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About influence of some superplasticizers on hydration and the structure of hardened cement paste

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Abstract. Current construction can not be imagined without the use of high-quality mortars and concretes obtained by using high-tech and workable mixtures with lower water content. Obtaining such mixtures in current conditions is impossible without the use of superplasticizers. The use of superplasticizers in concrete technology requires an answer to the question of the influence of superplasticizers on the deformation-strength properties of cement stone. There is a well-known dependence "composition-technology-structure-properties", from which it follows that the strength and deformation properties of cement stone directly depend on the hydration of cement stone in the early stages and structure formation. The influence of some types of superplasticizers on the hydration and structure of cement stone, namely, total, open and conditionally-closed porosity, total contraction, autogenous shrinkage, contraction porosity and hydration heat is considered in the article.

1 Introduction

Current construction can not be imagined without the use of high-quality mortars and concretes obtained by using high-tech and workable mixtures with lower water content. The production of such mixtures under current conditions is impossible without the use of superplasticizers (SP). Application of the SP in concrete technology requires an answer to the question of the influence of SP on the strength and deformation properties of cement stone. There is a well-known dependence "composition-technology-structure-properties", from which it follows that the deformation-strength properties of cement stone directly depend on the hydration of cement stone in the early stages and structure formation. In this connection, the investigation of the influence of the SP on hydration and the structure of cement stone is an important scientific problem [1-3].

In the literature there are very contradictory data on the influence of SP on such indicators as strength and deformation properties of cement stone. Numerous domestic and foreign studies have shown that the effectiveness of different SP depends on a number of parameters such as the type of cement used, cement grinding thinness, the type of aggregate, and the type of modifying additives used [4-8]. However, in the first place, it is necessary to take into account the influence of the SP on hydration and early structure formation, as the factors that predetermine the physic-mechanical properties of the cement stone.

The purpose of this work is to study the influence of some types of SP on hydration and the structure of cement stone. To achieve this goal, it is necessary to solve the following tasks: to study the influence of some types of SP on the hydration process, by studying the hydration heat and autogenous shrinkage in the early stages of hardening cement stone, and also to investigate the influence of the SP on early structure formation by studying the formation of porosity and own free deformations of the cement stone.

The influence of the SP was studied using Glenium ACE 430 (hereafter 430); Glenium 323 MIX (hereafter 323); Glenium 115 (hereafter 115); Melment F10 (hereafter M F10); Structuro (hereafter St); SikaViscocret (hereafter Si); Glenium 51 (hereafter 51); Rheobuild 181K (hereafter 181); Polyplast SP-1VP (hereafter SP1); Glenium 30 (hereafter 30) and Melflux 2641 (hereafter 2641) for total (Pt), open (Po) and conditionally-closed porosity (Pcc), total contraction (TC), autogenous shrinkage (CS), contractional porosity (CPr) and hydration heat of cement stone made of cement paste (CP) with a value of W / C = 0.27 using portland cement (PC) made by plants “Proletary” (3 batches) (hereafter, Pr1, Pr2 and Pr3), “October” (hereafter O), “Verkhnebakansky” (hereafter V), “Pervomaisky” (hereafter Pe), “Volskcement” (hereafter Vo) and CEM I 42.5 made in Europe (hereafter T).

2 Influence SP on porosity

As is known, porosity of cement stone predetermines all its physic-mechanical properties and, consequently, affects the properties of concrete. According to [9-12], the SP can influence the process of hydration of cement stone and, as a consequence, its porosity. According to the data of [12], the total porosity of cement stone in the presence of SP can vary from +5,5 to -4,7%, which causes a change in the strength of cement stone from -25 to +22%. Depending on the porosity of the cement stone,

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its modulus of elasticity, creep parameters, and shrinkage change [10, 11].

The dosage of the SP was selected from the condition for obtaining the magnitude of the limiting shear stress of a cement slurry with a value of W/C = 0.27 not more than 10 Pa, which, according to [10], makes it possible to obtain self-compacting concrete mixtures. The results of the studies are presented in Table 1.

Table 1. Porosity of cement stone.

№	Cement	SP	Porosity of cement stone		
			P_t	P_o	P_{cc}
1	Pr1	Not	0,285	0,262	0,023
2		430	0,271 (95)	0,265 (101)	0,006 (25)
3		181	0,319 (112)	0,302 (115)	0,017 (71)
4	O	Not	0,3	0,274	0,026
5		430	0,286 (95)	0,283 (103)	0,003 (11)
6		181	0,328 (110)	0,304 (111)	0,024 (93)
7		323	0,306 (102)	0,294 (107)	0,012 (46)
8	V	Not	0,292	0,273	0,019
9		430	0,295 (101)	0,285 (104)	0,011 (59)
10		323	0,298 (102)	0,281 (103)	0,019 (100)
11		115	0,295 (101)	0,281 (103)	0,013 (68)
12	Pe	Not	0,316	0,289	0,027
13		430	0,306 (97)	0,293 (101)	0,013 (47)
14		323	0,314 (99)	0,289 (100)	0,024 (90)
15		115	0,345 (109)	0,319 (110)	0,026 (94)
16		181	0,343 (108)	0,323 (117)	0,02 (73)
17	Pr2	Not	0,296	0,285	0,011
18		30	0,283 (96)	0,276 (97)	0,006 (62)
19		2641	0,294 (99)	0,286 (100)	0,008 (82)
20	Pr2 + NTF	Not	0,308 (104)	0,297 (104)	0,011 (108)
21		30	0,314 (106)	0,3 (105)	0,013 (126)
22		2641	0,311 (105)	0,296 (104)	0,014 (137)

As follows from the presented in Table 1 data, in the presence of a SP both the total and the open and, especially, the conditionally-closed porosity of the cement stone can change. The increase in open porosity with the introduction of the SP occurs to a greater extent with respect to the increase in the total porosity, and therefore the conditionally-closed porosity decreases.

If we adopt the following scale for assessing the compatibility of a SP with particular cement:

- the SP does not increase the total and open porosity of the cement stone relative to the standard - "excellent";
- SP increases either the total or open porosity of the cement stone relative to the standart by no more than 1.03 times - "good";
- SP increases either the total or open porosity of the cement stone relative to the standard more than 1.03 times - "satisfactory",

then the compatibility evaluation of the SP and cement studied will look like this:

Table 2. Compatible SP with cement.

PC	Assessment of compatibility of cements with SP		
	«excellent»	«good»	«satisfactory»
Pr	30; 2641	430	181
V		323; 115	430
O		430	181; 323
Pe	323	430	181; 115

As is known, in the provision of frost resistance of concrete an important role is played by the ratio of conditionally-closed and open porosity. According to [12], frost resistance of concrete can be determined by the formula

$$F = 307 \cdot K_{frs}^{0.57} \tag{1}$$

where as the criterion of frost resistance is used the ratio of conditionally-closed (Pcc) and open (Po) porosity:

$$K_{frs} = \frac{Pcc}{0{,}09 \cdot P_o} \tag{2}$$

In Table 3 shows the values of the criterion of frost resistance of cement stone in accordance with formula (2).

Table 3. Calculated values of the criterion of frost resistance of cement stone.

SP	The values of the K_{frs} criterion for cements (in parentheses - in% of the standard)			
	Pr	O	V	Pe
Not	0,985[1] / 0,411[2]	1,057	0,787	1,051
430	0,239 (24)[1]	0,117 (11)	0,327 (42)	0,485 (46)
181	0,608 (62)[1]	0,887 (84)		0,689 (66)
323		0,45 (43)	0,594 (76)	0,708 (67)
115			0,486 (62)	0,894 (85)
30	0,261 (64)[2]			
2641	0,335 (82)[2]			
Not [2,3]	0,425 (103)			
30 [2,3]	0,49 (119)			
2641 [2,3]	0,543 (132)			

Notes: 1 - for the first batch; 2 - for the second batch; 3 - with NTF

As follows from the presented in Table 1 and 3, when the SP is introduced into the CP, the frost resistance criterion worsens (formula (2)), mainly due to a decrease in the value of the conditionally-closed porosity. This fact can negatively affect the frost resistance of cement stone. In studies [10], a decrease in the frost resistance of cement stone was recorded with a constant value of W/C in the presence of some SP. In connection with this, when designing compositions of concrete with increased requirements for frost resistance, it is necessary to provide the required value of conditionally-closed porosity through, for example by using of air-entraining agent (AEA). It is not ruled out that in this case it is necessary to increase the dosage of the AEA to compensate for the missing value of the conditionally-closed porosity in the cement stone from the SP.

3 Influence SP on contraction

As is known, with PC hydration, the volume of product of reaction is less than the total volume of substances entering the reaction (cement + water). This phenomenon is called total contraction [13]. The total reduction in the volume of the hardening system «cement + water = cement paste» (TC) consists of a reduction in the external geometric volume of the hardening CP, i.e. CS or autogenous shrinkage, and uniformly distributed practically spherical cavities with a diameter of several tens of microns, so-called CPr, formed in the test volume. Thus, TC = CS + CPr [1]. The measurement of contraction is usually carried out by the Le Chatelier method, while the value of TC is measured on a non-isolated from the environment (liquid) CP, and the value of CS is measured on an isolated from the environment (liquid) CP. There are two main periods of development of contraction:

- before formation in the structure of the crystalline framework, when the CP is in the plastic state, and the values of TC and CS are equal;
- after the formation of a crystalline framework in the structure of the hardening CP, when the difference between the values of the TC and the CS is noted, and the formation of the CPr begins (this period in [11] is defined as the period of deformation development in the postplastic stage, and the value of the CS in this period, from the appearance of the crystalline framework, according to [11], has an influence on the early cracking of cement stone and concrete).

The development of contraction is directly related to the hydration of cement [13], therefore, the change in the hydration kinetics, in particular, in the presence of chemical additives, incl. SP can, due to a change in the duration of 1 and 2 periods of the process of contraction, both the magnitude of the CS, which determines the early cracking, and the magnitude of the CPr. In [10, 11], the changes in CPr and CS in the presence of SP and (or) some additives affecting the kinetics of hydration of PC were recorded.

In Table 4 presents the results of studying the influence of some SP produced by BASF on the process of contraction and the magnitude of CS and CPr. From the presented in Table 4 data is obvious:

- the kinetics of the process of contraction is influenced by both the type and dosage of the SP;
- in the presence of SP the value of TC at the age of 3 - 4 days slightly changes both in the direction of increase and in the direction of decrease, which indicates a some influence of the SP on the hydration process;
- the main result when using SP is an increase the value of the CS, which can be considered as a negative factor, in connection with which it can be asserted that a study of the influence of the SP on the CS value will make it possible to select a rational combination "PC + SP", which reduces the risk of early cracking due to development CS;
- there is a decrease in the value of CPr in the presence of a SP.

Table 4. Data on PC contraction in the presence of a SP.

Cement	SP	The values of the quantities			
		τ_1[1], h	TC, ml/ 100 g C[4]	CS, mm/m (share of TC)[5]	CPr, ml/100 g C (% volume of CP)
V	-	less 6	2,2[2]	3,0[2] (0,35)	1,43[2] (2,44)
	G323 0,47%	3	2,58	8,4 (0,64)	0,92 (1,57)
	G323 0,55%	12 - 24	2,42	3,4 (0,64)	0,86 (1,47)
	G115 0,35%	12	2,38	4,2 (0,41)	1,4 (2,39)
	G115 0,4%	24	2,43	4,3 (0,63)	0,89 (1,52)
	G430 0,37%	6 - 12	2,49	1,15 (0,76)	0,59 (1,0)
	G430 0,45%	36	2,4	0,95 (0,8)	0,47 (0,8)
Pe	-	12	2,15	1,89 (0,44)	1,2 (2,0)
	G323 0,47%	36	2,04	1,99 (0,68)	0,65 (1,1)
	G323 0,55%	12	1,82	3,1 (0,35)	1,17 (2,0)
	G115 0,35%	12	1,86	3,32 (0,44)	1,04 (1,77)
	G115, 0,4%	12	1,98	2,18 (0,28)	1,44 (2,44)
	G430, 0,37%	36	2,09	1,45 (0,78)	0,47 (0,8)
	G430, 0,45%	24	2,11	1,8 (0,61)	0,83 (1,4)
O	-	12	2,04	2,86 (0,5)	1,01 (1,7)
	G323, 0,47%	12	2,0	2,35 (0,3)	1,4 (2,38)
Pr1	G430, 0,37%	12	2,46	7,14 (0,59)	1,0 (1,7)
Pr2	-	5	3,0[3]	2,9[3] (0,32)	2,04[3] (3,48)
	G30, 0,32%	1	2,94	6,2 (0,44)	1,65 (2,81)
	M 2641, 0,36%	1 - 3	3,1	5,15 (0,36)	1,97 (3,36)

Notes: 1 - the duration of the first period of development of the process of contraction; 2, 3 - at the age of 96 and 72 hours respectively; G-series "Glenium"; M-series "Melflux"; 4 - C = cement; 5 - share of total CS from TC

Since, as noted above, the SP has an insignificant influence on the value of TC at 3 to 4 days of age, a significant change in the values of CPr and CS in the presence of SP is associated with the kinetics of the process of contraction (hydration) in the early period. In particular, on the first day of hydration there is a lag in varying degrees of the TC value of Verkhnebakansky cement with all SP from the sample without SP, which indicates some inhibition of the hydration process in the compositions with the SP in this period.

The change in the kinetics of the formation of a crystalline frame in the early period influences the change in the ratio between CPr and CS, i.e. an increase in time τ_o (duration of period 1) leads to a decrease in the CPr and an increase in the CS.

Thus, with the introduction of a SP into the composition of the concrete mixture, due to the possible influence of the SP on the hydration process of the PC and, as a consequence, on the kinetics of the contraction process, it is possible to change the duration of the period prior to the onset of intensive formation of the crystalline frame in the structure of the hardening cement stone, CPr and CS - with the increase of this period, i.e. when the hydration process slows down in the early period, the CPr increases and the CS decreases. Since CS has a significant influence on the cracking of cement stone (concrete) in the early period of structure formation [10, 11], and CPr has an influence on the frost resistance of concrete [12], and the ratio of CPr and CS of cement stone can vary widely [14], the question of the influence of a SP on these quantities requires special study.

4 Influence SP on hydration heat

According to [15-17], three main periods of cement hydration - induction, accelerated and delayed - are distinguished on thermokinetic dependence. In our opinion, the following three sections are of primary interest in the integral curve of heat of hydration of the PC in the early period of hydration: 1 - due to the heat of wetting and hydration of alkalis, free lime, partial hydration of C_3A and the formation of primary ettringite; 2 - the so-called induction period, during which the hydration heat is practically not fixed; 3 - period of intense hydration heat (accelerated) due to hydration of the basic clinker minerals. Then comes the period of slowing down the rate of hydration.

The SP can have a significant influence on the hydration heat parameters of cement [18], and for practical applications it is very important to select the most compatible "cement-SP" pair, since the SP can influence all the properties of the cement stone [9]. For each of these areas, certain quantitative indicators can be used, which depend on the type of cement, the presence of additives, and temperature conditions, i.e. can characterize the features of the hydration process. For the first stage, for example, the hydration heat quantity Q1 is important, since, as is known, the heat of wetting for powders depends on their dispersion. It is clear that in the amount of hydration heat Q1 in the first section there are "noises" - the heat of hydration of alkalis and free lime, partial hydration of C_3A and the formation of the primary ettringite. But if we consider the influence of the SP on the hydration heat in the first stage for particular cement, we can indirectly assess the influence of the SP on the dispersion of cement by changing the hydration heat Q1. As is well known, the heat of wetting for powders depends on their specific surface and varies, according to some data, in a very wide range, from 10^{-5} to 10^{-3} cal/cm^2, which, when recalculated on a PC, roughly corresponds to a value from 0.12 to 20 kJ/kg. It is clear that for PC this range will be much narrower.

According to the data of [15], hydration heat in the initial period with hydration of C_3S is 2.3 to 4.9 kJ/kg, depending on the dispersity of the binder, and the duration of this stage is from 20 to 38 minutes. In our studies (Table 5), the values for PC without SP, respectively Q1 from 2.15 to 6.6 kJ/kg, and the duration of the first period from 5 to 50 minutes.

Table 5. Influence of SP on the value of Q1 and the duration of the first stage of hydration.

SP	Hydration heat in the first stage kJ/kg / Duration of the first stage, min							
	Specific surface of cements, cm^2/g							
	2930	3270 – 3600						4140
	Cements							
	Pr1	Pr2	Pr3	V	O	Pe	Vo	T
Not	2,6 / 5	4,9 / 7	2,2 / 20	5,9 / 30	2,2 / 15	2,2/ 25	4,6 / 12	6,6 / 50
30	3,0/ 5							
2641	5,2/ 5							
SP1		11,6 / 10					8,7 / 10	6,4 / 26
M F10		9,9 / 19					10,4 / 19	6,8 / 7
St		10,2 / 22					8,8 / 19	13,8 / 44
Si		13,8 / 240					12,4 / 25	9,9 / 160
51		12,3 / 23					9,9/ 17	8,4 / 20
323				4,5 / 60	4,4 / 20	4,9 / 20		
430			2,4 / 10	5,8 / 60	1,4 / 175	1,8 / 180		
181			8,2/ 60		2,3/ 45	7,6/ 60		
115				2,6 / 70		2,6 / 20		

From the presented in Table 5 data, it is obvious that in cements without SP, the duration of the first period naturally increases with the decreasing size of cement particles, and the amount of hydration heat during this period depends not only on cement grinding thinness, which is also quite natural, since hydration heat in this period, as already noted, is related with the presence of free lime, etc.

With the introduction of the SP, the increase in the hydration heat in the first period is noted mainly, which can be estimated as the disperger influence of the SP (some exception is V + 115; O + 430; Pe + 430; T + SP1). It is also noted, as a rule, the extension of the first period. This may be due to both the growth of the actual specific surface due to the dispersion of cement and the retarding influence of the SP on the hydration of free lime and other compounds in the early period. It can be assumed that the more the hydration heat in the first period occurs with the introduction of the SP and the less the elongation of the first period, the more effective the SP with this cement is.

Estimating the duration of the induction period allows us to determine the influence of the SP on slowing down the hydration process in the early period, i.e. classify the SP on the influence on the setting time (SP with a retarding influence or not). According to [15], the duration of the induction period during hydration of C_3S is from 1.1 to 4 hours, depending on the dispersity. In our studies, the duration of the induction period for PC without SP was 1.8 to 3.1 hours (Table 6).

Table 6. Influence of SP on the duration of the induction period.

SP	The duration of the induction period, h							
	Specific surface of cements, cm^2/g							
	2930	3270 – 3600						4140
	Cements							
	Pr1	Pr2	Pr3	V	O	Pe	Vo	T
Not	2,5	1,8	3,1	2,2	3,0	3,0	2,5	2,3
30	5,5							
2641	6,5							
SP-1		2,3					5,6	3,5
M F10		7,0					5,3	3,9
St		6,6					22,5	22,5
Si		54,4					57	44,5
51		19,2					17,9	3,15
323				8,3	3,0	3,5		
430			9,1	5	10,5	5,2		
181			13		14,4	3,0		
115				5,8				

From the data presented in Table 6, it is obvious that when the SP is administered, as a rule, the duration of the induction period increases and in some cases, very significantly. It is clear that increasing the duration of the induction period to 44 and even 57 hours for practical use in most cases is undesirable. Some increase in the duration of the induction period can positively affect the increase in the stability of the concrete mix. Therefore, the influence of the SP on the change in the duration of the induction period can also be used as a criterion for assessing the compatibility of PC and SP.

The hydration heat rate in the third period can characterize the influence of the SP on the hydration process. According to [15], the duration of the third period of hydration because of C_3S hydration is 6.3 to 14.2 hours, depending on the size of cement particles, and the rate of hydration heat at this stage is from 8.2 to 19.8 kJ/kg · h. The total hydration heat at this stage is 44.8 to 90.9 kJ/kg. According to our data, the rate of hydration in the third period for PC without SP was from 2 to 25 kJ/kg · h, and the total hydration heat in the third period was from 26 to 94 kJ/kg (Table 7).

Table 7. The magnitude of hydration heat and its rate in the third period.

SP	The amount of heat released, kJ /Average hydration heat rate in the third period, kJ/kg · h							
	Specific surface of cements, cm^2/g							
	2930	3270 – 3600						4140
	Cements							
	Pr1	Pr2	Pr3	V	O	Pe	Vo	T
Not	69 / 12	94 / 14	81 / 15	55 / 7,5	26 / 2	45 / 5	62 / 11	87 / 25
30	68 / 13							
2641	68 / 15							
SP1		82 / 10					67 / 6	77 / 24
M F10		95 / 9					53 / 7	80 / 19
St		62 / 1					36 / 1	56 / 9
Si		42 / 3					26 / 0,5	46 / 7
51		59 / 7					40 / 4	79 / 7
323				87 / 9	52 / 1	34 / 1,5		
430			86 / 9	59 / 7	35 / 2	45 / 3		
181			80 / 6		41 / 0,6	30 / 0,4		
115				86 / 7		37 / 2		

The hydration heat rate in the third period can characterize the influence of the SP on the hydration process:

- since the hydration heat during hydration of various minerals is different, the change in rate can be a consequence of selective adsorption of the SP;
- it is obvious that the hydration heat will depend on the area of contact "cement-water", in connection with which the dispergation of cement particles in the presence of a SP can cause increasing of hydration heat.

From the presented in Table 7 data, it is obvious that the SP can have a significant influence on both the hydration heat in the third period and the rate of hydration. Such information can be very useful when selecting a «cement-SP» pair, for example, for concreting massive structures that require the minimization of the hydration heat of concrete. It is clear that minimum change the total hydration heat and the rate of hydration when using SP characterized small influence of the SP on the hydration process. As a confirmation, we can consider the relationship between the rate of hydration heat in the third period and the tensile strength of cement stone at the age of 28 days.

Thus, the analysis of the SP influence on the change the parameters of heat of hydratation of the PC gives information for a preliminary assessment of the "compatibility" of a particular PC with a particular SP, including taking into account the specific application (temperature conditions, requirements for the conservation of concrete mix and limiting hydration heat). To fully assess compatibility, it is necessary to identify the influence of SP on porosity, strength, and deformation properties of cement stone [18-19].

5 Conclusions

An analysis of the influence of the SP on the changes in the parameters of hydration and structure formation in the early periods provides information for a preliminary assessment of the "compatibility" of a particular PC with a particular SP, incl. taking into account the specific application (temperature conditions, requirements for the conservation of concrete mix and limiting hydration heat). For mix proportions of concrete with increased requirements for frost resistance and crack resistance, it is necessary to provide the required amount of conditionally-closed porosity, CPr, CS and their ratio. To fully assess the compatibility and values of the parameters of conditionally-closed porosity, CPr, CS and their ratio, it is necessary to determine the influence of the SP on the porosity, strength, and deformation properties of the cement stone.

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