

Influence of water saturation on strength of modified gypsum-alumina expanding cement at stage of delayed hardening

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Abstract. The article analyzes the influence of material composition of modified gypsum-alumina expanding cement with regard to mineral components ratio on its mechanical-and-physical properties change due to water saturation at the stage of delayed hardening. The expandable cementing medium applied in the survey, except for traditional components such as crushed gypsum rock and alumina cement, contained additionally portland cement and superplasticizer, based on polycarboxylic ethers. It has been established that depending on mineral components ratio water saturation of one-year-old cement rock can either improve or worsen its strength properties, provided that bending and compression resistance can change asynchronously and divergently. A regularity has been revealed regarding composite water resistance change depending on mass ratio of portland cement and gypsum rock (AC/GR). Within the variability of experimental factors a judicious ratio - AC/GR=0,2-0,95 has been established, where bending and compression resistance does not decrease as a result of cement rock water saturation during 48 hours.

1. Introduction

Concretes and mortars on hydraulic mineral binders are the most demanded structural materials in construction. Concrete technology has more than seven thousand years of history, but up to now the interest of researchers to cement composites does not become weaker. Improvement of concrete technology is at the moment carried out in various directions: resource conservation through the use of production wastes of different origin and secondary resources [1-7], nanostructuring of cement systems with formula process techniques [8-14], development of new or improved properties of existing mineral binders, etc. [15-21].

An interesting direction of modification of mineral binders properties is control over their own deformations, strength and rate of hardening. There are two ways of expansion achievement for a hardening binding substance: hydrosulfoaluminate expansion and oxide expansion. The most extensively studied way to control deformation and strength of mineral composites is the former.

In 1935-1941 V.V. Mikhailov introduced an astringent, which was called waterproof expanding cement (WRC), consisting mostly of alumina cement- up to 65% [22,23]. The deficiency of this binder was its very rapid setting, that could have been the result of gaging plaster use as a sulfate-containing component, thus hindering application of the astringent for technological reasons. The expanding gypsum-alumina cement (EGAC) introduced by I.V. Kravchenko and applied on an industrial scale in Russia since 1951 did not have such a shortcoming. This type of astringent is a hydraulic rapid-setting high- strength binder obtained as a result of intergrinding alumina clinker (or high-alumina slag) with



natural calcium sulfate dihydrate, given that content of the latter in a mixture does not exceed 30 %. This cement as compared to WRC has longer setting time and lower cost. Compositions based on EGAC showed adequate efficiency in manufacturing of waterproof concrete solutions for grouting precast concrete structures, oil well plugging, waterproofing of tunnel lining, etc.

WRC and EGAC did not contain portland cement. [24] shows composition of the fast-setting densifying mixture consisting of gypsum-alumina cement (27-30% by weight), portland cement (hereinafter PC, 27-30%), alumina cement (hereinafter AC 30-36%) and, in addition, asbestos (9.5 - 10%). With that gypsum-alumina cement includes calcium sulfate dihydrate (about 30%) as a sulfate-containing component. The shortcoming of the described cement types is absence of plasticizing agents as their component. Properties of these cement types, as well as mortar and concrete types based on those, are specified to a large extent by water-cement (water-binder) ratio when mixture is prepared. Absence of a plasticizer, capable of W/C (W/B) decreasing, stipulates inadequate efficiency of using binding and strengthening cement capacity.

[25] describes plugging material containing plasticizer. This material contains portland cement, an expanding additive (containing alumina cement or other aluminate-containing material), gypsum, curing regulator (accelerator) and a plasticizer with the following mass ratio, %: expanding additive - 2-15; gypsum - 7-9; curing accelerator-2-8; plasticizer - 0.3 - 0.8; lightweight additive - 3-10; artificial cement - the rest.

To date, the principle of hydrosulfoaluminate expansion is applied by researchers and practitioners to obtain a wide range of building composites with enhanced rate of strength gain, high physical-mechanical characteristics and controlled deformation properties [26-29]. Disadvantages of such materials could count thermodynamic instability and phase volatility resulting from hydrated calcium sulfoaluminate curing process. Some researchers are concerned about responsivity of set compositions to water saturation when in service. It is also mentioned in works [30-32] about high probability of strength and performance properties weakening for such mortars and concretes when saturated with water as a result of, for example, delayed ettringite formation.

It should also be kept in mind that genesis of strength and deformation properties of the given expanding binders depends enormously on the beginning, rate and completeness of hydrosulfoaluminate formation of the hardening cement rock. Obviously, this process will be also influenced by initial water balance of the mixture, i.e., by water-binder ratio. In this regard, application of modern efficient superplasticizers as part of modified EGAC stipulates relevance of specifying the ratio of mineral components of AC, PC and gypsum rock (hereinafter GR) in order to get the desired properties given the reduced initial water-binder ratio, as well as their influence on the composite properties change in conditions of water saturation at the later stage of service.

This work was aimed at clarifying influence of AC, PC and GR mineral components ratio, contained in the modified plasticizer based on EGAC polycarboxylic ethers, on water resistance of a one-year-old composite.

2. Materials and methods

At the initial stage, basic GR:AC ratio was identified on the basis of assumption that total concentration of SO_3 in EGAC should not exceed 17% in mass (GOST 11052). Taking into account, that concentration of pure calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in GR is about 95%, and mass fraction of SO_3 in calcium sulfate dihydrate is 46.5%, then concentration of pure SO_3 in gypsum rock will be equal to about $0.95 \cdot 46.5 = 44\%$. Therefore, concentration of gypsum rock in EGAC shall be not more than $0.17/0.44 = 38\%$. Based on experience of researchers, effective concentration of gypsum rock in EGAC is 28–32%. In our research we assumed GR:AC ration equal to 25:75, 30:70, and 35:65, while concentration of portland cement in the total mass of the three-component binder was assumed as being equal to 0%, 5%, 15%, 25%, and 35%. For ratio of mineral elements in the corresponding test compounds refer to table 1.

Table 1. Ratio of mineral elements: GR, AC, and PC.

Compound No.	PC Qty, %	AC Qty, %	GR Qty, %
1	0	65	35
2	0	70	30
3	0	75	25
4	5	62	33
5	5	66.5	28.5
6	5	71	24
7	15	55	30
8	15	59.5	25.5
9	15	64	21
10	25	49	26
11	25	53	23
12	25	56	19
13	35	42	23
14	35	44.5	19.5
15	35	49	16

As shown in the table, concentration of PC varies in the range of from 0% to 35%, AC – in the range from 42% to 71%, GR – in the range from 16% to 35%, at the same time ratio GR/(GR+AC) is within the range from 0.25 to 0.35.

The following materials were used in the surveys:

- AC – GC-40 OJSC Pashiysky Steel and Concrete Factory;
- PC – M500D0 OJSC Novoroscement;
- GR – gypsum rock from Shedokskoye Minefield inf Krasnodar Region;
- superplasticizer – Melflux 5581F (produced by BASF Construction Polymers);
- retarder – tartaric acid (hereinafter - TA).

40x40x160 mm samples have been manufactured as per GOST 310.4. Water/binder ratio (hereinafter - WBR) in all cases was equal to 0.21. Prior to the tests, the samples underwent dry curing (temperature $t=20-22$ °C, air relative humidity $W=55-60\%$). Bending strength and compression strength were identified as per GOST 310.4 for a sample of 1 year maturity. Strength capacities were identified using samples at natural humidity and using twin-samples exposed to water saturation for 48 hours by means of full submersion into water.

3. Results

Presence of a superplasticizer and PC in composition of modified EGAC (hereinafter MEGAC) imposes a number of features on the process of binder hydration. Thus, superplasticizer provides high fluidity of the mixture along with low W/binder ratio. Presumably, low water content of MEGAC inhibits active ettringite formation at early stages of hardening. Presence of PC in composition can intensify the ettringite growth due to increase of alkalinity level in the medium as a result of Portlandite by-product Ca(OH)_2 generation. At the same time, the presence of PC in composition provides prolonged growth of strength, which becomes higher the more efficient plasticizer works, that in aggregate enhances resistance of the composite against external and internal destructive effects. This is reflected, in particular, in waterproofing and increase of softening factor of compositions.

Compression and tension strength of compositions 1-15 under bending for dry and water-saturated MEGAC samples is given in Figure 1 and 2.

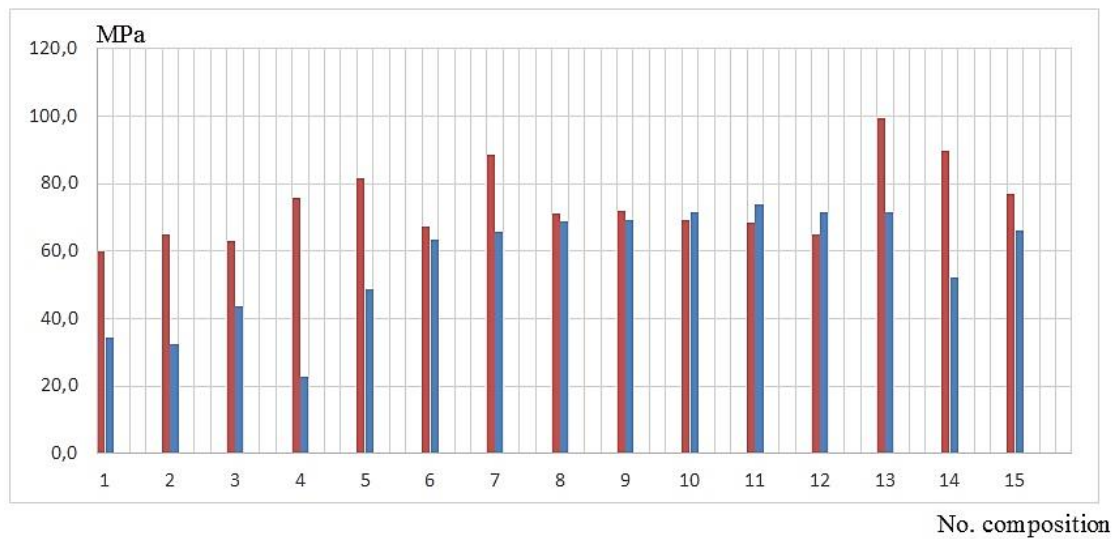


Figure 1. Compression strength of dry and water-saturated samples.

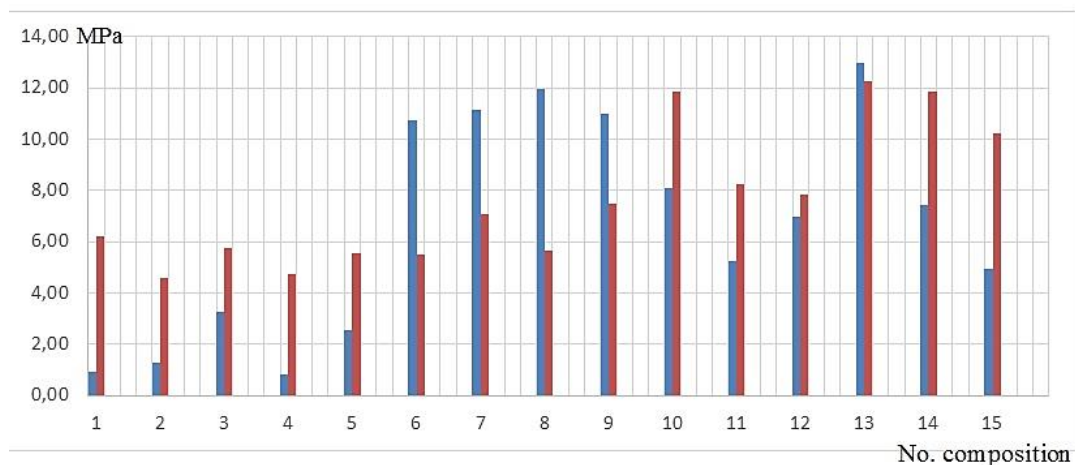


Figure 2. Bending strength of dry and water-saturated samples.

It follows from the data obtained that water-saturation of one-year-old samples influenced the strength characteristics. Along with that this impact is either positive or negative for different compositions, different in absolute terms, and for a number of compositions the impact on R_{comp} and R_{bend} is opposed.

Detailed analysis shows that compositions without PC or with minimum content of PC (compositions 1-5) have the lowest water resistance level: decrease of R_{comp} ranged from 31 to 70%, decrease of R_{bend} - from 43 to 85%. It can be concluded that presence of PC in compositions starting from 5% content with relative decline in the share of GR reduces response of artificial stone to water influx.

The following four compositions (compositions 6-9) with content of PC up to 15% have a slight decrease in R_{comp} within 3-6% (except for composition 7, showing the decrease of 26%). At the same time R_{bend} of all compositions of this group demonstrated growth by 47-111%. Slight decrease of

R_{comp} along with tangible increase of R_{bend} for compositions with PC share = 15% has important practical significance and scientific interest.

It is relevant to assume, that with such ratio of MEGAC components a structure is formed over the long term which has such parameters of strength and porosity that ettringite grains growing due to water saturation scarcely affect its compression strength properties, but significantly increase its bending resistance.

The following three compositions (compositions 10-12), containing 20% of PC, also demonstrate stable compressive strength with a slight increase, from 4 to 10%. R_{bend} , however, decreases significantly - by 11-36 %.

The last group of compositions (compositions 13-15) with PC content = 35% shows decrease of all strength properties resulting from water saturation conditions: R_{comp} decreases by 14-42%, R_{bend} - by 37-52% (except for composition 13, which showed a slight increase of R_{bend}).

Considering influence of increasing PC share from 0 up to 35% contained in MEGAC on strength characteristics in conditions of one-year-old water saturation, the following regularity can be admitted: absence of PC or low PC content = 0-5% does not provide water resistance of mixed binder cement rock and results in decreasing all strength characteristics; the content of PC = 15% provides stability of compressive strength along with significant increase of bending strength and can be considered to be optimal; increase of PC content up to 25% still doesn't affect R_{comp} but makes R_{bend} decrease; with PC content = 35% consistent negative impact of water saturation conditions on strength properties is observed: R_{comp} and R_{bend} decrease.

Presence of such non-linear PC content influence on MEGAC water resistance can be explained, apparently, by overlaying of two processes with opposed influence: on the one hand there is strengthening influence of growing share of waterproof hydraulic binder of portland cement, on the other hand, as the share of PC content grows the quantity of hydrated lime escaping during its hydration also grows. And growth of lime in the rock intensifies ettringite development under conditions of excess water.

Thus, with regard to occurrence of differently directed processes with the growing content of PC in MEGAC under conditions of water saturation of rock, optimum dose of PC lies within the range of 15-25%.

Along with that, it is clear that water resistance is influenced not only by the quantity of PC, but also by PC/GR ratio. Figures 3 and 4 show values of R_{comp} and R_{bend} increase or decrease depending on PC/GR ratio.

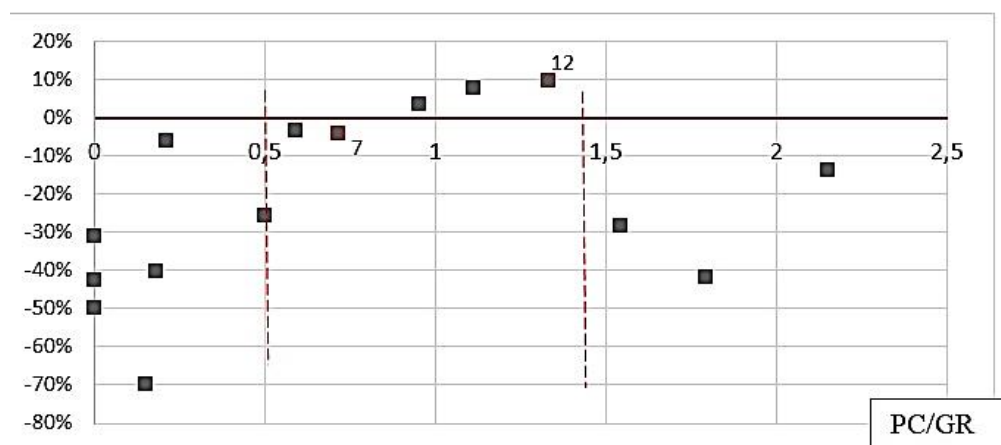


Figure 3. Change of compression strength depending on PC/GR ratio.

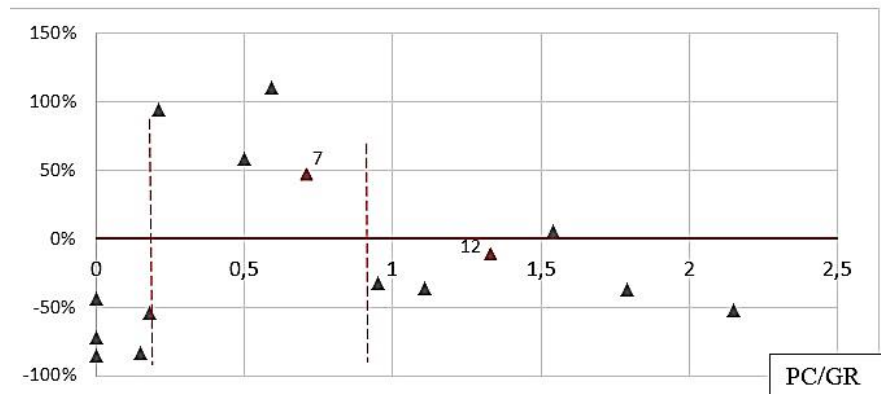


Figure 4. Change of bending strength depending on PC/GR ratio.

It is not possible to describe the correlation of change of strength and the PC/GR ratio presented in figures 3 and 4 with sufficient reliability of approximation ≥ 0.8 with second- or third-order equations, however, the following general conclusions may be drawn. In the graph for R_{comp} , an interval along axis PC/GR where decrease of strength is absent or minor can be highlighted: PC/GR = 0.5-1.5. The values of ΔR_{comp} to the left and to the right of the highlighted interval lie significantly below zero, indicating a low degree of water resistance of the respective compounds. For the graph of R_{bend} , the interval with majority of above zero values of ΔR_{bend} corresponds to the range of PC/GR = 0.2-0.95. Increase of R_{bend} is observed in this interval when hardened MEGAC stone is saturated with water.

It is clear that by overlapping the identified intervals, we can obtain the resulting range of PC/GR = 0.5-0.95, which shows increase of all strength characteristics. This conclusion has an important practical meaning.

Softening factor for R_{comp} and R_{bend} (F_{comp} and F_{bend} respectively) was calculated as the ratio of strength in water-saturated condition to the strength under dry conditions. Graphic interpretations of the obtained values are presented in Figures 5 and 6, which clearly show such ratios of portland cement, gypsum rock and gypsum-alumina cement, at which the softening factor $K \geq 1$, i.e. ranges of water-resistant compounds.

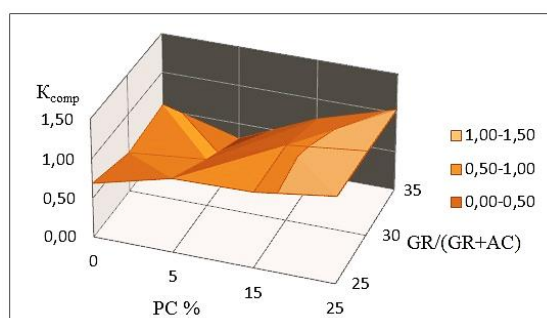


Figure 5. Influence of ratio of PC, GR and AC on softening coefficient under compression.

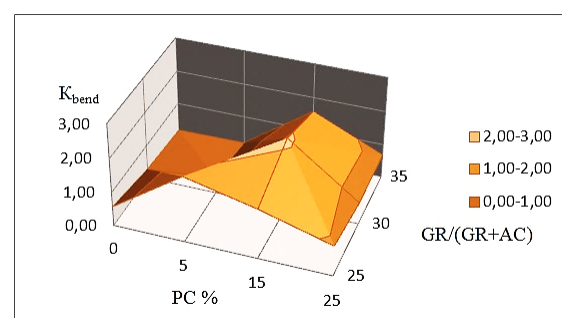


Figure 6. Influence of ratio of PC, GR and AC on softening coefficient under bending.

4. Conclusions

As a conclusion to estimation of water resistance of artificial stone made of MEGAC for a long term, it should be stated, that compositions with increased water resistance and, in some cases, with $K_{soft} > 1$, shall simultaneously comply with the following recipe conditions:

1. $GR / (GR + AC) = 0.25 - 0.35$;

$$2. PC / (GR + AC + PC) = 0.15 - 0.25;$$

$$3. PC / GR = 0.2 - 0.95.$$

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