Influence of superplasticizer additive on the strength of cement stone during wetting–drying cycles

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Abstract. This article discusses the issues of durability of reinforced concrete structures exposed to drying–wetting cycles. Transport structures are under the constant wetting and drying cycles, but rarely completely dry out, as the saturation process occurs faster drying. Such cycles cause moisture migration inside the concrete, which leads to leaching of calcium hydroxide Ca (OH)$_2$. The structure of the cement stone changes over time, and the dissolution of cement hydration products additionally leads to a strength decrease. Were tested the influence of the alternation of cycles of water saturation and drying of concrete on tensile strength, as the most sensitive characteristic to changes in the structure of the material. Since at present most concretes are manufactured using plasticizing additives, the tests were carried out with different content. The studies show that regardless of the amount of plasticizing additive in the samples, the flexural strength decreases. The compressive strength gradually increased, which is probably due to the ongoing process of hydration of the cement grains.

1. Introduction
Increase of operational reliability and durability of reinforcement concrete for transport buildings and structures is one of the most important tasks of materials science. The durability of concrete is determined not only by the qualitatively selected composition of the concrete mixture, its compaction and hardening conditions, but also by the influence of the environment. The influence of the environment has recently received more attention, for example, such processes as water penetration, concrete carbonation, chloride ion transport, sulfate exposure and others. The microstructure of concrete mainly determines the degree of their negative impact. At the moment, there are many studies studying the effect of mass transfer processes on the durability of cement materials. However, there are many factors affecting the processes occurring in the structure of concrete and it is very difficult to establish the significance of each of them.

Concrete structures typically experience constant wetting and drying cycles and rarely completely dry out. Drying leads to shrinkage and cracking, while when moistened, the microstructure fills with water and swells [1]. Hydration of exposed non-hydrated cement grains also occurs. The speed and type of mass transfer processes strongly depends on the content and rate of moisture migration. Wet/drying cycles cause the sorption-desorption hysteresis, when changes are characterized by complex behavior and depend on previous influences on concrete [1,2]. The drying process is slower than moisture saturation.

Highly active finely ground portland cements are used to prepare concrete for reinforced transport structures and to ensure their increased operational characteristics. This determines the fine capillary structure of the hardened cement stone. Alternating moistening and drying causes moisture migration
inside the concrete that leads to the leaching of Ca(OH)$_2$ from the interior of the concrete and its movement to the external surface near which calcium hydroxide crystallizes. Leaching hydration products entails the gradual loss of strength. This process has an especially negative effect on the flexural strength of concrete. The structure of the cement stone also changes over time. Changes in the structure of the cement stone over time and the additional effect of moisture migration facilitate to the dissolution of cement hydration products.

2. Shrinkage mechanism

Foreign studies [3,4,5,6,7,8,9] were carried out on the combined effect of moisture and drying cycles and different levels of constant load, as well as the effect of sulfates and the marine environment. There is a significant decrease in the strength of samples subjected to cycles of wetting and drying and it is also noted that the addition of mineral additives reduces the negative impact [1,3,6]. The drying regime is very important, since drying in the chamber to constant weight at a temperature of more than 105°C leads to the formation of cracks, which accelerate the process of moisture migration and hence the subsequent negative effects [2]. Studies [4] show that ettringite erosion becomes unstable and the erosion mechanism changes at temperatures above 70 °C [3].

As a result of domestic research [10], it was found that alternating water saturation and drying causes the appearance of internal stresses in the cement stone of concrete, which have a significant negative effect on tensile strength. Tests of samples made of cement stone subjected to moisture removal from only two sides at a constant temperature show that non-manifested capillary shrinkage causes normal shrinkage stresses in the sections of the sample along its thickness. Moisture is removed from pores and large capillaries during drying and volume contraction does not occur. Further drying, moisture begins to evaporate from smaller capillaries (less than 10$^{-7}$m). Shrinkage of concrete occurs due to the appearance of capillary pressure in the capillaries in the cement stone, where the water wetting the capillaries forms menisci. Capillary shrinkage increases with an increase in the porosity of the cement stone and a decrease in the radius of the capillaries. Initial shrinkage of wet cement stone is caused mainly by the action of capillary forces at high relative humidity of the air (60-98%). Shrinkage stresses cause irreversible changes in the structure, which leads to the appearance and development of microcracks. Bound moisture is removed from the tobermorite gel at a lower relative humidity (less than 68%).

The total free shrinkage is mainly determined by the chemical composition and the degree of hydration of the cement. The larger the volume of calcium hydroxide gel per unit volume of the cement stone, the higher the final free shrinkage. It is recommended to take measures aimed at reducing the free shrinkage of concrete and reducing the gradient of moisture content to reduce shrinkage stresses. Free capillary shrinkage caused by the evaporation of water from the cement stone gel decreases with a decrease in the amount of cement. Capillary shrinkage can be reduced by introducing surfactants that lower the surface tension of the liquid.

A large number of oscillation cycles of external environmental conditions lead to a change in the ratio of crystalline intergrowth/tobermarite gel in various parts of reinforced concrete transport structures. Crystalline intergrowth provides elastic operation of the cement stone under load and tobermarite gel provides plastic properties. Reinforced concrete spans are prestressed structures and are under constant stress from prestressing. A decrease in the volume of a crystalline aggregate in a cement stone of such structures leads to an increase in elastic deformations of concrete, which are already manifested as plastic deformations.

Currently, most of the manufactured concretes, especially high-grade concretes, are manufactured using plasticizing additives. In this regard, the effect of a plasticizing additive on the properties of concrete under prolonged cyclic exposure to moisture was studied. Specimen fabrication and strength tests were carried out in accordance with the current Russian requirements, and the cyclic wetting test mode was developed specifically for this study.
3. Description of experiments

Samples were made from a cement-sand mortar C: S = 1: 3, W / C = 0.4. River sand, fineness modulus 1.95, complies with GOST 8736-2014. Cement grade PC -500-D0-N. Cement indicators are given in Tables 1.2.

### Table 1. Characteristics of cement

| Characteristics                                      | Measure | Value |
|------------------------------------------------------|---------|-------|
| Fineness of cement according to the sieve residue (№008) % | %       | 0,6   |
| Fineness of cement of specific surface m²/kg          |         | 353   |
| Normal consistency %                                 |         | 26,5  |
| Initial set h-min                                    |         | 2-00  |
| Final set h-min                                      |         | 3-00  |
| W/C                                                  | -       | 0,40(112) |
| Flexural strength (for 28 days)                      |         | 6,41  |
| Compressive strength (for 28 days)                   |         | 55,54 |

### Table 2. Chemical composition of cement and clinker

| Chemical composition of cement                       | Chemical composition of clinker |
|------------------------------------------------------|---------------------------------|
| Insoluble residue, %                                  | Mass content of magnesium oxide, % 3,02 |
| Loss on ignition, %                                   | Mass content of free calcium oxide, % 0,96 |
| Mass content of sulfur dioxide (SO₃), %              | Saturation coefficient, %         | 0,93 |
| Mass content of chlorination, %                      | (CaO), % 65,00                  | (3CaO*SiO₂), % 62,81 |
| Mass content of alkaline oxides (Na₂O+0.658K₂O), %  | (Al₂O₃), % 4,63                 | (2CaO*SiO₂), % 13,34 |
|                                                     | (Fe₂O₃), % 4,11                 | (3CaO* Al₂O₃), % 5,30 |
|                                                     | (SiO₂), % 21,18                 | (4CaO* Al₂O₃* Fe₂O₃), % 12,49 |

Three series of samples, 4x4x16 cm in size, were made, three different compositions in the amount of 54 pieces (18 pieces in each batch). The samples were hardened before testing for 28 days in a normal hardening chamber. The composition of the samples is shown in Table 3.

### Table 3. Composition of samples

| Indicators                                      | 1 series | 2 series | 3 series |
|-------------------------------------------------|----------|----------|----------|
| Cement : Sand                                   | 1:3      | 1:3      | 1:3      |
| W/C                                            | 0,4      | 0,4      | 0,4      |
| Plasticizing additive (SP-1), % of the cement   | 0,3      | 0,5      | 0,6      |
| Samples amount, n                               | 18       | 18       | 18       |

The samples were subjected to heat and humidity treatment for 11 hours at a temperature of 70°C: 2 hours preliminary exposure, 3 hours rise in temperature to 70 ° C, 4 hours of isotherm, 2 hours of cooling.

Concrete structures are exposed to less extreme changes in humidity or temperature, shorter drying-wetting cycles, and less complete drying than in most experimental studies. Therefore, the test mode for the samples was taken as the closest to the real operating conditions. Humidification means immersing
the samples in water for 4 hours, drying means that the samples are kept in room conditions at a temperature of ± 18 °C and an air humidity of 60% for 4 hours. The maximum number of cycles performed was 90. Weight of each sample was measured before the start and end of each cycle, a pre-wiping pattern damp cloth. Flexural and compressive strength tests were performed after passing 30, 60, 90.

Out of 18 samples of each series, 3 samples were constantly in water and after 30 cycles passed the strength test. 2 samples were tested for strength after passing 30, 60, 90 cycles. The rest of the samples were subjected to 90 cycles of moistening and drying, during which their mass was regularly measured.

4. Experimental results
The obtained test results for the compressive and flexural strength of the samples are presented in Table 4. The table shows the average strength values of the tested samples.

| Characteristics                  | 1 series Plasticizing additive 0,3% | 2 series Plasticizing additive 0,5% | 3 series Plasticizing additive 0,6% |
|----------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Flexural strength, kg/cm²        | 128                                 | 135                                | 121                                |
| Compressive strength, kg/cm²     | 588                                 | 564                                | 592                                |
| Constantly in water for 2 months |                                    |                                    |                                    |
| Flexural strength, kg/cm²        | 135                                 | 146,5                              | 124,5                              |
| Compressive strength, kg/cm²     | 636                                 | 588                                | 658                                |
| After 30 cycles                  |                                    |                                    |                                    |
| Flexural strength, kg/cm²        | 120,5                               | 128                                | 117                                |
| Compressive strength, kg/cm²     | 635                                 | 617,5                              | 670                                |
| After 60 cycles                  |                                    |                                    |                                    |
| Flexural strength, kg/cm²        | 120,5                               | 128                                | 117                                |
| Compressive strength, kg/cm²     | 655                                 | 636                                | 650                                |
| After 90 cycles                  |                                    |                                    |                                    |

The test results show that, regardless of the amount of additive, the flexural strength of the samples subjected to wet / dry cycles gradually decreases. Moreover, the main deterioration occurs up to 60 cycles, and the difference between the results of flexural strength after 60 cycles and after 90 cycles is insignificant. The relative decrease in the flexural strength of the specimens after 90 cycles and specimens in water was 6%, 5%, and 3%, respectively, the amount of the added additive (0.3, 0.5 and 0.6%).

The compressive strength gradually increased, which is most likely associated with the ongoing process of hydration of the cement grains. The effects of cracks are likely to be mitigated by blockage due to condensation of moisture at narrow constrictions, swelling of C-S-H, and further hydration of exposed unreacted cement causing self-healing [1].
The mass of the samples was measured after each cycle. The figure 2 shows an enlarged graph of changes in the mass of samples with an additive content of 0.5% of the mass of cement. Weight measurements were performed after each cycle at the end of drying.

Each cycle consists of 4 hours of dampening and 4 hours of drying, and we tried to stick to this schedule. But since the tests are carried out entirely by hand, and some days fell on weekends and holidays, periodically it was necessary to increase the dampening stage to 64 hours in water and drying to 112 hours. The most noticeable curvature in the graph is related to the long holiday period during the 24th test cycle, when the drying time was 351 hours. Of the 90 performed cycles, only 10 were outside the specified time.
5. Conclusion

Studies have shown that wetting and drying cycles negatively affect concrete flexural strength. However, this effect is not strongly dependent on the amount of added plasticizing additive. In this direction, more research is needed, especially when exposed to constant bending load and nonextreme humidity and temperatures.

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