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INFLUENCE OF THE CALCIUM SULPHATE TYPE ON THE HYDRATION AND HARDENING PROCESSES OF SOME TERNARY BINDERS SILICATE-ALUMINATE-SULPHATE

Andreea MONCEA[1], Maria GEORGESCU[2]

In the last years, the ternary binders silicate aluminate sulphate had developed a greater interest because of their utilization for dry mortars. The main binders which compose these binders are Portland cement, calcium aluminate or high aluminate calcium cement and calcium sulphate. The last can be used in different forms (gypsum, hemi hydrate or anhydrite), the type and amount of them having an important influence on physical-chemical properties of the mortars.

Data concerning the influence of the calcium suphfate type, used as hemyhidrate and anhydrite on the physical-mechanical properties of the complex, ternary binders are brought in this paper. The data concerning the chemical processes occurring at the binder's hardening, resulted by X-ray diffraction analyses are also presented.

Keywords: high alumina cement, Portland cement, calcium sulphate, ternary binders

1. Introduction

It is very well known the calcium sulphate role in Portland cement setting time adjustment. In modern cement industry and especially in “dry mortars” domain [1], the complex binders containing calcium sulphate and calcium aluminate cement are of interest. An important category of dry mortars are made using silicate – aluminate – sulphate ternary binders [2, 3]. The last component is founding as gypsum, hemihydrate or natural anhydrite, it type significant influencing the mortars/concrete properties.

By adding of calcium sulphate in different amounts and forms, the physical-mechanical properties of the binders are influenced [4]. Calcium sulphate, Portland cement and high alumina cement association, leads to obtaining the binders with special properties like: rapid setting and hardening, good initial strengths development [5], controlled volume modifications during of the hardening etc.

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[1] PhD student, Depart. Science and Engineering of Oxide Materials and Nanomaterials, University POLITEHNICA of Bucharest, Romania, e-mail: moncea.andreea@gmail.com

[2] Prof., Depart. Science and Engineering of Oxide Materials and Nanomaterials, University POLITEHNICA of Bucharest, Romania

In the present paper, information regarding the influence of type and amount of calcium sulphate on physical-mechanical properties of some ternary binders silicate-aluminate sulphate are brought.

2. Experimental

2.1. Materials and binding compositions

For achievement of the ternary binders, the following materials were used:

- ordinary Portland cement, CEM I 42,5 (PC), (according to SR EN 197 – 1:2002) [6];
- calcium sulphate – hemyhidrate and anhydrite III ($C\overline{S}H_{0.5}$, $C\overline{S}$), characterized by a high fineness, with a specific surface area S_{sp} = 3590 cm^2/g; anhydrous calcium sulphate was obtained by thermal treatment at temperature of 600°C, for two hours and slow cooling in the furnace; it was identified by X-ray diffraction analysis [4];
- High alumina cement (HAC), GORKAL 50, with high alumina content, Al2O3 = 50%, with a good resistance at high temperatures ranging 1300 - 1400°C; the fineness was determinate by Blaine method (according to SR EN 196 – 6:1989) [7], was characterized by a specific surface area S_{sp} = 2188 cm^2/g.

The ternary binding compositions, prepared and investigated in terms of the main properties are presented in table 1.

Table1

Binder compositions

Materials [%]	**M_1**	**M_3**	**M_9**	**M_{10}**	**P_1**	**P_3**	**P_9**	**P_{10}**
OPC	90	85	20	10	90	85	20	10
HAC	5	10	50	60	5	10	50	60
$C\overline{S}H_{0.5}$	5	5	30	30	-	-	-	-
$C\overline{S}$	-	-	-	-	5	5	30	30

Binding pastes with water/binder ratio = ½, were prepared for some investigations. These were kept in sealed bottles at 20 ± 2°C for periods of 1, 7 and 28 days. At these periods of time, the hydration was stopped by acetone washing and oven-drying at 60°C for 2 hours. To highlight the initial compounds evolution in time and new compounds formation, X-ray diffraction analyses were performed on selected paste specimens and anhydrous powders, using a X-ray diffraction analyzer, SHIMADZU XRD-6000 diffractometer (with Kα; λ = 1.5418 Å with 0.02° and 2 dgr/min. pas).

Investigations concerning micro-structural particularities for each category of binders were selective performed using HITACHI S2600N microscope. The scanning electron microscopy (SEM) analyses were made on the samples coated with Au.

The setting time and the mechanical strengths development by the hardening of the binders were determined using the standard methods [8]. For compressive strengths determination, the specimens from mortar with binder/sand ratio of ½ and water/binder ratio of 0.5 were prepared and cured until 28 days in humid atmosphere (r.h = 95%).

3. Results

The graphic representations from Fig. 1and 2 reveal a different behavior of the ternary binders pastes from *setting time* point of view. For setting time determination, the pastes with standard consistency were used. HAC content and calcium sulphate type in binder's composition has influenced in important measure, the setting time.

For the binders with $C\overline{S}H_{0.5}$ content, the setting time becomes shorter in parallel with the increase of HAC content, in the range of 5-10%, for the binders M_1 and M_3. For the binders M_9 and M_{10} with 50-60% HAC the setting becomes very rapid (Fig. 1). This means a very high rate of hydration processes, which provides also, development of good initial strengths. As a result, these last compositions could not be considered for practical application, without the use to theirs preparation of a superplasticizer with retarding effect on setting time.

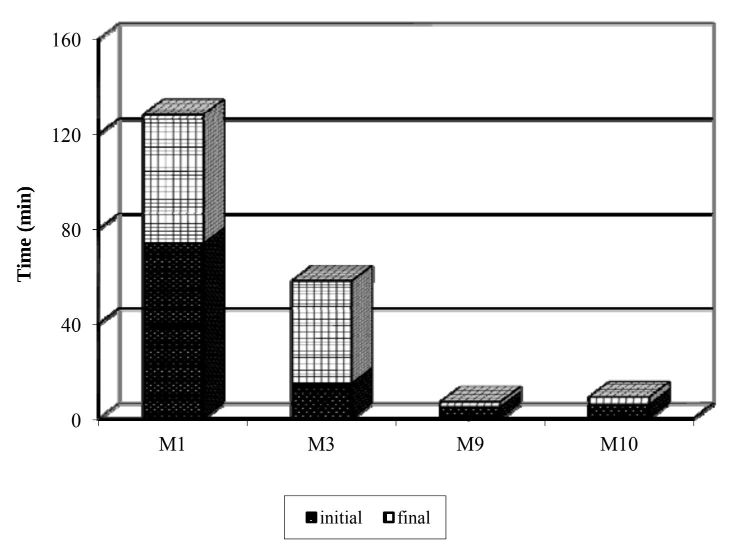

Fig. 1 Setting time of the ternary binders with hemihydrate calcium sulphate content

For the binders with $C\overline{S}$ content, the setting time variation in function of HAC content (Fig. 2) was not as regular as those for the binders with hemihydrate content (see Fig. 1). Is obvious the slower setting of the pastes with $C\overline{S}$ content and high contents of HAC – P_9 and P_{10} (Fig. 2). This behavior could be explained by the different solubility of the two forms of sulphate.

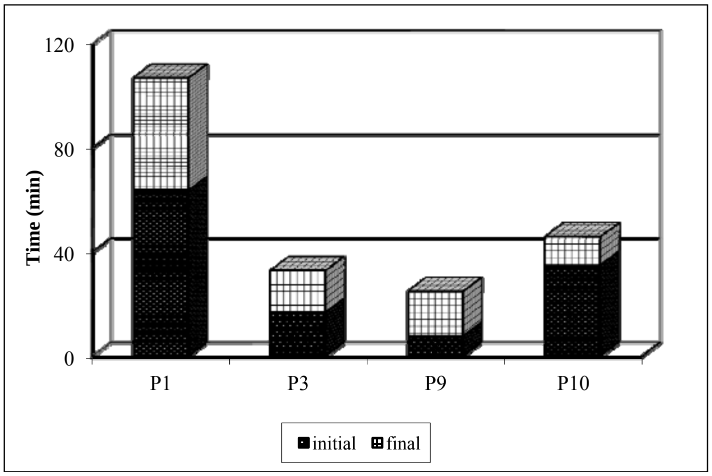

Fig. 2 Setting time of the ternary binders with anhydrous calcium sulphate content

With the object of preparation certain ternary binding masses with practical applicability, the use ob a polymer additive can be considerate [9-11]. For M_{10} binding composition with rapid setting and hardening the influence of hidroximethil ethilcellulose (HMEC) polymer additive was considered.

The influence of 0.4% and 0.7% polymer additive (HMEC) on setting time of M_{10} binder is shown in Fig. 3.

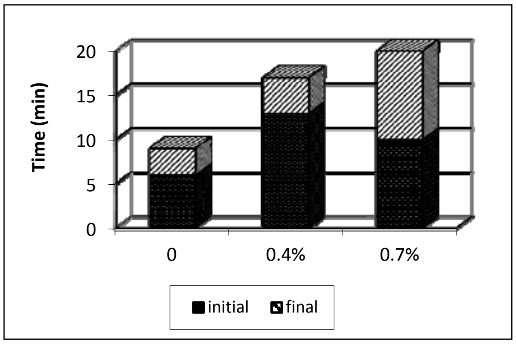

Fig. 3 Setting time variation function of HMEC amount, for M_{10} binder

The polymer additive is obvious beneficial for setting time increase. 0.4% HMEC addition increased the setting time, determining a double initial setting time. The increase of the HMEC proportion to 0.7% did not importantly modified the setting time, in comparison with 0.4% addition.

Considering the binders with hemihydrate sulphate content, the OPC/HAC ratio, affects especially the initial strength, in correlation with hemihydrate content (Fig. 4). In the case of binder with a low (5%) or very high (30%) calcium hemihydrate sulphate content, the compressive strengths are generally (including initial), lower for the binders with OPC/HAC higher ratio (M_1, M_3). A good evolution of compressive strengths in time with increasing values showed M_1 binder.

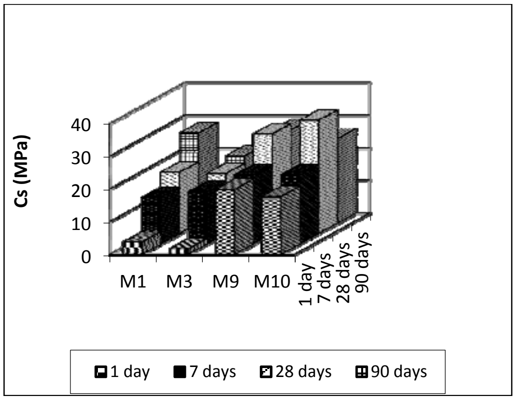

Fig. 4 Compressive strengths variation in time for the binders with C$\overline{S}$ $H_{0.5}$: 5% (M_1 and M_3) and 30% (M_9 and M_{10})

For this binder, the initial strength is relative low, but it increase importantly in time, at this evolution, the great quantity of Portland cement (90%) having an important contribution.

The binders with anhydrous calcium sulphate content developed generally, better compressive strengths in comparison with those containing hemihydrate. For this category of binders, the initial mechanical strengths are also, favorably influenced by smaller OPC/HAC ratio (P_1, P_3), the influence of higher HAC content being stronger for the compositions with 30% **C**$\overline{S}$ content – P_9 and P_{10} (Fig. 5).

The binders with higher content of calcium sulphate are noticeable by very high initial strengths. For these binders, the compressive strengths, after one day have values of approximately 20 – 34 MPa. But in time, even after 7 days the mechanical strengths diminished which can be a consequence of some internal stresses caused by rapid hydration processes or some transformation processes of initially formed hydrates, these binders having high content of HAC (50%).

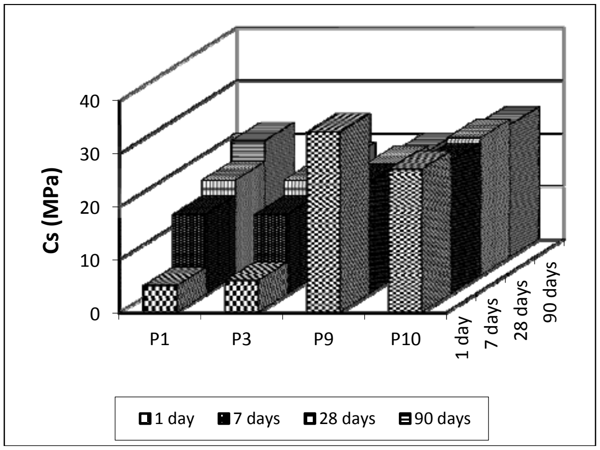

Fig. 5 Compressive strengths variation in time for the binders with C$\overline{S}$: 5% (P_1 and P_3) and 30% (P_9 and P_{10})

The X-ray diffraction analysis brings data that can be correlated with mechanical strengths evolution.

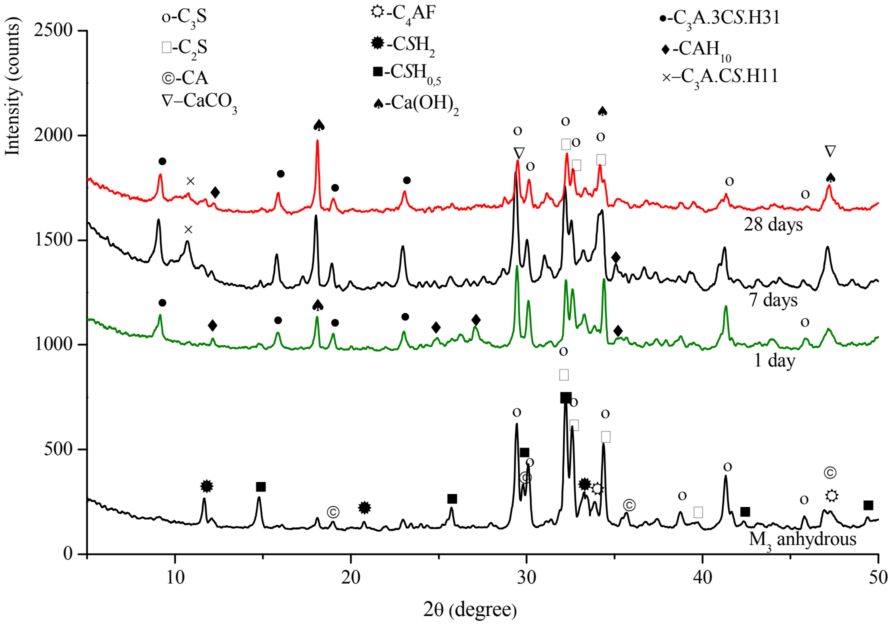

Fig. 6 X-ray patterns of M_3 binder – anhydrous and hydrated 1, 7 and 28 days

The X-ray patterns of M_3 specimen (Fig. 6) show the binder's hydration evolution, by diminish of specific peaks intensity for anhydrous compounds - C_3S,

C_2S and CA. Calcium sulphate $C\overline{S}H_{0.5}$ is totally consumed in the first day of hydration.

The main formed hydrates are calcium silicates hydrates, initially poorly crystallized. In time they evolve by polycondensation and crystallization phenomena, which lead to the hardening structure formation. As crystalline hydrates, even after the first day, calcium hydroxide and ettringite were detected. The ettringite is well evidenced after 28 days too but, beside it, on the X-ray pattern small peak specific to monosulphate aluminate hydrate appears. This last compound is formed by partially transformation of ettringite.

The hardening processes of the complex binders with anhydrous calcium sulphate are similarly to those discussed above for systems with calcium sulphate hemihydrate. Some differences can appear in the processes kinetic.

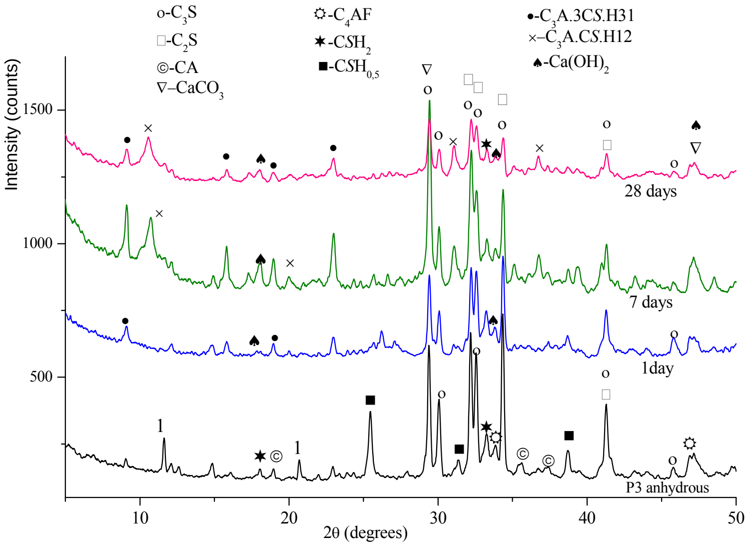

Fig. 7 X-ray patterns of P_3 binder – anhydrous and hydrated 1, 7 and 28 days

As can see in Fig. 7, anhydrous calcium sulphate, as well as dihydrated calcium sulphate brought by Portland cement in P_3 binder is consumed in the first day of hydration, with ettringite formation. This compound presence is evidenced on X-ray pattern by small peaks. These become higher in time, but after 7 days monosulphate compound appears, with more intense peaks than for M_3 binder (see Figs. 6 and 7). After longer period of time (28 days), these two sulphate aluminate hydrates coexist. This result is in good correlation with paper [12], in which an equilibrium state between the two complex sulphates salts is considered as possible.

Lower peaks of ettringite formed after one day of P_3 binder (containing $C\overline{S}$) hydration in comparison with M_3 binder (containing $C\overline{S}H_{0.5}$)suggest a lower speed formation of this compound from $C\overline{S}$ in good correlation with data in paper [12]. An explanation for this kinetic peculiarity could be the slower dissolution of $C\overline{S}$ in comparison with $C\overline{S}H_{0.5}$ the ettringite formation reaction being performed slower in the first case.

The SEM analyses were selective performed on M_3 and P_3 samples with preponderant Portland cement content and different calcium sulphate source. The initial hydrates, are calcium silicates hydrates, poorly crystallized, with irregular morphology (Figs. 8a and 9a). These hydrates are initially formed on the anhydrous grain's surface as seen in Fig. 8a. The presence of hexagonal lamellar shape crystals, assigned to CH can observe, for specimen hydrated 28 days (fig. 8b). The ettringite is also present as prismatic crystals as seen in Fig. 8b.

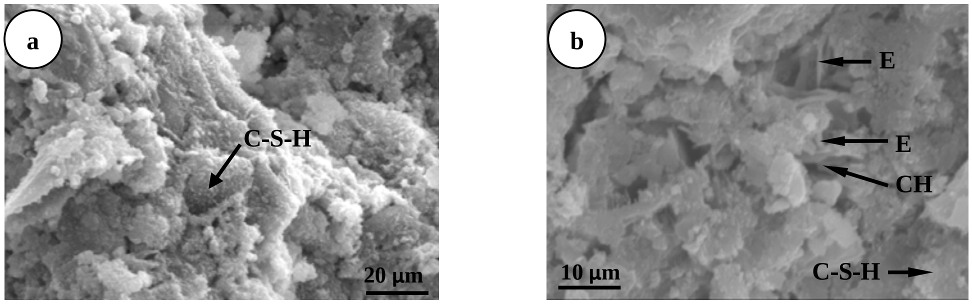

Fig. 8 SEM images of the M_3 binder hydrated: a-one day; b-28 days

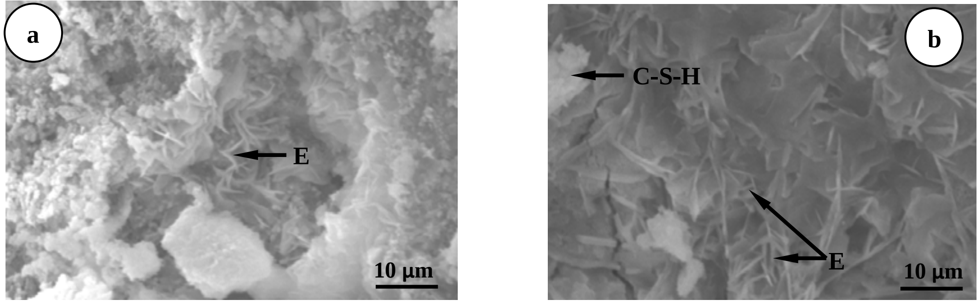

Fig. 9 SEM images of the P_3 binder hydrated: a-one day; b-28 days

The SEM micrographs realized for P_3 binder and presented in Fig. 9, suggest some differences from morphology point of view, in comparison with M_3 binder.

Even after one day of hydration it can appreciate a higher ordering degree of C-S-H phases. In the same time it can see the presence of frequent needles shape crystals belonging to ettringite. After 28 days the binder microstructure has an ordered character with a high crystalline degree of the ettringite. The needle shape crystals are interpenetrated (Fig. 9b); they are coexisting with monosulphate aluminate hydrate and a less ordered silicate hydrate phase.

The SEM images proved the microstructure differences of the ternary binders with different calcium sulphate forms. In the binder with $C\overline{S}$ having a lower solubility than HAC [13] the ettringite is developed like needle shape crystals (see Fig. 9). In this case the structure has a higher ordering degree, with favorable consequences on mechanical strengths. In the binder with $C\overline{S}H_{0.5}$ having a higher solubility than HAC [13], the ettringitte is developed like short prismatic shape crystals. In this case the ordering degree of the structure is lower and the mechanical strengths are also lower than those of binder with similar $C\overline{S}$ content.

4. Conclusions

The type and amount of calcium sulphate into ternary binders silicate-aluminate-sulphate influenced their setting time. So, the binders with higher $C\overline{S}H_{0.5}$ content (30%) are characterized by very short setting time, in comparison with the similar binders containing anhydrous calcium sulphate. The rapid set can be controlled with a 0.4 % HMEC addition.

The compressive strengths developed by the hardening of ternary silicate-aluminate-sulphate binders are also influenced by the type of calcium sulphate. This is a consequence of some particularities of the hydration processes kinetic and microstructural characteristics that the $C\overline{S}H_{0.5}$ or $C\overline{S}$ determines. So, in binder's case with $C\overline{S}$ content, the hydration processes are more rapidly and the main hydrate is ettringite. This compound is found like good developed needle shape crystals, which contribute to formation of a denser hardening structure, which ensures the development of initial mechanical strengths better than for the binders with similar $C\overline{S}H_{0.5}$ content.

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