Research into the Long-Time Strength of Cement Stone with a Modified Structure

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Abstract. The problem of a time-dependent gain of a cement dispersed system’s strength remains the focus of both domestic and foreign researchers in terms of its practical significance. To study the above problem, we used non-additive sulfate-resistant Portland cement grade 400 made by Volsk city plant with a normal density of 24 %. 9 series of samples were made from fresh Portland cement. The kinetics of changes in the cement stone’s physical and mechanical properties was observed on series’ samples for 9.5 and 18 years. The paper imparts the values of the cement, water, superplasticizer consumption and compaction ration derived from compacted cement paste after forming test pieces, numerical values of properties in check dates as a result of natural moisture exchange with the environment and drying of test samples to a constant mass at 105°C, as well as the degree of its hydration at the age of 18 years, which was determined by calculation from non-evaporable, that is, chemically bound, water, taking into account that its amount in fully hydrated cement comprises 23% of the cement mass. Changing of the superplasticizer introduction procedure, even with a minimum consumption of S-3, led to a change in the yield value of the cement stone. The experiments targeting to reveal the long-time behavior of a superplasticized cement stone allow us to speak of a clear trend in the influence of SP and its introduction procedure on changes in long-time strength values. However, this is only a trend, since there are many other factors of influence than those discussed in this paper, which testifies to the necessity for a more detailed study of this problem due to its complexity considering the development and application of a new generation superplasticizer and composite binders to construction practice.

1. Introduction

The problem of a long-time strength gain and its regulation is of particular interest in the current search for new-generation concretes including highly functional ones with very high strength, uniformity and low porosity, compliant with a novel concept of concrete science – to obtain a highly mobile matrix phase of a concrete mixture with a low water content attributable to the complex use of chemical and mineral admixtures with high rheological efficiency [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13].

However, publications on this problem mainly consider the early stages of hydration structure formation, and as for the later stages, as mentioned in [14], there is a long-before formed opinion that it is almost impossible to regulate the properties of cement stone during this stage, although there is a necessity for that. Following I.N. Akhverdov [15], the kinetics of cement stone time-dependent strength gain is described not by a smooth exponential curve, but by a function undergoing periodic discontinuities. According to Sychev [16], one of the many reasons for the “sawtooth” changes in the
time-dependent strength of "mature" concrete is the hydrolysis of Si-O-Si bonds, which account for up to 50-60% of cement stone strength.

In [17], it is said that the time factor causes the occurrence of two characteristic divergent processes in the concrete: the process of time-dependent strength gain (aging of concrete), defined by physico-chemical changes in its structure, and the process of strength loss of concrete under stress associated with the manifestation of the rheological properties – increase of deformation with time, leading to certain disruptions of the internal connections in the material at micro and macro levels.

The problem of regulating long-time strength gain is of particular interest in the current search for ways to obtain and use new-generation concretes including highly functional ones with very high strength, uniformity and low porosity compliant with a new concept of concrete science – to obtain a highly mobile matrix phase of a concrete mixture with a low water content owing to the complex use of chemical and mineral additives with high rheological efficiency. At the same time, the use of chemical additives is known to be the most effective method for managing the morphology of new formations in hydration cement structures, and, consequently, the patterns of their pore space.

In this regard, it is worth looking into the problem of procedure and concentration aspects of the effect on the formation of a long-time strength of cement stone and the possibility of regulating its macro-properties at the later stages of cement hydration after SP S-3 introduction into a cement-water suspension.

Research objective: To study the technological properties and long-time strength of cement stone with a modified structure.

Research tasks:
1. to obtain values on the yield strength and the diameter of the flow of cement paste, depending on the procedure for its preparation
2. to identify the dependences of changes in the density, porosity and hydration rate of cement stone on hardening time.
3. to reveal the influence of temperature-humidity treatment (THT) on cement stone’s structure and physical and mechanical properties.

2. Methods
To study the strength of cement stone, we took non-additive sulfate-resistant brand 400 Portland cement manufactured by Volsk city plant with a normal density of 24%. 9 series of type I samples were made from fresh Portland cement according to GOST 29167, 4x4x16 cm in size with a W/C ratio of 0.18; 0.20 and 0.27. Each series consisted of 12 samples. A year later, 6 more series of samples were made from the same Portland cement with a W/C of 0.24 for 15 samples in each series. When fabricating 13 compositions, the admixture SP S-3 was added in different dosages against the cement mass and with different procedures for its introduction into the cement paste. The water-cement ratios of cement paste used in the experiment correspond to modern recommendations for the production of new-generation concretes.

Table 1 shows the cement composition values, mixing of cement and introduction of the SP admixture into the cement paste in 15 series of samples. It should be emphasized that the preparation of all batches had two stages during 5 minutes. At each stage, 50% of the total content of mixing water was dosed, and the procedure for dosing SP was different in that, that in a number of compositions it was not introduced at the first stage but at the second stage it was added in full. In another part of compositions, on the contrary, both at the first and second stages of batching, SP was introduced together with water in ratio of 50% of the total volume, as can be seen from values in table 1.
Table 1. Yield strength and diameter of the cement flow, depending on the cement paste procedure.

| Sample series | W/C ratio | SP S-3, % | Cement paste procedure | d, mm | τ, Pa |
|---------------|-----------|-----------|-------------------------|-------|-------|
| 1             | 0.24      | –         | C+0,12H₂O+0,12H₂O       | –     | –     |
| 2             | 0.24      | 1.0       | C+(0,12H₂O+0,5SP)+(0,12H₂O+0,5SP) | 92.5  | 55.4  |
| 3             | 0.24      | 0.5       | C+(0,12H₂O+0,25SP)+(0,12H₂O+0,25SP) | 31    | 493.4 |
| 4             | 0.24      | 0.5       | C+0,12H₂O+(0,12H₂O+0,5SP) | 33    | 435.4 |
| 5             | 0.24      | 0.25      | C+(0,12H₂O+0,125SP)+(0,12H₂O+0,125SP) | 30    | 526.8 |
| 6             | 0.24      | 0.25      | C+0,12H₂O+(0,12H₂O+0,25SP) | 30    | 526.8 |
| 7             | 0.27      | –         | C+0,135H₂O+0,135H₂O     | 29    | 548.4 |
| 8             | 0.27      | 1.0       | C+(0,135H₂O+0,5SP)+(0,135H₂O+0,5SP) | 130   | 27.3  |
| 9             | 0.27      | 0.5       | C+(0,135H₂O+0,25SP)+(0,135H₂O+0,25SP) | 78    | 75.8  |
| 10            | 0.27      | 0.5       | C+0,135H₂O+(0,135H₂O+0,5SP) | 100   | 46.1  |
| 11            | 0.27      | 0.25      | C+(0,135H₂O+0,125SP)+(0,135H₂O+0,125SP) | 30    | 512.5 |
| 12            | 0.27      | 0.25      | C+0,135H₂O+(0,135H₂O+0,25SP) | 35    | 376.5 |
| 13            | 0.27      | 0.25      | C+(0,135H₂O+0,25SP)+0,135H₂O | 30    | 512.5 |
| 14            | 0.20      | 1.0       | C+0,1H₂O+(0,1H₂O+1,0SP) | –     | –     |
| 15            | 0.18      | 1.0       | C+0,09H₂O+(0,09H₂O+1,0SP) | –     | –     |

The samples were formed on a laboratory vibrating table with standard vibration parameters during 3-5 seconds. The shaped samples were placed above water in a closed hydraulic bath. After preconditioning for 17 hours, the samples were exposed to heat and humidity treatment in the laboratory as follows: temperature rise for 2 hours, isothermal exposure for 8 hours at a temperature of 85-90°C, natural cooling of the samples in the steaming chamber. After temperature-humidity treatment and removal of formwork, all samples were weighed to check changes in their mass and density over time as a result of moisture exchange with the environment. The samples were then placed in natural laboratory conditions, where, depending on the season, the temperature and relative humidity varied in the range from 8 to 24 °C and 56-90 %, respectively.

The kinetics of changes in the cement stone’s physical and mechanical properties on samples of series 1 – 6 was observed for 18 years, and on samples of series 7 – 15 for 9.5 years. At the same time, it should be noted that the assessment of the controlled parameters during all test periods was carried out in the laboratory at a temperature of 21-22 °C and a relative humidity of 58 - 60 %.

Table 2 shows the consumption values of cement, water, superplasticizer and compaction ratio derived from the compacted cement paste after forming the test samples. A more homogeneous distribution of dispersed cement in the composition No. 2 at a dosage of 1% SP of the cement mass was facilitative of a better value of the compaction ratio amongst the considered series of samples. The dosage of SP in the amount of 0.5 and 0.25 % did not have a noticeable effect on the compaction ratio.
Table 2. Cement paste composition.

| Component consumption per 1 m$^3$ of cement paste | Samples series |
|-------------------------------------------------|---------------|
|                                                  | 1  | 2  | 3  | 4  | 5  | 6  |
| C, kg                                           | 1746 | 1758 | 1732 | 1708 | 1736 | 1719 |
| Water, l                                        | 419  | 422  | 416  | 410  | 417  | 413  |
| SP S-3, kg                                      | -   | 17.0 | 8.6  | 8.5  | 4.3  | 4.2  |
| W/C                                            | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 |
| Compaction ratio, $C_r$                         | 0.977 | 0.984 | 0.970 | 0.960 | 0.972 | 0.963 |

3. Research outcomes and their analysis

Table 3 presents the numerical values of changes in the density and porosity of cement stone in check times as a result of natural moisture exchange with the environment and drying of experimental samples to a constant mass at 105 °C, as well as the degree of its hydration at the age of 18 years, which was determined by calculation from non-evaporable, that is, chemically bound, water, taking into account that its amount in fully hydrated cement is 23 % of the cement mass.

| Sample series | Cement stone’s density and porosity, $\text{kg/m}^3$ / % | Cement hydration rate, % |
|---------------|---------------------------------------------------------|--------------------------|
|               | After temperature-humidity treatment 28 days 420 days 18 years After drying at 105 °C | |
| 1             | 2165 / 8.4 2090 / 7.5 2081 / 8.4 1978 / 18.7 | 57.8 |
| 2             | 2197 / 10.6 2120 / 7.7 2052 / 14.5 1954 / 24.3 | 44.3 |
| 3             | 2156 / 4.6 2100 / 5.6 1991 / 16.5 1887 / 26.9 | 36.9 |
| 4             | 2126 / 3.3 2091 / 3.5 1990 / 13.5 1882 / 24.4 | 42.2 |
| 5             | 2157 / 3.7 2120 / 3.7 1990 / 16.7 1888 / 26.9 | 37.1 |
| 6             | 2136 / 4.5 2091 / 4.5 2081 / 5.5 1958 / 17.8 1857 / 27.9 | 33.9 |

Note: before slash – density, after slash – porosity.

From the analysis of the experimental data presented in table 3, it follows that in the first 28 days after temperature-humidity treatment (THT), a large moisture loss of 10.6% by its volume was found among samples of the second series, that is, cement stone with a dosage of 1 % SP S-3. Probably, this result can be explained by the fact that during adsorption and the appearance of a double electric layer (DES) in the dispersed system, the SP S-3 squeezes a certain amount of water into the outer diffuse part of the DES, thereby weakening its connection with the surface of cement particles. At lower dosages of SP S-3, on the contrary, there is less moisture loss.

At the age of 420 days, cement stone samples of series 1 and 2 displayed small absorption of water from the environment, while samples of series 3, 4 and 6 yielded a slight loss of moisture, which is probably due to the specific effect of SP S-3 on the formation of their pore space. However, at the age of 18 years, the kinetics of moisture loss from samples with SP S-3 began to significantly exceed the values of the control composition. As a result, the occurring porosity from evaporated water on samples prepared with SP S-3 began to exceed the similar values of the control composition by 60 – 112 %. Further drying of the experimental samples to a constant mass at a temperature of 105° C resulted in an increase in their porosity by about 10% for almost all series of samples. However, it should be underscored that the samples of series 2 – 6 prepared with SP S-3 showed a 30 – 49% greater total porosity from evaporated moisture in comparison with the control composition.

From the analysis of the values of cement’s hydration rate, it follows that a water-cement ratio of 0.24 cannot provide 100% hydration of cement. The use of SP reduces the hydration rate, despite the
fact that SP facilitates the dispersal of cement and increases the surface area of its grains. In this regard, it bears repeating that nothing should interfere with the hydration of cement.

Table 4 presents the values of a long-time compression resistance among 15 series of cement stone samples aged from 28 days to 9.5 years and 18 years, as well as the coefficient of time dependant strength gain $\beta_t$, equal to the ratio of the actual strength of cement stone in age $R_t$ to strength $R_{28}$. The check dates for the strength assessment were taken at random.

### Table 4. Long-time strength of cement stone.

| № of series | Compression resistance, MPa / coefficient $\beta_t$ |
|-------------|---------------------------------------------|
| 1           | 76.7 / 1.0                                  |
| 2           | 68.2 / 1.0                                  |
| 3           | 94.1 / 1.0                                  |
| 4           | 100.4 / 1.0                                 |
| 5           | 93.2 / 1.0                                  |
| 6           | 93.9 / 1.0                                  |
| 7           | 101.4 / 1.0                                 |
| 8           | 89.9 / 1.0                                  |
| 9           | 100.9 / 1.0                                 |
| 10          | 106.5 / 1.0                                 |
| 11          | 96.2 / 1.0                                  |
| 12          | 106.0 / 1.0                                 |
| 13          | 103.4 / 1.0                                 |
| 14          | 127.6 / 1.0                                 |
| 15          | 123.6 / 1.0                                 |

Note: before slash – compression resistance, after slash – strength gain coefficient $\beta_t = R_t / R_{28}$.

Analysis of values presented in table 4, with account to the introduction of SP in cement paste, porosity of cement stone and the rate of cement hydration, discussed above, confirms the opinion of many researchers that the final mechanical properties of cement stone is determined by the initial stages of its hardening. It can be highlighted that the change in time-dependant strength gain for all 15 series of test samples is wave-like, however the duration and amplitude of the wave for modified and unmodified hydration structures of cement stone hardening are different.

The results of a research into the strength gain of superplasticized cement stone fabricated with a dosage of SP S-3 in the range from 1.0 to 0.25% of the cement mass at a constant value of W/C as 0.24 and 0.27, indicate that the strength of superplasticized cement stone can be higher or lower than that of the control composition. The difference in strength in superplasticized cement stone can be mainly attributed to changes in the conditions of relatively rapid chemical reactions between cement and water during the time of mechanical grinding of the mixture, which determines the values of adsorption, viscosity and zeta potential in the cement dispersed system when changing the SP quantitative dosage and time of introduction. Also noteworthy are samples of compositions 10 and 15, which yielded values of the strength gain coefficient less than one at the age of both 4.5 and 9.5 years.

In conclusion, it should be said that the above experiments seeking to reveal long-time behavior of superplasticized cement stone allow us to state the presence of a clear trend in the influence of SP and the procedure of its introduction on long-time strength gain parameters. However, this is only a trend, since there is a lot of other factors of influence than those discussed in this paper, which speaks of the
complexity and necessity for a more detailed study of this problem, paying due attention to the development and application of novel SP and composite binders in construction engineering practice.

4. Concluding observations
1. The technological properties and long-time strength of cement stone with a modified structure were studied.
2. The influence of the superplasticizer content and the procedure for preparing cement paste on the parameters of yield strength and the diameter of flow of the cement paste was revealed.
3. Kinetic dependences of changes in the density, porosity, and strength of cement stone were derived for hardening periods of 9.5 and 18 years.
4. The research into the long-time behavior of superplasticized cement stone revealed a clear trend in the influence of superplasticizer and its introduction procedure on long-time strength parameters.

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