Cement Composition Materials Based on Electrochemically and Electromagnetic-activated Filling Water

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Abstract. A technology is proposed for producing electrochemically and electromagnetically activated water and, from the standpoint of resource saving, high-quality cement composite materials. The results of the physicochemical analysis and morphology of the sediment of naturally non-mineralized water activated by different regimes are presented. A quantitative and qualitative X-ray phase analysis, as well as the results of the study of the microstructure of cement stone samples based on mixing water activated in different modes, are given. The strength indicators of cement stone, mortar and concrete samples were established, and the results of a study of the water resistance of cement composites made with the use of activated mixing water were presented. It has been established that electrochemical and electromagnetic activation of mixing water contributes to a change in its physicochemical properties, influences the structure-forming factors of the cement stone and contributes to the improvement of the strength and performance indicators of cement composite materials.

1. Introduction
Currently, more and more attention is paid to improving the quality of concrete mixes and concrete based on them. This is especially true when using concrete products and structures at critical construction sites where high physical, mechanical and performance properties are required (strength and elastic-plastic properties, resistance in aggressive media, durability) [1-7]. At the same time, it is important to reduce the cost of materials produced and products based on them. The modern view of the science of structure formation of concrete from the standpoint of managing material properties and obtaining high-quality products and structures using energy- and resource-saving technologies determines the current direction of research in the field of building materials science.

The growth of the consumption market of monolithic concrete and reinforced concrete requires the solution of important problems in the field of improving the technology for preparing concrete mix. The existing production lines for the production of concrete mixes can be upgraded through the use of installations that allow to improve the technological process of preparing the mixture without significant changes to the used production lines. One of the directions in the area of improving concrete technology is the activation of raw materials, in particular, mixing water [8–13].
Activation of mixing water in the technology of preparing a concrete mixture affects both the processes of dissolution and coagulation, structure and hydrate formation, and the occurrence of condensation-crystallization structure of cement stone, which is formed due to direct chemical interaction of particles with the formation of a rigid bulk structure [14–16].

Treatment of mixing water by external influences, in particular, sequential electrochemical and electromagnetic activation, allows minimizing or eliminating chemical additives and automating the process of preparing a concrete mix [17].

When electrochemical and electromagnetic processing of natural water, along with the influence on the molecular structural characteristics of water, electrochemical processes occurring on the electrodes have a significant effect on the electrodes: the anode, which is under a positive potential, at which oxidation reactions occur ions with negative potentials and a cathode-electrode, which are under a negative potential, at which ion reduction reactions take place, having a positive potential [15]. The resulting compounds, which are in the ultradisperse phase (nanoscale from 1 to 100 nanometers), determine the activity of the water used to mix the mortars and concretes. The dispersed phase of iron oxides and hydroxides (anodic products) and calcium and magnesium hydroxides - due to the cathode reduction of water molecules, form a temporarily stable system of crystallization centers during the processes of transition of cement solutions into the phase of formation of gel structures and the formation of a solid phase with a smaller crystal structure.

The use of sequential electrochemical and electromagnetic activation of mixing water used for the preparation of concrete mixtures, allows to accelerate the setting time of cement paste and increase the strength of cement stone [12, 18]. Regulation of such activation parameters as electromagnetic field intensity, electric current density, water flow rate and processing time makes it possible to control the hardening and physicomechanical properties of binding materials. The optimal parameters of the electromagnetic and electrochemical activation mode and the achieved efficiency of the treatment of the mixing water depend on the properties of the used electrode materials, the physicochemical characteristics of the source water, and the holding time of the treated mixing water before introducing it into the concrete mix.

2. Results and discussion

In order to determine the factors influencing the structure formation of the mineral sediment based on the ionic components of natural water, an experimental study of the dispersed sludge phase, separated during water evaporation before and after its activation, was carried out. To exclude the time factor, the studied water was settled for two days, which led to the deposition of large dispersed particles in the initial water.

The study of the surface morphology of sediments was carried out using an atomic force microscope SPM9600 SHIMADZU with a wide scanning range of 125 µm × 125 µm × 7 µm and a radius of curvature of the probe not exceeding 20 nm in the mode of contact atomic force microscopy at a constant force of interaction of the probe with the surface in air.

For the preparation of electrochemically and electromagnetically activated water was used in the equipment of UPOVS 2-5,0 "Maksmir" [17].

Processing was carried out in three modes, the cipher of which is composed of alphanumeric designations. Mode (1-1) – activated water treated with an electric current with a density of $j_{\text{max}} = 5.65$ A/m² in the electrochemical activation chamber and an electromagnetic field of $H_{\text{max}} = 24$ kA/m in the working gap of the electromagnetic activation chamber; (3-3) – $j_{\text{max}} = 22.58$ A/m², $H_{\text{max}} = 75$ kA/m; (6-6) – $j_{\text{max}} = 43.55$ A/m², $H_{\text{max}} = 135$ kA/m. When treating water in the electrochemical activation chamber, an aluminum anode was used.

The study used tap artesian water of Saransk. The effect of activation treatment on the total and carbonate hardness, oxidability, spare and aggressive carbon dioxide content of the studied natural water is presented in Table 1.

Table 1. Results of physico-chemical analysis of samples of the investigated waters.
From the results of the analysis of the initial artesian water of Saransk, presented in table 1, it follows that it is characterized by average hardness. Low water oxidability, established in the range of 1.56–2.03 mg∙O₂/l indicates a low content of organic substances and inorganic reducing agents in water. The table shows changes in the hardness of the water. The common hardness index for treated water by the mode (3-3) has the lowest value – 7.43 mmol∙eq/l compared to other types. The lowest value of aggressive carbon dioxide was found in water treated by the mode (6-6) – 11.05 mg/l. With an increase in the current density and electromagnetic field under all modes of water activation, the content of aggressive carbon dioxide decreases.

The surface morphology of precipitates and their structure, formed during the evaporation of the water of an artesian well in the city of Saransk before and after activation is shown in Figure 1, 2.

**Figure 1.** Morphology of artesian water sediment Saransk city: a – not activated water; b – water activated by mode (1-1).
The morphology of sediment from various sources before and after activation is characterized by an average roughness and maximum crystal size (Table 2).

### Table 2. Roughness and maximum crystal sizes.

| Activation mode | Roughness $R_a$ (nm) | Maximum size of crystals (nm) |
|-----------------|----------------------|------------------------------|
| 0               | 11.152               | 153.79                       |
| (1-1)           | 4.636                | 70.54                        |
| (3-3)           | 7.96                 | 298.55                       |
| (6-6)           | 4.0                  | 218.34                       |

Analysis of the above data allows us to conclude about the undoubted influence of the parameters of electrochemical and electromagnetic water treatment on the structure formation of mineral sediment and large-scale dimensional levels of crystals. For artesian water, the city of Saransk, a decrease in roughness is observed during the transition from the activation mode (1-1) to the mode (6-6). A definite role in this process is exerted by the ionic composition of water and, in particular, by the level of the total hardness of water. In the course of changing electric and electromagnetic fields, the spatial equilibrium state of nanostructured precipitates is disturbed, which leads either to their consolidation and the formation of fine micrometric systems, or to the formation of nanodispersed systems with excess surface energy. The formation of nanodispersed systems with crystal sizes of 20–100 nm can serve as an additional source of nanometric centers of crystallization of the products of hydration of binders during their hardening.

In order to establish the structural changes occurring in the cement composites based on the activated mixing water, X-ray structural studies were performed, consisting in their analysis. The diffractograms were recorded on an ARL X’tra diffractometer (Switzerland), which is a full-size powder diffractometer q – q geometry with a goniometer radius of 260 mm and a source – a narrow-focus tube with a capacity of 2200 W (Cu anodes).
In the course of the experiment, Portland cement CEM I 42.5 N of the OJSC “Mordovcement” plant was used. Cement stone cubic samples were made of a size of 2 × 2 × 2 cm. The water-cement ratio for all the compositions was determined on the basis of the normal density of the cement paste. Samples hardened in normal conditions for 56 days. Cement stone made on untreated water was considered as a control sample. The obtained samples were ground in an agate mortar with an agate pestle with acetone until all the samples passed through a sieve with an aperture of 90 microns. The attrition samples were placed in round holders with a top loading inner diameter of 25.65 mm and a depth of 1.9 mm made of special steel.

During the qualitative analysis of diffractograms, it was found that the following minerals are present in the composition of all the studied samples of cement stone:

- $C_3S$ ($Ca_3SiO_5$) with $d = [3.044; ... 2.784; ...; 2.617; ...; ... 1.77; 1.629; ...]$;
- $C_2S$ ($Ca_3SiO_5$) with $d = [... 2.886; ... 2.784; 2.755; ... 2.617; ... 2.191 ...]$;
- $C_3A$ ($Ca_2.99Na_0.008Al_2O_3$) with $d = [2.702; ... 2.206; ...; 1.912; ... 1.3510 ...]$;
- $C_4AF$ ($Ca_2Fe_0.26Al_1.72O_5$) with $d = [7.321; ... 2.65; ... 2.058; ... 1.923 ...]$;
- $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite) with $d = [9.733; ...; 5.619; 3.872; ... 3.49; ...]$;
- $Ca(OH)_2$ (portlandite) with $d = [4.944; 3.04; 2.635; 1.927; 1.8; 1.69 ...]$.

Also in all samples there is SiO$_2$ (α-Quartz) with $d = [4.261; 3.348; 2.459; 2.283; ...; 2.13; ...; 1.819; 1.543; ...]$, whose concentration is in the range of 1-3% of the mass. depending on the sample. Further, this phase was not taken into account in the framework of quantitative X-ray phase analysis.

The results of a quantitative X-ray phase analysis of cement stone (Table 3) showed that for cements closed with activated water, on the first day of hardening there is a decrease in the number of phases of all clinker minerals compared to the control composition.

| Activation mode | The concentration of the phases (% of the mass.) | Amorphous phase (C-S-H) |
|-----------------|-----------------------------------------------|------------------------|
|                 | $C_3S$ $C_2S$ $C_3A$ $C_4AF$ Portlandite Ettringite |                        |
| 3 days of hardening | 22.2 11.50 2.50 10.90 8.00 3.70 | 41.20 |
| (1-1)           | 20.8 11.30 1.90 10.10 8.80 3.60 | 43.50 |
| (3-3)           | 18.8 11.40 2.10 9.80 9.00 3.70 | 45.20 |
| (6-6)           | 17.6 11.30 2.10 9.60 9.20 3.70 | 46.50 |
| 12 days of hardening | 10.5 9.40 0.60 8.90 15.30 3.20 | 52.10 |
| (1-1)           | 9.5 9.10 0.50 8.50 16.10 3.10 | 53.20 |
| (3-3)           | 8.8 9.20 0.50 8.30 16.50 3.20 | 53.50 |
| (6-6)           | 8.2 9.20 0.60 8.30 16.50 3.20 | 54.00 |
| 28 days of hardening | 8.5 8.50 0.00 7.10 14.20 3.20 | 58.50 |
| (1-1)           | 8.2 8.50 0.00 7.00 14.10 3.20 | 59.00 |
| (3-3)           | 7.8 8.40 0.00 6.90 14.00 3.10 | 59.80 |
| (6-6)           | 7.4 8.60 0.00 6.90 14.30 3.20 | 59.60 |
| 56 days of hardening | 7.8 7.10 0.00 6.20 13.50 3.10 | 62.30 |
| (1-1)           | 7.2 7.30 0.00 6.10 13.50 3.20 | 62.70 |
| (3-3)           | 6.6 7.20 0.00 6.00 13.60 3.10 | 63.50 |
| (6-6)           | 6.5 7.30 0.00 6.10 13.40 3.20 | 63.50 |
As a result, the amount of portlandite and calcium hydrosilicate increases. This process can be explained by the effect of electric current and magnetic field on the mixing water. When water is activated, the hardness salts dissolved in it become a different physical state – fine sludge, which forms additional crystallization centers, intensifying the processes of dissolution and hydration of cement [15, 16].

A quantitative analysis of the diffraction patterns of cement stone samples after 28 and 56 days of hardening also indicates a decrease in the number of C₃S in samples based on water treated with a magnetic field and an electric current, which indicates a greater degree of hydration of these samples.

An intensive increase in calcium hydroxide and hydrosilicates in cement stone on activated mixing water slows down by 28 days of hardening, which once again confirms the greater influence of external conditions on the structure formation of cement materials at a later time, compared with mixing water in the initial stages of hardening.

In the samples made on the activated mixing water, an intensification of the transition of C₃A to the solution is observed, which indicates a decrease in the probability of formation of ettringite in the later stages of hardening.

The use of mixing water in cement composites, treated with electric current and magnetic field, allows to intensify the processes of dissolution and hydration of cement, to increase the content of calcium hydrosilicates and, consequently, to increase the strength of cement composites.

In order to identify changes in the microstructure in the early stages of hardening of the cement stone with the use of activated mixing water, a microscopic analysis of the samples of cement stone was carried out. The study of the microstructure of samples at the age of 7 days was carried out using a Quanta 200 scanning electron microscope (Figure 3).

The results of microscopic analysis show that the cement stone with the use of activated mixing water has a more dense structure. The rheology of cement paste with the use of activated mixing water changes in the direction of increasing mobility and, consequently, reducing the volume of micropores of the cement stone.

An important stage of the research is the determination of the influence of the activated mixing water on the persistence of the effects of increasing the strength with the introduction of small and large aggregates. For this, samples were made of cement paste, mortar and concrete mix.
produced by the Mordovian cement plant was used as a binder, quartz sand with a fineness modulus 2.0 was used for fine aggregate, 5–10 granite crushed stone was used for coarse aggregate. The mixing water was used activated and non-activated. Water was activated according to the following modes: (1–1), (3–3) and (6–6). The amount of fine aggregate in the composition of the solution was selected from a ratio of 1: 3, and the composition of concrete was adopted from a ratio of 1: 1.053: 1.789 (cement: quartz sand: granite rubble). In each case, equal-moving trains were prepared. The test results are shown in Tables 4–6.

Table 4. Compressive and flexural strength of cement stone at different times of hardening.

| Activation mode | 3 days of hardening | 7 days of hardening | 28 days of hardening |
|-----------------|---------------------|---------------------|---------------------|
|                 | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           |
| inactive.       | 48.50              | 10.57               | 61.10              | 11.95               | 79.50              | 15.50               |
| (1-1)           | 52.38              | 10.67               | 69.00              | 13.15               | 96.20              | 18.00               |
| (3-3)           | 50.90              | 11.55               | 67.21              | 13.63               | 91.40              | 18.00               |
| (6-6)           | 49.00              | 12.54               | 70.30              | 13.03               | 100.20             | 15.50               |

Table 5. Durability at compression and a bend of solutions in various terms of hardening.

| Activation mode | 3 days of hardening | 7 days of hardening | 28 days of hardening |
|-----------------|---------------------|---------------------|---------------------|
|                 | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           |
| inactive.       | 11.00              | 7.50                | 24.00              | 8.57                | 26.50              | 9.55                |
| (1-1)           | 11.00              | 7.64                | 25.68              | 9.00                | 27.60              | 10.51               |
| (3-3)           | 11.22              | 7.62                | 26.40              | 8.83                | 28.40              | 10.70               |
| (6-6)           | 13.75              | 8.10                | 30.72              | 9.17                | 29.20              | 10.22               |

Table 6. Compressive strength and bending of concrete in different periods of hardening.

| Activation mode | 3 days of hardening | 7 days of hardening | 28 days of hardening |
|-----------------|---------------------|---------------------|---------------------|
|                 | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           | R_C (MPa)          | R_F (MPa)           |
| inactive.       | 32.25              | 5.83                | 38.04              | 6.82                | 46.42              | 8.04                |
| (1-1)           | 35.54              | 6.35                | 41.88              | 7.16                | 55.40              | 8.37                |
| (3-3)           | 32.29              | 6.05                | 47.29              | 7.10                | 63.25              | 8.15                |
| (6-6)           | 32.83              | 6.24                | 43.33              | 7.25                | 53.17              | 8.61                |

From the results of the study, it follows that all materials — cement stone, mortar, and concrete — are characterized by an increase in strength in the case of the use of activated mixing water.

Knowledge of the stability of cement composites when exposed to water is important because the building structures and products of many buildings and structures during operation are in aquatic environments.

Equal-moving cement compositions were considered for the study. The following were used as mixing water: 1) natural non-treated untreated (O), 2) natural, treated with an electromagnetic field with $H_{\text{max}} = 150$ kA / m (M), 3) natural, treated in an electrochemical activation chamber with $j_{\text{max}} = 43.55$ A / $m^2$ (E6A), 4) natural, sequentially processed by an electromagnetic field with $H_{\text{max}} = 150$ kA / m and electric current with $j_{\text{max}} = 43.55$ A / $m^2$ (M + E6A), 5) natural, processed sequentially in an electrochemical activation chamber with $j_{\text{max}} = 43.55$ A / $m^2$ and in the chamber of electromagnetic activation with $H_{\text{max}} = 150$ kA / m (E6A + M). The kinetics of changes in mass
content and coefficient of resistance of composites made on the mixing water activated by various modes, depending on the duration of the aging in the medium, is shown in Figure 4, 5.

**Figure 4.** The dependence of the change in mass content of cement composites on the duration of aging in water and the type of activation: 1 – O; 2 – M; 3 – E6A; 4 – M + E6A; 5 – E6A + M.

**Figure 5.** Dependence of change in the coefficient of firmness of cement composites on the duration of aging in water and the type of activation: 1 – O; 2 – M; 3 – E6A; 4 – M + E6A; 5 – E6A + M.

The kinetics of changes in the mass content of the examined compositions when kept in water has a similar character. In the initial periods of aging in water, an increase in the indicator under consideration occurs. By the three-month period, the samples are completely saturated with water and no further significant changes in the mass content are observed. Of the examined compositions, the most intensive water absorption is characteristic of composites on ordinary water, which have the highest water-cement ratio.
Analyzing the data obtained on the change in the coefficient of water resistance, we can draw the following conclusions. When kept in water for up to 90 days, the strength of all the considered composites increases, which is associated with the ongoing process of cement hydration. After 90 days, the kinetics of change in strength acquires a different character. So, with materials on ordinary water and water treated with a magnetic field, as well as under the combined action of a magnetic field and electric current, strength continues to increase, while materials with water treated by an electric current and under the joint action of electric current and magnetic field do not is changing.

3. Conclusions
Thus, the combined effect of mixing electric and magnetic fields of varying intensity on water significantly affects the structure of the dispersed particles formed and their activity, which allows us to expect an active effect of the treated water on the processes providing the quality characteristics of the concrete products obtained. The use of this technology contributes to the improvement of their operational properties due to the formation of fine-grained, more dense structure of cement stone.

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