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Mass Balance and Viscosity of the Pore Solution during the Hardening of Cement Paste

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Abstract: In the presented work, the results are provided of examining the properties of a pore solution during the process of cement paste hardening. Based on the experimental data of W. P. Halperin et al, the evolution of the mass balance of structured physical water is analyzed as a combination of interactions of capillary, gel, and other components. The formation and development have been studied of the pore solution viscosity. The comparison of the reported dependences of the water viscosity on the size of the pores with the experimentally determined values of the pores' radius has allowed estimating the rise of avid the pore solution viscosity in the process of hardening of cement paste. The separation of the structured pore solution's viscosity into capillary and gel components allows for a quantitative and qualitative consideration of the cement paste hardening as the process of forming a macrocapillary matrix, inside which a microporous structure is formed of the cement gel.

Key words: Structure, porosity, hardening, cement paste, pore solution, mass balance,viscosity.

1. Introduction

Cement concrete compositions, such as cement pastes, mortars, concretes, etc. (hereinafter: CCC), are moist capillary porous bodies, i.e., substantially heterogeneous systems. In real compositions, only individual microvolumes of the structure can, with some assumption, be considered as having a homogeneous structure. It is the heterogeneity, i.e., primarily the porosity that exerts a dominant effect on all constructive and operational properties of CCC without exception.

At any stage of the CCC hardening (at any time τ), the strength is determined by the state and properties of the forming structure. The solid skeleton of the structure is, in the first approximation, a volumetric sufficiently homogeneous configuration, albeit being built of elements of various mineralogical compositions, shapes, and sizes. The strength of the structure's solid-phase component is determined by the energy level of interactions between its component crystals, i.e., by the strength of inter-crystalline contacts at the atomic level.

However, this structure is inherently defective. The structure's defective nature is caused primarily by its porosity. It is the total amount of porosity and its properties, such as the pore size distribution, the ratio between the volumes of closed and communicating pores, the degree of saturation with a pore solution, etc. that directly determine the actual strength of the CCC, which is more than an order of magnitude less than the strength of the crystalline component of the capillary-porous structure. In this case, the liquid component of the structure—physical water, which connects solid-phase elements—has a special, fundamentally important influence.

Thus, the CCC strength is a macroscopic value, the study of which is only possible at the supramolecular level, i.e. phenomenologically, on the basis of empirical correlations.

2. Strength and Porosity of Cement-Concrete Compositions

The actual (final, 28-day) strength of hardening CCC can be achieved in completely different ways, depending on the specific combination of internal and

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external technological factors (composition of the mixture, compaction mode, hardening conditions, etc.), or even not achieved at all (!), with the wrong appointment or practical implementation of these factors. In the thermodynamic sense, strength is similar to work, the same value of which can be achieved by various variations in the applied force and the distance traveled.

This provision is the cornerstone of the problem under consideration. The whole point is that:

- strength is a measure of a material's resistance to mechanical failure, i.e. destruction—breaking the links between structural elements as a result of external influences of a different nature.
- strengthening is the reverse process of increasing the number of structural elements in the volume of the system and increasing the intensity of interaction between them; this process is the result of the development and action of internal forces of a chemical, colloid-chemical and physic-chemical nature.

Thus, strength is a static property of CCC, and strengthening is a dynamic process of formation and development of this property.

In general, the strength *S* of porous bodies: stone [1], ceramic [2], cermet [3] materials, and all types of CCC [4-9] is described by a power dependence of the form:

$$S = S_0 P^n \tag{1}$$

where P: porosity, S_0: strength at a zero porosity, n: power value that in the case of CCC varies within the range 2.5-3.5 [2, 3, 9, 10].

At any stage of CCC hardening (at any time τ), the strength is determined by the state and properties of the forming structure. The solid skeleton of the structure, in the first approximation, is a volumetric, fairly homogeneous configuration, although it is built from elements of different mineralogical compositions, shapes, and sizes. The strength of the solid-phase component of the structure is determined by the energy level of the interactions of the crystals that form it, i.e. the strength of inter-crystalline contacts realized at the atomic level.

However, this structure is inherently defective. The defectiveness of the structure is, first of all, its porosity. It is the general value of porosity and its properties (the distribution of pores by size, the ratio between the volumes of closed and communicating pores, the degree of saturation with a pore solution, etc.) that directly determine the real strength of the CCC, which is more than an order of magnitude less than the strength of the crystalline component of the capillary-porous structure.

So, the strength of CCC is a macroscopic value, the study of which is possible only at the supramolecular level, i.e. phenomenologically, on the basis of empirical correlations.

The first of these dependencies, which determines the strength as a function of the porosity of concrete, was proposed by R. Feret [4]. The Feret strength criterion, based on the "cement-space" ratio:

$$S = k\left(\frac{V_C}{V_C + V_W + V_S}\right)^2 = kP_{Fer}^{\ 2} \tag{2}$$

has served as a basis for obtaining most formulas for determining the CCC strength (V_c, V_w, V_s: are absolute volumes of cement, water, and sand, k: coefficient depending on the kind of cement and the hardening regimen, P_{Fer}: the Feret porosity).

D. Roy and G. Gouda [5, 6] suggested a different "reverse" logarithmic "Strength-Porosity" dependence:

$$S = -\frac{1}{k}\ln P_{Roy} \tag{3}$$

where $P_{Roy} = P/P_0$: the Roy porosity, P_0: the porosity at a zero strength, k: a constant equal to 2.6×10^{-5} 1/MPa.

The dependence Eq. (3) was obtained by the authors while studying the strength and porosity of cement paste samples obtained by hot pressing under high (up to 7,000 MPa) pressure. The 28-day strength of the samples had reached ~670 MPa at a porosity of about 2%.

It should be noted, that dependences Eqs. (2) and

(3), as well as the basic formula Eq. (1), determine the strength of hardened materials with constant structural and mechanical properties. However, in essentially nonstationary hardening processes, both the porosity and the strength vary over time, and it is exactly the $P(\tau)$ and $S(\tau)$ values that have to be used in the practical implementation of various scientific and engineering technological problems.

The Powers "gel-space" concept [7-9] is the most effective means of solving this problem, and the formula

$$S = S_0\left(\frac{V_{gel}}{V_{gel}+V_{cap}}\right)^n = S_0 P_{Pow}{}^n \tag{4}$$

determines the strength of a cement paste as a ratio of the volumes of the microporosity V_{gel} of the gel-forming inside the capillaries and the capillary space macro porosity V_{cap}, where S_0: the material strength at $P = 1$ (in which case all pores and capillaries are filled with the cement gel), P_{Pow}: the powers porosity, n is the power value varying within 2.5~3.7).

When studying the patterns of the CCC hardening and strengthening, it is necessary to keep in mind that the forming structure is a moist capillary porous body, while physical water, being a pore solution contained in the V_{cap} and V_{gel} volumes, is an equally significant structural component. The remarkable property of this water is that it always, i.e., at any moment of time τ, stays in thermodynamic equilibrium with the surfaces of the solid phase on which water is adsorbed (or by which it is absorbed). That is exactly why structured water while connecting/separating the solid phase structural elements, makes a direct contribution to the compressive strength balance of the forming structure. This effect is especially prominent at the stage of coagulation structure formation.

During the hardening process, the structural porosity is continuously transformed: the volume of the gel increases $V_{\mathrm{gel}}(\tau) \rightarrow \max$, while the volume of the capillary space decreases $V_{\mathrm{cap}}(\tau) \rightarrow \min$. As a result, the properties of structured water also change in strict correspondence with the structure development.

3. Evolution of the Cement Paste Mass Balance and Development of Structural Porosity in the Process of Hardening

From the phenomenological point of view, the hardening of cement paste should be regarded as an evolution of the mass general mass balance of a two-phase—"cement/water—chemically active composition:

$$m = m_c + m_w \tag{5}$$

where m_c: the mass of cement, m_w: the mass of water (the impact of the gaseous phase—the trapped air—can be neglected when analyzing the mass balance of such a system).

Already the primary structure of the CCC—the "compaction structure", formed during the packing and compaction of mixtures into molds, is characterized by an initial capillary porosity with pore sizes of about $(2.5\sim15.0)\times10^{-6}$ m [9, 11]. As the hardening processes develop, the initial porosity evolves while being transformed into a system of macro capillaries sized $\geq 10^{-7}$ m and microcapillaries sized $\leq 10^{-7}$ m. Besides that, a characteristic feature of CCC hardening is the formation, inside the capillary porous structure, of a cement gel with pore sizes of $(15\sim30) \times 10^{-10}$ m [7-9].

The general patterns of structural porosity formation and development during WPC (white cement paste) hardening are clearly illustrated by the Bhattacharja et al. [12] and Halperin et al. [13] experimental results, obtained using the NMR method. White cement mineralogical composition: $C_3S = 68\%$, $C_2S = 8\%$, $C_3A = 14\%$, $C_4AF = 1\%$; initial water to cement ratio $w/c = 0.43$. Fig. 1 shows the changes in the specific surface area, the amount of evaporable water m_{evp} according to T. Powers concept, and the average pore radius r in the process of WPC hardening. It is obvious that the average pore radius decreases by almost two orders of magnitude: from ~190 nm (at the age of 2.5 h) to ~2.2 nm (at the age of 1,440 h). This change in the average pore radius is consistent with previous studies' data [14]. The final value of the specific surface area $\omega = 225$ m^2/g is also in good agreement with the known results of [9, 15], and others.

Comparison of the results obtained by the NMR and MIP (mercury porosimetry) methods allowed the authors of Ref. [12] to separate the porosity formed during cement paste hydration into an open capillary and gel porosity (with pore sizes of 5 nm or less).

Based on these experimental data of Halperin et al. [13] and using the dependences of the "gel-space" concept [7-9], in Ref. [16] the changes have been calculated in the components of the mass balance of the liquid phase in the process of cement paste hardening:

$$m = m_{evp} + m_{n-evp} = m_{ch} + m_{ret} + m_{cap} + m_{gel} \quad (6)$$

where m_{evp}: the total mass of evaporable water, m_{cap}: the mass of capillary water, m_{gel} is the mass of gel water, $m_{n-evp} = m_{ch} + m_{ret}$: the total mass of non-evaporable water, m_{ch}: the mass of chemically bound water, m_{ret}: the mass of retained non-evaporable water.

It has been shown that chemical bonding of water ($m_{ch} \rightarrow$ max), formation of thin adsorption liquid films on hard surfaces ($m_{ret} \rightarrow$ max) and formation of cement gel ($m_{gel} \rightarrow$ max) occur on the account of reducing the mass of capillary water ($m_{cap} \rightarrow$ min) as a set of transitions:

- $m_{cap} \rightarrow m_{ch}$: a transition of capillary water into a chemically bound state.
- $m_{cap} \rightarrow m_{ret}$: a transition of capillary water into a strongly bound state of thin adsorption layers.
- $m_{cap} \rightarrow m_{gel}$: a transition of capillary water into a strongly bound state of gel water.

In order to obtain a complete picture of CCC hardening, the obtained results [16] must be complemented with the effects caused by the evolution of the cement paste's solid phase component, the mass m_{sol} of which is comprised of the masses of hydrated $m_{c(hydr)}$ and non-hydrated $m_{c(n\text{-}hydr)}$ parts of the cement, i.e.

$$m_{sol} = m_{c(hydr)} + m_{c(n\text{-}hydr)} \quad (7)$$

In its turn, the hydrated cement consists of the mass $m_{c(ch)}$ of the cement that has entered a chemical reaction and the mass m_{ch} of chemically bound water:

$$m_{c(n\text{-}hydr)} = m_{c(ch)} + m_{ch} \quad (8)$$

It should be taken into account that the maximum mass of water chemically bound in hydration and

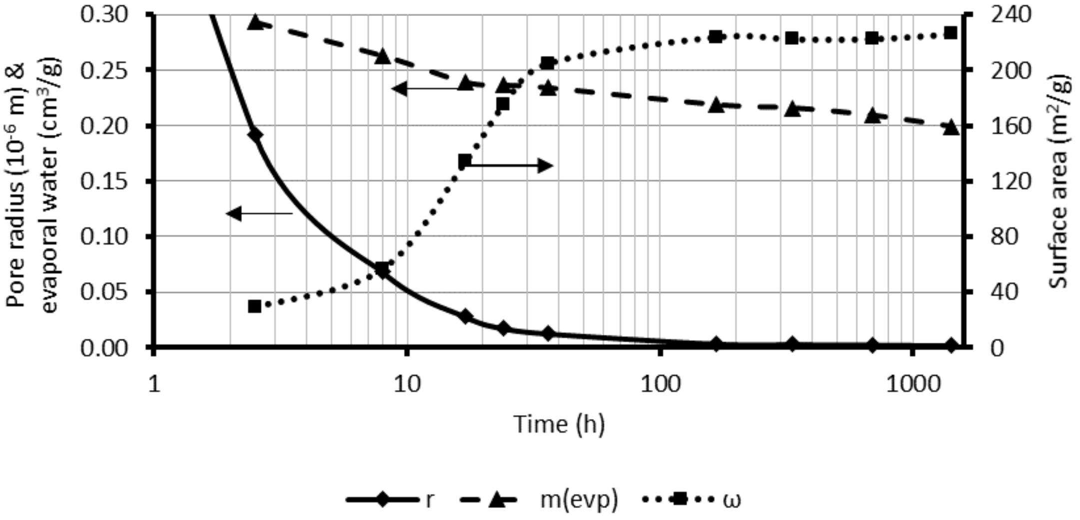

Fig. 1 Specific surface area *ω*, evaporable water m_{evp} and pore size *r* as a function of WPC hardening time (the curve $r = \Phi(\tau)$ was constructed according to experimental data of Fig. 3 [13]).

hydrolysis reactions of clinker minerals is equal to $m_{ch(\max)} = 0.23C$ for ordinary Portland cement [8, 17, 18].

The results of the joint analysis of the liquid and solid phases' evolution are presented in Fig. 2 in the form of a kinetic diagram. It should be noted that in this diagram the mass m_{ch} of chemically bound water, which is part of the solid phase, occupies the area confined by the dash-dotted line and the area of non-evaporable retained water m_{ret}.

Analysis of the set of transitions $m_{cap} \rightarrow m_{ch}$, $m_{cap} \rightarrow m_{ret}$ and $m_{cap} \rightarrow m_{gel}$ allows for evaluating the nature and intensity of the formation of capillary and gel components of the porosity of the hardening material (Fig. 3). The results of this analysis, in accordance with the "gel-space" concept by T. Powers [7-9], provide a direct way of assessing the strength value with Eq. (4).

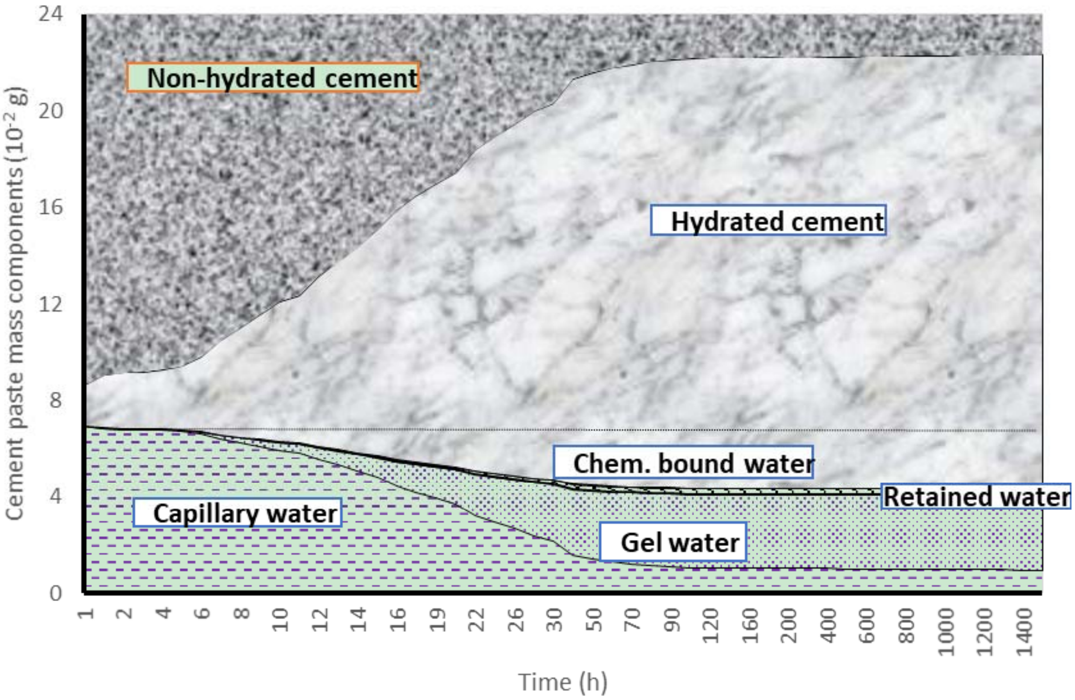

Fig. 2 Kinetic diagram of mass balance evolution during WCP hardening process.

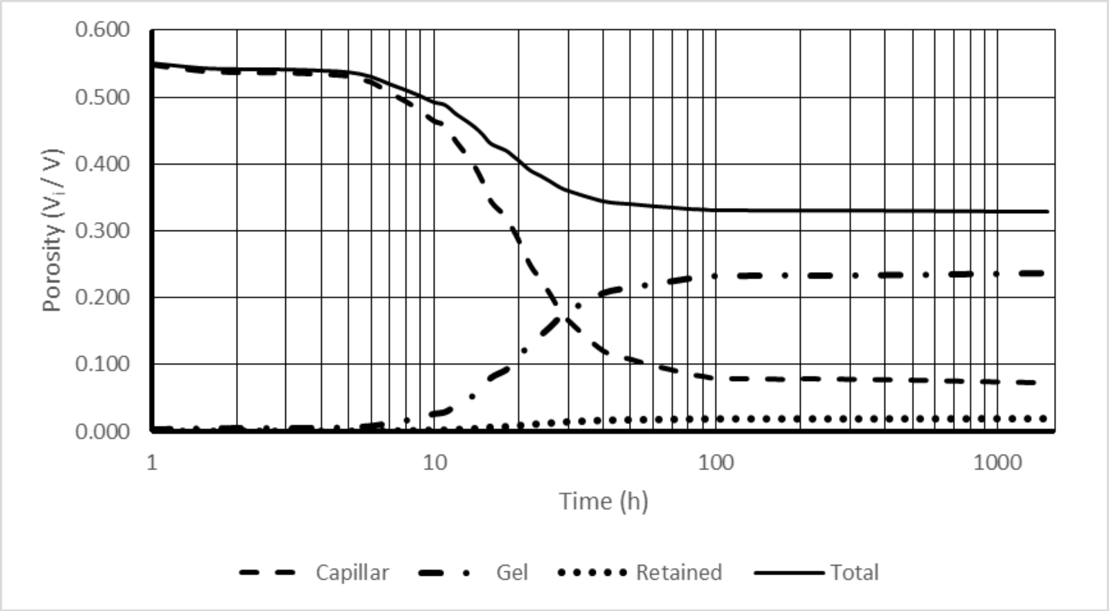

Fig. 3 Formation of porosity components in the process of cement paste hardening.

The values of the total porosity P_{tot} and its components P_{cap}, P_{gel}, P_{ret} are calculated as the ratio of the corresponding volumes of physical water V_i (i = cap, gel, ret) to the total volume V of the cement paste sample.

The "gel-space" concept of T. C. Powers makes it possible to calculate the components of the mass balance m_i "Eq. (6)" and the corresponding volumes v_i. According to this concept, the volume of gel water in the structure of the cement paste is determined by the following relationship:

$$v_{gel} = \frac{1-P_c}{v_{\mathrm{Pr}} P_c} \tag{9}$$

and the volume of capillary water is:

$$v_{cap} = v_w - (v_{n-evp} + v_{gel}) \tag{10}$$

Retained non-evaporable water is a full-fledged component of the water mass balance "Eq. (6)"; the volume of which (cm^3) is [8]:

$$v_{ret} = \gamma_{ret} \frac{\Omega_{hydr}}{3570k} \tag{11}$$

where Ω_{hydr} is the surface area of hydrated cement (m^2), k is a coefficient equal to the ratio of the theoretical mass of water required to moisten the entire surface to the mass of non-evaporable water.

In "Eqs. (9)-(11)": $P_c = 0.28$ is the porosity of the cement paste, $v_{pr} = v_c + (v_{n-evp} - 0.254)$ is the volume of solid products of cement hydration, $v_c = v / \gamma_c$ is the volume of non-hydrated cement, $v_{chem} = 0.23c\gamma_w$ is the volume of chemically bound, non-evaporable water.

The following values of the densities of the corresponding components were used in the calculations: γ_c = 3.15 g/cm^3 is the density of non-hydrated cement, γ_{Pr} = 2.16 g/cm^3 [10] is the average density of cement hydration products, γ_w = 1.0 g/cm^3 is the density of evaporated water. T. Powers used in his calculations [8, 9] the value of the specific volume of water v_w = 0.99 cm^3/g (γ_w = 1.01 g/cm^3) obtained by Copeland and Hayes [17]. H. Brouwers [19] when analyzing work [8] took the value of the specific volume of gel water equal to v_{gel} = 0.90 cm^3/g (γ_{gel} = 1.11 g/cm^3). Approximately the same value (γ_{ret} = 1.12 g/cm^3) is attained by the density of strongly bound non-evaporating water [10].

Fig. 3 summarizes in a graphic form the patterns of formation and development of the porosity components during the hardening of cement paste. The capillary component of porosity changes (decreases) most intensively, primarily due to the chemical binding of water ($m_{cap} \rightarrow m_{ch}$ in Fig. 2), as well as due to filling the capillary volume with the resulting gel ($m_{cap} \rightarrow m_{gel}$). In this case, porosity develops not only quantitatively, but also qualitatively. In particular, the change in the total porosity P_{tot} is determined by a corresponding decrease in macro-porosity (capillary porosity with $r \geq 10^{-7}$ m) and an increase in microporosity (gel porosity with $r \leq 10^{-7}$ m).

It should be noted that the data in Fig. 3 do not take into account the pore volume of entrained air, as well as the changes in the volume of hydrated cement.

4. Evaluation of the Pore Solution Viscosity in Hardening CCC

The increase in the specific surface area of the hydrated cement and the development of porosity in the process of the cement paste hardening (see curves $\omega = \psi(\tau)$ and $r = \phi(\tau)$ in Fig. 1) cause a continuous redistribution of the pore solution on the newly formed solid surfaces and a decrease in the average thickness h of the structured liquid layers. Besides that, intense chemical binding of capillary water makes a significant impact on the $h \rightarrow$ min effect. As a result, at a layer thickness of $h \leq 10^{-8}$ m, the energy level of strongly bound H_2O molecules increases to such an extent that the dielectric constant drops from 81 to 2 units, and water even acquires elastic properties: measurable yield strength and shear modulus [20]. Obviously, under such conditions, the viscosity η rises significantly, and its effect on the physical and mechanical state of the hardening material increases.

It should be borne in mind that a direct experimental determination of the viscosity of a structured pore solution in the process of hardening of any CCC is practically impossible. Nevertheless, the analysis of published experimental data obtained in studies of micro-and nanostructures of various types makes it possible to estimate the amount and character of changes in the water viscosity depending on the average radius of the pores. This, in its turn, provides new possibilities for interpreting the experimental data of Bhattacharja et al. [12] within the framework of the "gel-space" concept by T. C. Powers.

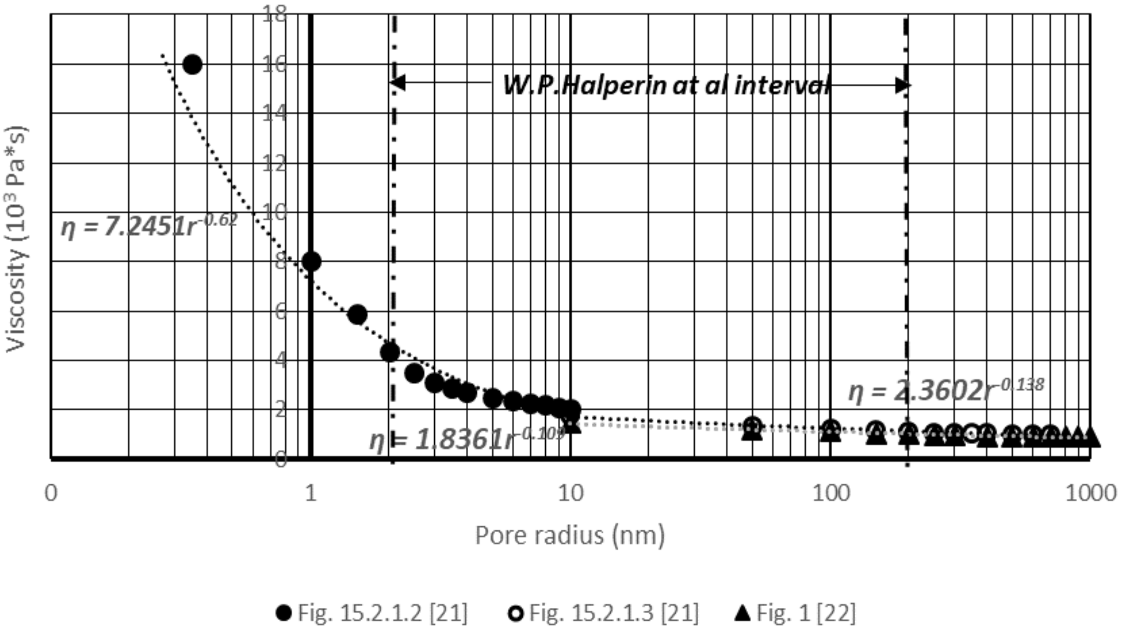

Fig. 4 Changes in dynamic viscosity of water η depending on the pore radius (according to the data from Ostrovsky [21] and Derjaguin and Churaev [22]).

Fig. 4 presents a graphic interpretation of dynamic viscosity of water as a function of the pore size (radius), obtained by joining two graphs borrowed from Ostrovsky [21]: Fig. 15.2.1.2 for the interval $0.5 \leq r \leq 10$ nm and Fig. 15.2.1.3 for the interval $0 \leq r \leq 750$ nm. These data correspond well with the results of direct measurement of water viscosity in quartz capillaries [22]. Both individual curves $\eta = f(r)$ in Fig. 4 and their set are approximated with power functions of the $\eta = ar^x$ type.

The experimentally determined changes in the average pore radius $r = r(\tau)$ (Fig. 1), designated here "*W. P. Halperin et al. interval*" were compared with the data of Fig. 4. This comparison made it possible to quantify evaluate the increase in the pore solution viscosity in the process of WCP hardening over the interval of r decreasing from ~0.2×10^{-6} m (at the age of 2.5 h) to ~0.2×10^{-8} m (at the age of 1,420 h) (Fig. 5). It can be seen that the viscosity increases steadily and almost monotonously up to 28 days of age (672 h), after which a sharper increase in η is observed. In order to explain the nature of the curve $\eta = f(\tau)$, it is necessary to link the change in η with the development of the structure of the hardening cement paste.

As the main structural factor that determines the state and properties of the liquid phase at any stage of hardening, we use Powers' porosity (see Eq. (4)).

$$P_{Pow} = \frac{V_{gel}}{V_{gel} + V_{cap}} \tag{12}$$

(here it is necessary to take into account that during the whole process $V_{gel} \rightarrow \max$, and $V_{cap} \rightarrow \min$). The advantages of the P_{Pow} parameter for studying the hardening and strengthening of CCC are discussed in detail in Section 1.

Transforming the data Fig. 5: Let us express the change in the dynamic viscosity of the pore solution η in the scale of the specific surface area ω of the hydrated cement (Fig. 6). The resulting dependence η-ω is characterized by the presence of two clearly defined rectilinear sections, the trends of which intersect at the point with the coordinates $\{\omega = 210.5, \eta = 1.489\}$. These coordinates, for cement paste investigated in the work [13], correspond to the hardening time τ = 36~40 h (we will use the average value τ = 38 h). This fact provides a reason to suggest that the intersection point determines such a state of the hardening cement paste in which the macroscopic capillary porous matrix is in fact already formed, and intensive formation begins of the gel component of the forming structure.

Similarly, in Ref. [12], based on the results obtained by NMR and MIP, it was proposed to separate the porosity formed in the process of cement paste hydration into the open capillary and gel porosity (with pore sizes of 5 nm or less).

As noted above, the viscosity $\eta = f(\tau)$ changes almost monotonically during hardening. At the same time, the curve $P_{Pow} = \psi(\tau)$ is characterized by different intensities of change in Powers' porosity over time. Therefore, it seems appropriate to analyze the change in the viscosity of the pore solution in the Powers' porosity scale (Fig. 6).

The resulting dependence "η-P_{Pow}" is characterized by the presence of 2 distinct straight sections:

"capillary"

$$\eta_{cap} = 1.0975 P_{Pow} + 1.2999 \tag{13}$$

which ends at the point with coordinates $\{P_{Pow} = 0.577;\ \eta = 1.93\times10^3$ Pa·s$\}$ by the time $\tau \approx 36$ h, and "gel"

$$\eta_{gel} = 103.77 P_{Pow} - 75.223 \tag{14}$$

the beginning of which is determined by the point with coordinates $\{P_{Pow} = 0.748;\ \eta = 2.48\times10^3$ Pa·s$\}$ on time $\tau \approx 108$ h.

At the initial ("capillary") stage of hardening ($\tau <$ 36 h), the slope of the straight line $\eta_{cap} = f_1(\tau)$ "Eq. (13)" relative to the "P_{Pow}" axis is very small, i.e. a significant increase in Powers' porosity has little effect on the increase in viscosity. This is apparently due to the fact that at this stage the bulk of physical water (mixing water) is contained in pores and capillaries of a rather large size.

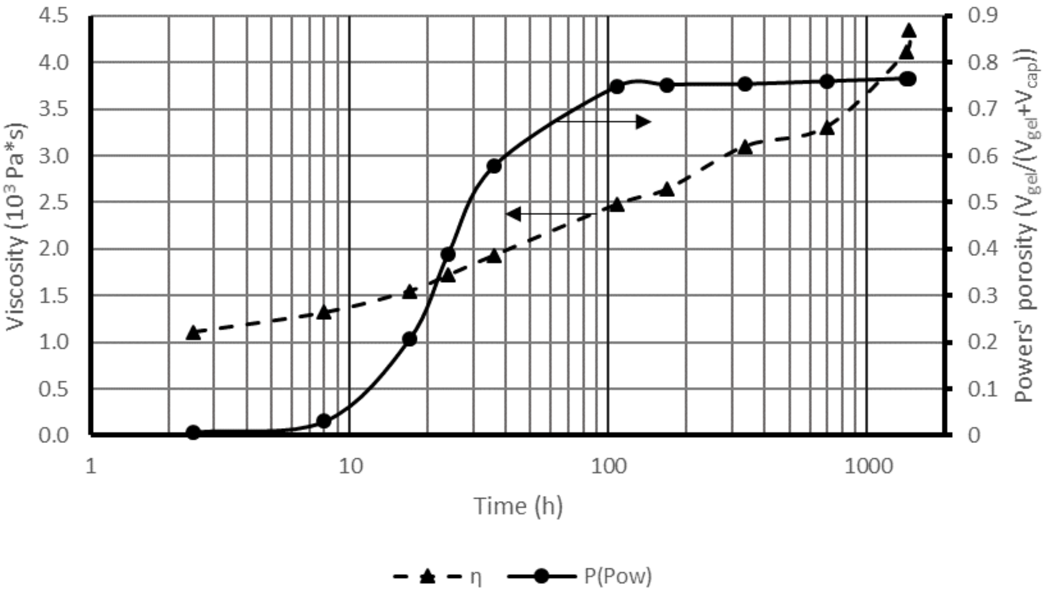

Fig. 5 **Changes in dynamic viscosity of pore solution η and Powers' porosity P_{Pow} during WCP hardening process.**

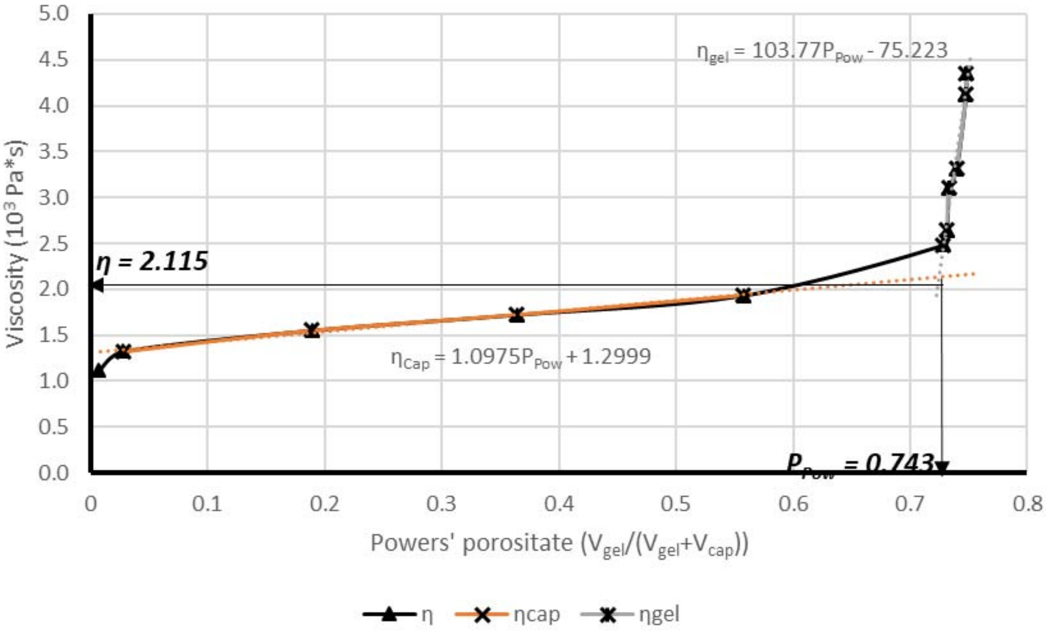

Fig. 6 **Pore solution viscosity η change in the Power' porosity P_{Pow} scale "Eq. (12)".**

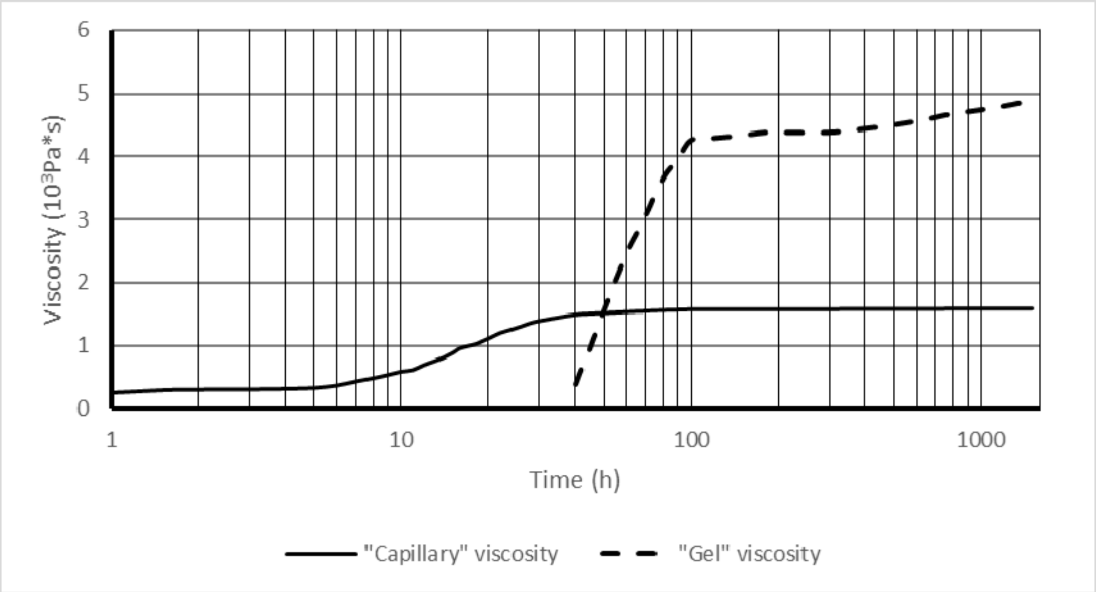

Fig. 7 Changes in capillary η_{cap} and gel η_{gel} components of the pore solution's dynamic viscosity in the process of cement paste hardening.

Approximately by this time ($\tau \approx 40\ h$), according to the scheme of J. Thomas and H. Jennings [23], the 3rd stage of hydration of the OPC is completed. At this stage, precipitation of hydration products (primarily C-S-H and C-H gels) into capillary pores occurs.

About the same time, a sharp rise begins of the viscosity's gel component η_{gel}, caused by the intensive formation of gel within the volume of the macro capillary matrix. This effect is observed until the time $\tau \approx 108$ h and after wards η_{gel} continues rising monotonously, albeit at a much lower intensity.

The next, intermediate interval (36 h < τ < 108 h) is determined by the fact, that the structure of the hardening cement paste is transformed from capillary-porous to gel-porous. In practice, this means that the separated volumes of C-S-H and C-H gels begin to connect inside the capillary pores.

The final, "gel" stage of hardening (τ > 108 h) is characterized by a significant increase in viscosity at an almost constant Powers' porosity, and the second rectilinear section of the graph $\eta_{gel} = f_2(\tau)$ is almost parallel to the "η" axis. As a result, the gel component of the structure intensively develops, characterized by the minimum pore size: r < 4 nm (see Fig. 1). The microstructure of the gel intensively absorbs, strongly binds capillary water, and the viscous properties of the pore solution become predominant (Fig. 7).

Fig. 8 demonstrates changes in the capillary and gel viscosities components as a function of the respective water mass balance components m_{cap} and m_{gel} (see Fig. 2). In this case, changes in the mass of water quantitatively characterize not the "moistening" or "dehydration" of the material, but the processes of formation of a capillary-porous macrostructure and the development of a gel-porous microstructure component inside it. It should be borne in mind that $m_{cap} \rightarrow$ min and $m_{gel} \rightarrow$ max, as shown by the arrows.

In particular, the analysis of the dependence $\eta_{cap} = f_1(m_{cap})$ shows, that the capillary viscosity η_{cap} increases insignificantly: from 0.239×10^3 to 1.572×10^3 Pa·s with a significant decrease in the mass of capillary water m_{cap}: from 6.91×10^{-2} to 1.23×10^{-2} g (curve $m_{cap} = f(\tau)$ in Fig. 2). It means that, due to the relatively large size of the pores and capillaries in this structure, the mobility of the ions of the capillary water is large enough, and the viscosity, is low, respectively.

Conversely, the graph $\eta_{gel} = f_2(m_{gel})$ shows that the gel viscosity increases sharply: from 0.38×10^3 to 4.63×10^3 Pa·s with a slight change in the mass of gel water:

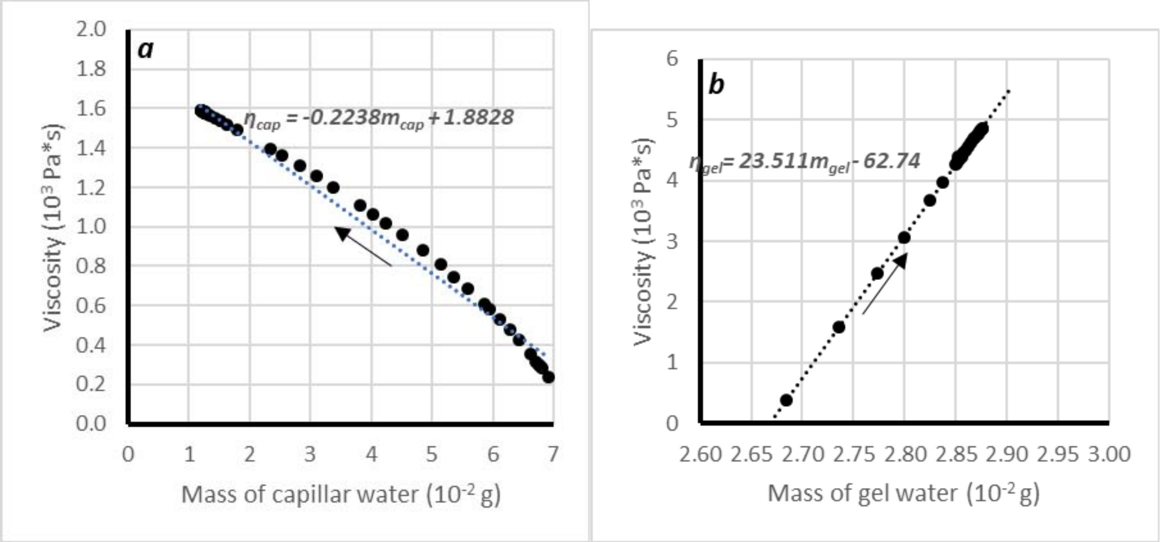

Fig. 8 Changes in capillary η_{cap} (*a*) and gel η_{gel} (*b*) components of viscosity as a function of the corresponding components of the water(arrows show the "direction" of the change in the mass of water during cement paste hardening process).

from 2.68×10^{-2} to 2.87×10^{-2} g. This indicates that the viscosity η_{gel} is indeed a property of thin films of strongly bound water that are characteristic of developed CCC structures.

Thus, the division of dynamic viscosity of a structured pore solution into η_{cap} and η_{gel} components allows considering the hardening of cement paste as the formation of a macrocapillary matrix, inside which a microporous structure of cement gel is formed. The analysis can be carried out on both a quantitative and a qualitative level.

In addition, the total value of the viscosity of structured water determines the measure of excess pressure in the deformed system [24], i.e. η is the coefficient of proportionality between the rate of deformation of the pore solution layer and the pressure acting in this layer. And this opens up new possibilities for studying viscoelastic effects, such as shrinkage and creep, in hardened CCC. However, the solution to these problems requires an additional set of analytical and experimental studies.

5. Conclusion Remarks

- CCC hardening is an alternative process in which, simultaneously with the material strengthening (formation of a condensation crystallization matrix), its defectiveness also develops (formation of capillary porosity). In this substantially non-stationary process, strength and porosity are time-variable values, i.e., $S = S(\tau)$ and $P = P(\tau)$.
- Physical water contained in the volumes of pores and capillaries, as well as in the cement gel, is always in thermodynamic equilibrium with the solid phase to which it is adsorbed (or to which it is absorbed). Therefore, water (pore solution) reacts quantitatively and qualitatively to all changes in the solid phase, and its (water) properties, primarily the viscosity, change in strict accordance with the formation of the hardening structure.
- Therefore, at all stages of hardening, structured physical water is an equally significant participant in the development of the CCC physical and mechanical state.
- In accordance with the experimental data of W. P. Halperin et al. [13] within the framework of the "gel-space" concept by T. C. Powers, the changes have been calculated in the components of the mass balance of the white cement paste in the process of its hardening.
- Comparison of the known dependences of the viscosity on the pore size $\eta = \eta(r)$ with the experimentally determined (W. P. Halperin et al. [13])

values of the decrease in the average pore radius $r = r(\tau)$ has made it possible to estimate the increase in the viscosity of the pore solution in the process of white cement paste hardening within the r decrease range from 0.19×10^{-6} m (at the age of 2.5 h) up to 0.22×10^{-8} m (at the age of 1,440 h).

- The division of dynamic viscosity of a structured pore solution into η_{cap} and η_{gel} components allows considering the hardening of cement paste as the formation of a macro capillary matrix, inside which a microporous structure of cement gel is formed.

Conflict of Interests

The author declares that there is no conflict of interest. They have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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