Role of potential-determining ions and water molecules in the structure formation of cement compositions

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Abstract. The paper is concerned with dealing with an urgent problem of present-day construction materials science and engineering such as increasing the strength of cement stone when using finely dispersed fillers. It has been found that the physical and mechanical properties of Portland cement-based materials largely depend on the strength of the cement matrix modified by finely dispersed fillers, in particular, on the electric surface properties of all components and pore walls (equilibrium electric surface potential and double electric layer with potential-determining ions and counter-ions and at the interface between the solid phase and water). Studies were conducted to determine the values of equilibrium electric surface potentials of perlite and glass hollow microspheres. The system-forming hierarchical structure of water acting as a matrix or a crystal-forming platform for the synthesis of spatial structures during the formation of a crystalline cage on the surface of micro-fillers was substantiated. The assembly elements of these systematized structures were investigated using electron microscopy. It should be noted that when water films are supersaturated with ions during cement hydration, crystals nucleate and grow on the surface of micro-fillers, which leads to self-compaction and hardening of the cement matrix at the microlevel.

Introduction
The works of the school of thought led by A.N. Plugin [1, 2] demonstrate that the hardening of cement binders depends on electro-heterogeneous interactions between the particles of cement hydration products, mineral additives and aggregates with unlike surface charges. In this context, the interaction is carried out through thin, monomolecular, in many cases, water interlayers that remain between the particles during the hydration hardening.

Currently, cement compositions keep on improving to obtain new properties by introducing various dispersed components such as perlite sand, fiberglass, glass microspheres, etc. [3-6]. Their electric surface properties, the nature of the distribution of water on their surfaces, and their role in the structure formation and formation of the properties of cement compositions remain poorly understood.
The purpose of the research is to clarify the electric surface properties of new disperse components of cement compositions, the laws of distribution of potential-determining ions and water over the surfaces of disperse particles, and their effect on the structure formation.

Literature Data Analysis
A specific feature of the electric surface properties of disperse materials is the discreteness of the surface charge, due to the fact that the double electric layer is formed by potential-determining ions on the surface of the solid phase, which are point charges located at a considerable distance from each other and which are essentially active centers on the surfaces of the disperse structure [1, 2].

According to the papers [1, 2], all structural elements of the concrete mixture and concrete have marked electric surface properties in the form of a surface charge, which is described by the density \( q^0 \), \( C/m^2 \), surface (electric surface) potential \( \psi^0 \), \( V \), and equilibrium electric surface potential \( \psi^0_p \), \( V \), and a double electric layer (DEL) at the interface of the solid phase and the water. The structure of DEL, including ions that are specifically adsorbed, is shown in figure 1.

![Figure 1. The structure of DEL [2]: \( \psi^0 \): electric surface (surface) potential; \( \psi_1 \): potential at the border between the dense and the diffusive parts of DEL; \( \zeta \): electrokinetic potential; \( \delta \): the thickness of the diffusive part of DEL.](image)

In the concrete mixture, the concentration of electrolyte, mainly \( Ca(OH)_2 \), quite quickly becomes significant (0.02 mol/L, and even higher at the beginning of hardening owing to the supersaturation of the liquid phase); therefore, all water physically and chemically binds to the surface of the structural elements and becomes part of DEL. The action in such a physically and chemically bound water layer within DEL is determined by the electric field that is created by the potential-determining ions of the particles, that is, the electric surface potential \( \psi^0 \), and the high polarity of the water, which transfers the electric field to a distance of 1 \( \mu \)m or more [1, 2, 7].

\[
\delta_{ac} = \frac{B/\rho^e_s}{H S^u} = \frac{H L B/\rho^e_s}{H S^u} = \frac{B/\rho^e_s}{H S^u} = \left[ \frac{1}{(m^2/kg)} \right] = m
\]

Having a huge specific surface area due to the most finely dispersed component, hydrosilicate gel, cement stone is a highly concentrated disperse system with a specific surface area of 250÷700 m\(^2\)/g = 250000÷7000000 cm\(^2\)/g.

As a result, the thickness of the water layer on the gel particles, and, consequently, other particles of cement stone, ranges from 0.63 nm 6.310\(^{-10}\) m, which corresponds to the size of the water associate [8], to 10 nm 1·10\(^{-8}\) m, which corresponds to the size of the pores in the particles and globules of the hydrosilicate gel [2].
Consequently, for cement stone with a low W/C ratio DEL is flat, with no diffusive part, which allows considering the interactions between the particles and the surfaces using the disjoining pressure equations for a flat DEL [2, 9]. In this case, the interaction is determined by the potential difference between the layer of potential-determining ions (PDI) and the layer of counter-ions (CI), which is named the electric surface potential in the papers [1, 2]. The absolute value of the electric surface potential $\psi_{ep}$ is determined using the experimental calculation method by the value of standard electrode potentials $E^0$ for simple substances [2].

The electric surface potential of a complex substance under standard conditions is determined by the equation:

$$\psi_{ep}^0 = \frac{\sum \psi_{ep,i} \times \nu_i}{\sum \nu_i}$$  \hspace{1cm} (2)

and the equilibrium electric surface potential (at different pH levels) $\psi_{ep}^p$ of complex substances is determined by the equation:

$$\psi_{ep}^p = \psi_{ep}^0 - 0.059pH$$  \hspace{1cm} (3)

**Findings of the research**

Equilibrium electric surface potentials of expanded perlite sand, fiberglass and glass microspheres were obtained based on the average stoichiometric composition and electric surface potentials of oxides.

The surface charge of glass (glass fiber and glass microspheres) was determined based on its average stoichiometric composition of $Na_2O$-$CaO$-$6SiO_2$ and the electric surface potentials of the oxides according to the method [2]:

Absolute electric surface potential:

$$\psi_{ep}^0 = (2.207 + 1.37 + 6 \times 0.56)/8 = +0.217 \text{ V}$$  \hspace{1cm} (4)

Equilibrium electric surface potential at pH = 12 (pore electrolyte of cement stone):

$$\psi_{ep}^p = \psi_{ep}^0 - 0.059pH = 0.217 - 0.059 \times 12 = -0.499 \text{ V}$$  \hspace{1cm} (5)

where 2.207; 1.37; 0.56 are the absolute electric surface potentials of $Na_2O$, $CaO$ и $SiO_2$, respectively.

The calculation of the electric surface potentials of perlite is shown in Table 1. As one can see, the grains of expanded perlite both in water (pH ~7) and in compositions based on Portland cement (pH ~12) have a negative electric surface potential and, consequently, a surface charge.

| Oxide    | $\psi_{ep}, \text{ V}$ | $x, \%$ | $x \cdot \psi^0$ | $\psi_{ep,perlite}^P, \text{ B}$ | $\psi_{ep,perlite}^P, \text{ V, at pH 12}$ |
|----------|------------------------|--------|-----------------|-------------------------------|---------------------------------------------|
| $SiO_2$  | -0.55                  | 72     | -39.6           | -0.19                         | -0.64                                       |
| $Al_2O_3$| 0.33                   | 15     | 4.98            |                               |                                             |
| $Fe_2O_3$| -0.32                  | 1.4    | -0.442          |                               |                                             |
| $CaO$    | 1.38                   | 2.2    | 3.036           |                               |                                             |
| $MgO$    | 1.13                   | 0.36   | 0.405           |                               |                                             |
| $K_2O$   | 2.35                   | 2.85   | 6.707           |                               |                                             |
| $Na_2O$  | 2.21                   | 2.85   | 6.308           |                               |                                             |
| $\Sigma$ | 96.66                  |        | -18.61          |                               |                                             |

Thus, in the environment of cement paste and stone, fiberglass, glass microspheres, perlite have negative surface potential values; fiberglass and microspheres: $\psi_{ep}^p = -0.499 \text{ V}$, and perlite:
\[ \varphi_{ep} = -0.90 \text{V.} \] Therefore, they can be a substrate for crystallization of hydration products with a positive surface charge, which corresponds to the diagram shown in figure 2.

![Figure 2](image)

**Figure 2.** Estimated structure of cement hydration products around fiberglass: C - fiberglass; K - crystalline hydrates of portlandite, hydroaluminates and hydrated calcium sulfoaluminates; \( \Gamma \) - particles of hydrosilicate gel.

Silicones used in cement mixtures are, as a rule, organosiloxane polymers (polyorganosiloxanes) with the structural formula \([R_2SiO]_n\), where R is an organic group (methyl, ethyl or phenyl), such as the simplest representative of silicones, polydimethylsiloxane:

![Figure 3](image)

**Figure 3.** The structural formula of polydimethylsiloxane and the spiral structure from it due to the dipole moment.

These groups can have a dipole moment relative to the siloxane chain and consequently enable the silicone film to have hydrophilic properties and an electric surface potential, that is, the ability to serve as a substrate for cement hydration products (by analogy with [6, 10]).

The dipole moment is determined by the structure of the siloxane group, which results in the polarization of the bond between silicon and hydrocarbon. The extremely flexible siloxane chain Si-C and Si-O reacts to the dipole moment and “tries” to arrange the siloxane units in such a way that the positively charged silicon of one unit is located opposite the negatively charged oxygen atom of the other unit, figure 3.6 (a). As a result, a singular spiral structure arises [11]. In this case, hydrocarbon radicals are directed outward, and hydrophilic associations are drawn inward. This structure allows water structures to be organically integrated into the lattice metrics. In the volume of water, the main structural element is also formed as a non-linear element, but twisted into a spiral. Moreover, the whole variety of combinatorial water structures on the surface of the polysiloxane chain will be a variety of the same spiral cycles of different symmetries [11].

In 1993, the American chemist Kenneth D. Jordan gave his suggestions of stable “quanta of water”, which consist of 6 molecules [12]. According to the ideas of Dr. Head-Gordon's group (2002), water molecules form “true bricks” of water through hydrogen bonds, which are topological chains and rings of many molecules, figs. 4 to 5.
The ideas about the structure of water, especially those related to the formation of large clusters, figure 5, are ambiguous. It is widely acknowledged that there is a common opinion on the existence of a quasistructure of water and initial associates of 5 water molecules on average. It is this structure that determines the interaction between water and the walls of capillaries. This arises from the ideas of A.N. Plugin on the dielectric permittivity of water [2], where the taking into account of the associates of 5 molecules of water with unidirectional dipole moments allowed deriving an equation for the dielectric permittivity of water, the calculation of which, unlike all existing equations, gave the value of $\varepsilon = 80$. In addition, it was shown that the dielectric permittivity of water at a charged surface varies from 2.16 to 80 at a distance to 1 $\mu$m from this surface, which corresponds to the propagation of an electric field of point charges through polar liquids according to G.I. Distler [7].

From this perspective, the following pattern of the behavior of water on the surface of the structural elements of concrete with charged surfaces seems most realistic. The structure of large water associates and the bonds between them are likely to be disrupted under the influence of the electric field of the surface and, more precisely, the PDI. Closely at the surface, the polar molecules of water will be adsorbed on the PDI. In this case, the adsorption of molecular associates of 5 molecules of water with unidirectional dipole moments should be most probable. In the intervals between the PDI, single unassociated molecules will be adsorbed, which will make it possible to obtain the most dense structure of cement stone, figs. 6 to 8.
Figure 6. The nucleation of the crystalline phase on fiberglass: 1) fiberglass; 2) nucleation of crystalline hydrates on the associates and individual water molecules.

Figure 7. Formations peculiar to portlandite and calcite form a dense structure on fiberglass.

The system-forming hierarchical structure of water act as a matrix or “scaffold” for the self-organization of spatial structures during the formation of a crystalline cage on the surface of a polyester fiber coated with a silicone film. The assembly elements of these systematized structures are visible in the electronic image, Figure 8a. When water films are supersaturated with ions during cement hydration, crystals grow on the surface of the polyester fiber, figure 8, b.
Figure 8. A through pore of perlite (a) and of a hollow glass microsphere (b), densely filled with cement hydration products; individual particles close to cubic shape: calcite from 0.6 microns in size.

Figure 9. Formation of a crystalline cage on a silicone film of a polyester fiber:
A - A structural model of a siloxane chain with an integrated spiral-shaped structural element of water; 
b - The growth of crystalline structures on the surface of a polyester fiber treated with a silicone sizing agent; c - A fragment of crystalline structures on a polyester fiber when magnified up to 3000x.
Findings
Therefore, it has been found that in a cement stone environment perlite, fiberglass and glass microspheres have a negative electric surface potential (charge) and can be used as a substrate for crystallization of hydration products with a positive surface charge.

The dipole moments and hydrogen bonds of water molecules promote the formation of the “structure” of water from molecular associates, consisting of about 5 molecules with dipole moments oriented in the same direction, and single water molecules.

From this perspective, the following pattern of the distribution of water by the charged surfaces of the structural elements of concrete seems most realistic. The structure of large water associates and the bonds between them are likely to be disrupted under the influence of the electric field of the surface and, more precisely, its potential-determining ions. Directly at the surface, the associates of 5 molecules of water are adsorbed mainly on the potential-determining ions, and in the intervals between the PDI, single unassociated molecules are adsorbed, which ensures the most dense structure of cement hydration products.

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