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Method of internal curing cement concrete used for 3D printing technology in construction

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KEYWORDS

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ABSTRACT

Currently, 3D printing technology in construction is becoming more popular every day in many countries and regions in the world. In parallel with the development of 3D printers, the research, design and application of materials as "ink" for this technology is also an urgent direction in materials science. Improvement of 3D printing technology with the use of concrete mixtures based on Portland cement largely depends on the sustainable solution of the problem of ensuring normal hardening of extruded concrete layers. A violation of hardening has known negative consequences and entails significant economic losses. It has been suggested to use polyacrylate solutions, preparation of which before application in concrete mixture allows controlling the process of their polymerization, postponing the sorption function of the additive in time to ensure the required rheology. Influence of super absorbent polymer (SAP) solution on structural formation processes and properties of cement materials is studied. Assessment of the degree of hydration was carried out by the calorimetric method for total thermal power using the isothermal calorimeter TAM AIR. Identification of main phases of cement stone (CS) by X-ray phase analysis was performed on XRD-6000 diffractometer. It is established that the use of SAP solutions has a positive effect on the mobility of cement mixtures due to the delayed polymerization and the corresponding water absorption by the polymer. The flexural strength range is 6.7–7.2 Mpa and the compression strength range is 68.5–71.7 MPa. It is established that the range of concentrations of SAP less than 1.5 % provides close to the reference composition (without SAP) the total hydration heat power of Portland cement at the age of 86 hours. The dependences of rheological and mechanical properties of cement materials on SAP concentration have been established. It has been proved that the use of SAP solutions is an effective engineering solution to ensure the hardening of concrete in adverse conditions. Further development of the topic may be aimed at studying the effect of SAP solutions on the properties of concrete mixtures of different compositions for 3D printing.

1. Introduction

The development of compositions with a set of properties that are indifferent to the influence of the environment during the setting and hardening of the binder is an actual task for material science in connection with the evolution of 3D-printers in construction. Conditions for intense moisture loss are occurred in the process of layer-by-layer 3D printing of cement materials. This leads to an imbalance of the water in the volume of the composite, a lack of liquid for hydration, a decrease in density, a rise of shrinkage and loss of strength. Thus, the preserve water for the hardening period including at the using hardening accelerators is important for "building ink" for 3D-printer.

As shown in [5], superabsorbent polymers (SAP) can be used to provide internal care for Portland cement hydration processes instead the saturation of lightweight aggregate by water in lightweight concrete. Most SAPs are made in the form of microsized granules, powders or fibers characterized by the possibility of water absorption in amount more than 50 times of the initial volume.

The use of superabsorbent polymers in cement mixtures has both positive and negative effects [6...10]. On the one hand, the use of SAP as a carrier of water supply to ensure the binder hydration is justified by the positive effect of reducing shrinkage. On the other hand, the granular polymers requires preliminary saturation by water (within 15-30 minutes) to best mobility of the mixture and operates in the structure of the composite as a source of additional pores that reduce mechanical properties. In this case, the kinetics of desorption is the most important for increasing the efficiency of SAP. Water should be migrated from the polymer to the cement system, and not in the opposite direction.

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Thus, the use of SAP solutions with delayed polymerization should provide the water reserve in the cement system for internal curing without loss of mobility of the mixture. An important condition is the establishment of "parity" concentrations of the polyacrylate solution at which sorption of water does not reduce the degree of cement hydration.

2. Material and methods

The influence of a solution of a superabsorbent polymer on the processes of structure formation and properties of cement compositions was studied in this paper. Portland cement CEM I 42.5 «Lipetskcement» was used as a binder. The multi-component acrylate composition «Renovir hydrogel» used for injection drainage of structures, it is proposed to use as SAP. SAP specifications are presented in the table 1.

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 $[-CH_2\text{-}CH(COONa)\text{-}]_n$). 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.

The mobility of cement mixtures was determined by the diameter of the spread from a truncated cone. The study of the physico-mechanical properties of cement stone was carried out at the age of 28 days after hardening under adverse conditions (temperature – 27 ± 2.5 °C, humidity – less than 60 %) according to the Table 2.

Table 1. Properties of polyacrylate superabsorbent polymer

No.	Indicator	Value
1	Density, kg/m^3	1100
2	pH	7
3	Polymerization rate, min	0.25…45
4	Bond strength, MPa	0.2
5	Tensile at break, %	300
6	Application temperature, ˚C	from 0 to 40
7	Biostability	stable
8	Vapor permeability	conditionally vapor tight

Table 2. The recipe for cement mixtures

Ratio	Value						
W/C	0.24						
B/A_1	–	0.06					
B/ΣA	–	95.0	47.0	23.0	18.2	15.0	11.0
SAP/C, %	0.00	0.25	0.50	1.00	1.25	1.50	2.00
Note. Ratio $A_2/A_1 = 0.02$ and $A_3/A_1 = 0.08$.							

The relative deformation of shrinkage was determined using a longitudinal horizontal comparator IZA-2 as the ratio $\varepsilon = \Delta l/l$, where Δl is the change of the distance between the benchmarks at the age of 28 days, l is the base distance between the benchmarks at the age of 24 hours.

The degree of hydration was estimated by the calorimetric method according using by the total thermal energy [11...13]. Isothermal calorimeter TAM AIR (TA Instruments) was used for calorimetric analysis of cement mixtures within 72 hours. Samples of cement mixtures were prepared at W/C = 0.5 and polymer content of 0.5-1.5 % by weight of Portland cement with a constant ratio B/A_1 = 0.06. The main phases of the cement stone (W/C = 0.24, SAP concentration 0-1.5 % by weight of the binder) were identified by X-ray diffraction analysis using a XRD-6000 diffractometer (Shimadzu). Shooting Conditions – cathode Cu, 15 kV, 100 μA.

3. Results and discussion

A calorimetric analysis of cement stone modified by solution of superabsorbent polymer with different concentrations was performed. Integral thermograms of the total heat release of cement stone are presented in the figure 1. It was established that the studied range of SAP concentrations (less than 1.5%) provides a heat release level close to the control composition (without SAP). This indicates a similar degree of binder hydration. The processes of structure formation of cement stone both with and without SAP are comparable. That is, the effect of SAP polymerization on Portland cement hydration is minimal.

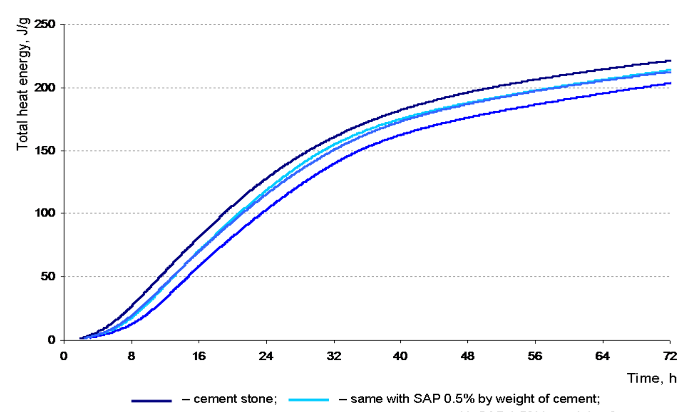

Figure 1. The kinetics of heat during the hydration of Portland cement with SAP.

An additional analysis of the influence of SAP on the processes of structure formation of cement stone can be established using X-ray phase analysis (figure 2). Diffraction reflections of the main phases of cement stone can be identified: low- and high-basic calcium hydrosilicates (CSH) with interplanar spacings d = 4.92, 3.03, 2.74, 2.61, 2.18, 1.93 and 1.80 Å, portlandite ($Ca(OH)_2$) with d = 4.92, 2.63, 1.93 and 1.80 Å, tobermorite (Tb) with d = 2.76 and 2.18 Å, calcite ($CaCO_3$) with d = 3.03 Å. Note that similar interplanar spacings may belong to cement clinker minerals that complicates the identification of phases and their number.

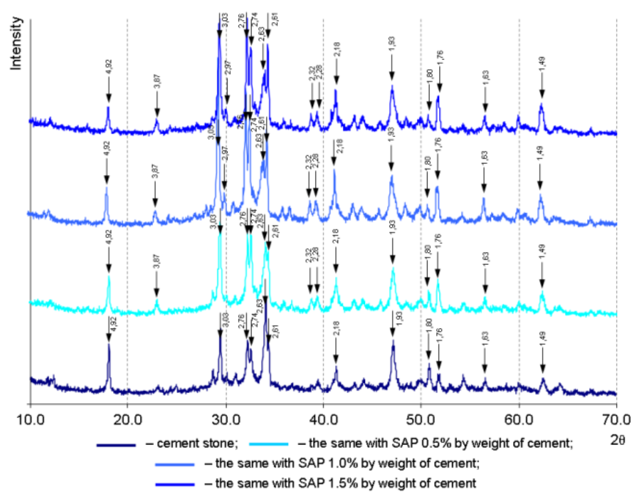

Figure 2. The X-ray phase analysis of cement stone.

An increase in the intensity of the main maxima can be noted on the X-ray graphs of cement stone with SAP (table 3). Cement stone with 0.5 % SAP by weight of Portland cement is characterized by an increase in the intensity of diffraction maxima at d = 3.87, 2.32, 2.28, 1.76, 1.63 and 1.49 Å, which relate to hydration products: calcium hydrosilicates, tobermorite, calcite and calcium hydrosulfoaluminates (CHSA). Naturally, this fact can be explained by the formation of more perfect crystals of hydration products. Such a positive effect of the superabsorbent polymer on the structure formation processes is also observed for cement stone with SAP in the amount of 1.0 % by weight of Portland cement. An almost twofold difference in the maxima of the products of hydration of Portland cement (CSH and Tb) can be distinguished at d = 3.03, 2.6, 2.74, 2.61 and 2.18 Å.

Obviously, an increase in the amount of SAP can have a negative effect on the structure formation of cement stone due to the creation of a physical barrier to the formation of crystals of hydration products. This is confirmed by X-ray graphs of cement stone after increasing in the SAP concentration to 1.5 %. Table 3 shows that the above called peaks of hydration products for such composition have a lower intensity compared to 1.0 % but greater than control composition.

Thus, calorimetric and X-ray phase analyzes show that SAP in an amount of not more than 1.0 % by weight of Portland cement has a positive effect on the structure formation processes of cement stone. The formation of a more perfect crystalline structure of cement stone is observed. An increase in the SAP concentration more than 1.5 % by weight of Portland cement leads to a decrease in the intensity of X-ray maxima corresponding to the products of hydration of Portland cement, which indicates the formation of a less perfect crystalline structure of cement stone.

The results of the study of the mobility of cement mixtures with SAP (Table 4) show a slight increase in the spread diameter at the increasing of the amount of polymer in the composition. This is due to the liquid state of the polymer part, which does not have a sorbing effect before polymerization and acts as an additional wetting component, in contrast to granular absorbent additives.

Table 3. Changes in the intensity of the diffraction maxima of cement stone

No.	d, Å	The concentration of the polymer part, % by weight of Portland cement				Interpretation
		0	0.5	1.0	1.5	
1	4.92	424	336	330	254	$Ca(OH)_2$; CSH
2	3.87	120	164	148	168	CHSA; CSH
3	3.03	536	728	1278	892	CSH; $CaCO_3$
4	2.97	212	194	294	236	CSH; Tb
5	2.76	448	648	1058	896	Tb
6	2.74	386	624	864	684	CSH
7	2.63	772	582	528	522	$Ca(OH)_2$
8	2.32	–	172	236	206	CSH
9	2.28	–	176	216	222	$CaCO_3$
10	2.18	260	322	464	380	CSH; Tb
11	1.93	446	396	416	408	$Ca(OH)_2$; CSH
12	1.80	262	214	194	200	$Ca(OH)_2$; CSH
13	1.76	202	292	320	320	CSH; Tb
14	1.63	164	184	246	190	CSH
15	1.49	162	228	280	260	$Ca(OH)_2$
Note. d is the interplanar spacing.						

Table 4. Rheological properties of mixtures and physico-mechanical properties of cement stone with a solution of SAP

No.	W/ΣA	ΣA/C, %	D_{sp}, mm	ρ, kg/m^3	R_{fx}, MPa	R_{com}, MPa	ε, mm/m
1	0	0.00	192.8	2100	7.15	70.4	2.4
2	95	0.25	197.8	2095	6.95	68.5	1.0
3	47	0.50	201.5	2095	6.85	70.7	1.2
4	23	1.00	197.8	2100	6.90	69.7	2.6
5	18	1.25	198.0	2100	7.00	71.7	2.7
6	15	1.50	206.5	2095	6.93	70.1	3.7
7	11	2.00	199.5	2100	6.70	70.8	4.9
Notes: D_{sp} is a spread diameter, ρ is the average density, R_{fx} is the flexure strength, R_{com} is the compressive strength, ε is the relative deformation at the age of 21 days.							

Table 4 shows that the effect of SAP on the average density of cement stone is insignificantly. The value of average density of cement stone varies within the margin of error. The value of indicators of mechanical properties changes analogously within 5 %: flexural strength varies from 6.70 to 7.15 MPa, the changing range of compressive strength is 68.5-71.7 MPa. A decrease in deformation of cement stone under adverse hardening conditions at the age of 21 days is also seen. The amount of SAP to 1% by weight of Portland cement leads to a decrease in shrinkage strain by 2 times. Thus, the use of SAP solutions shows the possibility of leveling the negative impact of sorption processes by polymer during the preparation, forming and initial hardening periods. SAP in a liquid state due to delayed polymerization does not absorb water and does not prevent wetting of the dispersed phase with stirring and hydration of the binder, but keep water further after polymerization.

The obtained dependences of the rheological properties of cement mixtures and the physicomechanical properties of cement stone show that varying the composition of the SAP solution to control polymerization allows to provide an internal care function and reduce shrinkage deformation. An effective concentration of SAP, ensuring the preservation of rheological properties, strength and also reducing deformations, is 0.5-1.0 % by weight of Portland cement.

4. Conclusions

Calorimetric and X-ray phase analyzes showed that the SAP solution in an amount of not more than 1.0 % by weight of Portland cement has a positive effect on the structure formation processes of cement stone. The formation of a more perfect crystalline structure of cement stone is observed. The SAP content of more than 1.5% by weight of Portland cement leads to a decrease in the intensity of the maxima in the radiographs corresponding to the products of hydration of Portland cement. In this case, the less perfect crystalline structure of the cement stone is associated with the formation of physical barriers by the SAP.

It has been shown that the solutions of superabsorbent polymers allow to keep water for hydration without loss of mobility, in contrast to granular additives. The obtained dependences of the rheological properties of cement mixtures and physico-mechanical properties of cement stone on the content of SAP indicate that the effective concentrations of SAP are 0.5-1.0 % by weight of Portland cement.

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