# INFLUENȚA UNOR FACTORI DE MEDIU ASUPRA COMPORTĂRII UNOR LIANȚI TERNARI SILICAT-ALUMINAT-SULFATICI▲
# THE INFLUENCE OF SOME ENVIRONMENTAL FACTORS ON THE BEHAVIOR OF TERNARY SILICATE – ALUMINATE – SULPHATE BINDERS

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***Considering some previous data concerning binding properties of silicate–aluminate–sulfate composites, the present paper brings complementary data regarding the influence of environmental factors (temperature, humidity), on the behavior of such kind of binders. Composite materials based on ternary binders with Portland cement, high aluminate cement and calcium sulfate (as hemihydrates or anhydrite III) content were investigated.***

***For selected compositions, taking into account their good binding properties in normal conditions, the influence of high temperatures and freezing–thawing effects on the mechanical strengths of such binders were investigated.***

***X–ray diffraction and thermal analysis were carried out for deeper research of involved processes in this complex masses behavior.***

***Considerând unele date anterioare, referitoare la comportarea liantă a unor mase complexe silicat–aluminat–sulfatice, lucrarea prezentă aduce informații complementare, referitoare la influența unor factori de mediu (temperatură, umiditate), asupra comportării unor astfel de lianți. Au fost investigați lianți ternari cu conținut de ciment portland, ciment aluminos şi sulfat de calciu (adus ca semihidrat sau anhidrit III).***

***Pentru compozițiile selectate pe baza determinărilor de proprietăți liante în condiții normale, s-au făcut investigații privind influența unor temperaturi ridicate, precum şi influența solicitărilor repetate de îngheț-dezgheț, asupra comportării unor astfel de lianți.***

***Pentru a obține informații cu privire la procesele implicate în comportarea lianților complecşi în astfel de condiții, la modificările compoziționale induse în anumite condiții, s-au făcut investigații prin analize de difracție cu raze X şi termo-gravimetrice.***

***Keywords:*** *High aluminate cement, Portland cement, thermal properties, ternary binders*

## 1. Introduction

Durability is one of the main characteristics of mortar/concrete composites and a principal criterion for choosing them for specific utilizations. The main indicators of mortars/concretes durability are the freezing-thawing resistance and the behavior to the corrosive media. The behavior in high temperature conditions is a characteristic that can have importance for some utilization.

Freezing-thawing exposure leads to physical degradation of the mortar/concrete composite, because of the induced stresses in its mass by increasing of water volume in pores by freezing. By this phenomenon alternated with exposure at normal temperature (T=20±2$^0$C), when thawing occurs, the hardening structure and therefore the mechanical strengths altering is unavoidably.

The freezing-thawing resistance of the mortars is influenced by different factors which can be grouped in [1-3]:

- factors depending of the concrete composition, binder's type and dosage, water to binder ratio, additives presence;
- processing factors –fresh mortar/concrete processing, curing conditions for hardening;
- environmental factors – exposure conditions of the concrete (humidity, temperature, chemical medium etc).

Beside the main characteristics at normal temperature, the composite materials realized with silicate-aluminate-sulfate complex binders, may present a good stability at high temperatures [4]. The thermal stability of the mortar/concrete composites depend on compositional characteristics:

- ✓ binders with high $Al_2O_3$ content have a good behavior at high temperatures (being even refractory);
- ✓ a lower $Al_2O_3$ content, the presence and nature of some impurities will significantly affect this behavior [5].

Considering some composites materials, realized with silicate–aluminate–sulfate binders, the

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mechanical strength development by hardening is assured by hydraulic properties of Portland cement and calcium aluminate cement. Thermal stability up to a certain temperature is conferred by the high alumina cement. Further, at higher temperatures (>1000$^0$C), the sintering phenomenon occurs and a ceramic binding between dehydrated materials and aggregates is ensured.

The present paper brings information concerning certain properties of ternary binders with Portland cement, high aluminate cement and calcium sulfate (hemihydrate or anhydrite), as: freezing-thawing resistance and high temperatures resistance. The compositions selected for these investigations have been showed a good mechanical behavior in normal curing conditions [6].

## 2. Experimental

The ternary binding masses were realized using as initial materials:

- Portland cement (PC), CEM I 42.5 (acc. to SR EN 197 – 1:2002) [7], characterized by a specific surface area of 2596 $cm^2/g$, determined by Blaine method [8];
- a high aluminate cement (HAC) Gorkal 50, with high alumina content ($Al_2O_3$ =50%) and good stability at temperatures till 1300 – 1400$^0$C;
- calcium sulfate – hemihydrate ($C\overline{S}H_{0.5}$) or anhydrite III ($C\overline{S}$) - obtained by heat treatment of hemihydrates at 600$^0$C for 2 hours.

For high temperatures behavior investigation, certain ternary binders with preponderant HAC content were prepared. Theirs compositions are evidenced in Table 1.

Prismatic specimens with 15mm×15mm×60mm sizes were prepared from mortars, with binder/sand ratio of ½, and water/binder ratio of 0.5. The specimens were compacted by vibration and cured in the following conditions: one day in covered moulds, at room temperature T=20 ± 2°C and after demoulded, the specimens were cured 7 days, on the water, at T=20 ± 2°C and relative humidity of 95% in covered enclosures.

The specimens were oven-drying at 60$^0$C for 24 hours, and then were heat treated at 200, 400, 600, 800, 1000 and 1200$^0$C for 2 hours. After heat treatment the mortar specimens were subjected to compressive strength tests.

For investigation of compositional hydrates changes with temperature, the binding pastes with water / binder ratio of 0.4 were prepared. They were cured and heat treated in the same conditions as was presented above. X-ray diffraction analyses (XRD) were made using a SHIMADZU XRD-6000 diffractometer (with Kα; λ = 1.5406 Å, 0.02º step and 2grd/min).

Some pastes cured in normal conditions for one and 28 days, were analyzed thermogravimetric method (TG), using a Shimadzu DTA-TG-50H instrument, operating in air, with a heating rate of 10ºC/min from RT to 1000ºC, in an open platinum pan.

Prismatic specimens were prepared also for freeze-thaw resistance determinations. For these investigations a big number of specimens were prepared with different PC/HAC ratio and different calcium sulfate nature and content. The considered compositions are presented in Table 2. The freezing-thawing resistance was determined on the specimens cured in following conditions: one day in covered moulds, at room temperature T=20 ± 2°C and after demoulding, they were cured for 28 days, at T=20 ± 2°C and relative humidity of 95%, in covered enclosures. Subsequent the mortar specimens were subjected to freezing-thawing cycles as follows [1, 9]:

- freezing in air at (-18±2)$^0$C for 12 hours;
- thawing at (+18±2)$^0$C for 12 hours in water.

After 10, 40 and 60 freezing-thawing cycles the specimens were subjected to visual assessment concerning species aspects and quantitative compressive strengths determinations.

**Table 1**

Binding compositions with hemyhidrate and anhydrite content
*Compoziții liante cu conținut de semihidrat şi anhidrit*

| Binder indicative *Indicativ liant* | Composition / *Compoziție* (%) | | | |
|---|---|---|---|---|
| | PC | HAC | $C\overline{S}H_{0.5}$ | $C\overline{S}$ |
| $M_9$ | 20 | 50 | 30 | - |
| $P_{11}$ | 15 | 55 | - | 30 |
| $M_{11}$ | 15 | 55 | 30 | - |

**Table 2**

Binding compositions exposed to freezing-thawing cycles / *Compoziții liante expuse la îngheț – dezgheț*

| Binder indicative /*Indicativ liant* | Compositions with hemihydrate content / *Compoziții cu conținut de semihidrat* (%) | | | |
|---|---|---|---|---|
| | PC | HAC | $C\overline{S}H_{0.5}$ | $C\overline{S}$ |
| $M_3$ | 75 | 20 | 5 | - |
| $M_7$ | 50 | 40 | 10 | - |
| $M_9$ | 20 | 50 | 30 | - |
| $M_{10}$ | 10 | 60 | 30 | - |
| $M_{11}$ | 15 | 55 | 30 | - |
| Compositions with anhydrite content / *Compoziții cu conținut de anhidrit* (%) | | | | |
| $P_3$ | 75 | 20 | - | 5 |
| $P_7$ | 50 | 40 | - | 10 |
| $P_9$ | 20 | 50 | - | 30 |
| P8 | 30 | 50 | | 20 |
| $P_{10}$ | 10 | 60 | - | 30 |
| $P_{11}$ | 15 | 55 | - | 30 |

## 3. Results

### *3.1 High temperature behavior*

Mechanical strengths variation of the heat treated specimens at temperature ranging 200 - 1200$^0$C, is shown in Figure 1. It can be observe that mechanical strengths decrease at temperatures above 600$^0$C or even at 400$^0$C – the $M_9$ binder with lover HAC content (50%) and lower residual strength values. This behavior is explained by loosing water from hydrates which ensure good mechanical strengths at normal temperature.

In Portland cement case, the calcium silicate hydrates (C-S-H) are gradually loosing water, even at temperatures lower than 100 $^0$C. Alluminates hydrates are gradually loosing water in correlation with theirs composition.

Dehydration process is totally over 600$^0$C, which explains the totally loosing of strengths at 800$^0$C. The compressive strengths increase for all binding compositions at temperature higher than 1000$^0$C. This evolution can be explained by sintering phenomenon that ensures the binding between dehydrated binders and aggregates. Initial chemical hardening at normal temperature is replaced with a ceramic binding. The images in Figure 2, realized after the heat treatment of specimens at 800 and 1200$^0$C, illustrate the above explained behavior.

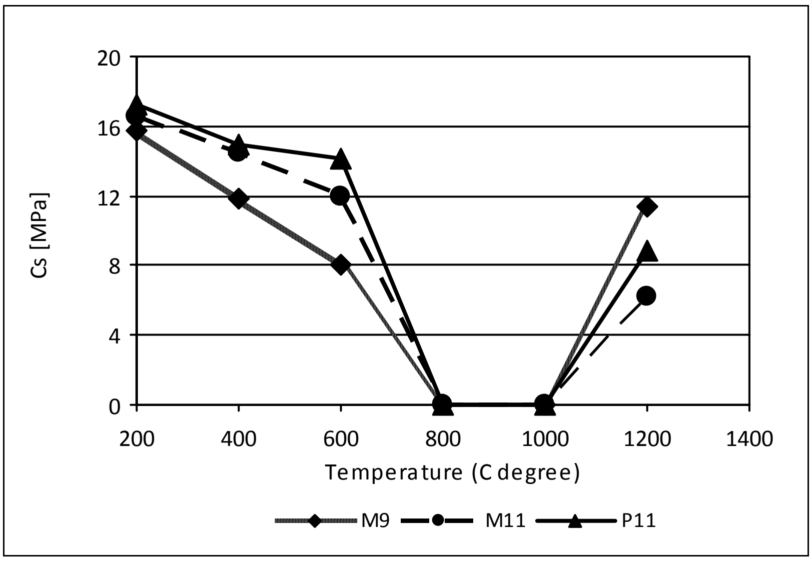
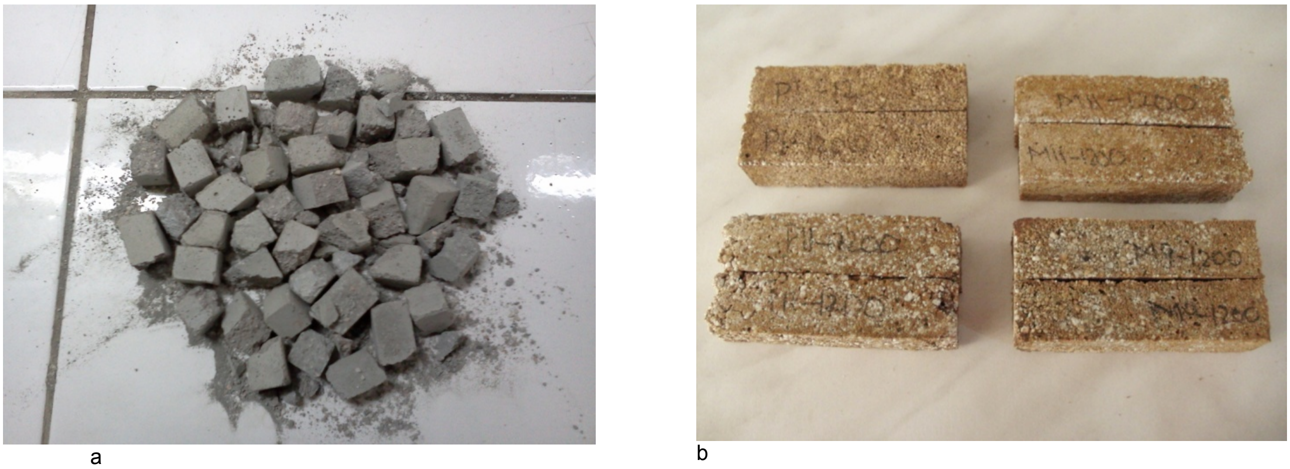
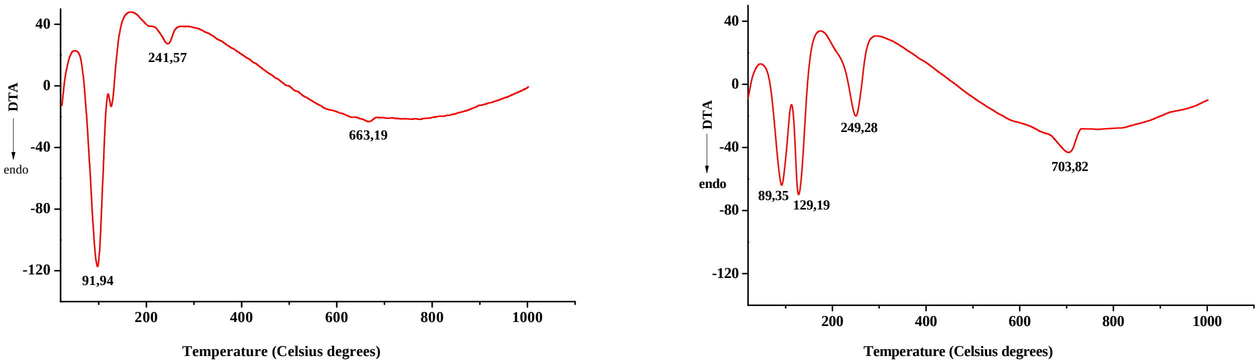



Fig.1 - Compresive strengths of the binding samples, heat treated at 200- 1200 Celsius degrees / *Rezistența la compresiune a probelor liante, tratate termic la 200-1200$^0$C.*



a b

Fig. 2 - Aspect of the specimens with high HAC content heat treated at 800 (a) and 1200 (b) Celsius degrees / *Aspectul probelor cu conținut ridicat de HAC, tratate termic la 800$^0$C (a) şi 1200$^0$C (b).*




a b

Fig. 3 - DTA curves of $M_9$ complex binder, hardened one day (a) and 28 days (b) in normal conditions.
*Curbe ATD ale liantului complex $M_9$, întărit o zi (a) şi 28 zile (b), în condiții normale.*

An image of dehydration processes of the hydrates formed by hardening up to 28 days of $M_9$ complex binder with 50% HAC content is provided by DTA curves in Figure 3. These curves reveal endothermic effects accompanied by mass losses caused by dehydration processes of different hydrates:

- a widely endothermic effects group, with maximum temperatures up to 129$^0$C, correspond to dehydration process of the aluminate sulfate hydrates (mainly ettringite) and calcium silicates hydrates formed in small quantities in binder;
- a less widely endothermic effect, with maximum temperatures between 241-249$^0$C, corresponds to final dehydration process of the ettringite [10];
- an endothermic effect with different amplitude and maximum temperatures for the two hardening periods of time: after one day it has a small amplitude and the maximum temperature at 663$^0$C and after 28 days its amplitude increases and the maximum temperature is 700$^0$C; this effect corresponds to the decarbonation process of $CaCO_3$ formed during specimens processing.

In general, the endothermic effects amplitude and weigh losses are obviously greater for 28 days of hardening, in correlation with greater hydrates quantity formed during hardening process.

X-ray diffraction analyses, presented in Figures 4 and 5, were realized on ternary binders with high HAC content (55%), and different calcium sulfate - $M_{11}$ with hemihydrate and $P_{11}$ with anhydrite, heat treated at 200, 600 and 800$^0$C.

X-ray pattern of $M_{11}$ binder heat treated at 200$^0$C (Fig. 4) reveals hydrates such: calcium sulfate hemyhidrate ($C\overline{S}H_{0.5}$), aluminum hydroxide (AH) and ettringite. These hydrates ensure hardening structure formation in normal conditions and not are found on the $M_{11}$ x-ray pattern heat treated at 600$^0$C. Certainly, the mentioned hydrates suffer a dehydration process even up to 200$^0$C.

At 600$^0$C, anhydrous calcium sulfate interferences appear with high intensity, because of dehydration process of hemihydrate. Beside $C\overline{S}$ it was found monocalcium aluminate (CA), the major mineralogical compound of HAC and $C_2S$, $C_3S$ - compounds of Portland cement.

The X-ray patterns of $P_{11}$ binder with anhydrous calcium sulfate (Fig. 5), present a shape and a heat treated temperature evolution simillar to $M_{11}$ binder,excepting the X-ray pattern of the $P_{11}$

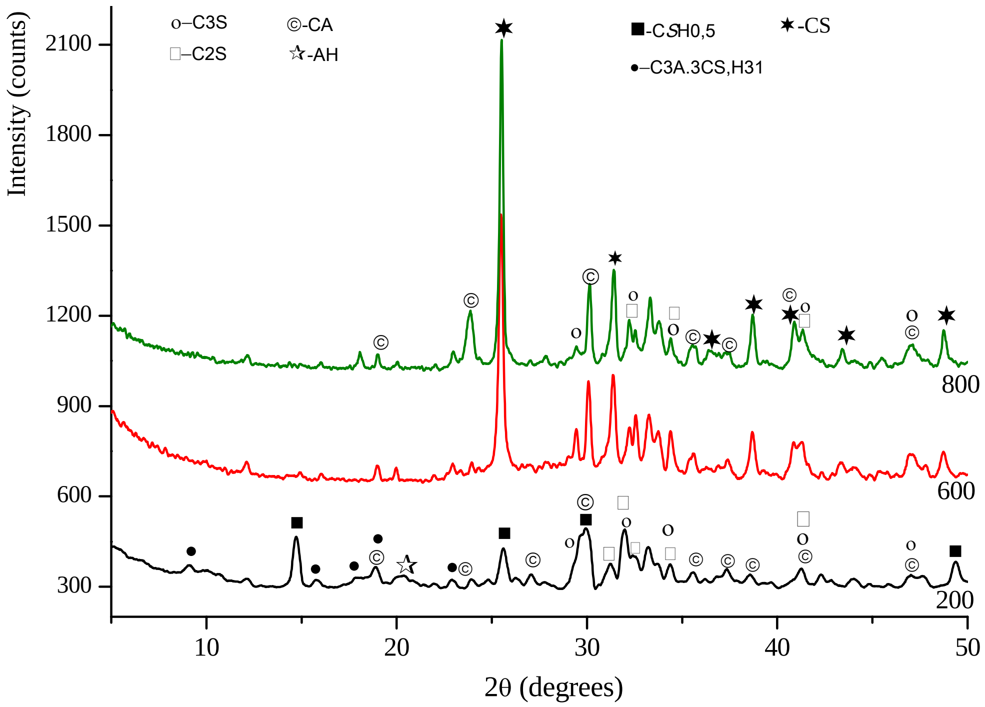



Fig. 4 - XRD patterns of $M_{11}$ binding composition, cured 7 days in normal conditions and after that, heat treated at 200, 600 and 800 Celsius degrees / *Difractograme ale masei liante $M_{11}$, întărită 7 zile în condiții normale şi tratată termic ulterior, la temperaturi de 200, 600 şi 800$^0$C.*

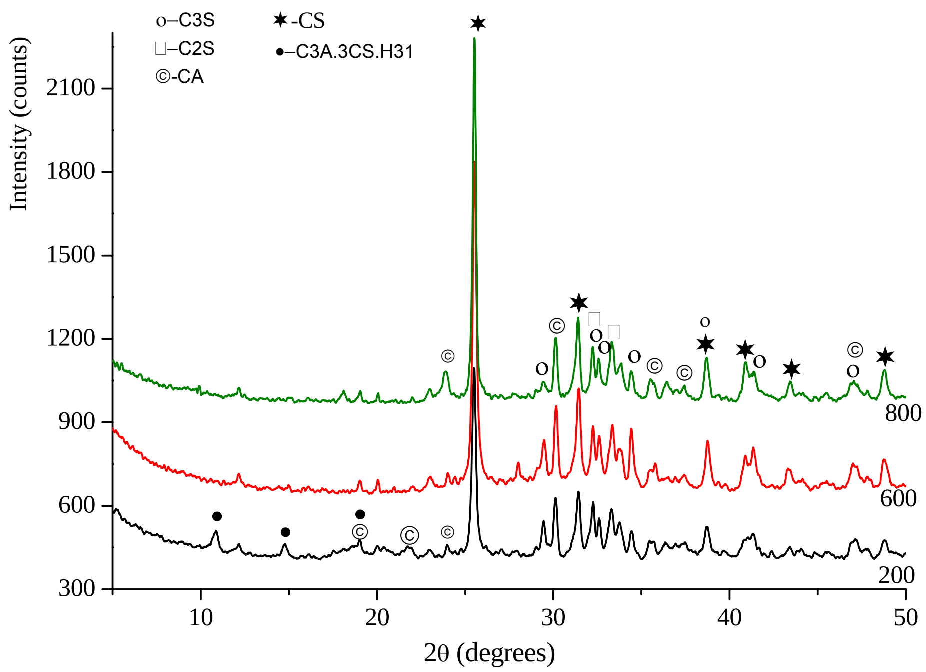



Fig. 5 - XRD patterns of $P_{11}$ binding composition, cured 7 days in normal conditions and after that, heat treated at 200, 600 and 800 Celsius degrees / *Difractograme ale masei liante $P_{11}$, întărită 7 zile în condiții normale şi ulterior, tratată termic la temperaturi de 200, 600 şi 800$^0$C.*

binder heat treated at 200$^0$C, which is different because hemyhidrate interferences disapear and anhydrous calcium sulfate speciffic interferations are present.

### *3.2 Freezing-thawing resistance*

The repeated freezing-thawing stresses of the mortars' specimens lead, as it was expected, to mechanical strength losses and finally even to their cancellation. Superficially damage of specimens is one of the first effects of repeated freezing-thawing stresses, which firstly appear by a deterioration in a surface layer (Fig. 6a), and after that destruction of specimens' edges and corners are visibly (Fig.6b). In parallel with number of freezing-thawing cycles increase, these processes are amplified and by inducing the cracks in the entire body of specimens lead to their full destruction.


a

b

Fig. 6 - Images of some mortar specimens after 60 (a) and 90 (b) freezing-thawing cycles / *Imagini ale unor epruvete de mortar supuse unui numar de 60 (a) şi 90(b) cicluri îngheț–dezgheț.*

The quantitative assessment of freezing-thawing resistance, for the investigated binding compositions was established by determination of strength losses in these conditions. The strength losses were calculated taking into account the initial strength (after 28 days of hardening in normal conditions) and the strengths of the specimens exposed to „n” number of freezing-thawing cycles, using the relation:

$$\Delta R = [(Rc-Rcn)/R_C] \times 100 \qquad (1)$$

In which: Rc is the specimen's strength after 28 days of hardening in normal conditions;

Rcn - compressive strength of the specimens after “n” freezing-thawing cycles.

The compressive strengths values, determinate for mortars' specimens exposed to 10-60 freezing-thawing cycles, are presented in table 3 and show progressive diminutions in parallel with the number of cycles increase. In Figures 7 and 8 the strengths variations of the binder specimens exposed to the freezing-thawing cycles, calculated with the above relation are presented.

For both specimen categories – with $C\overline{S}H_{0.5}$ content (Fig. 7) and $C\overline{S}$ content (Fig. 8), the compressive strengths diminish during freezing-thawing exposure is observed. This diminishing is amplified by the increase of the freezing-thawing cycles number. Considering the strength losses of the exposed specimens to the maximum number of cycles (60), it can observe that the binders with higher PC content and smaller HAC and $C\overline{S}H_{0.5}$ or $C\overline{S}$ content ($M_3$ and $M_7$, respectively $P_3$ and $P_7$) show smaller strength losses compared with the specimens containing higher HAC and $C\overline{S}H_{0.5}$ or $C\overline{S}$ ($M_9$ $M_{10}$ and $M_{11}$, respectively $P_{10}$ and $P_{11}$).

Such difference regarding the stability during freezing-thawing stresses is correlated with the porosity of specimens with different compositions. Capillary porosity of the binder matrices, which strongly influences the mortar specimen's permeability, must be considered as an important factor of influence for the freeze-thaw process [11].

**Table 3**

Compressive strengths of the binding specimens with hemihydrate and anhydrite content, after 10, 40 and 60 freezing–thawing cycles
*Rezistențe la compresiune ale probelor liante cu conținut de semihidrat şi anhidrit, supuse unui număr de 10, 40 şi 60 cicluri îngheț–dezgheț*

| Binder indicative / *Indicativ liant* | Compressive strength / *Rezistența la compresiune* [MPa] | | |
|---|---|---|---|
| | 10 cycles /*10 cicluri* | 40 cycles /*40 cicluri* | 60 cycles / 60 *cicluri* |
| E (Portland cement) | 17.33 | 15.26 | - |
| With hemihydrate content / *Cu conținut de semihidrat* | | | |
| $M_3$ | 18.37 | 13.78 | 13.63 |
| $M_7$ | 15.64 | 9.63 | 8.74 |
| $M_9$ | 16.8 | 14.22 | 11.56 |
| $M_{10}$ | 19.44 | 15.26 | 16 |
| $M_{11}$ | 22.64 | 14.67 | 15.11 |
| With anhydrite content / *Cu conținut de anhidrit* | | | |
| $P_3$ | 17.87 | 14.52 | 13.63 |
| $P_7$ | 13.81 | 12.59 | 10.96 |
| $P_8$ | 17.97 | 15.56 | 14.52 |
| $P_9$ | 19.27 | 18.67 | 15.85 |
| $P_{10}$ | 23.93 | 26.67 | 23.26 |
| $P_{11}$ | 20.41 | 15.26 | 14.96 |

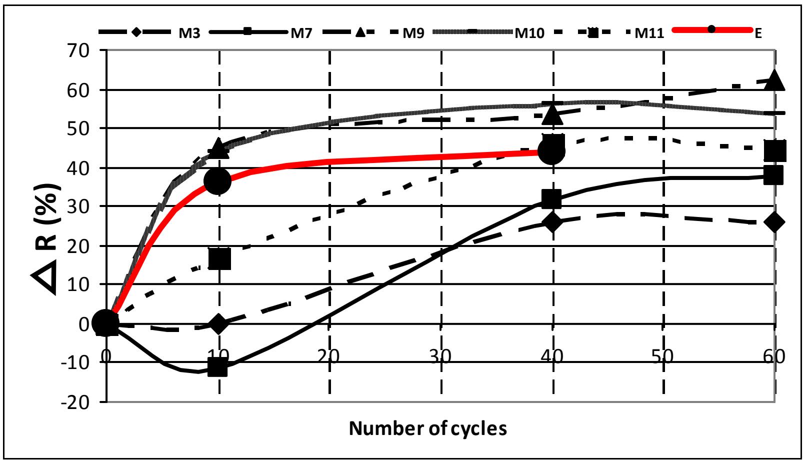



Fig. 7 - Strength modifications of the binding specimens with hemihydrate content after 10, 40 and 60 freezing-thawing cycles / *Modificări de rezistență ale probelor liante cu conținut de sulfat de calciu semihidrat, după 10, 40 şi 60 cicluri de îngheț – dezgheț:* + diminishes / *scăderi;* - increases / *creşteri* .

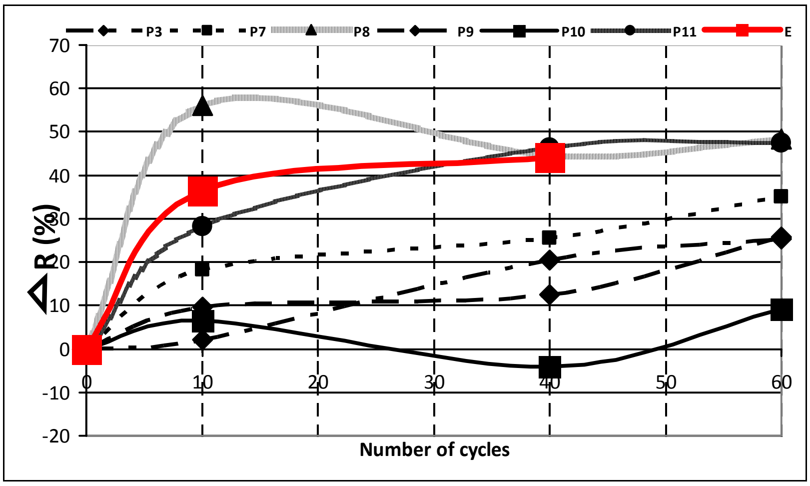



Fig. 8 - Strengths modifications of the binding specimens with anhydrite content, after 10, 40 and 60 freezing-thawing cycles / *Modificări de rezistență ale probelor liante cu conținut de sulfat de calciu anhidru, după 10, 40 şi 60 cicluri de îngheț – dezgheț:* + diminishes / *scăderi;* - increases / *creşteri* .

As volume and structure the capillary porosity (interconnected or interrupted pores) diminishes in time in parallel with evolution of hydration degree. Similar to Portland cement for which capillary porosity diminishes in time as measure the calcium silicate hydrates increase and partially obturate these pores, in the ternary binders case with high Portland cement content (>50), a similar phenomenon is assumed.

In ternary binder with high HAC and calcium sulfate content, the main hydrate - ettringite is crystallized therefore the calcium silicate hydrates resulted by Portland cement hydration are reduced. In consequence the capillary porosity can be higher for this binder's category. The next supplementary investigations will bring added value in this direction.

## 4. Conclusions

- Considering information regarding the binding properties of ternary binders of type silicate–aluminate–sulfate, ternary binding masses were realized and investigated from point of view of their behavior at high temperature and freezing-thawing resistance. The PC/HAC ratio and calcium sulfate nature and content ($C\overline{S}H_{0.5}$ and $C\overline{S}$ III) were varied.
- For all the binder specimens, exposed to heat treatment between 200 – 1200$^0$C, the diminishing of the compressive strengths was observed in parallel with the temperature of heat treatment increase until 1000$^0$C. This is correlated with the dehydration processes of hydrates resulted during binder's specimens hardening. For the binder with 50% HAC, the strength diminish was observed beginning at smaller temperatures, comparing to those containing 55% HAC. At higher temperatures (1200$^0$C), the mechanical strength values increased, due to sintering process, which assures a ceramic binding between the dehydrated binders and the aggregates.
- The ternary binders of type silicate–aluminate–sulfate with higher Portland cement content (>50% - $M_3$ and $M_7$, respectively $P_3$ and $P_7$) have had a better behavior at freezing-thawing stress. Their resistances have had small variations. This behavior must be correlated with compositional characteristics of the hardened binder, the porosity (especially capillary pores) having a key influence. We can assume that binder's specimens with higher PC content have a smaller capillary pores volume, because of their obstruction by calcium silicates hydrates formed by Portland cement hydration.

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