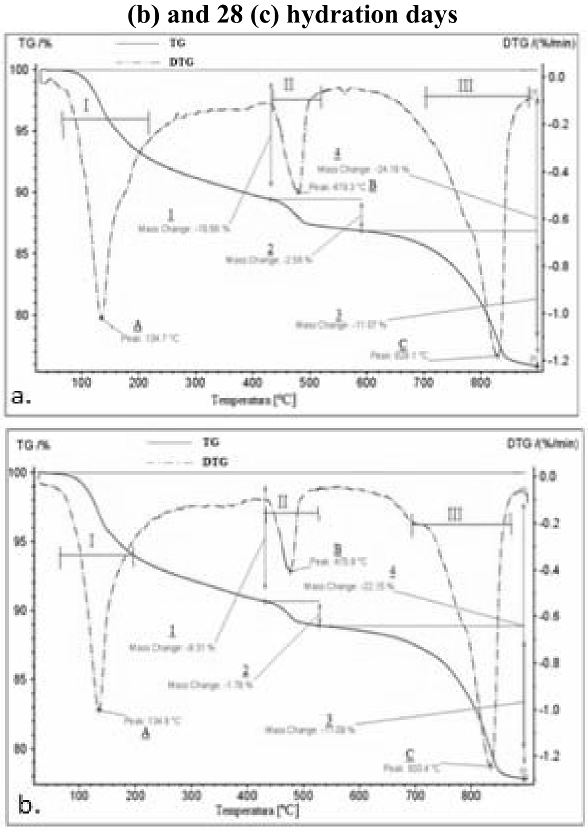


Fig. 3. Thermogravimetric analysis of simple cement paste, without superplasticizer additive, after 3 (a), 7 (b) and 28 (c) hydration days





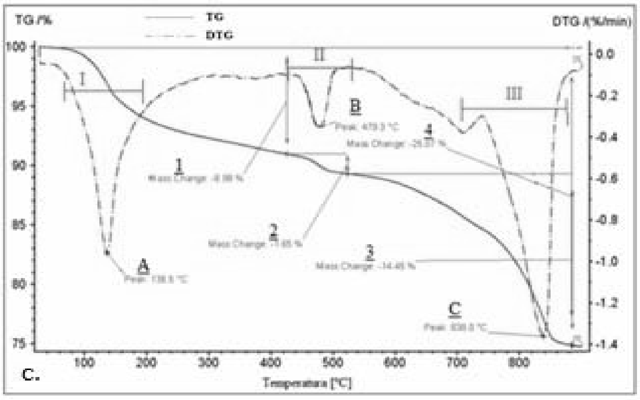


Fig. 4. Thermogravimetric analysis of cement paste with 2% superplasticizer additive Glenium Sky 526, after 3 (a), 7 (b) and 28 (c) hydration days

4. CONCLUSIONS

- X-ray diffraction of the sample without additive at 3 days highlighted the hydration product $Ca_6Si_2O_7SiO_4(OH)_2$ resulting from alite hydration, which is responsible for strength developing,
- X-ray diffraction spectra of the sample without additive highlighted the presence of hydration product $Ca(OH)_2$ at 7 days of hydration.
- X-ray diffraction of the sample with the addition of 2% Glenium Sky 526 has detected the presence of $Ca(OH)_2$ in all the hydration periods (3, 7 and 28 days). So, the Glenium Sky 526 additive favors the development of $Ca(OH)_2$, which result from the hydration of calcium silicates,
- Were revealed 3 temperature intervals where there are mass losses in the case of thermogravimetric analysis.
- The smallest mass losses has the simple cement paste, cured at 3 days, 20.31%, while the largest mass losses has cement paste sample, prepared with 2% superplasticizer additive Glenium Sky 526, cured at 3 days, whose value is 25.07%.
- It demonstrates the existence of a more important degree of hydration in the cement paste with 2% Glenium Sky 526 comparing with the simple cement paste sample.

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