Regulation of confining liquid for cement systems properties by means of electromagnetic fields

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Abstract. The paper studies theoretical aspects of methods for electrochemical, electromagnetic, magnetic activation of water as a confining liquid for cement systems. The ideas about processes of water structural organization are shown to be the basis for one of possible mechanisms of activating impact. Experimental data for electric conductivity, electric capacity on the example of distilled water treatment by means of magnetic field which confirm the change of water structure have been presented.

1. Introduction
The creation of resource-energy-saving technologies for obtaining the materials of different technological dedication possessing high production properties is considered to be one of the most important tasks of modern materials science. The application of external actions of different nature in the course of which an active state of water-containing dispersed system can be reached is thought to be the most technologically available, economically and ecologically efficient method. However it is quite evident that without identification of thermodynamic and kinetic regularities taking place at this phenomenon it is impossible to control effectively the creation of the materials with target properties. Despite the numerous investigations made by both national and foreign scientists [1-3], most aspects remain unclarified, and the theory of activation processes has been worked out at the phenomenological level predominantly. This fact doesn’t serve as an obstacle for application of the methods of external actions in practical purposes effectively, but it limits the possibilities of directed control over final properties of compounds based on binding agents. Taking into consideration the variety of methods for confining liquid activation, some definite types of low energy external actions on the cement systems are studied in this paper. From the authors’ view they have practical value in the technologies of products manufacture.

2. Theoretical ideas about low energy water activation
This paper is aimed at systematization and development of the ideas about physic-chemical entity of definite low energy external actions, possessing electromagnetic nature, and at experimental substantiation of theoretical aspects of a magnetic field and thermal impact influence on the processes of structure formation in water as confining liquid for cement systems.
The transformation of liquids from their inert state into chemically active one and the control over discrete structures of the system by means of slight changes in their structure and properties are thought to be the low energy activation of liquids. It also includes the control over kinetics of the process with the help of impact on the systems of the source with energy which equals to the thermal energy or a little less \((kT)\). The physico-chemical system can be considered as an active one if the internal potential energy store doesn’t temporarily correspond to its thermodynamic equilibrium values being the result of some external impact. In case it occurs, this impact is called as an activating one. It is believed that maximum possible values of energy for activating impact equal to 10 J/mol. In this case low energetic impacts can be effective because they influence the process of diffusely-developed intermediate structures in the system, in contrast to high energy impacts in which the transformation from one discrete state into another occurs as a “shock”. In the basis of this statement the regularities of experimentally observed facts can be found. For example, the phenomenon of disproportional dependency of energy-consuming processes development in the system of energetic equivalent inserted from outside.

Nowadays the following widespread methods of different media activation can be distinguished: magnetic, electromagnetic, electrochemical, hypersonic, thermal, mechanical, hydrodynamic, acoustic, plasmatic, disruptive-impulsive and chemical ones. They can be relatively divided into three groups [4]: physical (reagentless); chemical (reagent); combined. We will consider some definite methods of low energy activation of cement systems.

2.1 Electrochemical activation

In the course of water or water-salt solutions activation made by means of electrodes injection polarized with direct current, the active metastable compounds appear. Being used practically they quickly disappear, acting as a catalyst, an initiator and reagents in different chemical reactions, which occur predominantly on the interface “electrode - solution”. The formation of a double electrical layer at the surface of electrode with high potential \((10^6 - 10^7 \text{ V/sm})\) results in the occurrence of new metastable compounds which are capable to exist independently during a long period of time in the target thermodynamic conditions.

The peculiarity of this electrochemical activation is the formation of active microbubbles with the size of from 0.2 to 5 mkm which promote the qualitative change of the solution system organization. Such a spatial and temporal ordering of the system in the course of which the change in any of its parts (discrete factor) influences the interrelationship of other parts is assumed to be a system organization. For this reason the construction of a system organization model for the object being studied can be achieved only when all the possible interactions of separate structural units are taken into consideration.

In the course of electrodes polarization by means of alternating current a new mechanism of activating impact determined by the oscillating processes in the system appears. The origin of the process begins in a micro volume of water in an electrode sheath; then other parts of water volume are involved in an oscillating process as far as “pumping” of oscillating energy takes place. Since the process is an energetic one (the energy of oscillating process is proportional to a squared amplitude of oscillations), water activation doesn’t occur according to a diffusing mechanism and, hence, it can be finished during a short period of time. At the same time, according to modern theories, the oscillations with low frequency are generated at the stage of a fine-crystalline structure formation. In this case the origin and destruction of dynamically developed kinetic compounds the quantitative accumulation of which leads to new qualitative changes in a cement system are assumed. If the frequency of external field coincides with that of characteristic oscillation of structural compounds in a cementing system, it can be a source of code information to the reproduction of “self-alike” compounds. The reasons for “self-alike” structures reproduction are not completely cleared, but its source is a rhythmicity of electromagnetic coding external impact. It means that imposition of external frequency field can change the conditions of structures “selection” and lead to a cement stone formation which possesses the properties that differ from those created in the absence of external impact.
2.2 Electromagnetic activation
Generators of swirling electromagnetic waves of different types and structures (cavitational converters, hydrocavitational generators, monovibrators, etc.) are used for electromagnetic activation of cement systems predominantly at the early stages of structure formation. The principle of action for such generators is based on the initiation of non-linear processes of phasic transformation in a liquid-phase medium by means of a high-gradient electric, magnetic or acoustic field. As a result the discontinuity of a liquid medium and, consequently, the formation of a new structural organization of water or water solution are observed.

2.3 The impact by means of magnetic field of constant magnets
The impact is fulfilled with the help of a confining liquid transmission through the magnetic field lines of constant magnets with their following injection into the volume of a cementing compound. The treatment of the liquid by means of magnetic field activates the following processes at the early stages of concreting: the size of cementing compound grain is decreased, the dissipation and hydration of a cement part is intensified, new structures which differ from those obtained in ordinary conditions are formed, and the excreting of smaller crystal phases is observed. It is determined that the hardness of compounds on the basis of cement is increased under compression, the porosity is decreased and the cold resisting property of hardening systems is increased while the duration of setting and flow ability of cement grout is changed. In this case the necessary conditions of forced response appearance are the following: laminar liquid flow regime, gradient structure of magnetic field lines, and optimal concentration of the solution and temperature of the liquid. Literary data don't have a distinct theoretical basis that can make their systematization quite difficult.

We can claim, however, that one of possible mechanisms of external impact consists of the destruction of system-structural organization of the liquid revealed in changing the ratio of polymer and monomer components of water structure. In this case the constant ratio of separate water molecule dipoles and their associates is maintained unless the system-structural organization of liquid “determined” by the external action is destructed by thermal energy. This implies that in spite of its small energetic component, the magnetic field is able to widen the spectrum of possible fluctuations of spatial distribution of liquid particles and to create the conditions which allow for some possible temporal configurations of water dipoles to be energetically more efficient and, hence, more resisting ones compared with the initial state. These statements are the results of comparison of interaction forces for structural components of water-salt solution and forces of magnetic field [3].

For example, if in a system there is a target flow of the substance with a constant direction and an average speed of $U$, the particles with opposite charge must move in opposite directions under the influence of Lorentz force $F_{\text{max}} = z\epsilon_0 B(\nabla \times U)$ that results in a short-term redistribution of ions leading to the formation of microregions of spatial charge along the direction of liquid flow (RSC). With appearance of RSC the force of electrical field starts acting for a short period of time: $F = z\epsilon E$, where $E$ is the electric field intensity, $z\epsilon$ a particle charge, the direction of which coincides with that of magnetic force. $E$ equals to $(10^7 - 10^8)$ V/m. In this case the force of electric filed becomes comparable with the forces of ion - dipole (1) and dipole – dipole interactions (2).

$$F_{i-d} = d_m z\epsilon / 4\pi\epsilon_0\epsilon_r r^3 \approx 1.1 \times 10^{-13} H$$ (1)

$$F_{i-d} = d_m d_m / 4\pi\epsilon_0\epsilon_1 r^4 \approx 4.10^{-15} H$$ (2)

where $\epsilon_1, \epsilon_r$ is the force of ion-dipole interaction, $d_m$ is a dipole moment of water molecule $(6.02 \times 10^{-30} \text{Cl} \times \text{m})$, $\epsilon_0, \epsilon_1$ permittivity of vacuum $(8.85 \times 10^{-12} \text{F/m})$; $\epsilon_1, \epsilon_r$ permittivity of medium; $r$ radius of ion with ion atmosphere interaction region (in the region of long-distance hydration $\approx 10^{-9} \text{m}$).
The calculation of particles speed values, which they obtain in the region of spatial charge due to the action of magnetic field, also shows its excess over the average speed of thermal molecule movement. This result indicates that the processes of system-structural destruction of liquid organization and the decrease of ion hydrated film which have been mentioned above can be possible. So, at the target stable direction of a flow we can observe the destabilization of the system from thermodynamic equilibrium on the back of thermal molecule movement, especially at high speeds of liquid flow and values of magnetic induction.

Analysis of liquid media activation methods studied in this paper allows confirming that the ideas about the destruction of water structural organization are the basis for the mechanism of the processes taking place in these media. The external impact results in dissymmetry that means some well-ordered deviation from symmetry of liquid initial state stabilized by thermodynamic conditions is detected. It is well-known that if in symmetrically situated points of the system there arises a difference of charges, currents, potentials, forces, flows, concentrations, and the conditions satisfy to their scalar or vector interaction, and the distance between interacting elements is quite short, the state of dissymmetry makes its work. Therefore, according to our views it is necessary to investigate structural peculiarities of water and water solutions used as a confining liquid in order to develop our ideas about mechanisms of activating external impact.

3. Methods and materials

Some results of the experimental study estimating structural processes in distilled water on the example of external impact of magnetic field compared with thermal treatment of liquid are shown below.

The experiments have been carried out at the device that allows measuring the conductivity and electric capacity of liquids at the frequency of current in the range of 1 to 300 kHz. The distilled water having the capacity of \((1.3 - 3.0) \text{ mC/cm}^2\) has been used. The magnetic treatment of water has been done by means of its transmission through a funnel with two magnetic systems situated on both sides of its spout. Each system includes 6 magnets disposed gapless with the induction equals to 0.2 Tl, looking at each other with opposite poles. In order to compare the effect, water has been exposed to thermal impact without air because it is one of the factors which significantly changes structural organization of water. The measuring cell for conductivity estimation is a cylindrical glass vessel having a diameter of 7 sm, in which the investigated liquids of 200 ml have been placed, and two flat electrodes made of non-magnetic stainless steel (the square of each magnet equals to 22 sm²) which are situated on the distance of 22 mm. The measuring cell for capacity estimation is a cylindrical glass vessel having a diameter of 2 sm and length of 200 mm on which two armature of condenser (with square of 22 sm²) are situated with shifting relatively each other in parallel planes.

4. Results and discussion

In order to estimate possible mechanisms of water structure changes activated by magnetic field, electrical parameters have been measured after water heating from 20 °C to 60 °C and its following cooling until the initial temperature of 20 °C without air, after cooling until 10 °C and after heating up to 30 °C.

The results of experimental study are shown in Figure 1.
Figure 1. Relative changes of electric conductivity (a) and electric capacity (b) values of distilled water at different frequencies of reactive current in relation to the control sample: 1 – after treatment in magnetic field; 2 – after heating from 20 °C to 60 °C and then cooling until the initial temperature of 20 °C; 3 – after cooling to 10 °C; 4 – after heating up to 30 °C.

The results obtained reveal the decrease of electrical conductivity of distilled water after magnetic treatment of the liquid and they well coincide with the data of papers [5, 6]. In this case after heating of the liquid with its following cooling which is the same as in the experiments with activation made by magnetic field, the conductivity of distilled water is also decreased at the same frequencies of current. When the frequency of current is increased (100-300) kHz the effect is practically graded (Figure 1a). The dynamics of investigated parameters changes for distilled water at its heating up to 30 °C has an opposite direction. It means that electrical conductivity is increased at low frequencies and decreased at high ones. As far as the changes in electrical capacity of water at different external impacts concerns (Figure 1b), the presence of extreme points in the region of exploratory current frequency of approximately 10 kHz should be mentioned that is probably determined by the existence of associates made of water molecules with high concentrations which are close to structural compounds according to their size [7]. It should be noticed the presence of correlating dependence of water electrical properties at different types of external impacts that can indirectly confirm a close mechanism of liquid activation.

Changes in conductivity and electrical capacity of distilled water after its activation by magnetic field testify about changes in its structure as a result of dissymmetry in a system. It is evident that after activation in distilled water such changes of structure at which the mobility of water dipoles is altered at the frequencies of explorative reactive current can occur.

Analysis of fulfilled experiments results shows that electrical properties of water before and after its activation by magnetic field or by means of heating are changed at different frequencies of reactive current in different ways. In some cases the increase of parameters values is observed, in other cases the decrease of them is detected. Apparently, external impacts can lead to both system activation due to the increase of energy store and to the reactivation, - the process of “mollification”due to the binding of structural units in harder or more organized compounds. We can assume that in the systems two processes are observed – formation of clusters and their destruction. The former process is accomplished by the decrease of free energy and reactivity of the system as a whole, the latter results in their growth.
The application of a confining liquid activation by means of magnetic field allows regulating kinetics of structure formation processes [8] and such technological properties as hardness under compression, duration of cement grout setting, water absorption and thermal resistance of the samples.

5. Conclusion
1. On the basis of comparative evaluation of the processes for the system activated by means of electromagnetic field it is shown that the ideas about the processes of liquid structural organization destruction as a result of dissymmetry in a system are the most important reasons for possible mechanisms of activating impact.
2. The linear correlation between changes in conductivity and electrical capacity of distilled water in conditions of its activation, cooling and heating is revealed.
3. It is assumed that activation of distilled water by means of magnetic field, heating with following cooling without air and also water cooling induces the similar changes of its structure which include, probably, the increase of water clusters size. In this case the mobility of water dipoles is decreased at the frequencies of explorative reactive current of $(1 – 30) \text{ kHz}$, but it is increased at resonance frequencies of $(30 – 300) \text{ kHz}$.

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