Self-restoration hardening systems of high-strength concrete of a new generation

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Abstract. Preservation over time of the characteristics of high-strength artificial rock materials is currently the most important task. The operating practice critical structures, such as, for example, tall frame buildings, shows, unfortunately, the insufficient durability of the in-situ reinforced concrete from which these structures are constructed. Internal corrosion processes are complemented by external aggressive effects (temperature and humidity changes, changes in the gas composition of the ambient air, etc.). This article deals with issues of self-restoration (“autogenous healing”) of the concrete structure. Their solution is provided by a method of overgrowing the interaction products of elements of an aggressive solution (external factor) and components of hardening concrete (internal factor).

1. Introduction
In high-strength hardening systems, the acceleration of the self-organization process of the structure and its hardening leads to an earlier search by this system for a new path to another state and the rapid achievement of this new state (attractor). This transition occurs through the unstable state of the system, the imbalance of energy indicators (dissipation of the entire energy of the system), which also occurs more rapidly than in conventional hardening concrete systems. In other words, it is a manifestation of the universal law of nature: the scales should be balanced. To avoid reducing the construction and technical properties of high-strength concrete, it is necessary to make additional efforts to “pump” energy into the system to preserve the previously acquired state.

Due to the fact that the durability of concrete structures depends not only on nature, nature of multicomponent systems, but also, on the similarity of the properties of their constituent substances, techniques are needed to ensure the self-restoration of concrete in time. The proposed techniques are often very diverse and contradictory [1,2]. They do not always take into account the genesis of the applied raw materials, which is directly related to the manifestations of a certain chemical affinity in the interaction of the system with external substances and techniques.

2. Materials and methods
To study the kinetics of the overgrowing process of cracks, pores, and voids resulting from the destruction, we used the developed compositions of high-strength powdered concrete with technogenic materials. When developmental prototypes 40×40×160 mm was used powdered mineral modifier (PMM), which in addition to mineral substances contained: high alumina cement, microsilicasuspension (TC 14-139-121-89, $S_p \approx 350 \text{ m}^2/\text{kg}$), floured calcium carbonate, etc. as well as polymer superplasticizer Mlflux 2651 and floured quartzitic sandstone was extracted rock of the Kursk Magnetic Anomaly.
(KMA). Before mixing, the waste was ground to a specific surface $S_{w} = 500 \text{ m}^{2}/\text{kg}$.

The sulfide-containing slate of a fraction of 0.315-0.63 mm was used as fine aggregate, with the content of iron sulfide (pyrite, FeS$_{2}$) – 4%.

High strength composition was obtained on the basis of ordinary Portland cement PC 42.5H with superplasticizer. The content of PMM was 35-40%. The share of the Melflux 2651 superplasticizer was 0.9% of cement consumption.

Monitoring the state of the samples was carried out by determining the strength factor and linear dimensions. The maximum allowable value of expansion was considered 0.1-0.3% [3,4].

3. The study of the self-healing process of the concrete structure by crystalline compounds, the formation of which proceeds with an increase in the solid volume

By self-restoration (self-healing) the concrete structure means impeding destructive processes in a concrete stone by means of counter-processes spontaneously activated in concrete at the beginning of the product's destruction under the influence of external operating factors and preventing significant reduction of physical and mechanical characteristics.

Since the destructive power of the external corrosive environment is associated with the onset of crack formation, the essence of most self-restoration techniques is the immediate elimination of microcracks that appear. This is achieved in various ways, mainly involving the introduction into the concrete composition during the product remolding of special additives of organic or inorganic origin. When the reactive materials enter the cracks, these additives interact with them to form a dense substance in the crack that fills (“heals”) the crack. Another methods group involves the additional hardening and compaction of the material (the so-called “prestressing” of concrete) during hardening in order to create a high-density and high-strength structure that does not allow cracks opening. Achieving a high density of concrete stone is provided by the densest packing of filler and aggregate grains with the smallest volume of cementing matrix, which reduces the permeability of concrete to aggressive environmental components.

The studying results of the self-healing process of concrete by “overgrowing” the formed microcracks with hydrated new growths, which form in an aggressive sulphate solution with an increase in the volume of the solid phase, suggested that the rapid formation and accumulation of ettringite-like phases in cracks and pores in the calculated amount will lead to compaction of the structure, giving it solidity and the exclusion of further crack formation.

This paper proposes a combined method of self-healing of the concrete structure. Its essence lies, firstly, in the creation of a high-density and high-strength structure of the material and, secondly, in the introduction of the reactive mineral, which is part of the fine aggregate. That is, the self-healing process of the structure was investigated on samples of the developed high-strength multicomponent concrete, which included the mineral pyrite - iron sulfide. Such a combination ensured the appearance of ettringite-like iron-containing calcium hydrates in the thickness of the concrete stone during crack formation, which occurs with an increase in the volume of solid and condensed phases.

Developmental prototypes were made of concrete mix plastic remodeling method. After 1-2 days of curing in forms, they were subjected to heat and humidity treatment according to the regime of 2-6-3 h, and after 3 days of exposure were placed under a static load of 50 kg/cm$^{2}$.

Concrete was obtained with enhanced physicomanical characteristics of fine-grained concrete with the addition of a powder mineral modifier developed. The increase of compression and flexural strength was 31.3 and 21.6%, respectively. The indicators growth of construction and technical properties is due to the high density of the material, due to the introduction of the modifying additive into the composition, as well as the quality of the quartzitic sandstone aggregate and the degree of its adhesion to the hardening stone [5-7]. Characteristics of the developmental prototypes are presented in Table 1.

Table 1. Strength characteristics of developmental prototypes of high-strength concrete at the age of 7
3 days

| No. | Content in the composition, kg/m³ | Cement (Sp = 300 m²/kg) | PMM (Sp = 500 m²/kg) | Fine aggregate (0.14-0.315) | W/C | Compression strength, MPa | Flexural strength, MPa |
|-----|----------------------------------|-------------------------|----------------------|-----------------------------|-----|---------------------------|------------------------|
| 1a  |                                  | 1100                    | –                    | quartzitic sandstone        | 0.30| 88.73                     | 10.3                   |
| 16  |                                  | 1000                    | –                    | sulfuride slate             | 0.28| 93.25                     | 11.0                   |
| 1c  |                                  | 950                     | 124                  |                             | 0.25| 98.34                     | 11.9                   |
| 2a  |                                  | –                       | 1100                 |                             | 0.29| 84.67                     | 9.9                    |
| 26  |                                  | –                       | 1000                 |                             | 0.27| 90.35                     | 10.8                   |
| 2c  |                                  | –                       | 950                  |                             | 0.24| 97.60                     | 11.7                   |

In the testing process in a special solution were visually determined the magnitude of crack opening and the degree of overgrowth of their hydrated new growths.

The process mechanism is to convert the original colloidal form of ettringite to crystalline, which causes an increase in stress. When the stresses reach their optimal values, the crystals of ettringite stop growing radially in the cavities and voids formed due to the calculated number of crystallizing phases that do not lead to the concrete destruction. If the total porosity of the cement stone is taken equal to 0.15 cm³ / g, then the amount of calcium aluminate trisulfate hydrate (CATH), which theoretically should crystallize in the pores and cracks of the structure at its maximum water saturation, causing a stress of 5.0 MPa, is 0.08% masses of cement stone, respectively, the amount of gypsum - 0.3%. The recovery process is influenced by the arising dense protective films consisting of reaction products.

Studies were carried out on the basis of the hypothesis that aggregate sulfides can participate in hydrate formation processes and fill microcracks during the concrete destruction, and thereby affect its durability.

Knowledge of the parameters of hydrate formation reactions during the hardening of Portland cement, as well as the interaction reactions of iron sulfides with hardening cement, allows us to establish the possibility and preference of their course, and then predict the concrete properties.

The algorithm for writing a dynamic system according to the reaction scheme is uniquely defined. The direction of a particular reaction can be predicted by calculation using the free energy (Gibbs energy) [153].

The Gibbs free energy (Gibbs thermodynamic potential, free enthalpy) is one of the state functions of the system (G) determined from the expression:

\[ G = H - TS, \text{[J or J / mol]} \]

where \( H \) – enthalpy (heat content), J / mol; \( T \) – absolute temperature, K; \( S \) – entropy, J / mol.

The thermodynamic stability of hydro ferrites and hydrated calcium sulfoferrite under an elevated temperature was analyzed using the calculated Gibbs free energy values of the reactions listed in Table 2. The results obtained show that up to 348.15 K, thermodynamically more stable products of the reaction are calcium trisulfohydroferrite with gypsum (reaction 4, Table 3).
Table 2. Gibbs free energy change (ΔG) in hydrate formation reactions in hardening systems involving iron sulfides (CaO–FeS₂–O₂–H₂O)

| No. | Reaction equation | –G°<sub>298</sub> reactions kJ / mole |
|-----|------------------|----------------------------------------|
| 1.  | 4CaO+FeS₂+3.75O₂+10.5H₂O=0.5Ca₃FH₁₃+2CSH₂   | 1816.33                               |
| 2.  | 4CaO+FeS₂+3.75O₂+7.5H₂O=0.5Ca₃FH₁₃+0.5Ca(OH)₂+2CSH₂ | 1809.50                               |
| 3.  | 4CaO+FeS₂+3.75O₂+7.0H₂O=2Ca(OH)₂+2CSH₂ | 1802.73                               |
| 4.  | 4CaO+FeS₂+3.75O₂+17.5H₂O=0.5Ca(OH)₂+0.5Ca₃FH₁₃+0.5Ca₃FH₁₃+0.5CSH₂ | 1837.52                               |
| 5.  | 4CaO+FeS₂+3.75O₂+9.5H₂O=0.5Ca(OH)₂+0.5Ca₃FH₁₃+1.5CSH₂ | 1818.82                               |

Table 3. Dependence of Gibbs free energy on the temperature in the system (CaO–FeS₂–O₂–H₂O)

| The reaction number according to table 2 | –G°<sub>298</sub> reactions, kJ / mol, at a temperature, K |
|-----------------------------------------|-----------------------------------------------------------|
| 273.15                                  | 1831.35  1816.33  1801.13  1785.75  1770.21  1754.52 |
| 298.15                                  | 1822.22  1809.50  1796.73  1783.92  1771.07  1758.19 |
| 323.15                                  | 1833.22  1821.72  1810.23  1798.76  1787.30  1775.85 |
| 348.15                                  | 1858.02  1837.52  1816.59  1795.22  1773.46  1751.33 |
| 373.15                                  | 1833.13  1818.82  1804.37  1789.79  1775.10  1760.29 |

In this study, the principle of self-restoration was used with the use of both internal and external activator (substance) of the self-healing process of concrete: internal – aggregate iron sulfide, external – ammonium persulfate solution. In this way, a “smart” system was created, reproducing the process of natural self-restoring biological systems, as well as most materials in nature are self-regenerating according to a synergistic bifurcation mechanism (Figure 1).

Figure 1. The mechanism of the self-healing concrete structure when exposed to internal and external factors: (a) the beginning of the microcracking process; (b) the entry of cement hydration products and the oxidative process of sulfide into the microcrack (Ca²⁺, Al₂O₃, Fe₂O₃, SO₄²⁻), and water; (c) overgrowth of microcracks with crystalline new growth – Ca₆F₇(C₆)↓₃₂₂ and CsH₂; 1 – aggregate grains with iron sulfide inclusions, 2 – oxidizing agent in hardening concrete, 3 – the inclusion of iron sulfide in the filler, 4 – microcracks, 5 – increase in the size of cracks and their number, 6 – components of the secondary process of microcrack overgrowing, 7 – crystalline products of secondary hydrate formation in concrete microcracks.

The degree of self-healing was established according to the testing results of the resistance coefficient of preloaded samples and samples that were hardened under normal conditions, as well as by the speed of passage of the ultrasonic pulse. Confirmation was obtained when testing developmental prototypes of the developed high-strength
composition with the addition of floured iron sulfide (pyrite – FeS$_2$) under static load, placed in 4% ammonium persulfate solution. The load was created using a counterweight, laid on hardening samples and the specific pressure created 50 kg/cm$^2$.

The obtained data show that up to 28 days of age there is a steady increase in the mechanical properties of high-strength concrete samples under load, which indicates a decrease in the degree of concrete permeability for an aggressive reagent as a result of an intensive self-healing process of cracks: the compressive strength has changed almost to 97.83 MPa.

Thus, both thermodynamic calculations and experimental studies indicate the preference for the formation of iron-containing three-sulfate calcium hydrate associations at normal temperature in cracks and pores of the concrete and the conversion of Ft-phases to calcium monosulfoferrite at elevated temperatures.

The results obtained suggest that the interaction process of iron sulfides with hardening cement can be controlled by changing the oxidative system potential.

4. Conclusion
As a result of this work, new data were obtained on the study and development of compositions and technology for the use of high-strength compositions. The main task, which was solved in this direction finding ways to reduce the cost of raw materials and technological work.

The study of the kinetics of the formation of ettringite-like phases in the pores and voids of high-strength fine-grained concrete as a result of the interaction of internal and external sulfides and sulfates on model systems showed that the main hydrate minerals of cement clinker interact with an aggressive solution containing persulfate ions and oxidation products of sulfides placeholder. The products of this interaction are calcium trisulfohydroaluminate and gypsum, i.e. a destructive process proceeds, analogous to concrete corrosion of the third type. Binder, consisting of calcium silicates and tricalcium aluminate, with an increase in the amount of the latter, is characterized by a decrease in durability and corrosion resistance.

The nature of the overgrowing (self-healing) of cracks in concrete under load, as well as its kinetic parameters of the process, is established. The obtained data made it possible to determine the main methodological techniques for managing the self-healing process in aggressive solutions with sulfide-containing fine aggregate.

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