Relaxation processes during activation of cement mixing water

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Abstract. The analysis of relaxation processes in water activated thermally or ultraviolet irradiation is carried out. Activation of mixing water leads to earlier hardening of the cement. In this case, activated water loses its properties with a relaxation time that is equal to the activity time of melt water, which is explained by the general reasons for the origin of the increased reaction properties of activated water and melt water. These properties are due to the fact that upon activation, the content of free water molecules increases. In the usual state, part of the water molecules enters the voids of fractal-clathrate structures. During thermal or radiation activation processes characterized by certain relaxation times, these structures are destroyed and free water molecules are released. But after the cessation of activation, relaxation processes take place to restore thermodynamically equilibrium fractal-clathrate structures, and part of the free water is again captured by these structures. Therefore, the reactivity of water after the cessation of activation decreases.

1. Introduction
Various activating physical factors have been used [1-6] to strengthen concrete and improve the technology for its production.

The article discusses the properties of water activated by multi-frequency ultrasonic waves, and cement stone prepared on its basis [3]. The optimum time for the activation of mixing water was found to be 30 min. Ultrasonic treatment of mixing water allows to reduce the normal density of cement paste by 10-12% and increase strength at 7 days of age up to 45%, and at 28 days of age – up to 20%.

The authors considered the results of theoretical and experimental studies of the effect of mechanical treatment of mixing water and water-cement slurry in a mixer, which is a hydrodynamic installation, on the intensification of the structure formation process of cement stone and concrete. It was found that mechanical treatment of water causes an acceleration of setting and an increase in the strength of finished products [4].

A study of the physicomechanical characteristics of cement stone by the authors revealed a tendency to increase the strength characteristics of cement stone within 15-20%, depending on the type of cement, water-cement ratio and other factors in the same concentration range of the nanomodifier [5].

In [2], it was stated that ultraviolet (UV) radiation of cement mixing water increases the early strength achievable after the 7-day cement stone curing (Fig. 1, + signs) by 1.5.
The authors consider the effect of ultraviolet irradiation of mixing water on the strength of cement stone in the framework of the clathrate-fractal theory of the structure of liquid water. In accordance with this theory, liquid water molecules form a fractal structure, in the cavities of which a part of free water molecules is contained. In the processes of cement hydration, which determine the formation of a durable cement stone, free water molecules are involved that do not fall into the voids of the fractal structure. Under ultraviolet irradiation, the fractal structure partially collapses, free water molecules outside the fractal structure become larger, as a result of this, hydration is accelerated, and the strength of the cement stone increases. Theoretical relaxation time dependences make it possible to correctly describe the experimental data on the behavior of the relative strength of cement stone. In the calculations, the nonmonotonic time dependence of the strength of cement stone was reproduced by taking into account the influence of two competing factors: an increase in the free water content due to the destruction of the fractal-clathrate structure and a decrease in the free water content due to the reconstruction of the fractal-clathrate structure initiated by the photolysis products.

In [6], the non-uniform dependence of the cement stone strength on the radiation time [2] is explained by two relaxation processes determining the change in the concrete mix free water content. The fact is that according to the clathrate-fractal model of liquid water, some water molecules enter the fractal voids [7–9] and do not participate in hydration processes. The mechanism of the UV
radiation effect on concrete strength is that fractal structures are destroyed by UV radiation and water molecules are released from voids and participate in the cement stone formation. However, the UV radiation applied in [2] does not ensure direct water photolysis, as a result of which the hydrogen bonds fixing the fractal structure are destroyed. This RK-120 bulb radiation has a wavelength outside the H2O molecule absorption band [10]. Therefore, a gradual relaxation process of the thermally activated decomposition of the fractal liquid water structure occurs due to an increase in the local temperature when water molecules absorb UV quantum. The study is aimed to describe the parameters of this process [11-18].

2. Materials and Methods
The relative cement stone strength is described by the relation (1):

\[ \delta R = \frac{R(t)}{R(0)} \]  

Where, R(t) is the dependence of the cement stone strength on the mixing water activation time, and R(0) is the strength of cement stone prepared on inactive water.

The cement stone strength is proportional to the number of free water molecules that have not entered the fractal voids.

\[ R(t) = A_1 N_{f1}(t) \]  

Where, A_1 is the proportionality coefficient, N_{f1}(t) is the number of free water molecules that have not entered the fractal voids and therefore are easily accessible for hydration.

\[ N_{f1}(t) = N_{f2} + N_{f3}(t) - N_{f4}(t) \]  

Where, N_{f2} is the number of free water molecules that have not initially entered the fractal voids.

N_{f3}(t) is the number of free water molecules released from the fractal voids during the relaxation decomposition of these structures under the effect of radiation within a relaxation time \( \tau_1 \).

\[ N_{f3}(t) = A_2 [1 - \exp(-t/\tau_1)] \]  

N_{f4}(t) is the number of free water molecules that have entered the fractal voids of structures arisen within a relaxation time \( \tau_2 \) due to the emergence of fractal formation centers (the H+ ions) generated as a result of water molecules dissociation initiated by radiation [14].

\[ N_{f4}(t) = A_3 [1 - \exp(-t/\tau_2)] \]  

Where, A_2, A_3 are the proportionality coefficients.

3. Results
Figure 1 (solid line) shows the calculation results obtained using equations (2-5), which correlate with experimental data [2] at \( A_2/N_{f2} = 2.4, A_3/A_2 = 1, \tau_1 = \tau_{1y} = 6.1 \text{ min}, \text{ and } \tau_2 = \tau_{2y} = 11.1 \text{ min}. \) The relaxation time \( \tau_{1y} \) determining the fractal structure durability depends (6) on temperature \( T_{loc} \) increased as a result of the UV quantum absorption. Temperature increases in the local immediate surrounding area of the molecule, which has absorbed the quantum.

\[ \tau_{1y} = \tau_0 \exp(\varepsilon/(kT_{loc})) \]  

Where, \( \varepsilon \) is the hydrogen bond breaking energy of water molecules in the fractal structure, i.e., the activation energy of the fractal structure relaxation fracture.

Similar relaxation processes occur at thermal water activation, which leads to increased free water content and fluidity [15] (Fig. 2).
Dependence of the Relative Water Fluidity Change $\delta \varphi$ on the Thermal Activation Time at $T_{ac}=368$ K: Experimental [15] (+ signs) and Theoretical (solid curve).

The relative water fluidity change is described by relation (7).

$$\delta \varphi = (\varphi - \varphi_0)/\varphi_0$$  \hspace{1cm} (7)

Where, $\varphi(t)$ is the dependence of the water fluidity on the water activation time, and $\varphi_0$ is the initial water fluidity value.

The water fluidity is proportional to the number of free water molecules that have not entered the fractal voids $N_{f1}$.

$$\varphi = A_4 N_{f1}$$  \hspace{1cm} (8)

Where, $A_4$ is the proportionality coefficient.

The calculation results obtained using equations (3-5, 7, 8) correlate with the experimental data [15] at $A_2/N_{f2} = 1.28$, $A_3 = 0$, and $\tau_1=\tau_{1a}= 6$ min and are shown in Fig. 2 (solid line). The relaxation time $\tau_{1a}$, which in this case is determined by the thermal water activation temperature $T_{ac}=368$ K (9) turned out to be the same as that for the case of increasing concrete strength by activation.

$$\tau_{1a} = \tau_0 \exp(\varepsilon/(kT_{ac}))$$  \hspace{1cm} (9)

The equality of the relaxation times $\tau_{1a}$ and $\tau_{1y}$ confirms the identity of the thermal and UV water activation mechanisms and allows suggesting that $T_{ac}=T_{loc}$.

The state that arose at activation becomes metastable when cooling or upon the termination of UV radiation. The fractal structure returns to its original state in a relaxed manner. This will affect the free water content and, accordingly, the water fluidity [15] (Fig. 3).

The calculation results obtained using equations (3-5, 7, 8) correlate with the experimental data [12] at $A_2 = 0$, $A_3/N_{f2} = 1$, and $\tau_2 = \tau_{2k} = 450$ min and are shown in Fig. 3 (solid line). In this case, the
relaxation time $\tau_2 = \tau_{2k}$ is determined by the exposure temperature $T_{e}=293$ K (10) after thermal activation of water.

$$\tau_{2k} = \tau_0 \exp(\varepsilon/(kT_{k}))$$

(10)

Using equations (9) and (10), assuming that $\tau_0$ negligibly changes with temperature and considering the values $\tau_{1a} = 6$ min and $\tau_{2k} = 450$ min, we obtain $\varepsilon = 0.5$ eV. This corresponds to the energy of a single hydrogen bond and correlates with the fractal liquid water model [6].

At $\tau_{1a} = 6$ min, $\varepsilon = 0.5$ eV, and $T_{e} = 368$ K, equation (9) allows finding the value $\tau_0 = \tau_{0ex} = 15 \cdot 10^{-6}$ s. The $\tau_0$ value can also be estimated theoretically, while considering fractals as Brownian particles. To cause fractal with a size $R = 3 \cdot 10^{-6}$ m to be destroyed due to the hydrogen bond breaking [9], the smallest component with a size of $R_{min} = 10^{-9}$ m separated from the fractal and the rest of the fractal should be divided by a distance as long as $R_{min}$. Let us use the Einstein-Smoluchowski equation for $\langle x^2 \rangle$, i.e. the average value of squared distance passed by a Brownian particle of R size in a medium with viscosity $\eta$ over time $\Delta t$.

$$\langle x^2 \rangle = \frac{kT}{3\pi \eta R} \Delta t$$

(11)

Assuming $\langle x^2 \rangle = R_{min}^2$ and $\Delta t = \tau_0$, for an aqueous medium with $\eta \sim 10^{-3}$ Pa·s, we obtain $\tau_{0theor} = 6 \cdot 10^{-6}$ s that correlates with the experimental value $\tau_{0ex}$.

4. Conclusions
When water is activated, the clathrate-fractal liquid water structure is rearranged according to the relaxation mechanism, therefore, the effects of UV radiation and heat treatment on mixing water have
the same nature. In this case, the UV radiation effect can be described by introducing a local temperature. The activation time is determined by the energy of breaking hydrogen bonds between water molecules. Upon termination of activation, the state is metastable and fractal structures return to the initial state in a thermally activated manner at the same activation energy as excitation.

Hydration processes that lead to the formation of cement stone, amplified by ultraviolet radiation due to the release of free molecules water during the destruction of the fractal-clathrate structure of liquid water. Ultraviolet irradiation also leads to the dissociation of water molecules, with the formation of hydrogen ions, which are the nuclei of the formation of fractal-clathrate structures in water, which leads to a decrease in the content of free molecules in water due to entry into voids fractals. Thus, under ultraviolet radiation, two competing effects, which determine the nonmonotonic behavior of the early strength of cement stone from the time of ultraviolet irradiation of mixing water.

Theoretical relaxation time dependences allow one to correctly describe experimental data on the behavior of the relative strength of cement stone.

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