Theoretical foundations of the structure formation of cement stone and concrete

Bakhridin Khasanov¹*, Lyudmila Irmuhamedova¹, G Firlina and Temur Mirzaev²

¹Tashkent Institute of Irrigation and Agriculture Mechanization Engineers
Department of Technology and Organization of Hydromeliorative Works, 100000 Tashkent, Uzbekistan
²Lanzhou Resources&Environment Voc-Tech College, China

E-mail: mr.bakhridin@mail.ru

Abstract. The analysis of resource-saving technologies led to the main conclusion that up to now high-intensity methods for physical modification and hyper-consolidation of concrete mix and concrete have not been developed. Taking into account the physicochemical principles of the structure formation of cement stone and concrete, the production of particularly high-strength concrete (Kb > 100 MPa) is possible by using methods of modifying the concrete mixture, hyper-consolidation of the molded concrete taking into account the development of the optimal structure of the material, capable of significant stretch perception. The implementation of this idea in industrial production, apparently, is possible using simple technological methods for preparing concrete mixture, forming axisymmetric products, methods of hyper-consolidation of molded concrete and physical modification of concrete mixture, for example, by squeezing excess mixing water and entrained air [1].

1. Introduction
Management of the hardening processes of complex dispersed structures, such as cement stone and concrete, is possible on the basis of a deep understanding of the physical, mechanical and chemical-technological nature of their interaction. A significant number of studies on the kinetics of hydration of binders and technological analysis of hardening processes are devoted to this issue [2, 3, 4, 5, 6, 7, 8, 9]. Despite the large number of studies performed, there is still no general quantitative theory of hardening and structure formation of binders based composites. It is generally accepted that an astringent, reacting with water, turns into new chemical compounds that are fundamentally different from the original substance. The starting material has a greater solubility than the hydration products and the resulting solutions are saturated with respect to the hydrate.
V. Mikhazlis [10] believes that water molecules penetrate into the surface layers of the binder particles, lead to the simultaneous hydrolytic dissociation of anhydrous calcium silicates, and therefore a colloidal mass of tiny hydrate particles is formed.

According to A. A. Baikov [11], soon after mixing the binder with water, it dissolves, as in Le Chatelier [12]. But at the time the saturation concentration is reached, the process of dissolution of the starting material should stop, but its chemical conversion into hydrate cannot stop. Hence, A.A.Baikov, based on topochemical concepts, concludes that hydration products should be allocated in the form of a finely dispersed system due to the direct addition of water to the binder grains. The core that unites these theories is that, after the binding of binders to water, hydrates are formed in the form of tiny particles that have the properties of colloids and are in equilibrium with the environment. Regardless of whether these particles are formed as a result of precipitation from solutions, or during a topochemical hydration reaction, or due to dispersion of cement grains, hydrated particles possess all the properties of colloidal formations.

Le Chatelier and A.A. Baikov believe that the development and growth of crystalline hydrates goes through a solution. Mikhazlis explains the hardening of cement pastes from binders by the appearance of a coagulation structure between colloidal hydrate particles.

I.N. Akhverdov [2] considers the mechanism of the hydration hardening process from the point of view of the solution mechanism of cement particles with the subsequent crystallization of neoplasms from a supersaturated solution and crystal growth with the formation of a stone-like structure as a result.

A. F. Polak [4] argues as follows. Upon contact with water, the binder dissolves and a solution is supersaturated with respect to the hydrate, from which the embryos fall out. Growing hydrate crystals come together and join, forming a stone-like structure. In this case, it is justified to divide the complex hardening process into elementary stages:

1) dissolution of the original binder;
2) nucleation of a new phase - hydrate;
3) the growth of hydrate crystals;
4) the formation of colloidal and crystallization structures.

V. B. Ratinov [5] is inclined in favor of hydration hardening processes by the crystallization mechanism, in which dissolution plays an important role. Crystallization of neoplasms is also considered as a complex process of formation and growth of crystalline hydrates from supersaturated solutions. P.A. Rebinder and E.E. Segalov [13] adheres to the theory of crystallization structure formation, according to which the strength of the structure is caused by the coalescence of individual crystals with the formation of a bulk skeleton.

2. Methods
In [14, 15, 16], the simultaneous dissolution of the binder and the growth of neoplasm crystals are provided for. Moreover, calcium hydrate nuclei arise only in the induction period, and the form of these nuclei depends on interfacial energy and is a function of the coefficient of physicochemical heterogeneity.

Consider what processes occur during mixing of the cement with water, and it is necessary to take into account the important role of water, its density and viscosity. Since it is a change in its properties that determines the rate of dissolution of cement particles and the kinetics of the further processes of hydrolysis of cement minerals.

When cement powder is mixed with mixing water, a dispersed system is formed in which the properties of cement and water change depending on their quantitative ratio, temperature, pressure, and other characteristics [17]. Immediately after mixing, purely physical processes take place, consisting in the distribution and adsorption of water
on the surfaces of the cement particles, their sedimentation in microvolumes. At the same time, individual clinker minerals and initial hydration products are dissolved. There is a change in the chemical composition of cement particles, which plays an important role in the formation of the further structure. It is possible to imagine cement powder as a polydisperse uncompensated system in which small particles form aggregates with each other, characterized by lower surface potential and lower activity [2].

Curing and hardening of water-cemented cement from a chemical and physicochemical point of view is characterized by the processes of dissolution, hydrolysis, polymerization and hydration [2, 5].

Water enclosed between cement particles and having lost mobility is polarized due to diffuse phenomena, the dipole structure of particles, and the induction effect of polarized film water [6]. The orientation of the polar water molecules is maximally manifested in the adsorption layer near the interface.

In the process of the formation of solvate shells on the surface of gypsum particles (in the presence of gypsum), they interact under the influence of Van der Waals forces. When solvated cement particles come closer to the range of molecular attractive forces, they coalesce. Moreover, between the interacting surfaces there are still thin adsorption layers that impede further coarsening of the particles. Such systems are stable and form coagulation structures - a compact, group, closed, fragmented form [2].

When cement is mixed with water during mixing, a cement gel is formed - an inhomogeneous disperse system consisting of microagents and individual particles bound by Van der Waals forces, which ultimately leads to the formation of a coagulation structure; the formation of the coagulation structure of the cement gel occurs from the moment of cement mixing with water and ends, mainly, at the end of the induction period, which is in the interval between the beginning and the end of setting. This period is characterized by water adsorption on solid phase particles and its gradual saturation with cement hydrolysis products [16, 18].

There are several points of view on the mechanism of water binding by the surface of particles, but all of them recognize the dominant role of the force near-surface attraction field. The specific properties of adsorbed water affect the formation of the physicomechanical properties of cement gel and its transformation into a solid [19]. A cement particle interacting with a solution is a complex complex in which the solid phase is bound to the environment through a stabilizing double electric layer of ions, and in some cases through a solvation shell [2]. The degree of stability of the initially formed structure is determined mainly by the forces of interaction between particles.

The development of the coagulation process of a cement gel depends on the mineralogical composition and dispersion of the cement, as well as the presence of electrolyte additives in it, forming a double electric layer of the same sign at the surface of cement particles and preventing their adhesion. If the double electric layer of the same sign is absent, then near coagulation occurs, and the cement gel quickly thickens, turning into a stone-like body.

When cement is mixed with water, forces arise that ensure the formation of the coagulation structure of the cement gel, which has rheological properties, the ability to thixotropic transformations, compaction and hardening as ionic bonds arise at moments corresponding to the formation of crystallization centers. The areas of maximum probability of the formation of a new phase will be solvation layers.

The adsorption ability of cement, which determines the properties of the coagulation structure, changes dramatically depending on the physical activity of the force field, pressure, temperature, etc. The adsorption capacity of cement in a cement gel is enhanced by various force fields and promotes the interaction of dipole water molecules with attractive forces concentrated on the surface of the solid phase.

Strengthening the coagulation structure of the cement gel is accompanied by redistribution and partial binding of water - the convergence of solid particles, that is, contraction of the volume of the cement + water system. As a result
of this, volumetric compression of the cement gel occurs with the release of the liquid phase, which should especially be promoted by the force field. A reflection of these physicochemical processes of formation of the coagulation structure of the cement gel is a reduction in the setting time of the binder, since it transforms from a plastic-viscous state to a solid.

The end of the setting in its physical sense is close to the point in time at which the induction period of formation of the crystalline hydrate structure begins.

Further hardening of the coagulation structure is caused by the appearance and development of a crystallization process, in which ion-dipole and ion-ion bonds predominate, contributing to the loss of plastic properties by a cement gel [2].

Although the mechanism of hydrate formation during hardening, such as Portland cement, is still not clear, the following can be concluded. The penetration of water molecules into a binder particle during the topochemical hydration reaction can occur by surface diffusion through defects (surface hydration) or by volume diffusion of water. The solution mechanism is equally probable [6].

The formation of the crystal hydrate structure of the cement stone is based on electron-ion exchange processes between the dissociation products of cement minerals and dipole water molecules.

The products of the interaction of cement and water are transformed from molecules and ions with particle sizes \( r < 10\ \text{A} \) to colloidal particles (\( g \approx 10 \ldots 1000\ \text{A} \)) and well-formed crystal formations (\( g > 1000\ \text{A} \)) [17].

3. **Results and discussion**

The hydration process can be divided into the main stages [17]. In the first - on the binder grains there are insignificant shells of colloidal dispersion, quite loose and unstable. The second stage covers the further hydration of cement and is characterized by the formation of dense, stable shells on cement grains and low diffusion rates of water and back diffusion of hydrated ions into the solution. In this case, diffusion phenomena occur both in the area of external mass transfer in the liquid phase outside the grains of the initial components surrounded by shells of finely dispersed neoplasms, and in the region of internal mass transfer, that is, through amorphized shells of cement particles. The microscopic speed of a heterogeneous hydration process can be expressed by the semi-empirical equation

\[
\frac{dC}{d\tau} = -K \cdot C \tag{1}
\]

where \( \tau \) is the time;

\( C \) is the content of unhydrated cement;

\( K \) is a parameter characterizing the mineralogy of the initial substance.

These hydrates, which appear in the form of a film on cement particles, have polar groups in their structure and have a high specific surface, which allows them to bind a certain amount of water, turning it into a film. By limiting the amount of mixing water, conditions are quickly created for the formation of contacts between particles for their further interaction, mainly with forces of electrostatic and electromagnetic nature.

In [2, 18], the mechanism of hydration of Portland cement is presented as follows. First, a solution is created, supersaturated with \( \text{Ca}^{++} \) ions, then semi-permeable shells form on the surface of the cement solid particles. Then crystalline hydrates form under this shell and at a certain stage they destroy the primary shell, and this means the beginning of the main period of hydration. The formation of crystalline hydrate shells around cement particles determines the specific structure of cement stone.
According to [20], structure formation in a cement gel occurs in two stages. On the first, the primary structure (GSA framework) is formed due to crystallization contacts, and on the second, the secondary hydrosilicate structure. In [6], it was suggested that the primary structure is mainly based on inter-unit contacts of an electrostatic and electromagnetic nature, similarly to [17], and the secondary structure is based on valence nature contacts at the sites of overlapping gel shells.

According to the modern theory of hardening of Portland cement [3, 4, 5, 6], the hydration process is caused by the dissolution of clinker cement minerals in a certain volume of water — a solvent, and then crystallization of thermodynamically stable compounds from supersaturated solutions. Therefore, when dissolving, an increased volume of water is required, and during crystallization, a comprehensive reduction in its amount is required. At the beginning of the hydration process, the growth of binder hydrate crystals proceeds with a high degree of supersaturation of the solution in the kinetic region.

With a decrease in the density and viscosity of water and with an increase in internal pressure in the binder + water system, the dissolving ability of water increases and the processes that facilitate the transformation of cement gel into a solid accelerate. According to the Volter equation [21], the solubility of clinker minerals L and the formation of new phase nuclei should increase according to:

$$L = A \exp \left( \frac{-B \delta^3 V^2_c}{(RT)^3 \ln(C/C_0)} \right)$$  \hspace{1cm} (2)

where $\delta$ is the specific interphase energy;
$V_c$ is the molecular volume of the new phase, equal to the relative molecular mass $M$, referred to its density;
$T$ is the absolute temperature;
$C/C_0$ is the degree of supersaturation;
$A$ - pre-exponential factor;
$B$ is a constant gypsum coefficient.

The appearance of a solid phase from a supersaturated solution on the surface of the substrate is more likely than in the bulk of the solution.

The probability of their occurrence is determined by the formula (3), according to [9].

$$W_{ji} = W_{0ji} \exp \left( -\frac{A_{ji}}{kT} \right)$$  \hspace{1cm} (3)

where $T$ is the absolute temperature;
$A_{ji}$ is the work of the formation of a solid phase on a substrate.

The work of the formation of the solid phase ($j$) on the substrate ($i$) can be found from the formula:

$$A_{ji} = \frac{2(\varphi_j/kT)^2}{(\mu-\mu_j)^2} H_{ji}$$  \hspace{1cm} (4)

where $\varphi_j$ is the binding energy between the neoplasms of the phase ($j$);  
$\mu$ and $\mu_j$ are the chemical potentials of the solution and phase ($j$);  
$H_{ji}$ - coefficient of physico-chemical heterogeneity.
\[ H_j i = \frac{\delta_j - \delta_i + \delta_{ji}}{\delta_j} \] \hspace{1cm} (5)

where \( b_j, b_i, b_{ji} \) are, respectively, the free surface energy of the neoplasm (j), substrate (i) and the value of the interfacial energy localized in the places where phase (j) occurs, on the surface of phase (i).

A similar formula is given in [5]. According to it, the probability of nucleation of a new phase depends on the height of the energy barrier \( \Delta F_{\text{max}} \) and is described by the formula:

\[ \alpha = A \exp\left(\frac{-\Delta F_{\text{max}}}{RT}\right) \] \hspace{1cm} (6)

where \( A \) is a preexponential factor that takes into account the activation energy of the process \( U \):

\[ A = A' \exp\left(-\frac{U}{RT}\right) \] \hspace{1cm} (7)

An analysis of this formula shows that the rate of nucleation can be controlled by changing the internal pressure, temperature of supersaturation and changing the relative ratio (C/V), which can be controlled by various technological methods.

With a decrease in the degree of supersaturation of the solution, crystal growth as a result of the appearance of two-dimensional nuclei becomes energetically unfavorable, and the dislocation mechanism proposed by Barton, Cabrera, and Frank comes into force [22]. According to him, the surface of a real crystal contains steps, steps, free vacancies. Crystal growth will be the result of exchange processes between the molecules of the step, the adsorbed layer and vapor, as well as the diffusion of the adsorbed molecules in the direction of the steps. Obviously, the crystal nucleus can be either the smallest particle of a crystallizing substance, or any other solid particle that has the properties of adsorbing ions or molecules of a crystallizing salt on its surface [2].

The emergence and development of crystallization centers is associated with various force fields and with the concentration of the solution. The formation of nuclei and their subsequent growth are two successive stages of the process of formation of a new phase.

The crystallization theory does not consider the nature of the forces that would allow the crystals to come together for their further coalescence. Until now, the nature of the forces leading to macrorystallization has not been considered in hardening schemes. Here, hydrogen bonds, the van der Waals interaction, and various types of ionic interactions due to the presence of uncompensated electric charges play a certain role [23].

The problem of developing a model of crystallization and hardening, taking into account a number of physicochemical phenomena associated with the modification of the structure of concrete, is very relevant.

The forces of interaction between colloidal particles, manifested during the refinement of the liquid films separating them, can both accelerate coagulation and inhibit it.

The attractive forces [24] between two neighboring molecules (atoms) vary depending on the distance according to the law:

\[ F_{\text{attr}} = -\frac{A}{r^2} \] \hspace{1cm} (8)

Where \( A \) is a constant, and the repulsive force is defined as

\[ F_{\text{rep}} = -\frac{B}{r^m} \] \hspace{1cm} (9)
where \( m \geq 9 \); \( B \) is a constant.

The resulting attractive and repulsive forces is

\[
F_{\text{rea}} = -A/r^7 + B/r^m
\]

(10)

The electromagnetic nature of the interaction forces was predicted by Lebedev, and Lifshits [25] developed a theory of these forces, according to which the interaction between molecules is realized due to the existence of an electromagnetic field that fluctuates in space and time.

The forces of attraction between particles of the same nature as intermolecular forces. The adsorption of water by particles of cement minerals depends on these forces, and a Helmholtz double electric layer appears on the surface of the solid phase, followed by a Stern diffuse layer, the thickness of which depends on the physicochemical properties of the medium.

Repulsive forces - electric forces that arise as a result of selective adsorption by the interphase surface of one of the electrolyte ions present in the system. Since all particles of the dispersed phase are identical in nature and always adsorb a certain ion, they all acquire a charge of the same sign and this prevents them from moving closer to the distance of the action of contracting forces (adhesion forces). According to our ideas, A.E. Sheikin [26], all particles of cement in water have the same charge. On the other hand, the convergence of colloidal particles is prevented by the formation on their surface of a solvate shell of medium molecules or molecules of another component of the system. From a physical point of view, condensed solid systems are formed when conditions are created for the particles to come closer to a radius of action that provides a hardening structure. An important role is also played by the structure formation of water, which entails a decrease in its dielectric constant and causes the orientation of water at the surface. We did not find data on the mechanism of water adsorption on the surface of hydrates.

In the formation of the hardening structure, adhesive contacts of an electrical nature also play a role. According to the electrical theory of adhesion, the force required to break the adhesive bond is:

\[
F = 2\pi \cdot \delta / \varepsilon
\]

(11)

Where \( \delta \) is the surface charge density;

\( \varepsilon \) is the dielectric constant of the medium.

By the moment of structure formation, the cement particles (dispersed phase) turn into three-layer ones, where the core (inner layer) is the cement grain, the middle amorphized layer is a hydrate film, and the outer one is a structured water film.

In the process of converting a cement paste into a solid, the kinetics of crystallization of neoplasms, crystal sizes and the strength of intergrowth contacts depend on the composition of the liquid phase and its value relative to the new hydrated phases, which ultimately provides structural strength. Any influences that promote the growth and combination of crystalline hydrates favor the formation of a high-strength stone structure.

As a result of the processes of colloidation, crystallization, compaction of hydrated neoplasms and carbonization, a strong cement stone is formed [27]. The main condition that ensures the hardening of disperse systems will be the following: astringent properties in such systems are manifested if the neoplasms contain polar groups and the fat is also polar, and optimal conditions for structure formation are created. The surface of the crystals is coated with a moving adsorption layer. Internal pressure facilitates the approach to distances at which there are opportunities for the emergence of stable embryos between them and the appearance of molecular bonds between mobile molecules from opposite adsorption layers, this creates crystalline bridges between individual crystals. As a result, a crystalline stone-like structure is formed.
The structure of cement stone can be interpreted as “micro-concrete”, in which the unhydrated residues of cement particles — nuclei — serve as aggregates, and the neoplasm shells are the binding agent [2]. Hardening of cement stone is accompanied by a change in its density and porosity. The kinetics of cement stone hardening can be represented as a continuous process of increasing the number of submicrocrystals and their convergence while thinning the liquid layer between them and increasing the strength of ionic bonds.

An analysis of structure formation leads to the conclusion that it is possible to purposefully control this process using simple technological methods [1]. This, first of all, should include:

a) regulation of the quantitative ratio or concentration of binder in a unit volume of the aquatic environment;
b) change and development of the force field (pressure) during the formation of hydrated neoplasms;
c) reduction in volumetric water content of the "cement + water" system in the process of product formation (material modification).

The simultaneous fulfillment of these conditions presents significant technological difficulties, but in principle it is quite feasible. This is especially true for the development of structure formation of cement stone directly in concrete.

4. Conclusions

An analysis of structure formation leads to the conclusion that it is possible to purposefully control this process using simple technological methods. This, first of all, should include:

a) regulation of the quantitative ratio or concentration of binder in a unit volume of the aquatic environment;
b) change and development of the force field (pressure) during the formation of hydrated neoplasms;
c) reduction in volumetric water content of the "cement + water" system in the process of product formation (material modification).

The simultaneous fulfillment of these conditions presents significant technological difficulties, but in principle it is quite feasible. This is especially true for the development of structure formation of cement stone directly in concrete.

Acknowledgments

We express our deep gratitude to the leadership of the Kuylyuk experimental factory of bridge reinforced concrete structures in the city of Tashkent for their help in conducting pilot research.

References

[1] B Khasanov and T Mirzaev 2019 Production of extra-strong concrete axisymmetric products E3S Web of Conferences vol 97 06011
[2] Akhverdov I N 1981 Fundamentals of concrete physics (Moscow: Stroyizdat) p 464
[3] Butt Yu M and Timashev V V 1974 Portland cement (Moscow: Stroyizdat) pp 229-320
[4] Polak A F 1966 Hardening of monomineral binders (Moscow: Stroyizdat) p 208
[5] Ratinov V B and Rosenberg T I 1973 Additives in concrete (Moscow: Stroyizdat) p 207
[6] Sychev M M 1974 Hardening of binders (Stroy izdat, Leningrad branch) p 79
[7] Churaev N V 1972 On the calculation of Hamaker constants for bodies interacting through interlayers of liquid J. Kolloidn T 34 Vol 6 pp 959-963
[8] Manfred O 1935 Urbetnlfluutenbetonvacuum-beton J. Zement 28 p 24
[9] Vacum – Hartbeton – Boden 1984 / 38 / Fussbodern - ZTG. 5 pp 107-110
[10] Michaelis W 1893 Involuta later in alteveritas *J. Chemiker – Zeitung* 69 p 217

[11] Baikov A A 1948 Collection of works (Moscow: Publishing Academy of Sciences) 5 pp 20-38.

[12] Le Chatelier H 1919 Cristalloids against colloids in the theory of cement *J. Transactions of the Faraday* 14 p 47

[13] Segalova E E and Rebinder P A 1960 Modern physical and chemical mathematical ideas about the hardening processes of minerals binders *J. Building materials* 1 pp 21-26

[14] Polak A F 1963 Elementary hardening processes of monomineral binders *J. Problems of construction of oil refining and petrochemical enterprises in Bashkiria* Issue 3

[15] Ratinov V B Rosenberg T I and Rubinina N M 1962 Study of the kinetics of crystallization of calcium hydrosulfoaluminate *J. DAN SSSR*. T. 145 5 pp 1098-1103

[16] Ranen A 1976 ZumWirkungsmechanismus von Betonflussigern auf der Basis von Wasserloslichen Melaminharzen *J. Cement und Concrete Research* 1 pp 57-61.

[17] Volosyan L Ya 1973 Heat and mass exchange during heat treatment of concrete and reinforced concrete products (Minsk: Science and technology) p 256

[18] Akhverdov I N and Margulis L N 1976 Non-destructive quality control of concrete by electrical conductivity (Minsk: Science and Technology) p 174

[19] Butt Yu M and Rashkovich L N 1965 *Hardening of binders at elevated temperatures* (Moscow: Stroyizdat) p 222

[20] Mchedlov-Petrosyan O P 1971 *Chemistry of inorganic building materials* (Moscow: Stroyizdat) pp 224

[21] Volter M 1939 *Kinetik der Phasenbildung* p 220

[22] Barton V and Cabreran Frank F 1959 Crystal growth and the equilibrium structure of their surfaces *J. Sat. Elementary processes of crystal growth* pp 30-45

[23] Schiller K 1962 Mechanism of re-crystallization in calcium sulphate hemihydrate plasters *J. Iappl. Chem.* V12 3 pp 135-144

[24] Voyutsky S S 1975 The course of colloid chemistry *M.g. Chemistry* pp 512

[25] Lifshits E M 1955 The theory of molecular forces of attraction between solids *J. JETP* T 29 Release 1

[26] Sheikin A E 1974 *Structure, strength and crack resistance of cement stone* (Moscow: Stroyizdat) p 173

[27] Popov A N 1966 *Building materials and details* (Moscow: Stroyizdat) p 117