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FORMATION OF CEMENT STONE MICROSTRUCTURE IN THE PRESENCE OF COMPLEX CHEMICAL ADMIXTURES

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Abstract. This article experimentally investigates the possibilities of technological regulation of cement stone and concrete microstructure parameters through the introduction of chemical admixtures of various natures. Based on studies concerning the influence of chemical admixtures on cement hydration processes and cement stone microstructure, a comparative evaluation of the hardening and pore formation of cement stone with accelerating, plasticizing, and complex admixtures was performed.

Specifically, the study focused on the impact of complex chemical admixtures, including a superplasticizer like C-3 (likely a naphthalene sulfonate-based type) and LST (lignosulfonate) combined with accelerators such as NaCl or KCl, Na_2CO_3, K_2CO_3, Na_2SO_4, K_2SO_4 on the pore formation characteristics during the hardening of two types of cement: Portland cement PC CEM I 42.5R and slag Portland cement SPC CEM II B-S 32.5 R. These cements differ in their mineral composition, slag content, and consequently, their hydration rate and structure formation.

It was established that cement stone, whose porosity is characterized by a minimal pore radius and an optimal ratio between the volumes of gel pores and capillary pores, can be achieved through the complex application of an accelerator and a plasticizer. The synergistic effect of the superplasticizer reducing the water-cement ratio and improving particle dispersion, alongside the chloride accelerator speeding up early hydration, contributes to this refined pore structure.

Furthermore, a novel approach for evaluating the effectiveness of modifying the cement stone structure is proposed using the coefficient K_{ef}, defined as the ratio between the volumes of gel pores and capillary pores (ratio of dynamic microstructural indices). This quantitative information regarding the cement stone's microstructure and the limits of its regulation under the influence of internal and external factors allowed for the formulation of a concept regarding the possibilities of achieving specified concrete properties by modifying the corresponding parameters of the cement stone's microporosity.

Keywords: cement stone, microstructure, microporosity, chemical admixtures, structure formation, pore radius, pore size distribution.

Introduction. The pore formation process in cementitious materials is quite complex due to the presence of two developing, interacting structures: hydrosulfoaluminate and hydrosilicate. Hydrosilicates and calcium hydroxide play the main structure-forming role, constituting the bulk of the cementitious new formations. Despite the vast morphological diversity of other hydrated new formations within the cementitious material, their influence on certain physical and mechanical properties is deterministic and can be predicted in advance.

The primary properties of cementitious material – strength, permeability, frost resistance, etc. – are determined by the ensemble of micropores with a corresponding size distribution. Changes in pore sizes within the range of 2 to 100 nm can drastically affect the properties of the cementitious material, thus allowing for control over the nature of structure formation during the hardening phase. One of the levers for controlling the structure formation of cementitious material is the application of chemical and mineral admixtures, which in a specific way influence the course of hydration and hardening.

Analysis of Recent Research and Publications. The developmental trends in modern concrete technology are rooted in the increasing scientific intensity of concrete science. This field, in turn, is progressively integrating the principles and methodologies of physical and colloid chemistry, physics, and advanced simulation and statistical modeling techniques [1-2]. High indicators of strength, density, and durability in concrete are achieved at the microstructure level by incorporating highly effective chemical, mineral, and complex admixtures as crucial components. This approach enables the regulation of concrete properties by altering the ratio of capillary and gel microporosity within the cement paste structure and at the aggregate-cement paste interface [3-4].

The presence of pores in cement paste, ranging from 1 to 1000 nm in size and partially or completely filled with a liquid phase or vapor-air mixture, complicates their investigation. This is further compounded by the heterogeneous interaction of solid, liquid, and gaseous components, the diversity of their forms, the anisotropy of pore characteristics, and potential energetic changes at phase boundaries. Consequently, various methods are required for studying pore structure across different pore size distribution intervals (e.g., mercury porosimetry, nitrogen adsorption, thermoporosimetry). This also limits the methodological capabilities for quantitatively assessing the parameters of the evolving microstructure, the dispersity and strength of the solid phase of cement paste, the characteristics of bond forms, and changes in the indicators of pore liquid phase transitions under temperature or humidity influences, chemical, and other types of aggression [5-6].

One of the key factors for designing and producing concrete with desired properties, enhanced durability, and resistance to aggressive environments is the microstructure of the cement paste [7]. Currently, the primary method for regulating the properties of concrete mixtures and hardened concrete is the use of chemical and mineral admixtures. Chemical admixtures enable the targeted modification of the cement paste microstructure, which directly impacts the mechanical properties of concrete, including compressive strength, flexural tensile strength, elastic modulus, and deformation resistance [8-11].

Modifying the fundamental characteristics of the cement paste pore structure through chemical admixtures significantly influences concrete durability. Its parameters (pore size, pore volume, and size distribution) determine critical properties such as gas and water permeability, frost resistance, corrosion resistance, and more. Therefore, understanding the impact of chemical admixtures on the cement paste microstructure is fundamental for modern concrete engineering. This is not merely "important"; it forms the basis for innovation and solving complex challenges in construction. For these reasons, research into the influence of chemical admixtures on concrete properties and the nature of its structure formation remains highly prevalent in contemporary concrete science.

Aim and Objectives. The aim of this work is to regulate the structure formation processes of cement paste in concrete, based on thermodynamic analysis data of pore liquid phase transitions within confined pore volumes.

The objectives of this research are:

– To substantiate the application of differential scanning microcalorimetry for analyzing microporosity and phase transformations in hardening cementitious systems.

– To quantitatively assess the parameters of microporosity and their changes over time during the hardening of cementitious systems.

Materials and Methodology. This study investigated the influence of chemical admixtures on the pore formation characteristics of two types of cement: Portland cement PC CEM I 42.5R and slag Portland cement SPC CEM II B-S 32.5R. These cements differ in their mineral composition, slag content, and consequently, in their hydration rate and structure formation characteristics (Table 1).

The impact of several types of chemical admixtures was examined, including hardening accelerators with sodium and potassium cations, and plasticizers (Table 2). All admixtures conformed to the requirements of DSTU B V.2.7-65-97.

Quantitative assessment of pore structure parameters (pore size, pore volume, pore size distribution, pore shape) is performed based on scanning calorimetry data [12]. This assessment employs the principles of equilibrium thermodynamics and considers phenomena at phase boundaries. This approach addresses a complex set of tasks, including determining the parameters of liquid phase transitions during the freezing of porous dispersed materials, evaluating the energetic state of the liquid phase, assessing the degree of transformation during solid-liquid interactions, and evaluating the influence of technological factors and the effectiveness of concrete property modification with chemical admixtures.

Differential Scanning Calorimetry (DSC) belongs to the group of physicochemical thermal analysis methods used to determine energetic (enthalpy) changes in the substance under investigation. These methods are based on measuring temperature (Differential Thermal Analysis – DTA), spontaneous (Calvet calorimetry), or compensatory (DSC) heat flows [13].

Table 1 – Characteristics of Cements

Indicators		CEM I 42.5R	CEM III/B-S 32.5R
Actual Activity, MPa		52.0 (28 days)	23.7 (7 days)
Activity after Steaming, MPa		32.0	25.2
Fineness of Cement Grinding (passed through 008 sieve), %		91.0	91.0
Setting Time, hours-min: Start-End		3-20 4-20	1-50 7-00
For tests with river sand: Normal Consistency		28.0	28.1
Mineral Composition, %	C_3S	57.48	50.0
	C_2S	21.36	30.0
	C_3A	7.57	3.8
	C_4AF	12.35	16.2

Table 2 – Chemical Admixtures

Name	Chemical Formula	Regulatory Document
Potash (Potassium Carbonate)	K_2CO_3	DSTU B V.2.7-65-97
Sodium Carbonate	Na_2CO_3	DSTU B V.2.7-65-97
Sodium Chloride	$NaCl$	DSTU B V.2.7-65-97, ТУ 6-13-14-77
Potassium Chloride	KCl	DSTU B V.2.7-65-97, ТУ 6-13-14-77
Potassium Sulfate	K_2SO_4	DSTU B V.2.7-65-97, ТУ 38-10742-84
Sodium Sulfate	Na_2SO_4	DSTU B V.2.7-65-97, ТУ 38-10742-84
Technical Lignosulfonate (LST)	$\{C_{16}H_{15}O_8SNa\}$	TU 13-0281036-05
C-3	$\{C_{11}H_7O_3SNa\}_n$	TU 6-36-020429-625

The DSC method is based on heating (or cooling) a sample and a reference at a set rate while maintaining their identical temperatures. It measures the compensatory heat flow required to keep the sample's temperature within the programmed range. Experimental curves represent the dependency of heat flow (mJ/s) or specific heat capacity C_p (J/(g·K)) on temperature. The compensatory heat flow is directly proportional to the change in the sample's internal energy (enthalpy).

The thermoporosimetry method [14] is based on the thermodynamic dependence of the pore water crystallization temperature (T, K) on the pore radius ($R_{\text{п}}$):

$$R_{\text{п}} = 0.58 + 0.005(\mathrm{T}_0 - \mathrm{T}) - \frac{63.46}{\mathrm{T}_0 - \mathrm{T}},$$

where T_0=273.15 K. This allows for the determination of pore sizes in which a first-order phase transition (crystallization of pore liquid) is observed. The peak area, in turn, allows for the determination of the volume of liquid that underwent the phase transition.

Results. The pore formation process in cement paste is significantly more complex than in monomineral binders due to the presence of two developing and interacting structures: hydrosulfoaluminate and hydrosilicate. Hydrosilicates and calcium hydroxide play the primary structure-forming role, constituting the bulk of the cement paste's new formations. Despite the vast morphological diversity of other hydrated new formations in hardened cement paste, their influence on certain physical and mechanical properties is deterministic and can be predicted in advance. The main properties of cement paste – strength, permeability, frost resistance, etc. – are determined by the ensemble of micropores with a corresponding size distribution. Changes in pore sizes within the 2 to 100 nm range can drastically alter the properties of the cement paste, thus enabling control over the nature of structure formation during the hardening stage. One of the levers for managing cement paste structure formation is the application of chemical and mineral admixtures.

Hardening of the investigated cements within 1 day is accompanied by the formation of a pore structure with two micropore size distribution regions, characteristic of gel and capillary micropores. For Portland cement, these are in the range of 2.2-22 nm, with distribution maxima at 2.36, 2.45, and 14.6 nm. For slag Portland cement, the micropore distribution range narrows to 3.1-6.6 nm, with maxima at 3.4, 3.7, and 6.3 nm (Fig. 1, a). Simultaneously, the volume of micropores increases by 1.3 times compared to Portland cement (Fig. 1, b), reaching 0.46 cm³/g. This is attributed to the slower binding of mixing water during slag Portland cement hydration, the formation of hydrogelenite and hydrogarnets, as well as calcium hydrosilicates of lower basicity than those formed during Portland cement hardening. The consequence is a reduction in capillary micropore sizes and the formation of low-density (LD) C-S-H with porosity in the 3.1-4.2 nm range (Fig. 1, a).

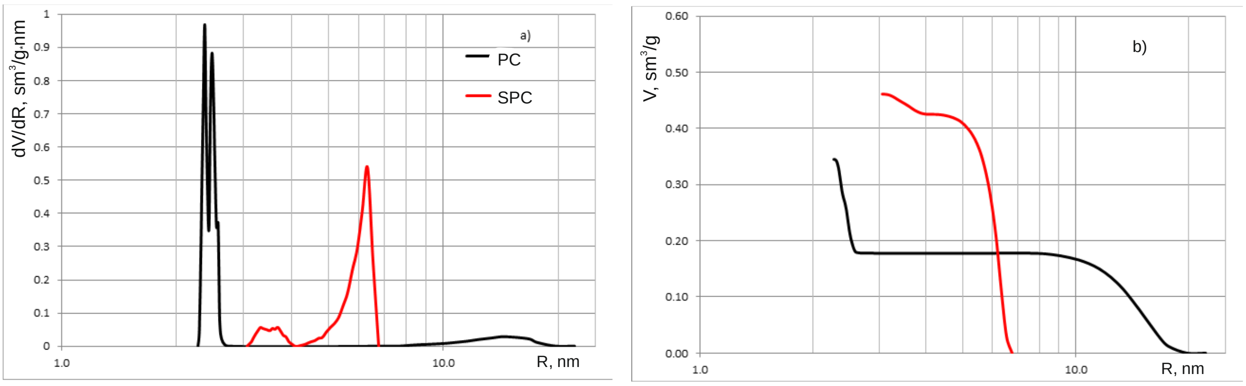

Fig. 1. Influence of cement type on the microporosity of cement stone:
a – pore size distribution; b – total pore volume

Gel microporosity in slag Portland cement (SPC) accounts for only 7.6% of the total porosity, whereas the analogous figure for Portland cement (PC) is 47%. Consequently, the amount of calcium hydrosilicates formed in the cement paste is 40% higher in PC than in SPC for the same hardening time.

In complex admixtures, each component complements the others and differs in its influence on the formation of the cement stone structure. For instance, the action of hardening accelerators is linked to increasing the solubility of the main cement minerals by altering the ionic strength of the solution and accelerating the crystallization of new phases. Sodium salt cations promote an increase in the alkalinity of the medium and exert a catalytic effect on the hydration of calcium silicates. The adsorption mechanism of Lignosulfonate (LST) and C-3 determines the reduction of surface tension at the phase interface, the release of immobilized water, etc., ultimately leading to the plasticization of mixtures. The effect of complex admixtures is more intricate due to the superposition of different component action mechanisms.

To enhance the efficiency of cement stone modification, further research is needed to identify the quantitative relationship between the composition of complex admixtures and concrete properties. The multi-component nature of admixtures and the associated complication of structure formation processes objectively lead to increased complexity of admixtures as objects of analysis and optimization. The influence of such chemical admixtures on the formation of cement stone microporosity was examined using sulfates, carbonates, chlorides of sodium and potassium as hardening accelerators, and plasticizing admixtures LST and C-3. Establishing patterns for the directed regulation of cementitious system parameters at the micro-level is a fundamental prerequisite for obtaining concretes with specified technical properties.

During the hardening of Portland cement over 1 day in the presence of C-3 (Fig. 2), two micropore size distribution regions are formed within the 4.6-9 nm interval. The ratio of gel and capillary micropores in the cement stone at this age is 12% and 88%, respectively, of the total volume.

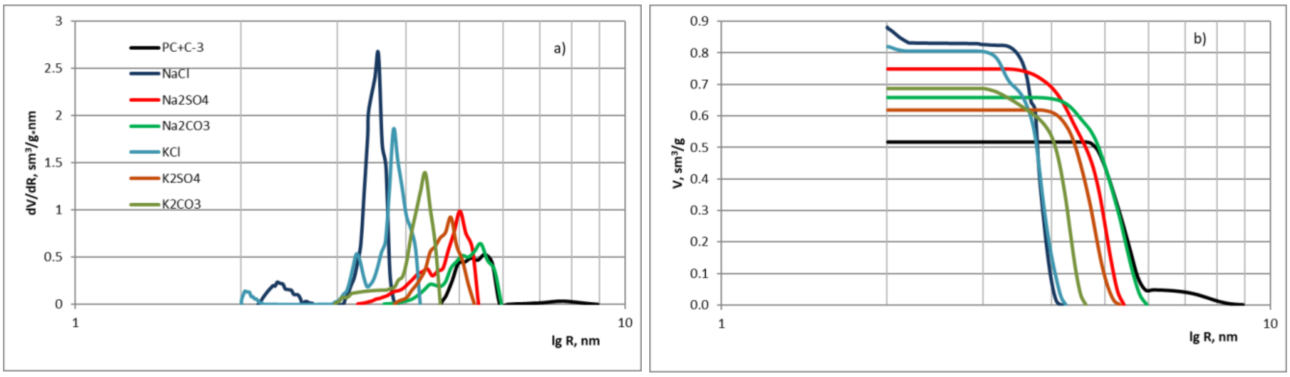

Fig. 2. Influence of complex admixtures based on C-3 on microporosity (Portland cement, 1 day): a – pore size distribution; b – total pore volume

During the hardening of Portland cement with complex admixtures based on Lignosulfonate (LST), a characteristic reduction in the total volume of micropores is observed when accelerators are introduced (Fig. 3). In this case, the percentage content of capillary micropores ranges from 70% (sodium and potassium sulfates, sodium chloride) to 85% (potassium carbonate). In combination with potash, LST is the most effective retarder at early hardening stages.

The ratio of gel to capillary micropores in the control sample is 69% and 31%, respectively. In the sample with KCl, the capillary micropore content is only 5%, and in the presence of sodium carbonate, they are entirely absent.

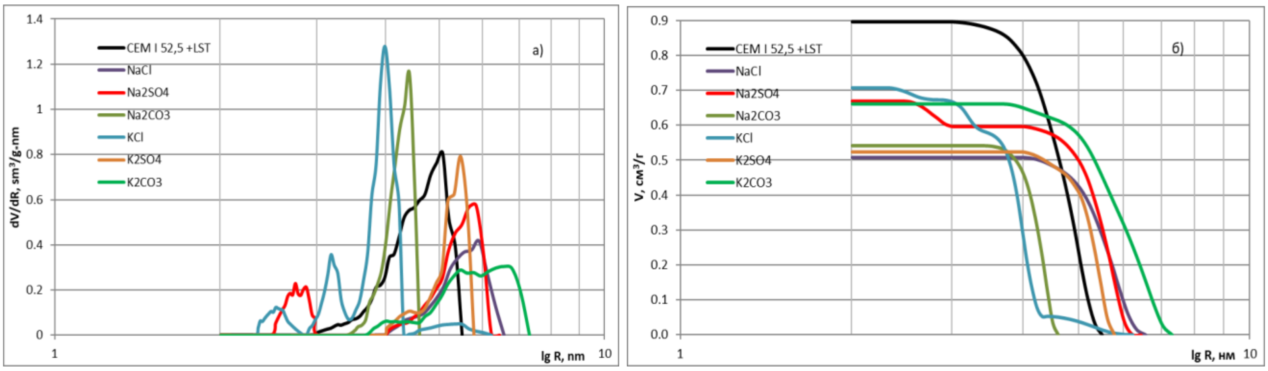

Fig. 3. Influence of complex admixtures based on LST on microporosity (Portland cement, 1 day): a – pore size distribution; b – total pore volume

During the hardening of slag Portland cement with complex admixtures based on C-3, the role of the anionic component of accelerators is clearly visible (Fig. 4). Potassium salt admixtures exhibit the best synergistic effect, contributing to the formation of microporosity with a minimal volume. In this case, the micropores of all samples are distributed within a narrow range of 3 to 5.2 nm.

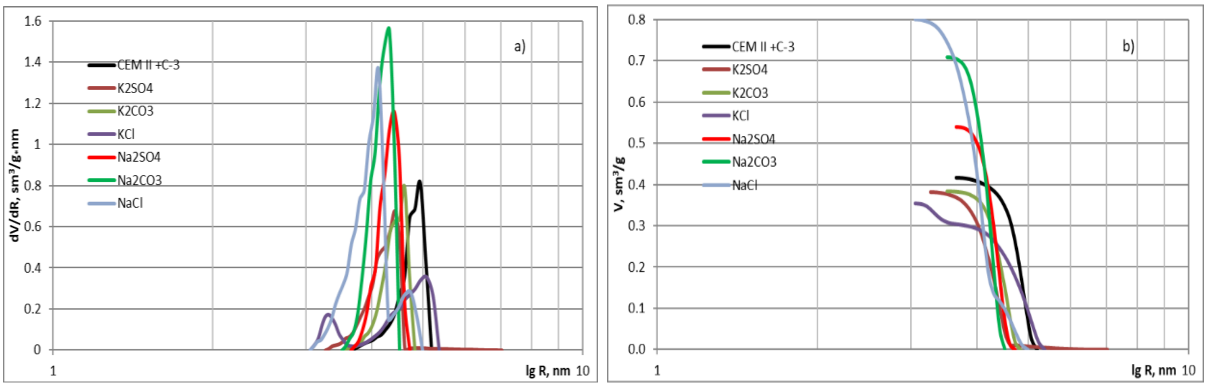

Fig. 4. Influence of complex admixtures based on C-3 on microporosity (Slag Portland Cement, 1 day): a – pore size distribution; b – total pore volume

For slag Portland cement with complex admixtures based on Lignosulfonate (LST), no clear patterns of structure formation are observed (Fig. 5).

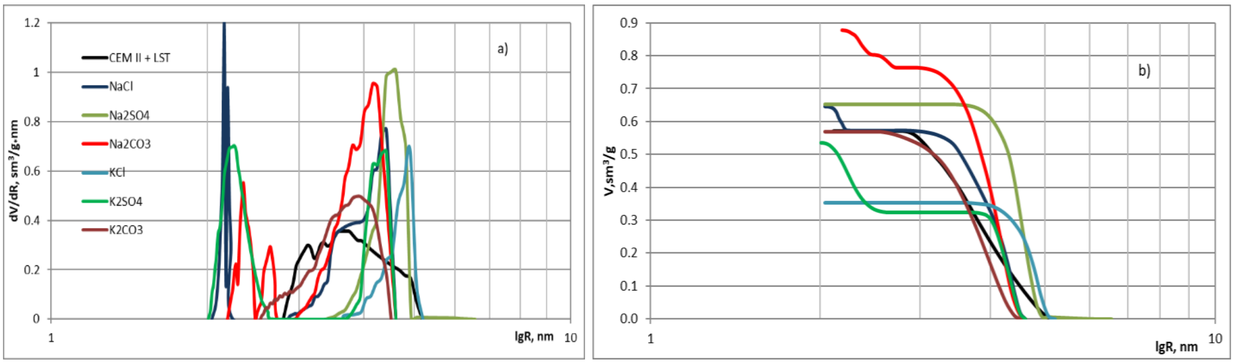

Fig. 4. Influence of complex admixtures based on LST on microporosity
(Slag Portland Cement, 1 day): a – pore size distribution; b – total pore volume

The distribution range expands from 2 to 55 nm. Admixtures of NaCl, K_2SO_4, and Na_2CO_3 contribute to the formation of high-density calcium hydrosilicates with characteristic gel micropore sizes.

The ratio of gel to capillary pores allowed for the determination of the efficiency coefficient K_{eff} as the ratio of dynamic microstructural indices:

$$K_{eff} = -\lg\left(\frac{|V_{cap1} - V_{gel1}|}{V_{total1}} \cdot \frac{V_{total0}}{|V_{cap0} - V_{gel0}|}\right), \qquad (1)$$

where V_{gel} is the volume of gel pores; V_{cap} is the volume of capillary pores, V_{total} is the total pore volume, index 1 corresponds to cement with admixtures, and 0 – without admixture.

The effectiveness of complex admixtures is determined by the combination of plasticizer and accelerator. As our studies have shown, for complex admixtures based on LST, potassium chloride is most effective for Portland cement, and sodium chloride for slag Portland cement (Fig. 6).

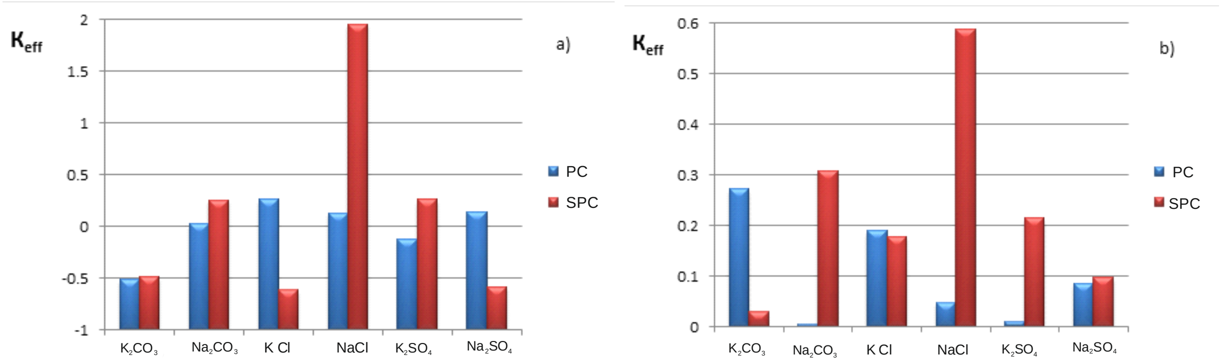

Fig. 6. Effectiveness of complex admixtures based on:
a – LST; b – C-3

For complex admixtures based on C-3, sodium chloride is also the most effective for slag Portland cement in terms of cement paste structure formation. For Portland cement, the combination of C-3 with potassium carbonate represents the most effective complex admixture option.

Chlorides are effective accelerators of cement hydration. They increase the ion concentration in the pore solution, promoting the rapid dissolution of C_3S and C_3A, which leads to faster formation of C-S-H gel and ettringite. Research [15] indicates that accelerators can initially form a more "open" or irregular structure due to rapid hydrate formation. However, the simultaneous use of a plasticizer (which reduces the water-to-cement ratio and improves dispersion) can compensate for this effect, leading to the formation of a more refined and denser porosity, which correlates with our obtained data.

Conclusions. The conducted research represents an important step in understanding the influence of complex chemical admixtures on the microstructure of cement paste. Specifically, the conclusion regarding the achievement of minimal pore radius and an optimal ratio of gel to capillary pores through the combination of plasticizer and accelerator, as well as the proposal of the K_{eff} coefficient as a microstructural index, open broad prospects for further research.

It is worth further investigating the specific mechanisms of their interaction with various cement minerals (alite, belite, C_3A, C_4AF) in the presence of plasticizers. A more detailed study is needed on precisely how these complex admixtures influence the formation, density, and internal structure of C- S-H gel – the main component determining concrete strength.

References

[1] S. Mahmoud, "Sayed Ahmed Statistical Modelling and Prediction of Compressive Strength of Concrete", *Concrete Research Letter*, 2012. vol. 3(2), pp. 452-458. https://www.researchgate.net/publication/233415183

[2] *Computational Modelling of Concrete and Concrete Structures*. Meschke, Pichler & Rots (Eds), EURO-C 2022 conference. Vienna, Austria, 2022. 767 p. https://library.oapen.org/bitstream/id/5ee90490-2d47-45fa-918f-3ff6dedacbd2/9781000644715.pdf

[3] A.A. Hilal, "Microstructure of Concrete", *High Performance Concrete Technology and Application*. InTech, Oct. 05, 2016. http://dx.doi.org/10.5772/64574.

[4] H.M. Jennings, "A model for the microstructure of calcium silicate hydrate in cement paste", *Cement and Concrete Research*., 30(1), pp.101-116, 2000. https://doi.org/10.1016/S0008-8846(99)00209-4.

[5] K.K. Aligizaki, *Pore Structure of Cement-Based Materials. Testing, interpretation and requirements*. New York: Taylor & Francis, 2006. https://api.pageplace.de/preview/DT0400.9781482271959_A38165198/preview-9781482271959_A38165198.pdf

[6] Jianzhuang Xiao, Zhenyuan Lv, Zhenhua Duan, Ch. Zhang, "Pore structure characteristics modulation and its effect on concrete properties. A review", *Construction and Building Materials,* 397(10), 132430, 2023. https://www.researchgate.net/publication/373588522.

[7] J. Plank, E. Sakai, C.W. Miao, C. Yu, J.X. Hong, "Chemical admixtures – Chemistry, applications and their impact on concrete microstructure and durability", *Cement and Concrete Research*, vol. 78, Part A, pp. 81-99, 2015. https://doi.org/10.1016/j.cemconres.2015.05.016.

[8] Z. Tuskaeva, S. Karyaev, "Influence of various additives on properties of concrete", *TPACEE-2019, E3S Web of Conferences*, 164, 14007, 2020. https://doi.org/10.1051/e3sconf/202016414007.

[9] W. Kujawa, I. Tarach, E. Olewnik-Kruszkowska, A. Rudawska, "Effect of Polymer Additives on the Microstructure and Mechanical Properties of Self-Leveling Rubberised Concrete", *Materials*, 15(1), 249, 2022. https://doi.org/10.3390/ma15010249.

[10] N. Asatov, "Concrete structure with complex additives", *IOP Conference Series Materials Science and Engineering*, 1030, 012014, 2021. https://doi.org/10.1088/1757-899X/1030/1/012014.

[11] V. Sopov, L. Pershina, L. Butskaya, E. Latorets, O. Makarenko, "The role of chemical admixtures in the formation of the structure of cement stone", *Transbud-2017. MATEC Web of Conferences*, 116, 01018, 2017. https://doi.org/10.1051/MATECCONF/201711601018.

[12] P. Sobhanipour, R. Cheraghib, A. A. Volinsky, "Thermoporometry study of coagulation bath temperature effect on polyacrylonitrile fibers morphology", *Thermochimica Acta*, no. 518, pp.101–106, 2011. https://doi.org/10.1016/j.tca.2011.02.015.

[13] A.V. Usherov-Marshak, V.P. Sopov, "Thermoporometry of cement stone", *Colloidal journal*, vol. 56, no. 4, pp. 600-603, 1994. https://www.researchgate.net/publication/293212305_Thermoporosimetry_of_cement_stone

[14] W. Hemminger, G. Höhne, H.-J. Flammersheim, *Differential Scanning Calorimetry*. Second Edition. Springer, 2003.

[15] A.F. Simedru, O. Cadar, A. Becze, D. Simedru, "Restructuring the Basic Design of Several Accelerator-Based Concrete Mixes by Integrating Superplasticizers", *Materials,* 17, 5582, 2024. https://doi.org/10.3390/ma17225582.

ФОРМУВАННЯ МІКРОСТРУКТУРИ ЦЕМЕНТНОГО КАМЕНЮ В ПРИСУТНОСТІ КОМПЛЕКСНИХ ХІМІЧНИХ ДОБАВОК

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Анотація. У статті експериментально досліджуються можливості технологічного регулювання параметрів мікроструктури цементного каменю та бетону шляхом введення хімічних добавок різної природи. На основі досліджень впливу хімічних добавок на процеси гідратації цементу та мікроструктуру цементного каменю було проведено порівняльну оцінку твердіння та пороутворення цементного каменю з прискорювальними, пластифікуючими та комплексними добавками.

Зокрема, дослідження зосереджено на впливі комплексних хімічних добавок, які включають суперпластифікатор С-3 (на основі нафталінсульфонату) та LST (лігносульфонат), у поєднанні з прискорювачами, такими як NaCl або KCl, Na_2CO_3, K_2CO_3, Na_2SO_4, K_2SO_4 на характеристики пороутворення під час твердіння двох типів цементу: портландцементу PC CEM I 42.5R та шлакопортландцементу SPC CEM II B-S 32.5 R. Ці цементи відрізняються своїм мінеральним складом, вмістом шлаку, а отже, швидкістю гідратації та структуроутворенням.

Було встановлено, що цементний камінь, пористість якого характеризується мінімальним радіусом пор та оптимальним співвідношенням між об'ємами гелевих та капілярних пор, може бути досягнутий шляхом комплексного застосування прискорювача та пластифікатора. Синергетичний ефект суперпластифікатора, що зменшує водоцементне співвідношення та покращує дисперсність частинок, а також прискорювач, що прискорює ранню гідратацію, сприяють утворенню покращеної структури пор.

Крім того, запропоновано новий підхід до оцінки ефективності модифікації структури цементного каменю з використанням коефіцієнта K_{ef}, який визначається як співвідношення між об'ємами гелевих та капілярних пор (співвідношення динамічних мікроструктурних індексів). Ця кількісна інформація щодо мікроструктури цементного каменю та меж її регулювання під впливом внутрішніх та зовнішніх факторів дозволила сформулювати концепцію щодо можливостей досягнення заданих властивостей бетону шляхом модифікації відповідних параметрів мікропористості цементного каменю.

Ключові слова: цементний камінь, мікроструктура, мікропористість, хімічні добавки, структуроутворення, радіус пор, розподіл пор за розмірами.

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