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ANALYSIS OF THE MICROSTRUCTURE OF CONCRETE FRACTURES IN STRUCTURES THAT WORK ON COMPRESSION AND ITS IMPACT ON STRENGTH

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Abstract. Comparative microanalysis and elemental analysis of the structure of chips of concrete composites of different strength from compressive structures were used. Analysis of the microstructure of concrete chips was performed using a scanning electron microscope from Oxford SU 70 using a CCD detector. Elemental analysis of objects was performed using energy-dispersive X-wave spectroscopy (EDC analysis). The method of energy-dispersive X-wave spectroscopy is used. The character of opening of cracks of concrete samples in the course of their destruction is analyzed. From the data of X-ray and spectral analysis it follows that in a series of samples of strength of 120 MPa in the process of hydration of clinker minerals during hardening of concrete a number of chemically active substances is formed. These are primarily potassium oxide hydrate, calcium silicate hydrate (HSC) and structural gel models such as Janite and Tobermorite. Modification of the concrete composite with a complex of MK and MTK create conditions for the conversion of unstable and soluble calcium hydroxide into a strong crystalline hydrate of calcium silicate.

The structure of concrete compacted in this form gives a significant increase in strength. The influence of ultrafine modifiers on the microstructure of cement stone formed during the operation of the structure and the strength of concrete are determined. The results of the scanning electron microscopy analysis show that the phase sizes differ slightly, but are not larger than ≈20 μm. Characteristic destruction of the sample with a strength of 120 MPa occurred in the main cracks, which develop due to the greater number of phases in contrast to the nature of the destruction of the sample with a strength of 50 MPa, which broke mainly on one structure. The complex of modifiers based on microsilica and metakaolin in the concrete mixture creates conditions for the conversion of unstable and soluble calcium hydroxide into a strong crystalline hydrate of calcium silicate. When using cement with a low content of C_3S less than ≈50% significantly complicates the production of high-strength concretes, in particular when using silica and metakaolin, because the effectiveness of these additives implies the presence of excess portlandite $Ca(OH)_2$ in the curing system, while systems with low C_3S content is characterized by a reduced content of $Ca(OH)_2$.

Keywords: concrete, compressive structures, ultrafine modifiers, energy-dispersion x-wave analysis, scanning electron microscopy.

Introduction. The implementation of a complex of physicochemical methods for diagnosing the state of the structure of concrete composites in structures is an urgent task today. Since the new approach to the chemical modification of the commercial concrete mixture poses the problems of substantiating the cause-and-effect relationships of structure formation and quality control of the raw material, which is a necessary condition for obtaining high-strength concrete.

The development of ways to reduce structural defects and limit the deformable properties of concrete becomes an important task for both research and engineering practice. In particular, this is

relevant for high-strength concrete composites, for which the filling density at the micro- and nanostructural level is an important characteristic. Among the technological factors that affect the formation of a concrete matrix of high structural strength and density is the modification of the concrete composite with a complex of finely dispersed modifiers based on amorphous condensed silica with a specific surface area of ≈250 m²/g [1]. Highly active pozzolans lead to a decrease in porosity and $Ca(OH)_2$ content, which, in turn, affects the generation of calcium hydrosilicates [2].

The paper analyzes data from scanning electron microscopy [3] of chips of concrete composites of different component composition and strength, which was determined experimentally. Energy dispersive X-wave spectroscopy was used to determine the elemental composition of the formed fracture phases.

Analysis of recent research and publications. The experience of international research [4-10] indicates that the structure of high-strength concrete is formed mainly from low-base calcium hydrosilicates (CSH-I) and such structural models of cement gel as Jenite and Tobermorite. However, there are a number of factors that can affect the physical and mechanical properties of concrete. First of all, these are microcracks caused by autogenous shrinkage [11-15], which significantly reduces the resistance of concrete to aggressive environments, and defects in the interphase transition zone between the cement matrix and large aggregate aggregates [16].

The purpose of the work is to substantiate the cause-and-effect relationships of the processes of concrete stone structure formation and their influence on strength indicators for physical and mechanical tests. For this purpose, two experimental recipes of concrete mixture from structures were selected.

Research materials and methods. To compare the structure, samples with a compressive strength of 50 MPa (sample #1) and 120 MPa (sample #2) were selected, which was modified with a complex of finely dispersed modifiers based on microsilica (MC) and metakaolin (MTK).

Analysis of the features of the microstructure of concrete chips was carried out using a scanning electron microscope of the Oxford SU 70 company using a CCD detector. Elemental analysis of objects was carried out using energy dispersive X-wave spectroscopy (EDX analysis).

A high vacuum (10-7 mBar) was created in the microscope chamber to eliminate the interaction of electrons with air molecules. To eliminate impurities and create a vacuum, the chamber was additionally equipped with a vessel cooled by liquid nitrogen, designed to condense impurities and cool the X-wave radiation spectrum analysis detector.

Physical and mechanical tests of concrete samples were carried out in accordance with current normative documents DBN B.2.7-64, DBN B.2.7-65, DBN B.2.7-69, DSTU B B.2.7-96, DSTU B B.2.7-114. The determination of compressive strength was carried out on a P250 hydraulic press, the loading of the samples was carried out continuously at a speed that ensures an increase in the calculated stress in the sample until its complete destruction within (0.6 ±0.4) MPa/s.

Research results. The microstructure of the concrete composite plays a decisive role in the formation of the mechanical properties of the concrete composite. With high stress gradients that occur in reinforced concrete structures, thermal shocks, freezing of water, the homogeneity, dispersion and phase composition of the cement matrix affects the development and character of deformations.

From the scanning electron microscopy data in Fig. 1 and energy dispersive X-wave spectroscopy Fig. 2. the list and relative content of elements characterizing the phase composition of the fracture surface of sample No. 1 was determined. The list of elements in Table 1 and their percentage content indicates the presence in the concrete matrix of fractured calcite $CaCO_3$, which was formed as a result of the reaction of calcium oxide with atmospheric carbon dioxide in the presence of moisture and has a spherical structure with low adhesion and cohesion to cement stone. High concentrations of calcite on the fracture surfaces are present due to the fact that the fracture of the concrete structure mainly occurs in areas of lower strength, in which such a phase is present, which is confirmed by EDH analysis data. From the results of EDH spectroscopy, it can be assumed that the greater the dispersion of the phase components of calcite, the higher the concentration of aluminum atoms and the lower the concentration of silicon atoms.

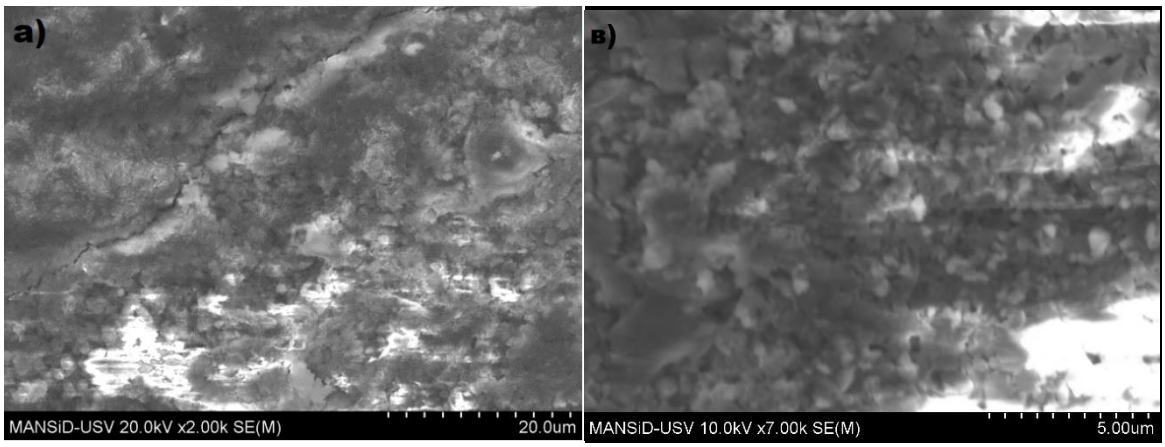

Fig. 1. Electronic raster images of the surface of concrete fractures from structures of sample No. 1 of various scales

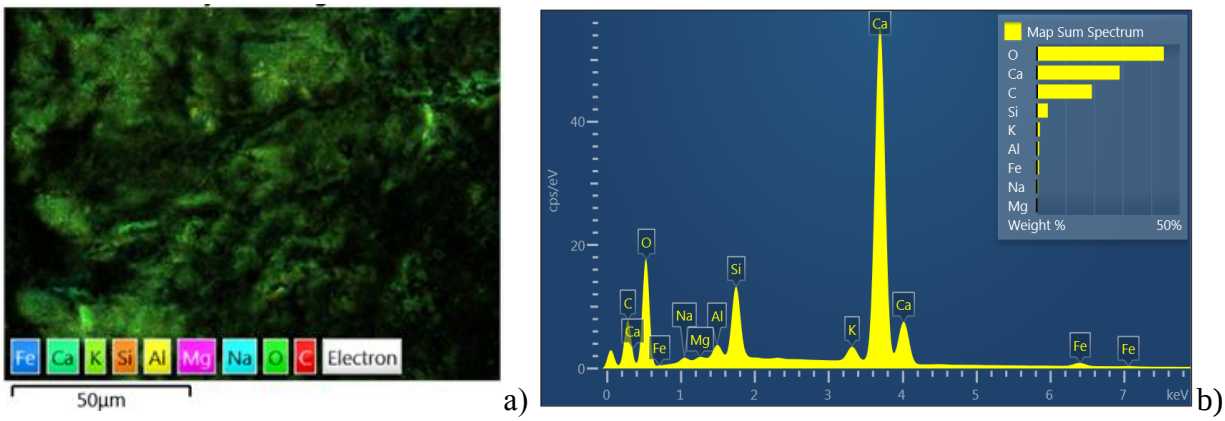

Fig. 2. Elemental map of concrete sample No. 1 according to the results of EDH analysis (a) and the results of energy dispersive X-wave analysis (b)

Table 1 – Elemental composition of broken concrete of sample No. 1

Element	Apparent Concentration	Wt%	Standard Label
C	108.28	**19.27**	C
O	285.15	**44.50**	SiO_2
Na	5.13	0.45	Albite
Mg	2.27	0.21	MgO
Al	10.60	0.82	Al_2O_3
Si	55.79	3.86	SiO_2
K	19.90	1.07	KBr
Ca	495.17	**29.03**	Wollastonite
Fe	10.54	0.79	Fe

In Fig. 3, 5 show fragments of raster electron microscopy images of sample #2. Elemental analysis in Table 2, which indicates the presence of mainly low- ($CaO/SiO_2 \approx 1.8$) and high-basic ($CaO/SiO_2 \approx 2.6$) phases of calcium hydrosilicates, as well as unreacted microsilica particles, in the concrete structure. Compared to sample No. 1, the structure of sample No. 2 is characterized by a greater number of phases and their heterogeneity. It can be assumed that this is what significantly increases the compressive strength for sample #2, which is associated with a higher specific surface area of pozzolan particles, which are able to react faster with $Ca(OH)_2$, forming a denser microstructure.

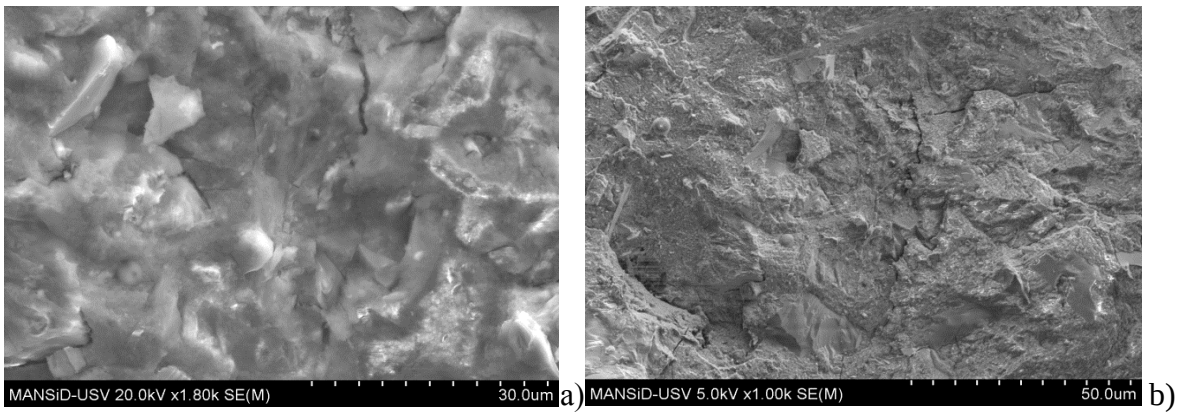

Fig. 3. Electronic raster images of the fracture surface of concrete from structures of sample No. 2 of various scales

The failure of the concrete sample under a pressure of 120 MPa occurred with the formation of fractures with a predominant amount of calcium hydroxides, which are denser and stronger than the structure prevailing in the fractures of samples No. 1, in which the fracture occurred through calcite with a Mohs hardness of 3. All phases of hydration in the second sample is more evenly distributed, unlike the first. From the results of the analysis of scanning electron microscopy, it follows that the sizes of the phases differ slightly, but are not larger than ≈20 μm. The characteristic failure of sample No. 2 occurred along the main cracks, which develop due to a greater number of phases, in contrast to the nature of the failure of sample No. 1, the failure of which occurred mainly along one structure.

From the X-ray and spectral analysis data shown in Fig. 4, it follows that in a series of samples with a strength of 120 MPa, a number of chemically active substances are formed in the process of hydration of clinker minerals during concrete hardening. These are primarily potassium oxide hydrate, calcium silicate hydrate (GSK) and such structural gel models as Jenite and Tobermorite. Modification of the concrete composite with the MK and MTK complex creates conditions for the transformation of unstable and soluble calcium hydroxide into strong crystalline calcium silicate hydrate. The structure of concrete compacted in this way gives a significant increase in the strength index.

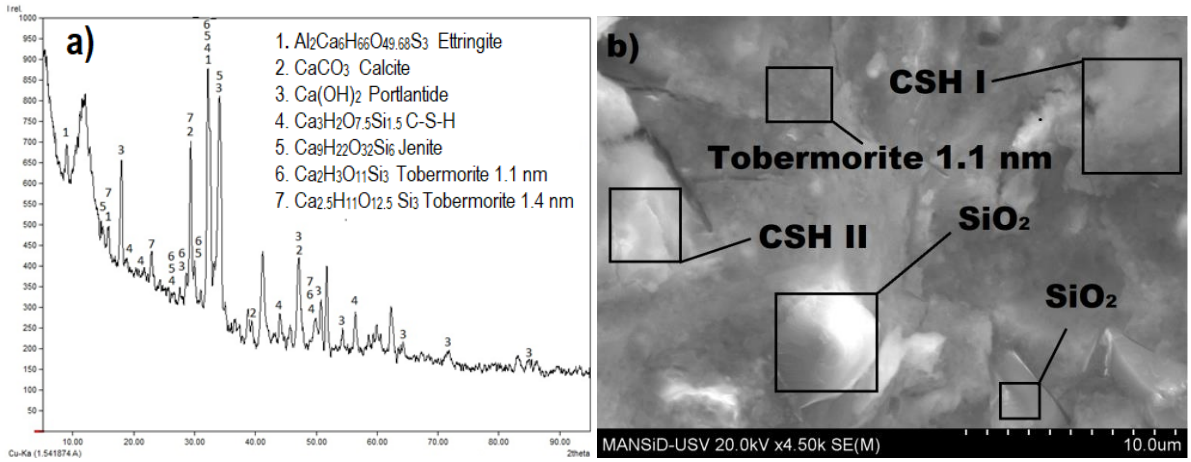

Fig. 4. X-ray analysis of concrete (a), and SEM image of the microstructure of a section of the concrete surface of sample #2 (b)

In addition, when MK is introduced into the liquid phase of the cement dough, a silicon oxide gel is formed, which subsequently adsorbs free Ca2+ and OH ions with the formation of weakly crystallized low-basic HSCs. Under limited conditions, low-base HSCs lead to an increase in the number of gel pores and a decrease in open porosity. Such closed pores prevent the propagation of cracks in the depth of the solid body, because the stress drops very quickly from high values on the surface of the pore to low values in its inner parts, that is, small closed pores prevent the process of material destruction.

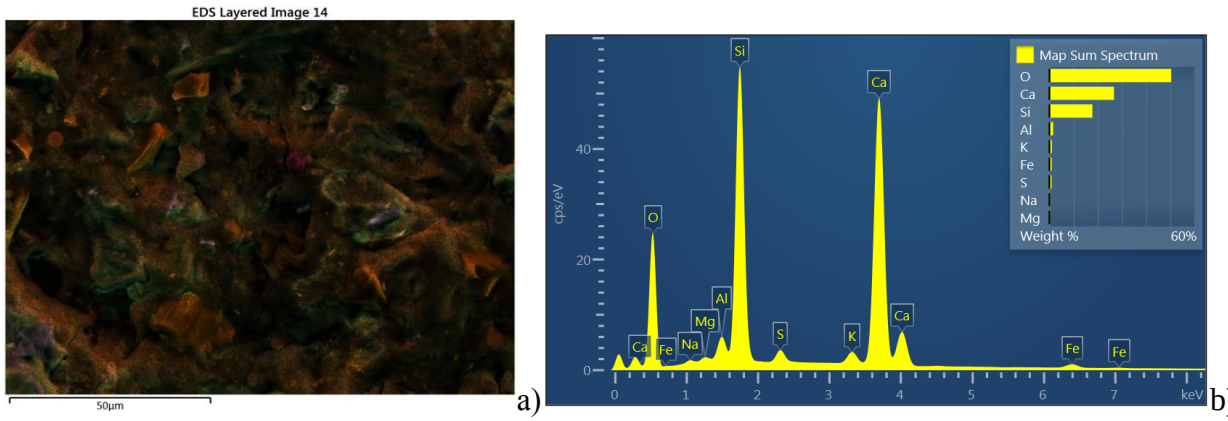

Fig. 5. Elemental map of the concrete sample of formulation No. 2 according to the results of EDH analysis (a) and the results of energy dispersive X-wave analysis (b)

Table 2 – Elemental composition of fracture of the concrete sample of formula #1

Element	Apparent Concentration	Wt%	Standard Label
O	**393.92**	**50.40**	**SiO_2**
Na	3.87	0.34	Albite
Mg	3.43	0.31	MgO
Al	19.98	1.52	Al_2O_3
Si	**257.48**	**17.81**	**SiO_2**
S	12.53	0.90	FeS_2
K	17.78	1.03	KBr
Ca	**439.97**	**26.75**	**Wollastonite**
Fe	12.70	0.94	Fe

Conclusions: a complex of modifiers based on microsilica and metakaolin in the concrete mixture create conditions for the transformation of unstable and soluble calcium hydroxide into strong crystalline calcium silicate hydrate. The concrete structure compacted in this way increases the strength and durability of reinforced concrete structures. In addition, when MK is introduced into the liquid phase of the cement dough, a silicon oxide gel is formed, which subsequently adsorbs free Ca2+ and OH ions with the formation of weakly crystallized low-basic HSCs. Structural models of cement gel, such as Tobermorite and Jenite, are essentially a complex nanomaterial consisting of many separate layers of molecules with different properties, which are formed into a kind of structural composite. Determination of the physical and mechanical properties of these structures requires a more in-depth study using already existing diagnostic methods.

It should also be noted that the use of cement with a low C_3S content of less than ≈50% significantly complicates the production of high-strength concrete, in particular when using silica and metakaolin, since the effectiveness of the use of these additives requires the presence of excess portlandite $Ca(OH)_2$ in the hardening system, while how systems with a low content of C3S are characterized by a reduced content of $Ca(OH)_2$.

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АНАЛІЗ МІКРОСТРУКТУРИ ЗЛАМІВ БЕТОНУ В КОНСТРУКЦІЯХ, ЯКІ ПРАЦЮЮТЬ НА СТИСК ТА ЇЇ ВПЛИВ НА МІЦНІСТЬ

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Анотація. Проведено порівняльний мікроаналіз та елементний аналіз структури сколів бетонних композитів різної міцності з конструкцій, які працюють на стиск. Для порівняння структури вибрано зразки із міцністю на стиск 50 МПа, та 120 МПа який модифіковано комплексом дрібнодисперсних модифікаторів на основі мікрокремнезему (МК) та метакаоліну (МТК). Аналіз особливостей мікроструктури сколів бетону проводили за допомогою скануючого електронного мікроскопа фірми Oxford SU 70 з використанням CCD-детектора. Елементний аналіз об'єктів проводився за допомогою енергодисперсійної Х-хвильової спектроскопії (ЕДХ-аналізу). Використано метод енергодисперсійної Х-хвильової спектроскопії. Проаналізовано характер розкриття тріщин бетонних зразків в процесі їх руйнування. З даних Х-променевого та спектрального аналізу слідує, що в серії зразків міцності 120 МПа в процесі гідратації клінкерних мінералів при твердінні бетону утворюється ряд хімічно активних речовин. Це в першу чергу – гідрат калію окису, гідрат силікату кальцію (ГСК) та такі структурні моделі гелю, як Дженіт і Тоберморіт. Модифікування бетонного композиту комплексом МК і МТК створюють умови для перетворення нестабільного і розчинного гідроксиду кальцію в міцний кристалічний гідрат силікату кальцію.

Ущільнена в цьому вигляді структура бетону дає значний приріст показника міцності. Визначено вплив ультрадисперсних модифікаторів на утворену в процесі експлуатації конструкції мікроструктуру цементного каменю та міцність бетону. З результатів аналізу скануючої електронної мікроскопії слідує, що розміри фаз дещо відрізняються, але не є більшими ніж ≈20 мкм. Характерне руйнування зразка з міцністю 120 МПа відбулося по магістральним тріщинам, які розвиваються через більшу кількість фаз на відміну від характеру руйнувань зразка з міцністю 50 МПа, злам якого відбувся переважно по одній структурі. Комплекс модифікаторів на основі мікрокремнезему та метакаоліну в бетонній суміші створюють умови для перетворення нестабільного та розчинного гідроксиду кальцію в міцний кристалічний гідрат силікату кальцію. При використання цементу з низьким вмістом C_3S меншим за ≈50% значно ускладнює одержання високоміцних бетонів, зокрема при використанні кремнезему і метакаоліну, оскільки ефективність застосування цих добавок передбачає наявність в тверднучій системі надлишкового портландиту $Ca(OH)_2$, в той час як системи з низьким вмістом C_3S характеризуються зниженим вмістом $Ca(OH)_2$.

Ключові слова: бетон, конструкції які працюють на стиск, ультрадисперсні модифікатори, енергодисперсійний х-хвильовий аналіз, скануюча електронна мікроскопія.

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