the internal curing of concrete is shown in [5]. The decreasing of autogenous shrinkage of concrete from 500 to 120 µm/m with the admixture of SAP was shown. The similar positive effect – reducing shrinkage on drying (by 12.6%) and autogenous shrinkage (by 15.5 %) of self-leveling mortars is described in [4]. Such a shrink-inhibiting effect is most significant at the age of 28 days.

The authors [6, 7] investigated the effect of differently dispersed SAPs on the reduction of plastic shrinkage of cement systems (fractions 0...200 µm and 200...500 µm) in different heat and humidity conditions. Longitudinal deformations for compositions with a dispersion of SAP less than 200 µm and 200...500 µm have decreased by 20 and 17 %, respectively.

In accordance with [6], an increasing in the content of superabsorbent polymers in cement mortar lead to the decreasing of the tensile and compression strength by 20.5 and 25.8 %, respectively. This is explained by the changing of porosity [11] which is additionally formed after the desorption of SAP (Figure 1).

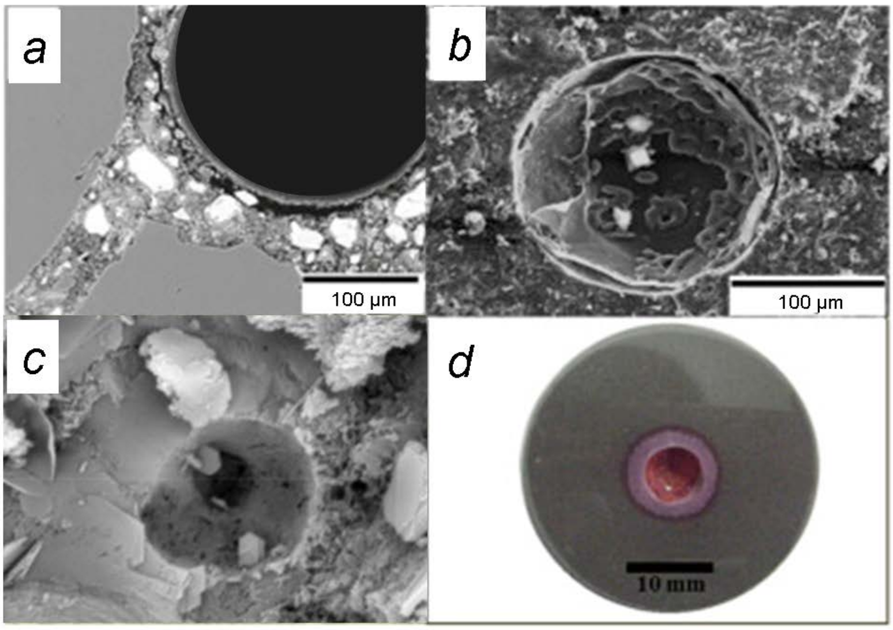

Figure 1. Structure of cement mortar [6] (c) and a, b, d [11].

In [10], it was shown that the introduction of SAP in cement composites does not lead to a significant changes in flexural strength at the age of 28 days. However, cement stone samples containing SAPs show an insignificant increasing in flexural strength by 9.05 and 2.91 %, for a particle size of < 200 µm and fraction 200...500 microns, respectively, just in the early stages of hardening (3 days) [9]. A negative trend is observed in the later periods (28 days). Flexural strength decreases by 25.4 and 37.2 % and compressive strength by 13.6 and 21.8 % for SAP granules with a size of less than 200 microns and fraction 200...500 microns, respectively. In this case, the particle size of the SAP is essential. Large SAP granules have the greater reduction in the strength of the cement stone.

Studies of the SAP with different average particles size (from 324 to 1065 µm), density of anionic groups and crosslinking density from acrylic acid and acrylamide [9, 13] show a significant decreasing of compressive strength of mixtures with very high density of anionic functional groups. In this case, the desorption of water from the SAP occurs prematurely. This leads to an excess of water and forms additional porosity. A small decreasing or saving of strength is observed in cement mixtures with SAP with a lower concentration of anions.

The authors [14] based on the analysis of the effect of SAP on the mechanical properties of concrete at the age of 28 days conclude about an unambiguous negative influence. Compressive strength by 8...35 % under high humidity hardening and 28 % in conditions of low humidity is reduced. The tests of the samples that have been hardened under sealed conditions show inconsistent results For example, the flexural strength is decreased by 33 % [15] or increased by 7 % for different compositions, but the compressive strength is decreased by 10...13 % [16].

Thus, the use of superabsorbent polymers in cement composites is characterized by both positive and negative effects. On the one side, the use of SAP is justified by the positive effect of reducing shrinkage. On the other side the granular polymer requires pre-saturation (up to 30 minutes) to ensure sufficient mobility of the cement mixture and is in the composite structure as a source of additional pores, reducing mechanical properties. The desorption kinetics of SAP provides the most important for increasing efficiency. Water migration should be carried out in sufficient quantities from polyacrylates to the cement system in sufficient quantities, and not the other way around. The properties of polymer cross-linking, the shape and size of the granules, and the properties of the sorbate are important factors for controlling the desorption process [9].

Based on the above analysis, the following hypothesis can be formulated: the forming of thin films of polyacrylates in the structure of the cement materials by delayed polymerization of acrylic acids in water solution provide the water reserve for internal curing without the loss of mobility of the mixture and strength properties of the composite. This is especially actual to develop recipes of building «inks» for 3D-printers [17–20].

2. Materials and Methods

In this paper the effect of the “Renovir-hydrogel” superabsorbent polymer on the properties of cement stone was investigated. The SAP solution is obtained by mixing water (W) with the three components of the polymer part ($\Sigma A = A_1 + A_2 + A_3$) and catalyst ($B$). The component “$A_1$” is acrylic acid (propenoic acid CH_2=CH−COOH) or salt (sodium polyacrylate [-CH_2-CH(COONa)-]$_n$). The component “A_2” is a crosslinking agent in which poly-saturated compounds are widely used. The component “A_3” is an initiator from peroxides, hydroperoxides, hydrogen peroxide, persulfates, azo compounds or redox systems. Varying the concentrations of each component allows to control the polymerization process and form a different degree of crosslinking and polymerization speed. Main characteristics of the “Renovir-hydrogel” superabsorbent polymer are presented in [21].

The determination of the influence of the SAP components “Renovir-hydrogel” (Table 1) on the physical and mechanical properties of the cement stone is the main aim of this study. The study was carried out in the framework of a full two-factor experiment. The amount of catalyst B/A_1 (X_1) and the ratio of water to polymer part $W/\Sigma A$ (X_2) were chosen as factors. The average density and compressive strength were used as controlled indicators.

Table 1. Compositions of superabsorbent polymer solutions “Renovir-hydrogel”.

No	Composition	Amount, %			Factors	
		ΣA	B	W	X_1	X_2
1	C-0.003/5.0	16.67	0.042	83.29	0.003	5.0
2	C-0.009/5.0	16.44	1.390	82.71	0.009	5.0
3	C-0.003/8.5	10.44	0.880	88.68	0.009	8.5
4	C-0.009/8.5	10.53	0.027	89.44	0.003	8.5

The Portland cement CEM I 42.5 produced by “Stone Flower” was used to prepare a series of cement test samples with W/C-ration 0.3. The SAP solutions were used as water in the cement mixtures. The control composition (C-0/0) was prepared without a solution of SAP. Hardening of the samples was carried out in normal conditions. The average density and total pore volume were determined by methods in according with regulatory and technical documents Russian State Standards GOST 12730.1-78 and GOST 12730.4-78. The average density was determined by the ratio of the mass and volume of the samples, and the true density by the pycnometric method. Six cubic-samples 50 mm in each series were tested to compressive strength according to EN 196-1 at the age of 7; 14; 21 and 28 days. The tests were carried using static loading by the servo-hydraulic press «Advantest 9».

The study was performed by equipment from the Head Regional Shared Research Facilities of the Moscow State University of Civil Engineering. Technical specifications of the equipment are available on [22].

3. Results and Discussion

Cement pastes with SAP visually were not characterized by differences in workability unlike the control composition. Presumably, the process of SAP polymerization in the selected range of components is began after the formation of samples. This provided a delay in the water sorption by SAP and in the deterioration of workability pastes. Previously [23], the studies of the polymer solutions "Renovir-hydrogel" were carried out by NMR-relaxometry method. The start and end times of polymerization of this SAP were established for studied concentrations. According to this study, the period of viability of the polymer solutions "Renovir-hydrogel" is from 14.2 to 105.2 minutes. That is, the limiting time of preservation of viscosity sufficient for technological operations exceeds 10 minutes before each of the mixtures was formed.

Analysis of the kinetics of setting and hardening of Portland cement with the addition of acrylate allows to estimate its impact on the process of structure formation of cement stone in time. The kinetics of the compressive strength of the cement stone with the hydrogel solutions of different composition were obtained in this study (Figure 2).

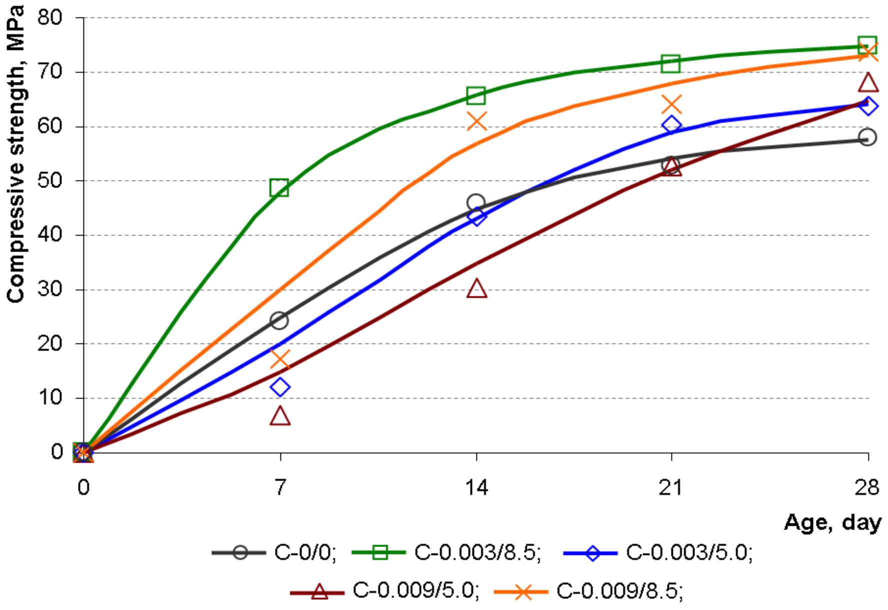

Figure 2. Kinetics of hardening cement stone with SAP.

The obtained results show that the cement stone modified by solution of the acrylate superabsorbent polymer is characterized by greater strength at the age of 28 days by 10.2 ... 29.5 % than the composition with water (Table 2). However, the different effect of the ratio $W/\Sigma A$ and B/A_1 on the strength in the early periods of hardening is shown in Figure 2. It can be noted that the compositions with the amount of polymer $W/\Sigma A$ = 8.5 (regardless of the amount of catalyst) are characterized by faster hardening kinetics than the control composition. At the same time the cement stone where the ratio of water to polymer part is equal to 5.0 has less strength than the control composition at the age of up to 14 days. This indicates an excess of polymer in the composition, which has a negative impact on the structure formation of cement stone.

Table 2. Rheological properties of cement pastes and physical-mechanical properties of cement stone with SAP at the age of 28 days.

No	Composition	ρ, kg/m³	S_ρ, %	P, %	S_P, %	R_{com}, MPa	S_R, %
0	C-0/0	2065	0.93	8.0	2.33	58.0	4.24
1	C-0.003/5.0	2100	0.30	3.5	3.13	63.9	3.22
2	C-0.009/5.0	2070	0.60	3.8	3.27	64.2	4.26
3	C-0.003/8.5	2135	0.79	3.3	2.61	75.1	4.13
4	C-0.009/8.5	2095	0.57	3.5	3.55	73.7	3.72

Notes: ρ is average density; P is total pore volume; R_{com} is compressive strength; S_ρ, S_P, S_R are standard deviations for average density, total pore volume and compressive strength respectively.

The studies have allowed to establish an experimental equation for estimation of the dependence of the compressive strength on selected prescription factors:

$$Y = 69.23 - 0.275X_1 + 5.175X_2.$$

The analysis of the structural parameters of the cement stone in the Table 2 show that an increase in the amount of catalyst to 0.009 leads to a slight decrease in the average density and an increase in the porosity of the cement stone due to the faster polymerization process of acrylate. In the initial period of preparation of the mixture due to absorption, the polymer reduces the amount of free water in the system and impairs mobility and workability. Delayed polymerization is achieved with a smaller amount of catalyst. In this case the polymer does not interfere the distribution of water in the volume and performs an absorbing function after molding the product. This has a positive effect on the compaction of the mixture and on the hydration of Portland cement, which provides a lower porosity of cement stone (more than 2 times) (Table 3). The introduction of the SAP solutions in the studied range of variable factors leads to an increase in the strength of cement stone by 10.2...29.5 %.

Thus, it was shown that the using of water solutions of acrylic acids with controlled polymerization does not lead to the loss of the strength of the cement stone. The studied SAP solutions allow to delay the absorption of water from the cement mixture in contrast to the granulated SAP. Obviously, additional studies are required to determine the action mechanism of SAP solution on the process of structure formation of cement stone and to establish the dependences of influence of prescription and technological factors on the deformation properties.

Table 3. Changes of properties of cement pastes and cement stone compared with the control composition (C-0/0).

No	Composition	ρ, %	P, %	R_{com}, %
1	C-0.003/5.0	+1.7	-56.3	+10.2
2	C-0.009/5.0	+0.3	-52.5	+10.7
3	C-0.003/8.5	+3.4	-58.8	+29.5
4	C-0.009/8.5	+1.5	-56.3	+27.1

Note. «+» or «–» show an increase or decrease in the indicator.

The results show that the introduction of polymer solutions with controlled polymerization in cement compositions provides an increase in compressive strength from 58.0 to 63.9...75.1 MPa in contrast to the using of granulated SAP when compressive strength is decreased by 8...35 % [4, 6, 12].

Positive world experience in the use of granulated SAP for reducing shrinkage and the results of this study suggest the effectiveness of using SAP solutions with controlled polymerization in cement systems hardening in bad conditions. Such a solution may have further development and practical application in 3D-printing technology, where extruded concrete structures are subject to intensive moisture loss.

4. Conclusions

Based on this research the following conclusions were made:

1. The formulated hypothesis is confirmed in this paper. It has been shown that the super absorbent polymer solutions with a controlled polymerization process can be used in cement composites to control water balance for improving physical and mechanical properties.

2. An experimental equation for estimation of the dependence of the compressive strength on the amount of catalyst and the ratio of water to polymer part was obtained.

3. The investigated SAP solutions allow to increase the average density and compressive strength of cement stone. The introduction of the SAP solutions (for studied range of variable factors) leads to decrease the porosity from 8 to 3.3…3.5 % and increase the compressive strength of cement stone from 58.0 to 63.9...75.1 MPa or by 10.2 ... 29.5 % in comparison with the composition without SAP.

Acknowledgement

The work was carried out within the framework of the agreement No 14.583.21.0072 on granting subsidies for the implementation of the federal target program «Research and development in priority areas for the development of the scientific and technological complex of Russia for 2014-2020» (project identifier - RFMEFI58318X0072) with the financial support from the Ministry of Education and Science of the Russian Federation.

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Contacts:

Aleksandr Inozemtcev, +7(499)1880400; InozemcevAS@mgsu.ru
Evgeniy Korolev, +7(499)1880400; info@nocnt.ru
Thanh Qui Duong, +8(499)1880400; quiduongthanh@gmail.com

Инженерно-строительный журнал

ISSN 2071-0305

сайт журнала: http://engstroy.spbstu.ru/

DOI: 10.18720/MCE.85.15

Физико-механические свойства цементного камня с раствором суперабсорбирующих полиакрилатов

А.С. Иноземцев*[*], Е.В. Королев, Т. Зыонг
Национальный исследовательский Московский государственный строительный университет, г. Москва, Россия
** E-mail: InozemcevAS@mgsu.ru*

Ключевые слова: суперабсорбирующий полимер, механические свойства, прочность при сжатии, внутренний уход, твердение, усадка

Аннотация. В связи с распространением 3D-принтеров актуальным является разработка рецептур, обладающих индифферентным к влиянию окружающей среды набором свойств в период схватывания и твердения вяжущего. Гидратация цементных композитов в агрессивных условиях требует поиска решений, обеспечивающих внутренний уход за бетоном. Одним из таких способов может быть использование специальных высокопоглощающих или суперабсорбирующих полимеров (САП). В отличие от традиционного введения гранулированных САП, формирование в структуре цементного композита тонких пленок полиакрилатов с отложенной полимеризацией акриловых кислот в водном растворе обеспечивает систему резервом воды для внутреннего ухода за процессами гидратации без потери подвижности смеси, способствуя снижению усадочных деформаций при сохранении прочностных свойств композита. Целью исследования является установление влияния соотношение компонентов в составе САП «Реновир-гидрогель» на физико-механические свойства цементного камня. В работе использованы стандартизированные методы испытаний в соответствии с ГОСТ с применением современного оборудования и инструментов. Установлено, что использование растворов САП с управляемым процессом полимеризации способствует увеличению средней плотности и прочности цементного камня. В исследуемом диапазоне варьируемых факторов введение раствора САП приводит к повышению прочности цементного камня до 29.5 %. Получена экспериментально-статистическая модель, описывающая зависимость предела прочности при сжатии от количества катализатора и отношения воды к полимерной части для обеспечения требуемых характеристик композита.

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Контактные данные:

Александр Сергеевич Иноземцев, +7(499)1880400; эл. почта: InozemcevAS@mgsu.ru

Евгений Валерьевич Королев, +7(499)1880400; эл. почта: info@nocnt.ru

Тхань Куй Зыонг, +7(499)1880400; эл. почта: quiduongthanh@gmail.com