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THE INFLUENCE OF TOTAL WATER-TO-CEMENT RATIO ON THE MECHANICAL PROPERTIES OF CEMENTITIOUS COMPOSITES INTERNALLY CURED WITH POLYACRYLIC SUPERABSORBENT POLYMERS (SAP)

WPŁYW CAŁKOWITEGO WSPÓŁCZYNNIKA WODA-CEMENT NA WŁAŚCIWOŚCI MECHANICZNE KOMPOZYTÓW CEMENTOWYCH PIELĘGNOWANYCH WEWNĘTRZNIE POLIAKRYLOWYMI POLIMERAMI SUPERABSORPCYJNYMI (SAP)

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Abstract

Superabsorbent polymers (SAP) allow for the introduction of changes to the pore network characteristics in cementitious composites and the course of binder hydration. Therefore, SAP addition contributes to significant changes in multiple properties of concrete. The effect of internal curing differs depending on its design process – the initial content of curing water in the concrete mix, polymer characteristics and water absorption properties, the state in which it's added (non-saturated/hydrogel), and the design method regarding curing water content in the entire water content. The authors investigated those variables' influence on selected concrete properties – compressive strength, water absorption, and shrinkage. All independent variables significantly influenced the studied properties of concrete. The increase in the total water-to-cement ratio led to a significant decrease in the mechanical properties of cementitious composites. Modification with the use of SAP added in the form of hydrogel had the most positive influence on the properties of concrete..

Keywords: concrete internal curing, superabsorbent polymers, cementitious composites, hydrogel, SAP

Streszczenie

Polimery superabsorpcyjne (SAP) umożliwiają wprowadzenie zmian w charakterystyce sieci porowej kompozytów cementowych i w przebiegu hydratacji spoiwa. W efekcie dodatek SAP przyczynia się do znaczących zmian w wielu właściwościach betonu. Efekt pielęgnacji wewnętrznej różni się w zależności od metody jej zaprojektowania – początkowej zawartości wody pielęgnacyjnej w mieszance betonowej, właściwości fizycznych polimeru, w tym zdolności do absorpcji wody, stanu, w jakim jest on wprowadzony (nienasycony wodą/hydrożel), oraz metody uwzględnienia wody pielęgnacyjnej w całej zawartości wody zarobowej. Autorzy zbadali wpływ tych zmiennych na wybrane właściwości betonu, w tym na wytrzymałość na ściskanie, nasiąkliwość i skurcz całkowity. Wszystkie zmienne niezależne w istotny sposób wpływały na badane właściwości betonu. Wzrost całkowitego współczynnika woda-cement spowodował istotne pogorszenie właściwo-

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ści mechanicznych kompozytów cementowych. Najbardziej pozytywnym wpływem na właściwości betonu charakteryzowała się modyfikacja za pomocą dodatku SAP wprowadzonego w postaci hydrożelu.

Słowa kluczowe: pielęgnacja wewnętrzna betonu, polimery superabsorpcyjne, kompozyty cementowe, hydrożel, SAP

1. INTRODUCTION

Internal curing of cementitious components presents an interesting approach to shaping the properties of hardened concrete. With its significant influence over hydration dynamics and pore network characteristics, internal curing affects the mechanical properties of concrete and its resistance to different corrosive agents and, therefore, concrete's durability. The idea of internal curing, introduced decades ago using water-saturated lightweight aggregate, focuses on limiting the negative effects of the hydration process – self-desiccation of the hardening cement matrix, and its most visible impact – autogenous shrinkage [1, 2]. Although this issue can be neglected in regular concrete, properties of cementitious composites of low and very low water-to-binder ratios can be significantly impacted by the aforementioned phenomenon [3].

During the hydration of the binder, mixing water in the hardening composite is slowly used to form hydrates, making a cement matrix. During this transition, as the overall volume of hydration products is smaller than that of substrates, the difference in volume marks the creation of a pore network. Due to ongoing hydration, those gel pores gradually contain less water and subsequently collapse due to pressure differences as the composite has not gained its designed stiffness. The scope of those changes is most visible during the first 24 hours of hydration when the skeleton of the cement matrix is still forming.

The idea behind internal curing was to introduce another material in the mix, which would not participate in the hydration process but instead allow a portion of mixing water to be stored in its structure [2]. Initially, it would not be used for hydration purposes but rather for maintaining high relative humidity during the initial formation of the pore network, preventing or reducing the scope of pore collapse, causing volumetric changes, and, therefore, decreasing autogenous shrinkage [4, 5].

Different agents can provide internal curing of cementitious composites and can be divided into two main groups differing in the phenomena linked to water absorption potential [6]. The first includes materials with an extensive pore network – mainly lightweight aggregates (LWA) and organic fillers (sawdust, wood pellets, etc.). In their case, the water absorption mechanism is purely physical and consists of water adsorption due to high specific external and internal surfaces. During hydration, as the access to stored water within the internal curing agent is limited, the decrease in relative humidity within the composite can be prolonged, and, therefore, the scope of negative aspects associated with hydration is limited. Due to its grain structure, although a modification of concrete with that type of material allows for mitigation of autogenous shrinkage, high porosity and below-average mechanical properties of the modifier often result in an overall decrease in mechanical properties of concrete as a side effect.

The other group of modifiers consists of superabsorbent materials. Although those have some potential for surface water adsorption, the main cause of their ability to absorb water is electrochemical in nature. As such materials are introduced into the water environment, the absorption process occurs within the entire volume of the modifier [7]. Due to its structure, consisting of long and entangled polymeric chains and a high content of ions (sodium, potassium, etc.), to reduce the initially high osmotic pressure, water molecules are absorbed in its structure and non-permanently entrained in it [8]. The efficiency and scope of that process can depend on various factors, among others, on the chemical composition of any given superabsorbent polymer and the properties of the environment in which the absorption process takes place [9]. The absorption capacity of any given SAP varies in different environments, as the absorption process ceases to occur once the equilibrium state is reached between osmotic pressure within the polymer, its polymeric structure strength, and external pressures of various origins. Different manufactured and natural polymers have such properties – the most commonly used are polyacrylic polymers (artificial) and cellulose-based ones (natural).

The effect of cementitious composites' internal curing varies significantly in using SAP compared to other internal curing methods [7, 10, 11]. The effect regarding self-desiccation of cement matrix is more effective, as the granulation of SAP used in concrete technology can be much finer than in the case of LWA and can ensure access to stored water throughout the volume of the cement matrix. Also, due to the much higher water absorption capacity, changes to the pore network characteristics of a cementitious composite (mainly its total volume and median pore diameter) can be introduced after its desorption from the polymer structure [12]. Those can positively or negatively impact concrete's durability and mechanical properties and depend heavily on the design process of internal curing. Modification with SAP introduces an additional phase to cementitious composite, sometimes referred to as 'quasi-pores' [13], which, after water desorption from SAP structure, transitions towards the regular pore phase, influencing both mechanical properties of the composite, as well as its resistance towards aggressive environmental factors, freeze-thaw or carbonation for instance [14, 15]. The influence over the pore network of the composite due to internal curing can result in a significant deterioration of the mechanical performance of concrete. Methods presented in this paper focus on exploiting SAP properties in different water absorption environments to reduce negative effects associated with internal curing methods, both for fresh and hardened concrete.

2. RESEARCH SIGNIFICANCE

The effects of internal curing with superabsorbent polymers can vary significantly over numerous properties of cementitious composites [16-18]. SAPs of varying origins and properties have different water absorption and desorption potentials in different environments. Also, as the proposed modification usually includes adding extra mixing water, its presence in the composite impacts the hardened composite's pore network characteristics. To investigate this issue, the authors compared and analyzed the properties of internally cured concretes differing in the polyacrylic SAP mass content in the concrete mix. Also, the influence of its dosing method was investigated. SAP can be added to other ingredients in different states regarding its initial water saturation: in a non-saturated state (the process of water absorption takes place while mixing with other ingredients phase – in cement paste environment), saturated/hydrogel state (the process of water absorption takes place prior to mixing SAP with other ingredients in water environment), and a superposition of both (SAP is pre-saturated not to full capacity with water prior to its addition to other ingredients of concrete mix). All those variants have a different effect on one of the essential characteristics of an internal curing agent – the dynamics of water desorption from its structure and, therefore, the effectiveness of internal curing.

Except for the type, amount and addition method, the influence of additional curing water (water absorbed by superabsorbent polymer) increasing the total water-to-cement ratio was determined as one of the critical factors impacting the effect of SAP on various concrete properties. As curing water is introduced into the concrete mix, its water-to-cement ratio changes. In internally cured composites, its three variants can be distinguished: total water-to-cement ratio – $(w/c)_{tot}$; effective water-to-cement ratio – $(w/c)_{eff}$; entrained water-to-cement ratio – $(w/c)_e$. The dependence between them can be described as:

$$(w/c)_{tot} = (w/c)_{eff} + (w/c)_e \quad (1)$$

Determining the actual value of the entrained water-to-cement ratio is burdensome. It includes mainly the analysis of water absorption test results of any given internal curing agent in the environment simulating cementitious composite or changes in the consistency of SAP-modified and reference concrete mixes. Based on that information, the amount of water stored in the internal curing agent at the time of the test can be estimated, and therefore, $(w/c)_e$ can be calculated. Usually, as in the case of other types of internal curing agents (for example, LWA), additional water is included in the mix to compensate for water stored in the internal curing agent to prevent consistency loss. In previous work, authors investigated and described a significant negative effect of this method on the mechanical properties of concrete and its resistance to corrosive agents. The authors determined the influence of those four variables to be crucial to the effectiveness of internal curing in concrete technology and designed an experiment plan to verify its influence over selected concrete properties.

The use of internal curing agents in concrete technology usually contributes to a deterioration in the workability of fresh concrete. Although there are multiple methods to increase mix fluidity, in the case of modification with the use of SAP, it is still most common to counteract those changes through the addition of extra water (curing water) to the mix. Authors believe and wanted to confirm it through experimental means, that any changes to the water-to-cement ratio have a statistically significant impact on the performance of hardened concrete.

3. MATERIALS AND METHODS

In total, 20 series of concrete samples were prepared. Eighteen of those were modified with superabsorbent polymers. Modified series varied in SAP type, amount, dosing method, and the designed total water-to-cement ratio. The range of each quantitative variable was set to mimic cementitious composite in which internal curing would have merit. It was decided to simplify the composition of the mix to reduce the probability of unintended interactions between its different ingredients. The concrete mix consisted of cement CEM I 42.5 R as a binder, river sand 0/2, gravel coarse aggregate 2/4, 4/8, and 8/16, PCE superplasticizer (2.3% m.c.), and mixing water. No other additions or admixtures were used (Table 1).

Table 1. Composition of reference series

Material	Mass per 1 m^3 [kg]	
	REF 0.30	REF 0.36
River sand 0/2	668	643
Gravel 2/4	95	91
Gravel 4/8	477	459
Gravel 8/16	668	643
CEM I 42.5 R	450	
Total water	135	162
$(w/c)_{tot}$ [-]	0.30	0.36

Two superabsorbents of different material characteristics were used, varying in polymer composition and water absorption properties (Table 2). SAP A represented a fine-graded SAP of high water absorption capacity and rapid character of the water absorption process (up to 15 min from an introduction into absorption environment). On the other hand, SAP B granulation in a non-saturated state ranged from 2 mm to 2.5 mm (Fig. 1), its absorption capacity was much lower than SAP A's, and its water absorption took up to 24 hours. Due to a prolonged water absorption process, it was decided not to include in the experiment the variant of concrete modification with SAP B added in a non-saturated state to the mix.

Table 2. Material characteristics of polyacrylic superabsorbent polymers

Grain size in a non-saturated state [µm]	SAP A	SAP B
<90	<8%	0%
90-150		0%
150-750	86-95%	0%
750-2000	≤6%	0%
2000-2500	0%	100%
Water absorption capacity in mixing water environment [g/g]	160.0	69.2
Water absorption capacity in cement paste environment [g/g]	16.0	7.5
Grain morphology	Irregular	Spherical

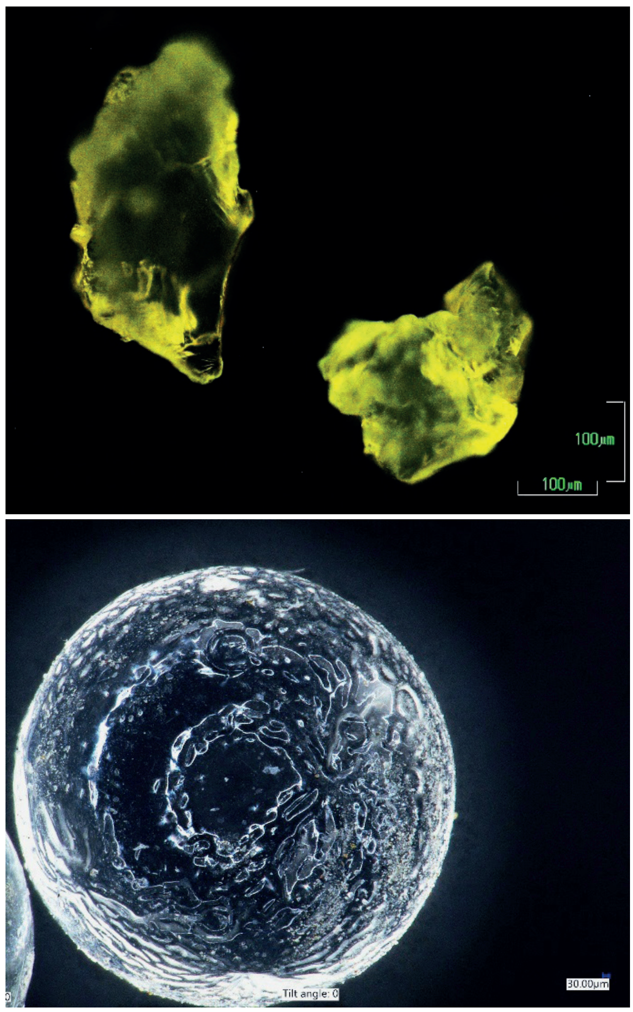

Fig. 1. Morphology of SAP A (irregular) and SAP B (spherical) grains in a non-saturated state

The water absorption capacity of superabsorbent polymers was determined via the commonly used "teabag method", which consists of placing a sachet with a known mass non-saturated SAP in the water absorption environment and its mass measurements after time spent in the water absorption environment. Based on that information, it is possible to calculate water absorption capacity in different environments (the maximal mass of water that SAP can absorb into its structure). The presented research determined water absorption capacity for two environments – mixing water and cement paste of water-to-cement ratio equal to 0.50 (simulating water absorption capacity in concrete mix). The maximal SAP mass increase caused by water absorption was determined – water absorption capacity in each of those environments was determined.

The analysis of obtained test results was conducted via screening design. The designed experiment included four independent variables – $(w/c)_{tot}$, polymers type, amount of mixing water absorbed initially by SAP, and dosing method of SAP into the mix (Table 3). The total water-to-cement ratio of SAP-modified cementitious composites ranged from 0.30 to 0.36. Polymer type variable was varied through its granulation (parameterized – 0 for fine granulation, 1 for coarse granulation). The dosing method was varied through the part of SAP introduced in a hydrogel form (100% for the hydrogel dosing method, 0% for the non-saturated method). The last variable was the initial amount of mixing water absorbed by the internal curing agent in relative units (%). The mass content of SAP was calculated based on its water absorption capacities in different environments and assumed portion of mixing water that was to be absorbed according to formula (2), where m_{SAP} – mass content of SAP [% m.c.], β – designed portion of mixing water to be absorbed by SAP [%], α – water absorption capacity of SAP in water absorption environment (in the case of conducted study, either mixing water environment or concrete mix environment), (w/c) – water-to-cement ratio (in the conducted research is equaled to 0.30).

$$m_{SAP} = \frac{\beta \cdot \left(\frac{w}{c}\right)}{\alpha} \tag{2}$$

The mass of additional water increasing the total water-to-cement ratio in AW was determined experimentally by testing the consistency of individual concrete mixtures using the slump test method – $(w/c)_{tot}$ was raised until the same consistency as in the case of REF 0.30 was reached. This method was used to determine the effect of the additional water in the mix composition of the properties of hardened concrete.

Table 3. Plan of the experiment in the conducted research with its independent variables – total water-to-cement ratio, SAP type, SAP dosing method, and designed amount of mixing water to be initially absorbed by SAP

Series ID	$(w/c)_{tot}$ [–]	SAP content [% m.c]	Mixing water absorbed by SAP [%]	SAP type	Dosing method
a	b	c	d	e	f
AH 25	0.30	0.047	25	SAP A	Hydrogel
AH 50		0.094	50		
AH 75		0.141	75		
AH 25 AW	0.32	0.047	25		
AH 50 AW	0.34	0.094	50		
AH 75 AW	0.36	0.141	75		
AN 2.5	0.30	0.047	2.5		Non-saturated
AN 5.0		0.094	5.0		
AN 7.5		0.141	7.5		
AN 2.5 AW	0.32	0.047	2.5		
AN 5.0 AW	0.34	0.094	5.0		
AN 7.5 AW	0.36	0.141	7.5		
BH 12.5	0.30	0.054	12.5	SAP B	Hydrogel
BH 25		0.108	25		
BH 50		0.216	50		
BH 12.5 AW	0.32	0.054	12.5		
BH 25 AW	0.34	0.108	25		
BH 50 AW	0.36	0.216	50		

The effect of designed internal curing of different intensities over various concrete properties was investigated. The total shrinkage of concrete was tested according to PN-84/B06714/23 and ITB instruction nr 194 [19, 20]. In concrete beams (100 x 100 x 500 mm), measurement units were installed, and using the Amsler apparatus, the relative change in sample length was measured. Tests began one day after sample preparation and lasted for 480 days. Samples were stored in a climatic chamber in a controlled humidity and temperature environment (RH above 95% and T = 21 ±2°C).

Water absorption of concrete was tested based on PN-88/B-06250 [21]. Cubic samples (100 x 100 x 100 mm) were stored in water for 28 days after forming. Afterward, samples were moved to air-dry conditions for 24 hours to remove excess water from concrete surfaces. In the next step, samples were dried at 105°C until their mass stabilized. The result of the test – water absorption of concrete – was then calculated as a quotient of the difference in wet mass and dry one to dry mass, multiplied by 100 [%].

Compressive strength was investigated according to PN-EN 12390-3 [22] on cubic samples (150 x 150 x 150 mm). Samples were cured in the same climatic chamber for 28 days. After that time, they were compressed in a hydraulic press using the aforementioned standard.

The consistency of fresh concrete mix was determined via the slump test method according to PN-EN 12350-2 [23].

4. RESULTS

Consistency was determined using the slump test method. The consistency test was used in the series with additional water (AW) to determine the mass of extra water that should be introduced into the mixture to maintain the mix's rheological properties at a level similar to the reference series (REF 0.30). The results of the tests carried out are presented in Table 4. As the mass of water initially absorbed by the SAP increases, the fluidity of the mixture significantly decreases. This phenomenon is caused by the reduced mass of water available to liquify the cement paste in the concrete mix. It can be solved by introducing additional water into the system, increasing the total water-cement ratio. For series of concrete mixes to which extra water was added to counteract the decrease in the mix's workability, its amount was determined experimentally and presented as a new total water-cement ratio $(w/c)_{tot}$: 0.32, 0.34, and 0.36, respectively. Although this is a design method commonly used for internal curing, it contributes to a change in the proportions between all ingredients in the mixture – the additional volume of water is introduced at the expense of the volume of the remaining ingredients, making the final composition of the mix different from the composition of the reference series.

Table 4. Slump test results for fresh concrete mixes

Series ID	Total water-to-cement ratio [-]	Slump [mm]
REF 0.30	0.30	65
REF 0.36	0.36	125
SAP AH 25	0.30	60
SAP AH 50		40
SAP AH 75		30
SAP AH 25 AW	0.32	70
SAP AH 50 AW	0.34	65
SAP AH 75 AW	0.36	70
SAP AN 2.5	0.30	60
SAP AN 5.0		50
SAP AN 7.5		20
SAP AN 2.5 AW	0.32	60
SAP AN 5.0 AW	0.34	65
SAP AN 7.5 AW	0.36	65
SAP BH 12.5	0.30	30
SAP BH 24		15
SAP BH 50		0
SAP BH 12.5 AW	0.32	60
SAP BH 25 AW	0.34	65
SAP BH 50 AW	0.36	70

The effects of internal curing significantly varied depending on all assumed quantitative variables. In all prepared concrete series, internal curing met its goal of reducing linear changes caused by shrinkage deformations. An empirical model of linear changes caused by shrinkage deformations was developed (3), where ε_t – linear changes caused by shrinkage deformations [10^{-6} m/m], t – time from sample preparation after which linear changes were measured [day], c – asymptote of the model (maximal linear changes caused by shrinkage [10^{-6} m/m], d – correction coefficient [$\sqrt{day}$].

$$\varepsilon_t = c \cdot tgh\left(\frac{\sqrt{t}}{d}\right) \tag{3}$$

In all analyzed variants of internal curing, its effects contributed to a reduction in linear changes caused by shrinkage deformations (Fig. 2).

The scope of those changes varied – the most positive effect was observed for modification with SAP A added in hydrogel state, in mass content, allowing for an initial absorption of 75% of mixing water, with an additional volume of water added to

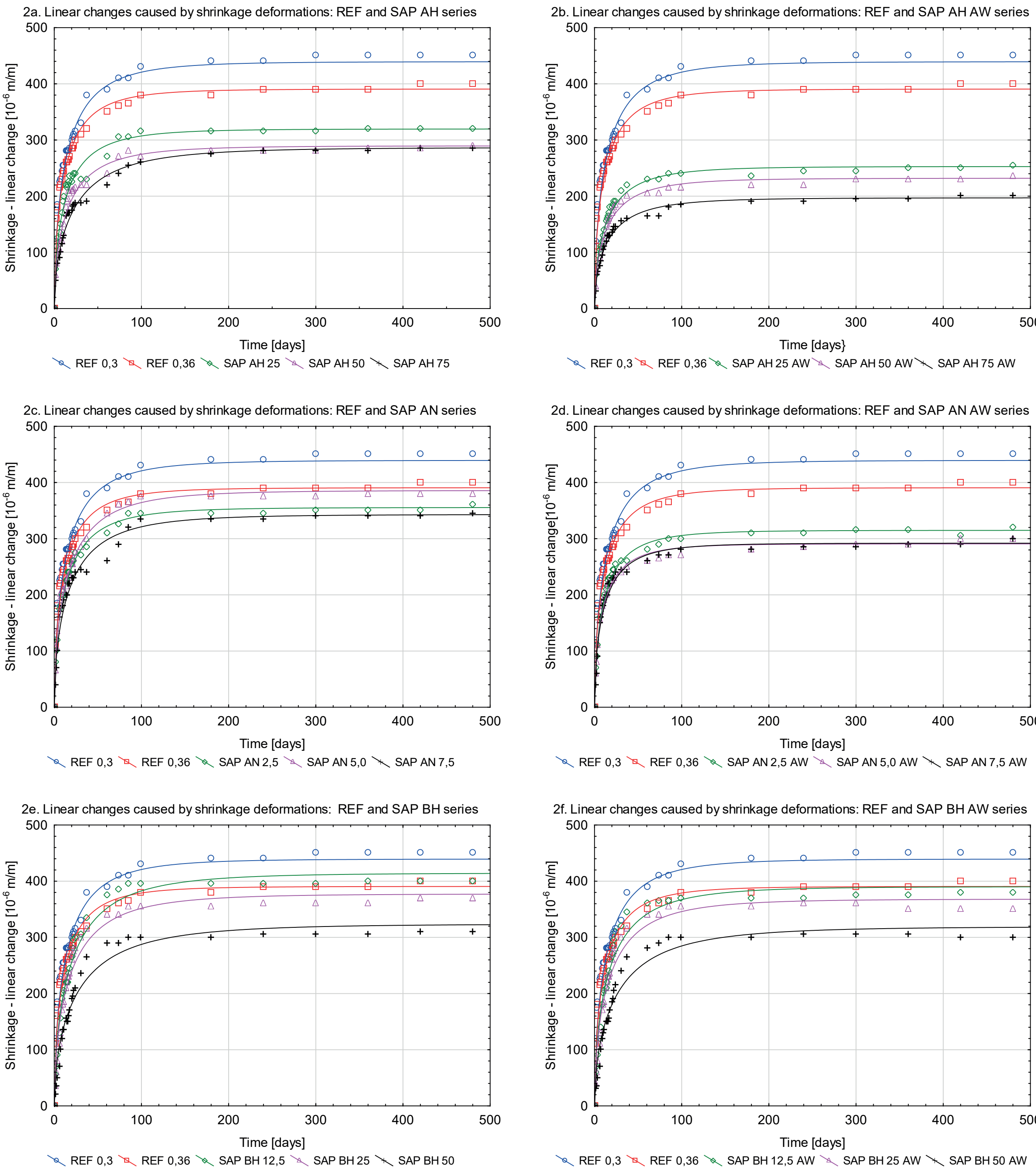

Fig. 2. Aggregated test results for linear changes caused by shrinkage deformations carried out for cement composites modified with superabsorbent polymers in various variants and reference compositions: 2a) SAP A added as a hydrogel; 2b) SAP A added as a hydrogel with additional water to maintain reference consistency; 2c) SAP A added in a non-saturated state; 2d) SAP A added in a non-saturated state with additional water to maintain reference consistency; 2e) SAP B added as a hydrogel; 2f) SAP B added as hydrogel with additional water to maintain reference consistency

the concrete mix to compensate for the consistency loss. The least efficient was modification with SAP B, regardless of its dosing method. In most cases, linear changes for internally cured series of total water-to-cement ratio equal to 0.30 were lower than for reference concrete with a total water-to-cement ratio of 0.36.

The influence on the concrete's water absorption wasn't that unambiguous (Fig. 3). Water absorption is one of the properties that allow estimating the continuity of the capillary network in the cement matrix. For reference series, water absorption was determined at 4.04% for REF 0.30 and 4.56% for REF 0.36. Concretes modified with SAP A in a hydrogel state were characterized by significantly lower water absorption than the reference series. In the case of SAP AH 75 was nearly 50%. The effect of reducing water absorption was not observed in the case of concretes in which SAP A was added in a non-saturated state to the remaining ingredients of the concrete mix. Concretes modified with SAP B polymer, with a grain size unsaturated with water of 2-2.5 mm, were characterized by a significant increase in water absorption compared to the reference series, up to 25%.

of adding SAP (SAP AO series) caused an almost 10% increase in compressive strength compared to the reference series REF 0.30. There are several reasons for this phenomenon. If SAP is introduced in a hydrogel form into the concrete mix, the SAP particles are characterized by the lowest electrochemical activity. Osmotic pressure reaches the lowest possible level due to water absorption in a mixing water environment before SAPs mix with the other ingredients. This significantly reduces the intensity of agglomeration of SAP particles, contributing to their more even distribution in the cement matrix. Therefore, the internal curing performed this way leads to more effective binder hydration.

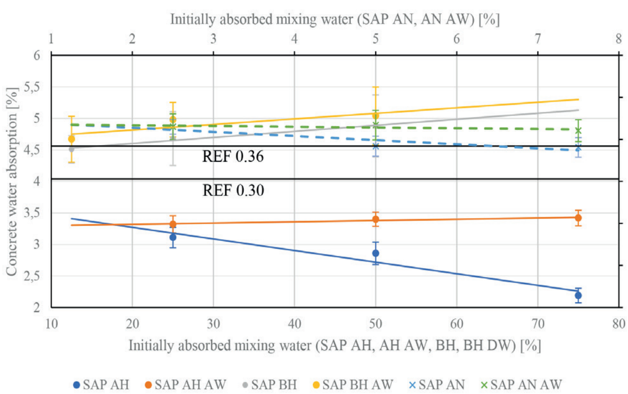

Fig. 3. Concrete water absorption for internally cured hardened concrete samples. SAP A was added to the concrete mix in different states (non-saturated/hydrogel). Due to differences in water absorption capacity in different environments, the same mass of polymer led to varying amounts of water that could be absorbed into the polymer structure, hence two axes of abscissae

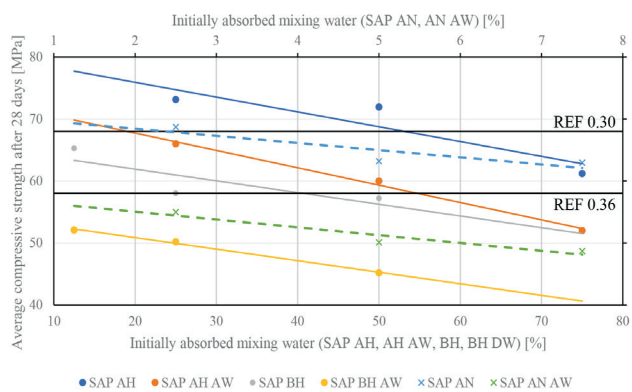

Fig. 4. Average compressive strength for internally cured concrete after 28 days of curing in a climatic chamber. SAP A was added to the concrete mix in different states (non-saturated/hydrogel). Due to differences in water absorption capacity in different environments, the same mass of polymer led to varying amounts of water that could be absorbed into the polymer structure, hence two axes of abscissae

In most cases, the compressive strength of concretes modified with superabsorbent polymers was lower than that of the reference series (REF 0.30) (Fig. 4). This effect was intensified by increasing the total water-to-cement ratio with additional curing water to maintain concrete mix consistency. Concretes modified with SAP A in a hydrogel state and added in the amount allowing for initial absorption of 25% and 50% of mixing water, were the exception – an increase in the mechanical performance of concrete was observed in those cases.

The influence of superabsorbent polymers on the strength characteristics of concrete is associated with the formation of SAP agglomerates, contributing to changes in the composite's pore network. This effect disappears in the case of fine-grained SAP (SAP A), added in the form of a hydrogel. Changing the method

The negative impact of increasing the total water-to-cement ratio $(w/c)_{tot}$ on the compressive strength of internally cured concretes was significant. The introduction of additional water to the concrete mix (increase $(w/c)_{tot}$) to maintain the consistency at a level similar to the reference series (REF 0.30) contributed to a significant decrease in compressive strength, in the extreme case by up to 33% (SAP BO DW50 series). An important issue is the problem of determining the reference level for internally cured concrete to which water has been added that is not included in the effective water-to-cement ratio. The REF 0.36 reference series was prepared to demonstrate the impact of SAP at different $(w/c)_{tot}$. However, the reference level to which the results of all series modified with superabsorbent polymers refer was concrete with a specific initial water content $w/c_{tot} = 0.30$ (REF 0.30).

Internal curing aims to improve the material's durability and reduce the material's susceptibility to linear changes caused by shrinkage deformations. The impact on the strength characteristics of the material is not the primary purpose of using internal curing of cementitious composites using SAP, but designing it to limit the negative impact on strength is desirable and expedient.

5. DISCUSSION

Internal curing is usually considered a way of modyfing concrete to prolong its durability and impact shrinkage behavior due to the binder's hydration. However, its addition to the concrete mix can have an unintended negative influence on the mechanical performance of the composite and its other properties. In conducted research main variables that can manifest during internal curing design were considered. The analysis parameterized two independent variables: SAP grain size and the addition method. Each of these variables was considered at two levels.

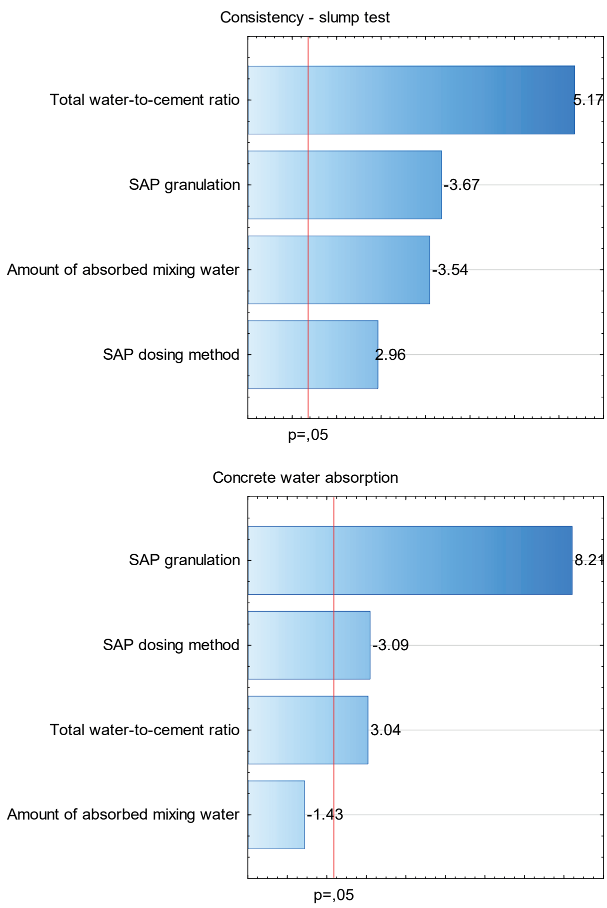

Fig. 5. Pareto chart of the absolute value of standardized effect estimate of variables considered in the study on the consistency of fresh concrete mix and hardened concrete's water absorption

All of the investigated properties were influenced by internal curing. Assumed independent variables had a statistically significant impact on the properties of the fresh mix (Fig. 5). In this graph, the effect ratings obtained by the ANOVA procedure are ordered from the highest absolute value to the lowest. The value of each effect is represented by a bar and a line that indicates how large the effect should be to be statistically significant (in the conducted research, the p-value was chosen at a standard value of 0.05). It was observed that with an increase in the internal curing agent's content, the concrete mix's rheological properties changed significantly, reducing the fluidity of the mix. The granulation of SAP in a non-saturated state most influenced concrete water absorption as it most certainly contributed to significant changes in the pore network, the effect of which can also be observed in the mechanical properties of concretes modified with SAP B.

In the case of compressive strength, a significant effect of all adopted variables can be observed (Fig. 6). A negative effect (decrease in compressive strength) was observed when increasing the total water-cement ratio, using SAP B (with a larger size of polymer particles in the water-unsaturated state), and increasing the percentage of mixing water absorbed by SAP. Introducing SAP into the mix in a hydrogel state was the only variable positively influencing concrete's mechanical performance.

In the case of linear changes caused by shrinkage deformations, the significant variables were polymer grain size (increase in linear changes with increasing grain size in the non-saturated state), total water-to-cement ratio (reduction of linear changes with increasing w/c), and the percentage of mixing water initially absorbed by the SAP (reduction of linear changes with the increase in the mass of water trapped in the SAP). It should be noted that in the research carried out, the percentage of initially absorbed mixing water was related to the method of adding SAP to the mixture concrete – concretes containing SAP added in a non-saturated state in an amount allowing for the absorption of 25%, 50% or 75% of the mixing water were not investigated. A modification of this type would result in an overestimation of the mass SAP content by approximately ten times compared to other cases, disturbing the analysis. For this reason, the only compositions with a much higher initial percentage absorbed mixing water were compositions to which SAP was added as a hydrogel, in the same mass amount as in the case of it being added in a non-saturated state.

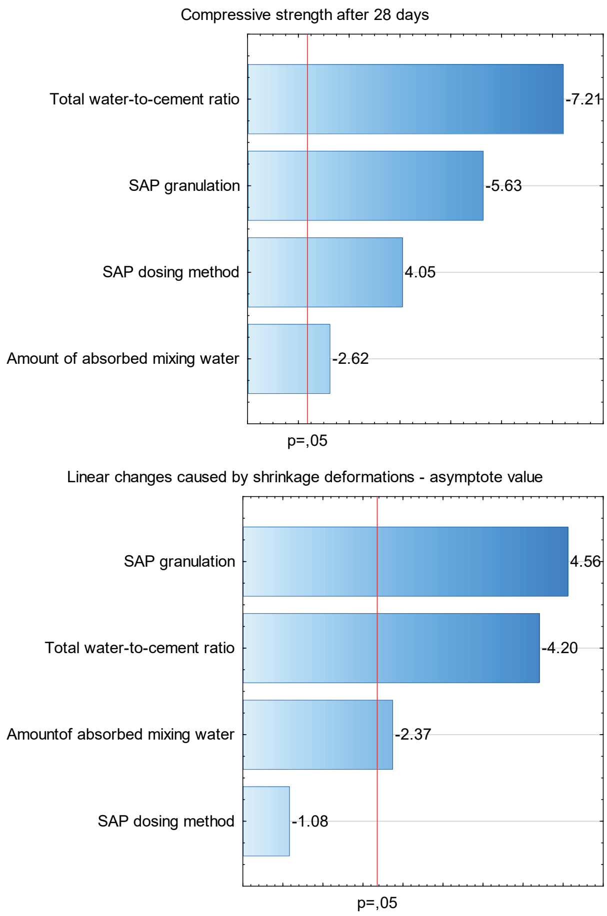

Fig. 6. Pareto chart of the absolute value of standardized effect estimate of variables considered in the study on concrete's compressive strength after 28 days of curing and asymptote value from the proposed model on the linear changes caused by shrinkage deformations

After their addition to the cementitious environment (cement paste, concrete mix), SAP grains are distributed within the cement matrix. It was proven in [24], that depending on the SAP state in which it is added to the mix, different phenomena impacting the quality of the aforementioned distribution occur. Entangled polymeric chains that make SAP's structure allow it to increase volume during water absorption while maintaining grain shape. This behavior is possible due to the elongation of the entire polymeric skeleton of SAP. However, in such a state, it is possible to fragment SAP grains by external forces.

This phenomenon can be observed as SAP is added to the concrete mix in hydrogel form. Water content in such a state exceeds 99% of SAP grain volume – polymeric skeleton expands to its limits. Under such conditions, when introduced to an environment with a high content of grains of different origins (cement, fine, and coarse aggregate), during the mixing phase of concrete mix, hydrogel SAP grains change their granulation – a mechanical fragmentation occurs.

Hydrogel fragmentation can have different impacts on the properties of SAP and concrete modified with it. As this phenomenon occurs, SAP structure can be damaged to the extent that its water absorption capacity in different environments is detrimented, which has a negative effect on the efficiency of internal curing. In the research, neither SAP A nor SAP B manifested changes in water absorption properties due to fragmentation.

On the other hand, as SAP is introduced in a non-saturated state, water absorption occurs in the cementitious environment. In the case of polyacrylic polymers, due to high ionic strength in the water absorption environment, SAPs' water absorption capacity is severely impaired (approx. ten times lower than in the case of a tap water environment). The less water SAP absorbs, the less its volume increases; therefore, the less its polymeric skeleton is susceptible to fragmentation. It can be assumed that this phenomenon occurs to a minimal extent if SAP water absorption occurs directly in the concrete mix environment.

The change in the way SAP is introduced into the mix has a significant impact on concrete properties. Fragmentation aside, due to a different initial water content stored in SAP grains, the dynamics of its desorption (the main SAP property affecting properties of internally cured concrete) varies. In the previous study by the authors, due to a different initial water content and fragmentation phenomenon, the difference in the volume of curing water used can vary 10-fold for the same mass of SAP introduced to the concrete mix in different states [9].

The other issue associated with the efficiency of internal curing is the distribution of SAP grains within the cement matrix. The phenomenon of SAP agglomeration, while added in a non-saturated state, is often described in the literature on the subject [25-27]. As SAP is introduced in a non-saturated state, all phenomena associated with water absorption occur during and straight after the mixing process. With significantly lesser volumetric increase caused by reduced water absorption capacity in an alkaline concrete mix environment, the osmotic pressure within polyacrylic SAP grains remains relatively high. The properties of the absorption environment affect the agglomeration risk of SAP grains. In this case, an additional water absorption environment can be distinguished – the outer layer of SAP grain, constituting an interim layer between the absorption environment and SAP internal structure (Fig. 7).

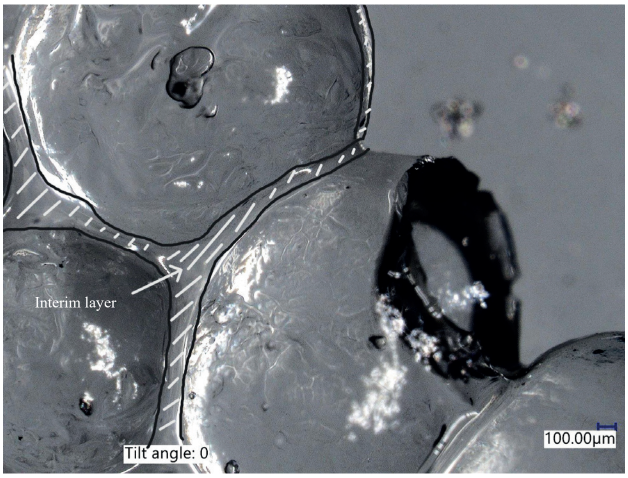

Fig. 7. The interim water layer on the outside of the water-absorbing SAP grains contributing to an increased risk of SAP grain agglomeration

Both physical and electrochemical aspects influence the aforementioned behavior. Surface tension and ionic strength due to high osmotic pressure in SAP grain are potent enough to attract water from the outer layer of neighboring SAP grain, therefore causing grain agglomeration.

As SAP grains agglomerate, the internal curing agents cease to be distributed evenly within the entire volume of the composite. As this occurs, the effectiveness of internal curing significantly reduces. Also, it contributes to forming a network of large pores in the cement matrix once water is removed after water desorption from agglomerated grains. Therefore, a deterioration in the mechanical properties of such concrete is highly probable. It has been reported that the aforementioned phenomena can contribute to significant deterioration in the mechanical performance of internally cured cementitious composites [28]. In the case of fresh concrete mix properties, SAP addition contributes to a significant deterioration in the workability of the fresh composite [29]. Due to this, it is common to counteract the aforementioned effect with an increase in total water content in the composition of concrete [30-32]. Although the exact interaction mechanisms between superabsorbent polymers of different origins and superplasticizing admixtures are still elusive, disregarding that method of controlling the rheology of the mix and including an additional volume of water in the composition to counteract SAP influence over viscosity leads to an increase in the porosity of the cement matrix. With introduced changes, the deterioration in the mechanical performance of the cementitious composite is expected, even if internal curing allows for a local increase in the degree of hydration of the binder. The effect of reduced mechanical performance with an increase in total water-to-cement content was also true in the case of concretes that are not subject to internal curing (in the case of the performed research, series REF 0.30 and REF 0.36). The increase in total water-to-cement ratio caused by increased water content in the mix that is added to counteract SAP's influence over concrete mix rheology also contributes to other, more mundane issues. With its introduction, the mass content of all ingredients per m^3 changes. In the performed research, the additional water volume was compensated through changes in the aggregate content in the mix. However, any non-intended changes between reference and modified series can deteriorate the quality of performed experiments and introduce additional variables influencing studied properties.

The SAP addition method isn't the only factor influencing the effectiveness of internal curing. Both the type and internal curing agent's properties significantly impact the characteristics of fresh concrete mix and hardened concrete properties. Any superabsorbent polymer's water absorption capacity depends on its chemical composition. SAP consists of polymeric chains interconnected via crosslinker. Its quantity indicates the level of entanglement between independent chains, its potential for volumetric change, and, therefore, its water absorption potential. As a polymeric network is less susceptible to elongation, it is also less prone to be impacted by mechanical fragmentation. Due to this, after water desorption, a network of large pores (defects) can be observed in the cement matrix, deteriorating the overall properties of concrete. It is the main reason behind recommendations for limiting the maximal grain size to be useful from the perspective of internal curing if added in a non-saturated state.

6. CONCLUSIONS

Conducted research allowed to determine the influence of variables related to designing internal curing using superabsorbent polymers on the properties of cementitious composites. It was found that:

- Pre-saturation of fine-graded SAP A in the tap water environment before its addition to other ingredients of the concrete mix contributed to an increase in the efficiency of internal curing – a more significant reduction in linear changes caused by shrinkage deformation was observed while reducing the negative impact on the mechanical properties of concrete.

- Regardless of the type of SAP used, its mass content, the amount of mixing water initially absorbed by SAP, and its addition method to other ingredients, internal curing leads to a decrease in linear changes caused by shrinkage deformations in relation to reference series.
- Internal curing's side effects affecting the mechanical properties of concrete were avoided only in the case of particular modification using SAP A – an increase in mechanical properties of concrete (or no influence at all) was observed in the case of modifying concrete with fine-graded SAP A added in a hydrogel form to the concrete mix. Its effect on mechanical performance was dependent on the amount of initially absorbed mixing water by the internal curing agent.
- An increase in the mass content of SAP contributed to a significant decrease in the fluidity of concrete mix.
- Modification of concrete with SAP of coarse granulation (SAP B), regardless of the design method, contributed to a significant deterioration in the mechanical performance of concrete caused by its non-homogenous distribution within the cement matrix.
- An increase in the total water-to-cement ratio allowed the consistency of concrete mixes to be maintained on a level of a reference series; however, it contributed to a significant deterioration of the mechanical performance of concrete.

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