The influence of activated binders (cement) on the process of their hardening

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Abstract. Introduction. The paper studies hardening activation with regard to binding systems (cements) and justifies the possibility of its implementation in construction engineering to prepare construction mixes when erecting buildings and structures out of cast-in-situ concrete and reinforced concrete. During hardening of binding systems (cements), hydrated cement phases are formed and the substance becomes solid, affecting the formation of cement stone and its strength.

Purpose of the study. We aimed to study the mechanism of phenomena that occur during activation and hardening in binding systems as well as explore the possibility of their implementation and boosting in order to improve the physical and mechanical, processing, and performance properties of construction mixes.

Methods. The properties and stability of binding (cement) systems, which are lyophilic systems, qualitatively characterize the interaction between a solid body and a fluid. The lyophilic behavior implies good wetting, low interfacial tension, and resistance of the surfaces to mutual adhesion.

Results. A holistic approach to studying the mechanism of hardening activation in binding systems at the level of colloidal chemical phenomena as well as the energy of interaction between the binder and water in construction mix preparation will make it possible to determine the main directions of boosting the processes in binding systems through various types of energy impacts: mechanical, chemical, non-reagent, ultrasonic, electrostatic, and other methods.

1 Introduction

Since construction sites require high-quality concrete mixes, concrete mix preparation is the most critical procedure in concreting. To enhance the quality of concrete mixes, we need to continuously seek new reserves and opportunities to improve their properties and concreting quality.

In-depth studies on the mechanism of phenomena that occur during activation in binding systems (which, in certain physical conditions, set and harden, thus forming artificial stone as a result of chemical interaction between the initial components and their physical and chemical transformations) will allow us to determine possible directions of their boosting.

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2 Materials and Methods

![Diagram showing the process of coagulation and crystallization of cement stone](image)

Fig. 1. Coagulation structureization of cement gel and coagulation-crystallization structureization of cement stone.
3 Results and Discussion

In terms of physics, setting means the formation of a thixotropic reversible coagulation structure that strengthens in time. Strengthening occurs due to an increase in the number of colloidal-sized particles of the solid phase per unit volume. Setting is caused by water binding by the surface of cement grains and new formations. The formation of these new structures is an independent process that precedes and significantly affects water-cement paste hardening. As a result of setting, intense water binding occurs, and, as a consequence, permittivity decreases due to water structuring in new high dispersion hydrated phases. When introduced, AlCl$_3$, Al$_2$(SO$_4$)$_3$, FeCl$_3$, Fe$_2$(SO$_4$)$_3$ shorten the setting time but do not result in an instantaneous setting. It means that setting depends not only on Al$^{+3}$ impact but also on intense water binding [17].

The aggregative stability of a dispersion system largely depends on the composition of the dispersion medium and can be altered through the introduction of electrolytes. For lyophilic systems, electrolyte introduction increases the coagulation rate, and, when a certain (critical) electrolyte concentration is reached, the coagulation rate reaches its limit. A charged surface (a statistical value) represents alternating areas with positive and negative charges (with one type of charge dominating, which predetermines the overall charge of the surface). Therefore, when the surface of cement grains is negatively charged, adsorption, engagement of multivalent ions into the adsorption layer, and their impact on the electrical double layer (EDL) are possible. The sign of the potential-determining ion layer charge and the value of the diffusion layer characteristic in cement dispersions are largely related to the ion composition of the dispersion medium. During hydration, the potential value and charge sign change.

The ionic composition of a dispersed medium changes as a result of phase transformations, the action of fields and electrolytes. In addition, a change in the ionic composition of a dispersed medium is possible when sparingly soluble substances are introduced into the system, whose ions, due to adsorption, can affect the composition of the potential-determining layer of the dispersed phase [18].

The pH value of the medium significantly affects the ζ-potential (the potential difference of the dispersed medium and the liquid layer surrounding the particle), since the ions H$^+$ and OH$^-$ and due to their dipole nature and small sizes are easily adsorbed and thus the pH increases in the cement slurry, which also leads to change ζ-potential.

Coagulation processes play an important role in the formation of cement stone due to the discharge of particles, reduction of their potential, and compression of the diffusion portion of the electrical double layer. By reducing the potential of the adsorption layer or compressing the diffusion portion of the electrical double layer (or the interparticle distance), it becomes possible to control the setting time or initial density of grains in stone. Reduced permittivity decreases the thickness of the diffusion layer. Therefore, water binding decreases the thickness of water films, within which the EDL thickness is reduced, i.e., setting becomes less hindered. The hydration process leads up to setting, which is based not only on chemical water binding (an increase in the solid/liquid (S/L) ratio) but also on liquid permittivity reduction.

The introduction of active ions affects the potential of the adsorption layer and, therefore, the EDL characteristics, the structuring degree of boundary water layers, and transport of active particles, i.e., colloidal chemical and condensation phenomena. Besides, through their charge state and the nature of the chemical environment [19-22], active ions affect the activity of the centers. The electrolyte ions with a charge opposite to that of the particle surface produce the coagulation effect. The higher the valence and the larger the radius, the more intense the effect. A reduction of the ζ-potential to approx. 30 mV leads to coagulation.
With trivalent ions introduced, e.g., Al$^{+3}$, the capacity arises to reduce the zeta potential more intensely in comparison to monovalent ions, which is important: their appearance in the setting process at ion hydration.

Being highly active, multivalent ions demonstrate a strong adsorption capacity in relation to the solid phase, they more easily (in comparison to other ions) penetrate the electrical double layer of ions with the opposite charge and replace there the potential determining ions, thus changing the charge of the solid phase surface.

To reduce energy consumption during thermal activation (steam curing) of concrete hardening, it is necessary to ensure acceleration of hydration and strength gain at an early stage.

The cement stone strength increases with the speed exceeding the directly proportional hydration degree of the binder and is characterized by the quantity and quality of bound water. Water filling the pores and cavities of the binder represents a solution with a complex physical and chemical composition that interacts with solid particles and is, to a certain extent, a bound solution. The kinetics of chemical water binding predetermines the structure of new cement stone formations, which develops during setting.

The dependence of the concrete strength on the water/cement ratio is associated with the cement stone structure formation process. When the water/cement ratio increases (water surplus), the hydration process slows down, and concrete porosity increases, which has an adverse effect on strength. Low porosity of cement stone is ensured by a decrease in the water/cement ratio.

A decrease in the water/cement ratio accelerates crystal formation in cement stone, is accompanied by qualitative changes in its structure, and increases the concentration of alkalis in the liquid phase, this boosting the hydrosilicate formation process.

The interaction between cement particles and water with ions of some chemically active compounds can significantly accelerate the induction period—cement gel setting time and the formation of crystal hydrate complexes causing its transformation and passage into a stone-like state, which affects the kinetics of cement stone strength gain.

Extremely small concentrations of ions capable of compressing the double layer due to the action of counterions are necessary for impact on the electrical double layer. The introduction of foreign ions into the hydrosilicate structure leads to changes in the energy characteristics of the bond, which affects the plasticity of the mix and cement stone strength.

The pH level of the medium plays an important role in hydrate formation (hardening). The pH level of the medium intensifies the hydration of clinker grains and the pH level of the liquid phase, thereby increasing their solubility since OH$^-$ radicals have a smaller size in comparison to water molecules and penetrate the pores of the new formations’ shield film more freely. The acceleration of the hydration of silicate phases is ensured through an increase in the concentration and intensity of active centers on the surface of cement minerals as well as through the introduction of ions participating in the formation of the binding system into dispersion.

The activity of the binding system can be controlled by means of not only chemical modification of the surface but also surface electron processes due to changes in the concentration of free charge carriers in the surface vicinity, e.g., through exposure to an electric field.

Ions that can modify the surface chemically can simultaneously affect the system properties as potential-determining ions. The ion composition of the liquid phase affects the intensity of active centers, colloidal chemical properties of dispersion, morphology of cement phases, properties of cement phases. Ion exchange makes it possible to affect the defectiveness degree of surface atoms and the activity of adsorption centers as well as the colloidal chemical properties of the surface (the sign and intensity of the charge). The surface/liquid interaction, in terms of electrostatic forces that manifest in bonds of atoms or...
ions of the surface and structure of the liquid in boundary and free layers, affects the consistency of the mix. The introduced substances, depending on their nature, chemically modify the surface of minerals in such a way that the activity of the surface in reactions with water disappears or noticeably increases. Such changes in the ion composition of the surface also have an effect on its charge and the whole gamma as well as colloidal chemical phenomena that manifest at the phase boundary, on the one hand, and mobility (stiffness) of the whole heterogeneous system, on the other hand.

Possible methods of activation, considered at the level of colloid-chemical phenomena, are summarized and presented in Figure 2.

**Fig. 2.** Activation of hardening processes at the level of colloid-chemical phenomena

### 4 Conclusion

- Impact on DES; increase in zeta potential and dielectric constant; compression of the diffuse part of the DEL; impact on aggregation processes
- Impact on the activity of the centers
- Impact on DES; decrease in zeta potential; change in the charge of the solid phase
- Impact on DEL due to the involvement of multivalent ions in the adsorption layer
- Changing the value of the zeta potential and setting time
- Influence on coagulation rate

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Conclusion: As a result of the performed generalizations and the analysis of studies addressing the hardening of binding systems and its implementation in construction at the level of colloidal chemical phenomena, and the energy of interaction between the binder and water in construction mix preparation, we have determined the main directions of boosting the processes in binding systems through various types of energy impacts. To ensure hardening activation, the following is required:

- Impact on the composition of the potential determining layer of the dispersion phase;
- An increase in the pH level, which results in changes in the zeta potential and possible charge exchange;
- A decrease in the interparticle distance or reduction of the diffusion portion of the electrical double layer.

The introduction of active multivalent ions contributes to the reduction of the zeta potential. Besides they can become potential-determining ions in the system. They affect the...
intensity of active centers, colloidal chemical properties of dispersion, morphology and properties of cement phases.

The introduction of foreign ions into the hydrosilicate structure leads to changes in the energy characteristics of the bond, which affects the plasticity of the mix and cement stone strength.

Studies on phenomena that occur during binding system hardening activation as well as the implementation of the mechanism of these phenomena will make it possible to apply various methods of construction mix components (cement, mixing water, fillers) activation during preparation more widely in order to improve the physical and mechanical, processing, and performance properties of mixes.

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