Research of porosity of a cement stone with a zeolite containing filler and a superplastic stifier

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Abstract. This research paper discusses the influence of the zeolite-containing filler of the Beltau deposit and the polycarboxylate superplasticizer on the formation of the porosity of the cement stone. The results of experiments to establish the effect of zeolite-containing filler and plasticizing additive on pore size distribution are graphically presented. The data obtained confirm the feasibility of using this type of filler in concrete.

1 Introduction

Design, development of new materials, improvement of the required property indicators, and comparative analysis and research of mechanical, physicochemical, structural, and other properties. As a result, the strength indicators of the materials being developed (ultimate strength in compression, tension, etc.) are established, the physicochemical parameters of the forming interactions occurring in the medium, the nature of the adhesive-cohesive bonds formed in the pore space (type of pores, dispersion, size distribution, the presence of conditionally closed pores, etc.) [1].

Materials with pores differ from dense materials in some properties: the ability to absorb or pass water through themselves to adsorb water vapor from the air. The high porosity of the composite provides low sound and thermal conductivity. However, for a certain group of materials (concrete, ceramic wall materials, special finishing materials, etc.), when solving the required strength problems, certain frost resistance and maximum impermeability of water and various gases must be provided [1].

Numerous studies have established that the physical and mechanical properties of cement stone such as strength, deformability, permeability, frost resistance, etc. are directly dependent not only on the presence of crystalline neoplasms in the structure of the cement stone but also on the size of pores, their configuration, and quantity. Concrete is a capillary-porous material permeated with pores and capillaries of various sizes [2, 3].

The knowledge gained from the study of the pore space in many respects allows predicting the material's behavior during further operation. In this aspect, how the pores of the cement stone are classified is of certain interest.

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Currently, there is no generally accepted method for dividing the pores of capillary-porous bodies by size. However, it can still be noted that this issue was most fully developed by M.M. Dubinin [2, 3]. The international organization IUPAK provides for the division of pores by size into micropores (less than 2 nm), mesopores (2-50 nm), and macropores (more than 50 nm).

The complete data on the influence of certain categories of pores on the properties of cement stone are presented in Table 1.

The classification shows that physical and mechanical parameters (strength and deformability), contraction deformations (shrinkage), special properties (water resistance, frost resistance, etc.) are largely determined by the emerging pore structure of the cement stone.

A large number of works are devoted to the formation of the structure of a cement stone in unfilled systems [3]. As for the filled ones, the influence of industrial waste and man-made products on the formation of the structure of cement stone has been studied to a certain extent. In this regard, it is of certain scientific interest to study the issues of structure formation of cement compositions modified with an active mineral additive of a certain dispersion from zeolite-containing rocks.

Table 1. Classification of pores by size in cement stone

Pore size	Characteristic	Condition of water in the pores	Properties of cement paste, which are influenced by the pore size
1000 – 15µm	Large spherical voids	Has bulk phase properties	Strength, permeability, frost resistance
15-0.05 µm	Large capillaries	Also	Also
50-10 nm	Capillaries are medium in size. Pores between particles	Moderate surface tension action	Strength, permeability, high humidity shrinkage
10 – 2.5 nm	Small (gel) capillaries	Strong surface tension action	Shrinkage
2.5 – 0.5 nm	Micropores, gel pores, pores between crystals	Strongly adsorbed, no menisci are formed	Shrinkage, creep
0.5 nm	Micropores are "interlayer"	Structural	Shrinkage, creep

This article shows the results of studies of the effect of zeolite-containing (ZCR) filler (natrolite) and superplasticizer on the formation of the pore structure of a cement stone.

2 Materials and methods

In the studies, Portland cement without additives from the Akhangaran cement plant, grade M400, was used as a binder (Table 2). Mineralogical composition: C₃S-58%, C₂S-14%, C₃A-7%, C₄AF-16%, CaSO₄-2%.

The ZCFC of the Beltau deposit (Central Kizilkum) with a specific surface SP-11A 3400 cm²/g. The chemical composition of ZCR.

The surfactant used was a polycarboxylate superplasticizer (SP) POLIMIX from ARMENT CONSTRUCTION CHEMICALS.

The water-reducing effect of SP is 30%, the optimal dosage is 0.8% of the binder mass. The porosity characterization of the cement stone was determined using a Thermo

Scientific Pascal 240 mercury porosimeter (Italy). For the experiment, samples of 20x20x20 mm in size were made and immersed in a CD3 dilatometer to form a vacuum on the evacuator. After the formation of a vacuum, the dilatometer was filled with mercury and immersed in the autoclave compartment of the porosimeter to obtain porograms. Porograms were calculated automatically using the SOLID EVO software, and the following characteristics were determined: specific pore volume (mm^3 / g), relative pore volume (mm^3 / g), and total porosity (%).

During the experiments, four types of compositions were made:

1. Composition № 1 - control composition of pure cement;
2. Composition № 2 - cement + ZCR (30%);
3. Composition № 3 - cement + joint venture (0.8%);
4. Composition № 4 - cement + ZCR (30%) + SP (0.8%);

The mixing of the binder components was carried out separately - first, the filler from ZCR ground to a specific surface of $3400 \text{ cm}^2 / \text{g}$ and cement were mixed with part of the mixing water, and then with the rest of the water and the additive. The cement-bonded particle board filler consumption is assumed constant and equal to 30% of the cement mass, and the SP dosage is 0.8%.

3 Results and Discussion

According to the shape, the pores in the cement stone are divided into closed (pores are rounded and isolated from other pores), channel-forming (pores are open at both ends and can be straight, worm-shaped and loop-shaped), and dead-end (open only at one end and can, has straight, worm-like, loop-shaped configuration). By origin, the pores in the cement stone are subdivided into the air, sedimentation (capillary, sedimentation), and contraction pores. Air pores are formed as a result of technological factors, sedimentation as a result of external and internal water separation. With external water separation, part of the mixing water goes out, forming a system of communicating capillaries, and the rest accumulates in the contact zones and contributes to the formation of sedimentation pores.

Contraction pores are formed due to the manifestation of contraction of the "cement-water" system during hardening of the cement stone. There is an assumption [3-7] that the contraction pores have sizes characteristic of capillaries. Of undoubted interest are studies on the formation of the structure of multicomponent systems "cement-mineral-additive-superplasticizer." The characteristics of the study of pore parameters are shown in Fig. 1, 2. Based on the processing of the experimental results shown in Fig. 1, 2, the characteristics of the pore structure of the studied samples were obtained (Table 3.). Analysis of these tables shows that compositions № 3, 4 differ from the control ones: with the introduction of a finely ground additive, insignificant changes in porosity are observed. The porosity of composition № 2 is reduced by 14.95%, the specific and relative volume by 21.53% relative to the control. The introduction of the filler helps to reduce the pore size in the region of 4.8682-0.1846 microns, which, according to the classification [2], [3-10], affect strength, frost resistance, and water resistance. In our opinion, a decrease in porosity in such systems occurs due to the formation of low-basic neoplasms due to interactions arising with the participation of active silica and alumina with calcium hydroxides.

Fig. 1. Specific pore volume by size of the studied compositions

In composition № 3, there is a significant decrease in porosity by 32.16%. Specific and relative pore volumes are reduced by 39.45%. In our opinion, this is due to the water-reducing ability of the SP. As a result, capillary porosity decreases, and a denser structure of the cement stone is formed.

Based on the classification [3], we can also conclude that pores less than 10 nm do not affect the mechanical properties. Dangerous pores that reduce strength, frost resistance, permeability, etc., are larger than 10 nm. Further, we carried out studies of the influence of individual pore categories in terms of size on the strength and durability of the cement stone (Figure 3).

Table 2. Characteristics of the porous structure of the test samples

Pore structure parameters	Structure №1	Structure №2	Structure №3	Structure №4
Total pore volume (mm ³ / g):	81.32	63.81	49.24	34.42
Total pore surface area (m ² / g):	6.576	5.112	4.908	3.269
Average pore diameter (μm):	0.0995	0.0388	0.0385	0.028
Total porosity of the sample,%	17.532	14.91	11.894	8.678

The best performance is observed in the composition № 4: the porosity of the cement stone decreases relative to the control by 50.5%. Due to a significant decrease in porosity, composition № 4 has the highest strength index. The reason for the change in the pore structure is, apparently, the transformation of Ca(OH)₂ into ow-base compounds due to interaction with active silica and a decrease in the amount of mixing water.

Fig. 2. Total porosity by size of the studied compositions

Figure 3 it can be seen that the dangerous porosity of composition № 1 is 16.663%. With the introduction of SCR microfiller, the dangerous porosity of the composition № 2 is reduced by 33.17% and is 11,135. The introduction of SP in the composition № 3 reduces the number of dangerous pores in the cement stone by 43.52%. In composition № 4, the dangerous porosity is reduced by 66.95% and reaches 5.507%.

Based on the classification [3], we propose to divide the capillary pores of the cement stone into the following three groups: 1. Macropillaries - 15-0.5 microns (affect strength, permeability, frost resistance); 2. Mesocapillaries - 50-10 nm (affect strength, permeability, and shrinkage at high humidity); 3. Microcapillaries - 10-2.5 nm (affect shrinkage). To establish the presence of capillary pores formed due to hardening of the multicomponent system cement + ZCR + SP, studies were carried out to determine the quantitative content of such pores in the developed composite (figure 4).

Fig. 3. Dangerous and safe pores of the investigated compositions

Comparing the pore structure of a cement stone with different content of modifying additives showed that the most favorable in reducing the macro-, meso- and microcapillaries increasing the strength of the cement stone is composition № 4.

Fig. 4. The number of macro-, meso- and microcapillaries of the studied compositions

4 Conclusions

The research results obtained can be summarized as follows:

- introduction into the mixture of a finely ground filler made from ZCR helps to reduce the porosity of the cement stone by 2.622%;
- introduction of SP into the mixture provides a significant increase in stone density and a decrease in porosity (by 5.638%);
- as a result of using a filler from ZCR + SP it helps to reduce the porosity by 8, 854% (50% in relation to the control).

The results obtained indicate the positive effect of the composition based on finely ground ZCR and CP based on polycarboxylate ethers on the formation of the required parameters of concrete properties and contributes to the creation of the necessary conditions for a deeper flow of hydration processes in the system "cement + water + CP + ZCR"

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