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Structure and properties of modified shungite concrete during electrode heating

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Abstract. Concrete composition modifying by different electrically conductive components is one of less laborious but relatively effective methods between wide variety of electrode concrete heating effectiveness improvement methods. The purpose of this study is investigation of special aspects of cement systems modified by powdered shungite (Ssp 400 m2/kg) in combination with active mineral and plasticizing admixtures that harden under electrode heating at below zero temperatures. By the method of differential thermal analysis anomaly of exothermic reaction of cement stone specimens was discovered, that is due to formation of hydrated calcium silicate C2SH (A) discovered by the method of quantitative XRDA, and is verified by results received from scanning electron microscopy method, which among other factors provides higher strength and low permeability to these composites. Stability of cement systems modified by shungite and curing under electrode heating has been proved.
Keywords: concrete, electrically conductive mineral, shungite, electrode heating, percolation, structure

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1. INTRODUCTION

One of the disadvantages of electrode heating that limits its widespread application in construction industry is increase of power costs conditioned by increase of electric resistance of concrete because of decrease of volumetric content of electrolyte, mainly, of chemically unbound water, which is caused by conduct of hydration processes and its evaporation under heating.

To deal with the given problem different methods of electrode heating effectiveness increase find application, that are based on introduction of electrically conductive particles to raw mixes (steel fiber, mineral carbon-contained particles et al.). In the paper by Golovnev S.G., Molodtsova B.A., Koval S.B. it is shown that existence of steel fibers considerably varies value and nature of the change of

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specific electric resistance that differs by more evenly behavior and much lesser rate of its increase with time in comparison with original composition [1]. In the papers [2,3] improvement of the effectiveness of electrode heating of steel fibers reinforced concrete is confirmed by computational simulation method. In the paper [3] it was demonstrated that modeling of temperature fields gives an opportunity to locate heating loss and to correct characteristics of heating for improvement of the effectiveness of electrode concrete heating. During introduction of steel fibers to the mix (from 0 to 4 %) value of electric conductivity of steel fiber reinforced concrete at regular fibers distribution linearly increases [4]. The disadvantages of steel fibers using in the capacity of electrically conductive particles are complication of its regular distribution in the volume of concrete and, correspondingly, homogeneity of percolation effect, and also relatively high cost.

Another way of giving electrically conductive properties to composites is based on introduction of carbon-contained particles to its composition [5-7]. A number of studies [8–14] shows an opportunity of carbon nanotubes application for electrically conductive properties increase, however, high cost and complication of its regular distribution of carbon nanotubes in composite volume confine the scope of practical use of this technological concept.

Analogous concepts of giving electrically conductive properties to composites can be observed in a series of studies oriented to solution of a problem of critical infrastructure roads heating (airports, highly traveled by people and transport areas), where carbon particles [15-17], graphite powders [18], steel, copper and aeneous turnings [19, 20] are used in the capacity of electrically conductive components.

According to our reckoning, more effective and applicatory way of concrete electric conductivity increase in technology of electrode heating is introduction of powdered (Ssp 100-500 m2/kg) carbon-contained particles, for example, shungite, to concrete mix [21-25], including using active mineral [26–33], chemical and organomineral additives [34-37]. In previously completed studies we defined optimal degree of fineness (Ssp 400 m^2/kg) and content of shungite (5 % by mass of cement) that provide percolation effect during electrode heating [38].

The papers of Lukutsova N.P., Pykin A.A [39], Kravchenko T.G. [24], Shilin A.D. [40,41] and others are devoted to development and investigation of micro- and nanodispersed admixtures based on shungite-contained rocks for concrete. In the papers [39,42] it is observed that application of admixture with desired content of shungite filler in the quantity of 5% in the composition of fine grained concrete leads to concrete compressive strength improvement in 3 days of hardening by a factor of 4.4 over test composition, in 28 days – by a factor of 1.5. The paper [43] shows positive effect of carbon-siliciferous nanomodifier (CSNM) synthesized by the way of ultrasonic material dispersion made of riddlings after crushing of shungite-contained rocks of the III kind from Zazhoginskoe occurrence (Karelia) on the properties of cement stone (CS) and fine grained concrete (FGC). Ecological safety of this nanomodifier development technology is proved. According to the data from XRDA it is found that during introduction of CSNM in the quantity of 10 % redistribution of portlandite in hardening CS appears. In 1 day of CS hardening reflection intensity of portlandite is dramatically enhanced from 203 to 850 pps, further in 3 days of hardening of CS its decrease from 695 to 525 pps appears, in 7 days – from 592 to 426 pps, in 28 days of hardening – from 332 to 213 pps. Structure of CS with CSNM at 28 days differs by fibrous columnar crystals with the length from 0.5 to 10 μm, with the width from 0.3 to 1.5 μm existence in cracks and micropores. Morphology of these crystals specific to hydrated calcium silicate of the type CSH (I). The authors established that formation of additional quantity of hydration products, that help to structure consolidation and CS strength improvement, appears as a result of interaction of intensively producing portlandite with amorphized surface of siliciferous phase of modifier. At the same time carbonic nanoparticles serve as crystallization centres of new growths during hardening of cement system, which promotes acceleration of setting and hardening of cement-water paste. Maximum growth of CS strength can be observed during introduction of CSNM in the quantity of 10% by mass of cement. In addition, at 1st day of hardening strength was increased by a factor of 2.4, at 28th day – by a factor of 1.6. At the same time introduction of CSNM to FGC in the quantity of 10% promotes decrease of medium sized pores by a factor of 2 and decrease of total porosity – from 17.8 to 13.6 %, which arises from formation of cement matrix of additional quantity of new growth in pore volume that promote consolidation of concrete structure.

Without reducing relevance of discussed above studies it should be noted that special aspects of structure formation and properties of concrete modified by powdered shungite in combination with active mineral and plasticizing admixtures under electrode heating are underinvestigated, which represents substantial interest for scientific rationale of technological concept that we have suggested [22].

The purpose of this study is investigation of special aspects of cement systems modified by powdered shungite (S_{sp} 400 m^2/kg) in combination with active mineral and plasticizing admixtures that harden under electrode heating at below zero temperatures.

Object of research – modified shungite-contained cement composite hardening under electrode heating.

Subject of research – morphology of cement stone, phase composition of hydrated new growths, pore structure and physico-engineering properties of concrete.

2. METHODS AND MATERIALS

In the capacity of raw components for production of cement stone and concrete hardening under electrode heating we used the following ones:

1) portland cement (PC) CEM I 42.5N produced by OAO "Sukholozhsktsement" corresponding to GOST 31108-2016, with the following material and chemical composition: SiO_2 – 21.0; Al_2O_3 – 4.8; Fe_2O_3 – 3.9; CaO – 61.7; MgO – 2.8; alkali – 0.7; Cl – 0.012. Selection of portland cement of given type is conditioned by popularity and accessibility, widespread use in the capacity of binder on concrete mix plants, and also due to lack of mineral admixtures in its composition, which helps assess the impact of powdered shungite on hydration products and properties of cement compositions hardening under electrode heating at negative free air temperature more nearly.

2) fractionated quartz sand of Kamsko-Ustinskoe occurrence of the Republic of Tatarstan, fulfilling conditions of GOST 8736-2014.

3) granite macadam with fraction 5-20 of A sort made according to TS 5711-006-00186938-2017 produced by AO "EVRAZ Kachkanarskij gorno-obogatitel'nyj kombinat".

4) metakaolin MKZHL produced by ZAO "Plast Rifei" according to 5729-097-12615988-2013, with specific surface 1357 m^2/kg received after heat treating of enriched kaolin of ZHuravliniy log occurrence in the Chelyabinsk Region with the following chemical composition: Al_2O_3 – 42.0 %; SiO_2 – 55.8 %, Fe_2O_3 – 0.7 %, TiO_2 – 0.4 %; K_2O – 0.9 %; Na_2O – 0.05 %; CaO – 0.15 %.

5) plasticizing admixture (PA) – hydrous solution of polycarboxylate ester "Glenium Ace 430" produced by OOO "BASF Stroitelniye sistemy" with density at 20°C – 1.06 g/sm^3, pH – 4-7.

6) powdered shungite of Zazhoginskoe occurrence (Karelia Republic) produced by OOO NAUCHNO-PROIZVODSTVENNYJ KOMPLEKS "KARBON-SHUNGIT", Petrozavodsk, with the following chemical composition: SiO_2 – 57.0 %; TiO_2 – 0.2 %; Al_2O_3 – 4.3 %; MgO – 1.2 %; CaO – 0.3 %; Na_2O – 0.2 %; K_2O – 1.5 %; S – 1.5 %; C – 28.0 %; H_2O – 3.0 %. Shungite grinding was made by means of spring-loaded mill to the value of specific surface equal to 400 m^2/kg.

7) potable tap water meeting requirements of GOST 23732-2011.

For experimental investigation we have blended shungite-contained concrete mixes [22] and cement stone samples that present matrix of the following compositions:

Sample 1 – check composition (PC-370 kg, fine aggregate – 444 kg, coarse aggregate – 1000 kg);

Sample 2 – composition modified by shungite in the quantity of 5 % by mass of cement;

Sample 3 – composition modified by metakaolin and PA "Glenium Ace 430" in the quantity of 10% and 1 % by mass of cement correspondingly;

Sample 4 – composition modified by shungite, metakaolin and PA "Glenium Ace 430" in the quantity of 5%, 10 % and 1 % by mass of cement correspondingly.

Concrete heating was made at sub-zero air temperature, schematic of electrode heating is shown in fig. 1.

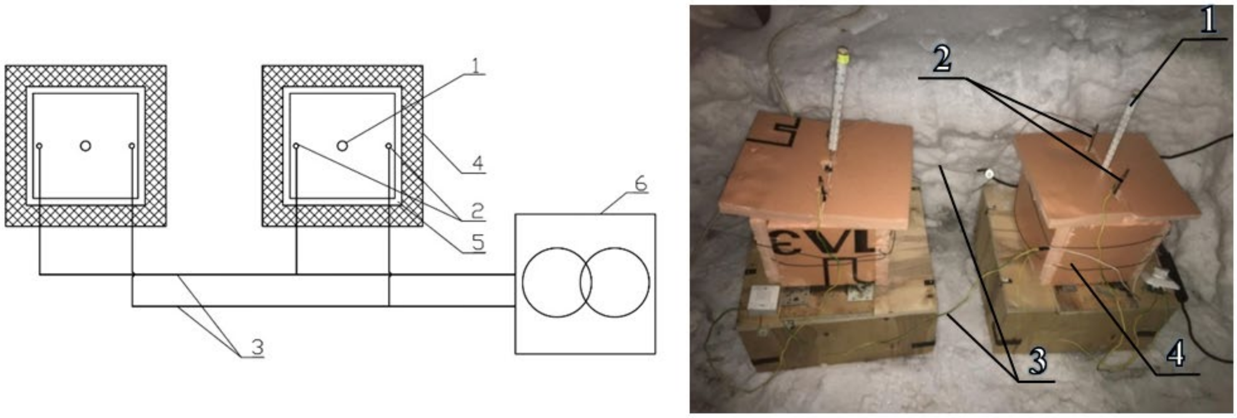

Fig. 1. Schematic of electrode heating of concrete hardening at sub-zero air temperature: 1 – thermometer dipped in concrete body; 2 – electrodes; 3 – conducting wires; 4 – thermal insulation, 5 – frame, 6 – power converter.

Pore structure of concrete was studied through GOST 12730.4-78, physico-engineering properties – through GOST 10180-2012.

Complex thermal analysis was made by means of NETZSCH STA 449 F3 Jupiter apparatus with permission TG – 0,1 μg, DSK < 1 μW. Lidded platinic crucibles were used as specimen's holding tool, calcined aluminum oxide was reference standard. In the course of investigations thermogravimetric (TG), differential thermogravimetric (DTG), differential thermal (DT) and temperature (T) curves were registered.

X-ray diffraction analysis (XRDA) was made by means of X-ray diffraction meter D8 ADVANCE (Bruker Axs) with Bragg-Brentano-Geometrie in the interval of angles equal to 5-65° 2θ and with spin speed of goniometer equal to 1°/min. The specimens were prepared by means of powder pressing of investigated substance in disk-shaped cuvette. Diffraction patterns that we have received were processed with the use of EVA program integrated to software of diffractometer called DiffractPlus. Pfase composition is determined through the use of international base of X-ray evidence PDF-2.

Electron-microscopic analysis was carried out with the use of field-emission scanning election microscope called Merlin (Carl Zeiss) equipped with spectrometer of energy dispersion named AZtec X-Max (Oxford Instruments). Resolution of spectrometer is 127 eV.

Definition of concrete waterproofing was made by means of "AGAMA-2PM" implement produced by "VNIR" company according to GOST 12730.5-2018. Operating principle of this implement based on pressure measuring in chamber with pre-vacuum that increases due to natural air penetration into the chamber through test material (concrete). Integrated electronic microprocessor provides recalculating of measured results of concrete resistance to air penetration and concrete watertightness grade (W from 0 to 20) according to GOST 12730.5-2018.

Concrete strength test that hardens under electrode heating and normal curing conditions was carried out on cube specimens with the size of 10x10x10 cm in accordance with GOST 10180-2012 by the use of compression-testing machine IP-1000.

Freeze-thaw resistance was determined at cube specimens with dimensions of 10x10x10 cm in accordance with GOST 10060-2012 "Concretes. Methods for determination of frost-resistance" [44]. The test was carried out in freezing compartment "KMD – 0.15" meant for carrying out the control of freeze-thaw resistance by accelerated (the third) method at the temperature minus (50±2) ^{o}C. Cube concrete test specimens before strength test and main concrete samples before freezing were saturated by 5% hydrous solution of sodium chloride with the temperature (20±2) ^{o}C.

3. RESULTS AND DISCUSSION

On the first stage of the research pore structure of initial and modified shungite concrete was observed. Concrete modifying by powdered shungite, AMA and PA decreases total porosity and materially changes pores structure (Table 1).

Table 1. Pore structure parameters of concrete compositions under investigation after electrode heating.

Concrete composition	Pore structure parameters				
	Full pore volume, (P_f)	Volume of open capillary pores, (P_o)	Volume of open noncapillary pores, (P_{no})	Volume of relatively closed pores, (P_c)	Microporosity rate, (P)
Initial	20.98	10.65	0.93	9.4	0.79
Shungite – 5%	20.86	10.42	0.84	9.6	0.91
AMA – 10%, PA – 1%	17.26	6.61	0.45	10.2	1.79
Shungite – 5%, AMA –10%, PA – 1 %	15.69	4.47	0.32	10.9	1.95

Introduction of powdered shungite into the control concrete composition decreases full pore volume from 20.98 % to 20.86 %, reduction of volume of open capillary pores from 10.65 % to 10.42 % and volume of open noncapillary pores from 0.93 % to 0.84% are observed, at the same time volume of relatively closed pores increases from 9.4 % to 9.6 % and microporosity rate also increases from 0.79 % to 0.91 %. Introduction of powdered shungite into the composition modified by AMA and PA decreases total porosity and highly changes pore structure. Reduction of full pore volume from 17.26 % to 15.69 % is observed. During simultaneous decrease of total porosity material redistribution of open capillary, open noncapillary and relatively closed pores volume appears. In that way, volume of open capillary pores decreases from 6.61 % to 4.47 %, volume of open noncapillary pores decreases from 0.45 % to 0.32 %, volume of relatively closed pores increases from 10.2 % to 10.9 % and microporosity rate increases from 1.79 to 1.95.

Obtained results accord with [43], and also with findings that we have obtained through studies of physical and mechanical properties where average density and strength of modified CS at 28 days of hardening are higher in comparison with check sample (by 5.67% and 14.63% correspondingly), which shows the effectiveness of using powdered shungite, AMA and PA for concrete structure modifying that subjected to electrode heating.

On the second stage we have undertaken studies of CS samples with the use of differential thermal analysis. Analysis of endo- and exothermic effects is shown in figures 2-5 in a form of thermograms, thermogravimetric (TG) and differential thermogravimetric (DTG), differential thermal (DTA) and differential calorimetric (DC) curves of cement stone specimens.

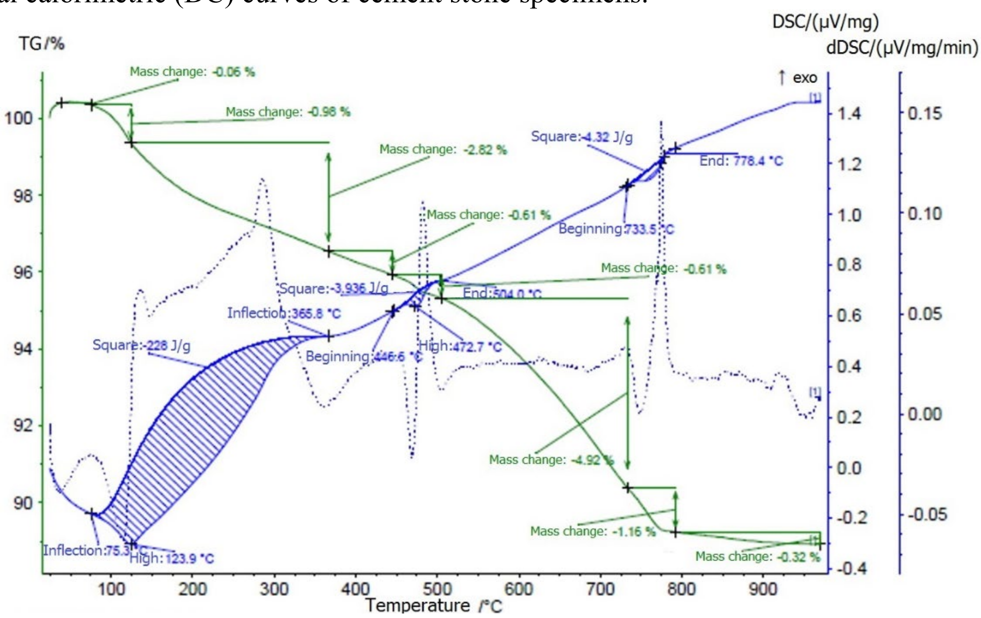

Fig. 2. Thermogram of CS of check specimen (sample No.1).

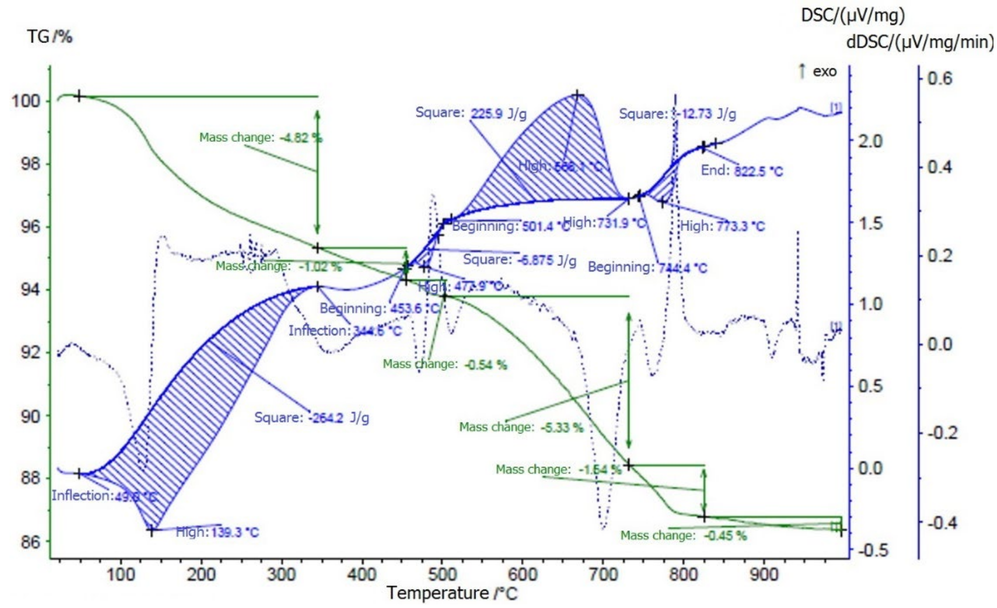

Fig. 3. Thermogram of CS specimens modified by powdered shungite (sample No.2).

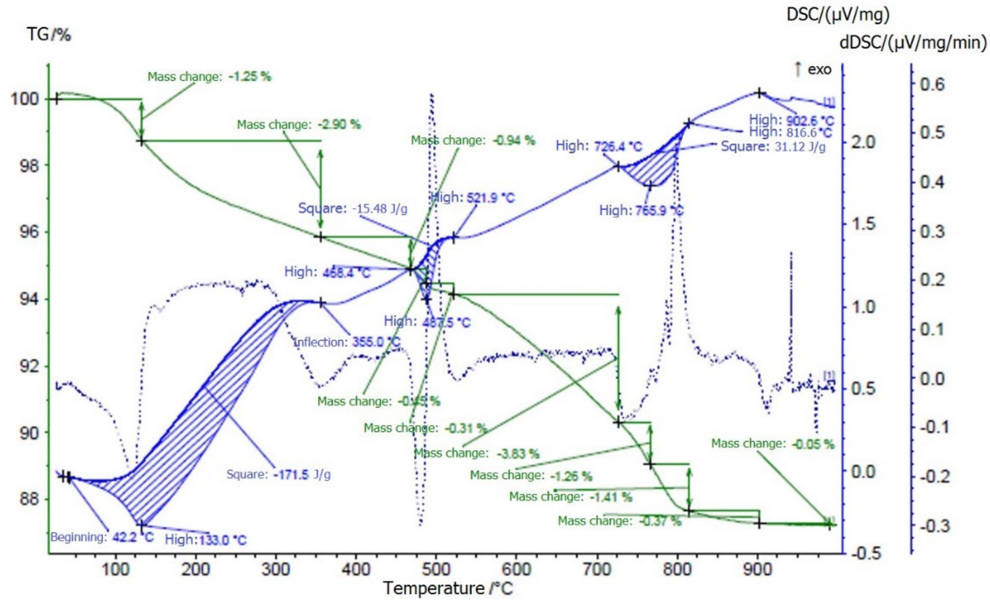

Fig. 4. Thermogram of CS specimens modified by PA and AMA (sample No.3).

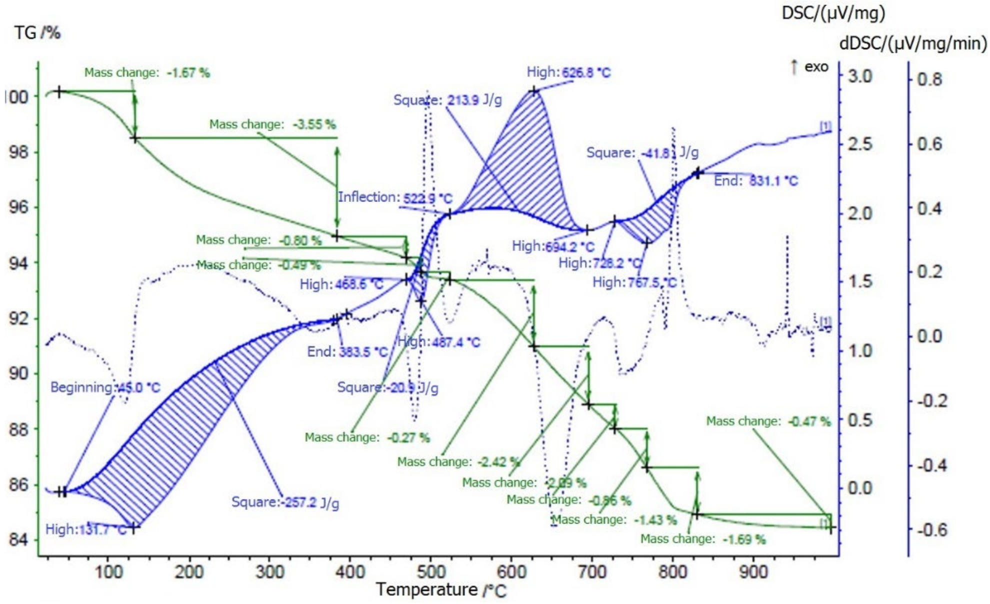

Fig. 5. Thermogram of CS modified by shungite, PA and AMA (sample No.4).

As we can see in fig. 2-5, for all samples of CS three main endothermic effects typical for these systems can be found: the first one with the maximum at temperature 123.9-139.3 °C resulting from removal of adsorbtion water from gel hydration products and crystallization water from hydrated calcium sulfoaluminate; the second one with the maximum at temperature 472.7 – 487.5 °C conditioned by dehydration of calcium hydroxide [45]; the third one with the maximum at temperature 733.5 – 773.9 °C resulting from dissociating of calcium carbonate and decompounding of calcium silicate hydrate. Along with endothermic effects in specimens of CS with addition of powdered shungite (fig. 3) and modified by shungite, AMA and PA (fig. 5) exothermic reaction appears that connected with full burn-off of shungite carbon at temperature 624.2 – 731.9 °C, which is coherent with research results obtained by other scientists [46]. For the specimen of CS with shungite addition (sample No.2) maximum value of exothermic effect is achieved at temperature 626.8 °C, for the specimen modified by shungite, AMA and PA (sample No.4) – at temperature 566.1 °C.

Area of endothermal effects (of the specimen with addition of shungite – 264.2 J/g, 6.88 J/g, 12.73 J/g; for cement stone modified by AMA and PA – 171.5 J/g, 15.48 J/g, 31.12 J/g; for cement stone modified by shungite, AMA and PA – 257.2 J/g, 20.9 J/g, 41.8 J/g), is higher in comparison with the check specimen (228 J/g, 3.94 J/g, 4.32 J/g), which shows more decompounding new growths in modified compositions of cement stone, and more complete conduct of hydration processes. It leads to improvement of physical and mechanical properties of concrete under electrode heating at cold-weather concreting in comparison with initial unmodified composition. Increase of entalphy of the second endoeffect that concerned with dehydration of portlandite for modified specimens is probable connected with increase of hydration products volume of the present compositions.

Modified compositions of cement stone are characterized by large mass change for the first and the third endoeffects in comparison with check specimen, which confirms existence of higher quantity of hydrated calcium silicate in modified compositions, that promote the increase of strength values of composites.

By means of differential thermal analysis difference of exothermic effects of samples No.2 (CS with shungite) and No.4 (CS with shungite, AMA and PA) was found. At the same time the sample No.4 is characterized by less square by 5.3% of exotherm (213.9 J/g) in comparison with the sample No.2 (225.9 J/g), and also less (by 15.4%) loss of mass, which arises from new chemical bonds and new growths formation in the presence of binder, shungite, plasticizers and AMA. On the next stage of the research X-ray diffraction analysis was carried out for definition of new growths in hydration products of the present CS compositions.

On the second stage according to the data from XRDA it was found that the mail hydration products of test specimens are portlandite, non-hydrated minerals of clinker – alite and belite, and also hydrated calcium silicates with different basicity (fig. 6-9).

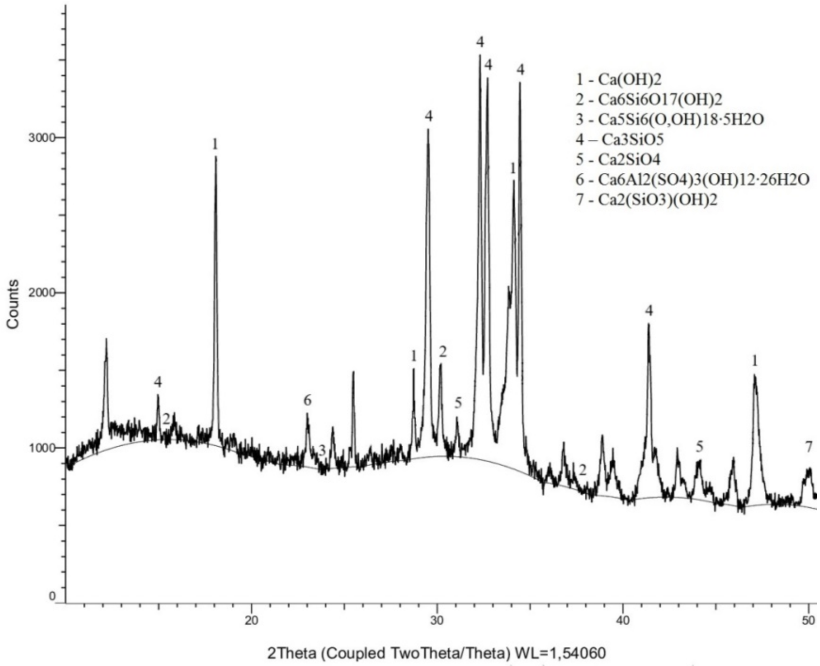

Fig. 6. X-ray pattern of check specimen of CS.

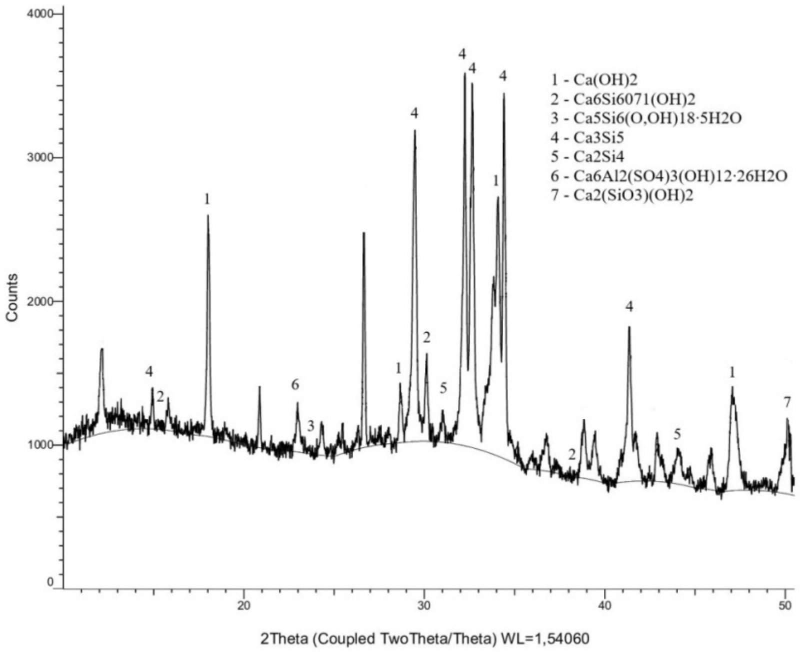

Fig. 7. X-ray pattern of CS specimen modified by powdered shungite.

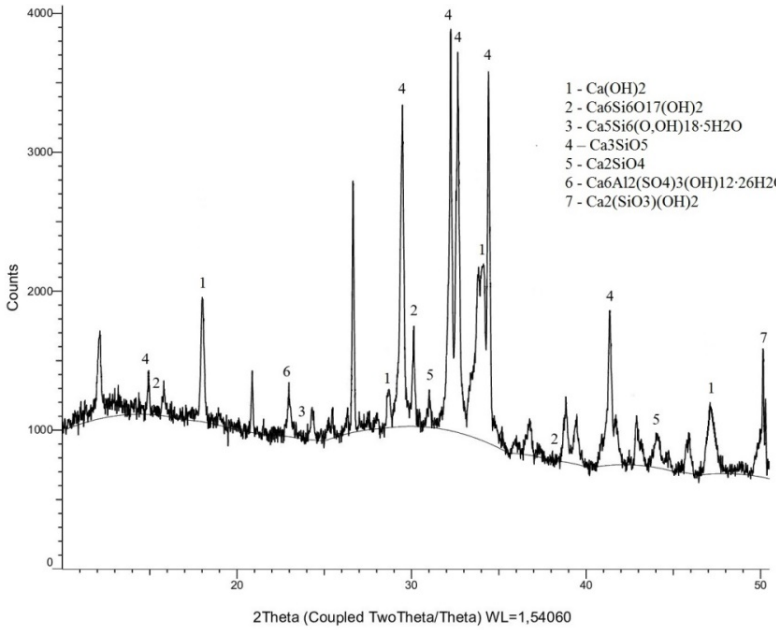

Fig. 8. X-ray pattern of CS specimen modified by PA and AMA.

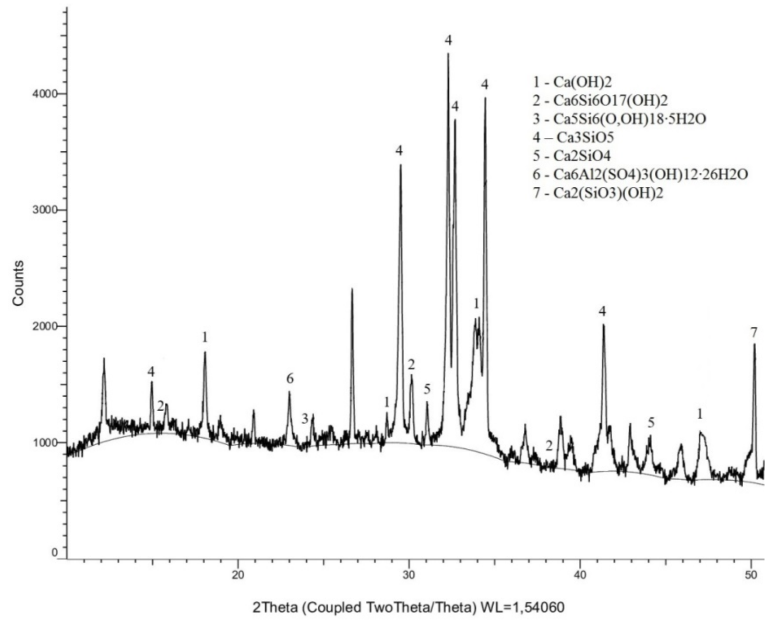

Fig. 9. X-ray pattern of CS specimen modified by shungite, PA and AMA.

In modified specimens (fig. 7-9) intensity reduction of portlandite diffraction reflections, higher content of low-basic hydrated calcium silicates C_3S_3H (xonotlite), minerals of tobermorite group $C_4S_5H_5$ and dellaite minerals C_6S_3H in comparison with check specimen (fig. 6) can be observed. It provides improvement of stress-strain properties of concrete modified by shungite, AMA and PA, which was established at previously undertaken studies [47]. Obtained results favorably compare with the data from quantitative XRDA: content of portlandite, xonotlite, tobermorite and dellaite in check specimen is equal to 8.14, 6.68, 6.82, 1.64 % correspondingly; in the specimen modified by powdered shungite – 5.78, 6.95, 7.94, 2.88 % correspondingly; in the specimen modified by AMA and PA – 3.22, 7.16, 8.53, 3.47 % correspondingly; in the specimen modified by shungite, AMA and PA – 2.92, 11.08, 9.18, 4.72 % correspondingly.

Increase in content of low-basic hydrated calcium silicates in the modified specimens provides high stability of cement stone against hydrothermal recrystallization, and also such hydrosilicates as xonotlite and tobermorite provide high strength and low water and gas permeability, which is confirmed by research results of air permeability and water impermeability of concrete (Table 2).

Table 2. Influence of shungite, metakaolin and PA on water impermeability of concrete hardening under electrode heating.

No.	Content of running modifying components, % by mass of PC	Freeze-thaw resistance, cycles	Concrete water-tightness grade
1	–	F200	W8
2	Shungite Ssp 400 m^2/kg – 5%	F300	W12
3	Metakaolin – 10% PA “Glenium Ace 430” – 1%	F300	W16
4	Shungite Ssp 400 м2/кг – 5% Metakaolin – 10% PA “Glenium Ace 430” – 1%	F400	W20

Ettringite existence primary has an impact on microstructure formation of cement stone at early stage of hydration in comparison with hydrated calcium silicates in the light of their large size [48].

It should be noted that in the specimens with shungite addition (No.2 and No.4) in contradistinction from check sample (No.1) and the sample modified by AMA and PA (No.3) hydrated calcium silicate C2SH (A) formation in the quantity of 0.76 and 3.19% correspondingly can be observed, which among other factors provides higher strength and lower permeability in comparison with the check specimen. In our opinion, the reason of difference between values of exothermic reactions in the specimens with shungite addition (No.2 and No.4) is hydrated calcium silicate C_2SH (A) formation.

On the third stage of experimental investigation special aspects of morphometric features of CS structures of initial composition, with desired content of shungite, modifying agents and under electrode heating were studied by means of electron-microscopic analysis (fig. 10-12).

Electron micrographs of CS specimens’ spalls

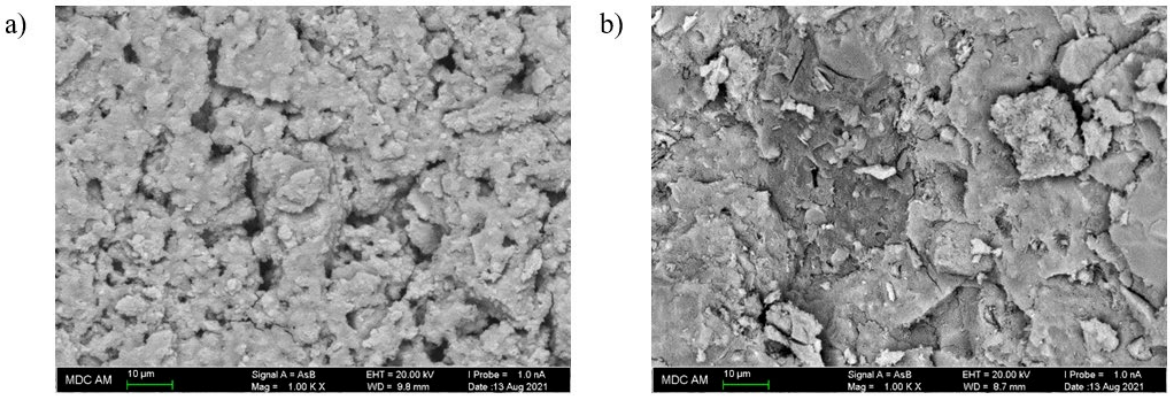

Fig. 10. Electron micrographs of cement stone (at increase x1000): a – composition with no agent; b – composition with shungite, AMA and PA.

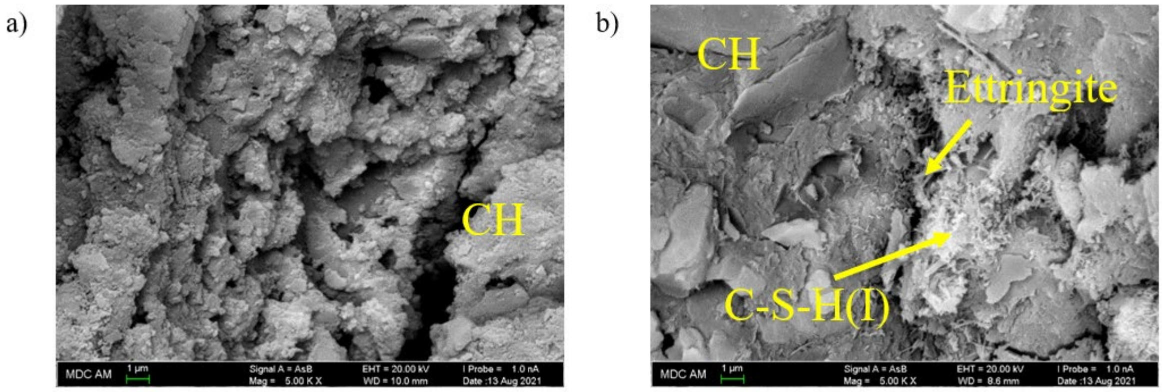

Fig. 11. Electron micrographs of cement stone (at increase x5000): conventional symbols refer to fig. 10.

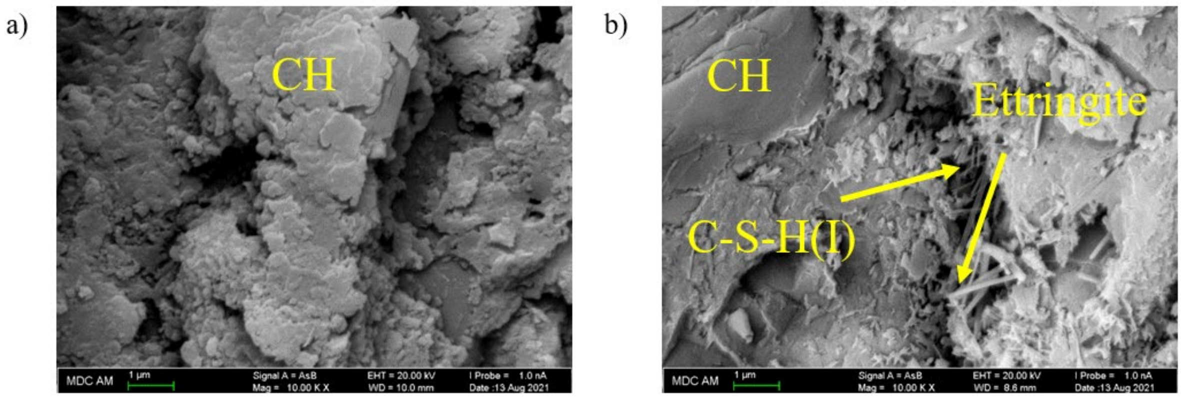

Fig. 12. Electron micrographs of cement stone (at increase x10000): conventional symbols refer to fig. 10.

Generally, structure of the test specimens has porosity characteristic to composites of given type, however, pore size, shape and total pore volume have differences, which arises from size and shape of hard structure elements, pattern of distribution in space, state of their aggregation and compaction degree. Concrete compositions modified by shungite, AMA and PA under electrode heating are characterized by topological structure condensation in comparison with check composition (fig. 10,11).

It is found that introduction of shungite with degree of fineness equal to 400 m^2/kg in the quantity of 5 % by mass of PC in combination with 10 % of metakaolin and 1 % of PA "Glenium Ace 430" (figures 11 b – 12 b) to portland cement composition leads to more compact and homogenous structure formation between cement stone compositions under investigation with inclusions of additional quantity of new growths in the form of compact clusters of fibrous crystals in cracks and pores, and also leads to more regular distribution of shungite in cement stone volume in comparison with the specimen modified only by powdered shungite in the quantity of 5 % by mass of PC.

In the described figures 11-12 (b) domination of new growths in cement stone modified by shungite, AMA and PA clearly traces, and these new growths are presented as fibrous jellous phase similar in structure and content to tobermorite – CSH(B), CSH(I) (basic mass), as crystal line phase composed of laminas and scales (about 1 μm across) of calcium hydroxide $Ca(OH)_2$, hexagonal lamellas of hydrated tetracalcium aluminate, acicular and whisker crystals of ettringite.

Attained results about influence of powdered shungite content on special aspects of concrete structure formation and properties under electrode heating is coherent with IR spectroscopy results of the compositions under investigation [49] and experimental investigations of shungite impact on concrete properties and effectiveness of electrode heating [47].

On the fourth stage of experimental investigation compressive strength test for concrete specimens hardening under electrode heating and during 28 days of normal curing was made for comparison of obtained results of XRDA, DTA and scanning electron microscopy method with strength properties of the developed compositions (Fig. 13).

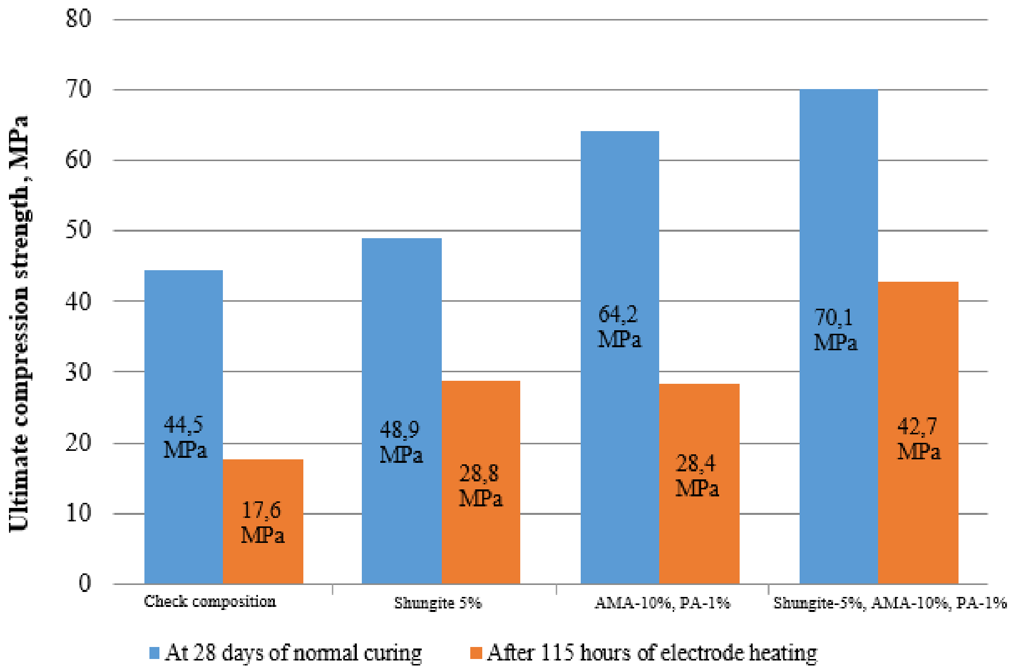

Fig. 13. Strength of specimens under investigation.

As it can be observed from data in Fig. 13, powdered shungite with hydraulic activity and characteristics of pozzolanic addition in combination with its capability to act as crystallization centers makes a contribution to concrete strength improvement under normal curing, moreover, its electrically conductive properties considerably help to increase the effectiveness of electrode heating.

It is found that introduction of shungite it the quantity of 5% into initial concrete composition curing under electrode heating provides a means of compressive strength increase by 63.6 %. Introduction of 5 % of shungite in combination with AMA and PA leads to its compressive strength improvement by 142.6 % in comparison with the initial non-modified composition and by 50.3 % in comparison with analogous composition without shungite.

Results analyzing of strength properties of the compositions under investigation shows positive effect of powdered shungite in concrete curing under normal conditions and electric heat treatment process.

4. CONCLUSIONS

1. Concrete composition modifying by shungite, AMA and PA decreases total pore volume from 18.1 % to 14.8 %. During decrease of total porosity substantial volume redistribution of open capillary pores, open noncapillary pores and relatively closed pores appears. For instance, volume of open noncapillary pores decreases from 0.9 % to 0.3 %, volume of open capillary pores decreases from 6.3 % to 5.2 %, and volume of relatively closed pores increases from 9.31 % to 10.9 %, microporosity value increases from 0.79 to 2.05.
2. By means of DTA method it is found that modified compositions of cement stone are characterized by larger mass change for the first and third endoeffects during shungite introduction in comparison with the check composition, which is confirmed by larger square of endothermic effects and larger loss of mass for the first and third endoeffects in comparison with the check composition, which shows its deeper hydration.

3. By means of XRDA it has been established that modification of cement compositions by shungite, AMA, PA leads to decrease of diffraction reflection intensity of portlandite, increase of diffraction reflection intensity of low-basic hydrated calcium silicates (especially of xolonite), minerals of tobermorite group, that are responsible for their physical and mechanical properties improvement. Besides, introduction of shungite, AMA and PA provides minor change of qualitative composition of new growths of modified specimens, where high-basic hydrated calcium silicate of hillebrandite group C2SH can be observed, that promotes improvement of freeze-thaw resistance of cement compositions according to literature data.

4. By means of scanning electron microscopy method it is found that introduction of powdered shungite in the quantity of 5 % by mass of PC in combination with 10 % of metakaolin and 1 % of PA "Glenium Ace 430" to portland cement composition leads to more compact and homogenous structure formation between CS compositions under investigation with inclusions of additional quantity of new growths in the form of compact clusters of fibrous crystals in cracks and pores, and also leads to more regular distribution of shungite in cement stone volume in comparison with the specimen modified only by powdered shungite in the quantity of 5 % by mass of PC.

5. By means of DTA method anomaly of exothermic reaction of CS specimens modified by identical quantity of powdered shungite was discovered, that consists in enthalpy increase by 5.6% of the specimen No.4 in comparison with the specimen No.2, which can be explained by hydrated calcium silicate C2SH (A) formation in the quantity of 0.76 and 3.19 % in the specimens No.2 and No.4 correspondingly, that was found by means of quantitative XRDA, and what is confirmed by the results obtained with the use of scanning electron microscopy method, which provides, among other factors, higher strength and lower permeability in comparison with the check specimen.

6. It is found that introduction of shungite it the quantity of 5% into initial concrete composition curing under electrode heating provides a means of compressive strength increase by 63.6 %. Introduction of 5 % of shungite in combination with AMA and PA leads to its compressive strength improvement by 142.6 % in comparison with the initial non-modified composition and by 50.3 % in comparison with analogous composition without shungite.

7. Summing up what has been said, in the result of experimental studies analysis it is found, that generally structure of developed shungite-contained concrete is common with structure of traditional cement stone and concrete, which bears witness of familiar theoretical models about cement concrete structure formation on prescribed system of shungite concrete hardening under electrode heating. Stability of cement systems modified by shungite and hardening under electrode heating has been proved, on account of which it is reputed that science and technology solution, that we have developed, be substantiated.

REFERENCES

[1] Golovnev S.G., Evseev B.A., Koval S.B., Molodtsov, M.V. Heat treating of newly-laid steel fibre reinforced concrete at temperature below freezing. Use of steel fibre reinforced concrete in transport construction. 1998. P. 26.

[2] Matus E.P. Numerical simulation of electric curing of fiber reinforced concrete with fibers of high conductivity. Bulletin of Eurasian Sciences. 2019. 2 (11). P. 1 – 9.

[3] Dudin M.O., Vatin N.I., Barabanshchikov Y.G. Modeling a set of concrete strength in the program ELCUT at warming of monolithic structures by wire. Magazine of Civil Engineering. 2015. 54 (02). P. 33 – 45.

[4] Armoosh S.R., Oltulu M. Effect of Different Micro Metal Powders on the Electrical Resistivity of Cementitious Composites. IOP Conference Series Materials Science and Engineering. 2019. 471 (3).

[5] Liu Y., Wang M., Tian W., Qi B., Lei Zh., Wang W. Ohmic heating curing of carbon fiber/carbon nanofiber synergistically strengthening cement-based composites as repair/reinforcement materials used in ultralow temperature environment. Composites Part A Applied Science and Manufacturing. 2019. 125. P. 105570.

[6] Tian W., Liu Y., Qi B., Wang, W. Enhanced effect of carbon nanofibers on heating efficiency of conductive cementitious composites under ohmic heating curing. Cement and Concrete Composites. 2021. 117. P. 103904.
[7] Gomis J., Galao O., Gomis V., Zornoza E., Garcés P. Self-heating and deicing conductive cement. Experimental study and modeling. Construction and Building Materials. 2015. 75. P. 442 – 449.
[8] Bataev V.A., Kudashov A.G., Teplykh A.M., Ognev A.Yu., Alexandrova V.M. Polymer composite based on epoxide resin and strengthened by multi-wall carbon nanotubes. Scientific Bulletin of Novosibirsk State Technical University. 2009. 37 (4). P. 115 – 122.
[9] Mikitaev A.K., Kozlov G.V. Description of strengthening rate of nanocomposites by polymer/carbon nanotubes as part of percolation models. Physics of the Solid State. 2015. 57 (5). P. 961 – 964.
[10] Kondrashov S.V., Gunyaeva A.G., Shashkeev K.A., Barinov D.Ya., Soldatov M.A., Shevchenko V.G., Muzafarov A.M. Electrically-conductive hybrid polymer composite materials on the basis of noncovalent functional carbon nanotubes. Proceedings of VIAM. 2016. 2 (2). P. 10 – 10.
[11] Ryabov S.A., Zakharychev E.A., Semchikov Y.D. Investigation of influence of functionalisation time of carbon nanotubes on physical and mechanical properties of polymer composites based on them. Bulletin of Lobachevsky University of Nizhny Novgorod. 2013. 2-1. P. 71 – 74.
[12] Bocharov G.S., Eletskii A.V., Knizhnik A.A. Nonlinear resistance of polymer composites with carbon nanotube additives in the percolation state. Technical Physics. 2016. 61 (10). P. 1506 – 1510.
[13] Semenov K.V., Drummers Y.G. Thermal crack resistance of massive concrete foundation slabs and its provision in construction winter period. Construction of unique buildings and structures. 2014. 2. P. 125 – 135.
[14] Blokhin A.N. The influence of carbon nanotubes on electric conductivity of epoxy matrix. Issues of modern sciences and practices. Vernadsky University. 2012. 41 (3). P. 384 – 386.
[15] Tian W., Liu Y., Wang M., Wang W. Performance and economic analyses of low-energy ohmic heating cured sustainable reactive powder concrete with dolomite powder as fine aggregates. Journal of Cleaner Production. 2021. 329. P. 129692.
[16] Sassani A., Ali A., Halil C., Sunghwan K., Kasthurirangan G., Taylor P.C., Nahvi A., Polyurethane-carbon microfiber composite coating for electrical heating of concrete pavement surfaces. Heliyon. 2019. 5 (8). P. e02359.
[17] Malakooti A., Theh W.S., Sajed Sadati S.M., Ceylan H., Kim H., Mina M., Cetin K., Taylor P.C. Design and Full-scale Implementation of the Largest Operational Electrically Conductive Concrete Heated Pavement System. Construction and Building Materials. 2020. 255. P. 119229.
[18] Fulham-Lebrasseur R., Sorelli L., Conciatori D. Prefabricated electrically conductive concrete (ECC) slabs with optimized electrode configuration and integrated sensor system. Cold Regions Science and Technology. 2022. 193. P. 103417.
[19] Abolhasani A., Pachenari A., Razavian S.M., Mahdi A.M. Towards new generation of electrode-free conductive cement composites utilizing nano carbon black. Construction and Building Materials. 2022. 323. p. 126576.
[20] Malakooti A., Abdualla H., Sajed Sadati S.M., Ceylan H. Experimental and theoretical characterization of electrodes on electrical and thermal performance of electrically conductive concrete. Composites Part B Engineering. 2021. 222. P. 109003.
[21] Mukhametrahimov R.H., Galautdinov A.R., Garafiev A.M. Patent No. 2725715 Russian Federation, C1 C04B 40/02, 111/20, 103/32, 14/36, 28/00 The method of cold water concreting. pubd. 03.07.2020, Bul. 19.: 2725715. RF.
[22] Mukhametrahimov R.Kh., Galautdinov A.R., Garafiev A.M. Patent No. 2750772 Russian Federation, C2 C04B 40/02, 111/20, 103/32, 14/36, 28/00 The method of cold water concreting of structures. pubd. 02.07.2021, Bul. 19.

[23] Mukhametrahimov R.Kh., Galautdinov A.R., Garafiev A.M. Patent No. 2750883 Russian Federation, C2 C04B 40/02, 111/20, 103/32, 14/36, 28/00 Concreting procedure at temperatures below freezing. pubd. 05.07.2021, Bul. 19.
[24] Kravchenko T.G., Tereshko A.G., Khromilin E.I. Modified electrically conductive shungite concretes. 1985. P. 77 – 84.
[25] Stroganov V.F., Amel'chenko M.O., Mukhametrakhimov R.K., Vdovin E.A., Tabaeva R.K. Increasing the Adhesion of Styrene-Acrylic Coatings Modified by Schungite Filler in Protection of Building Materials. Polymer Science, Series D. 2022. 15 (2). P. 162 – 165.
[26] Lesovik R.V., Klyuyev S.V., Klyuyev A.V., Netrebenko A.V., Kalashnikov N.V. Fiber concrete on composite knitting and industrialsand KMA for bent designs. World Applied Sciences Journal. 2014. 30(8). 964 – 969.
[27] Makul N., Fediuk R., Amran H.M.M., Zeyad Abdullah M., Azevedo A., Klyuev S., Vatin N., Karelina M. Capacity to develop recycled aggregate concrete in south east asia. Buildings. 2021. 11(6). 234.
[28] Fediuk R., Amran M., Klyuev S., Klyuev A. Increasing the performance of a fiber-reinforced concrete for protective facilities. Fibers. 2021. 9(11). 64.
[29] Klyuev S., Fediuk R., Ageeva M., Fomina E., Klyuev A., Shorstova E., Zolotareva S., Shchekina N., Shapovalova A., Sabitov L. Phase formation of mortar using technogenic fibrous materials. Case Studies in Construction Materials. 2022. V. 16. P. e01099.
[30] Klyuev A.V., Kashapov N.F., Klyuev S.V., Zolotareva S.V., Shchekina N.A., Shorstova E.S., Lesovik R.V., Ayubov N.A. Experimental studies of the processes of structure formation ofcomposite mixtures with technogenic mechanoactivated silica component. Construction Materials and Products. 2023. 6 (2). P. 5 – 18.
[31] Rakhimova N.R. Rakhimov R.Z., MorozovV.P., Eskin A.A. Calcined low-grade clays as sources for zeolite containing material. Periodica Polytechnica Civil Engineering. 2021. 65 (1). P. 204 – 214.
[32] Klyuev S., Klyuev A., Fediuk R., Ageeva M., Fomina E., Amran M., Murali G. Fresh and mechanical properties of low-cement mortars for 3D printing. Construction and Building Materials. 2022. № 338. P. 127644. DOI:10.1016/j.conbuildmat.2022.127644.
[33] Klyuev S.V., Klyuev A.V., Shorstova E.S. The micro silicon additive effects on the fine-grassed concrete properties for 3-D additive technologies. Materials Science Forum. 2019. 974. P. 131 – 135.
[34] Khozin V., Khokhryakov O., Nizamov R. A. «Carbon footprint» of low water demand cements and cement-based concrete. IOP Conference Series: Materials Science and Engineering. 2020. 890. P. 012105. 2020.
[35] Klyuev S., Fediuk R., Ageeva M., Fomina E., Klyuev A., Shorstova E., Sabitov L., Radaykin O., Anciferov S., Kikalishvili D., de Azevedo Afonso R.G., Vatin N. Technogenic fiber wastes for optimizing concrete. Materials. 2022. V. 15(14). P. 5058.
[36] Mukhametrakhimov R.K. Investigation of plasticizing additives based on polycarboxylate esters on the properties of concretes formed by 3D printing. Construction Materials and Products. 2022. 5 (5). P. 42 – 58.
[37] Aleksandrova O., Quang N., Bulgakov B., Fedosov S., Lukyanova N., Petropavlovskaya V. The Effect of Mineral Admixtures and Fine Aggregates on the Characteristics of High-Strength Fiber-Reinforced Concrete. Materials (Basel). 2022. 15 (24). P. 8851.
[38] Garafiev A.M., Mukhametrakhimov R.K. Investigation of percolation of electric current in modified cement composites area for conservation of energy in electrode heating technology. II All-Russian Scientific Conference, dedicated to the centenary of the Moscow State Construction University MISI – MGSU. 2022. P. 109 – 112.
[39] Lukutcova N.P., Pykin A.A., CHudakova O.A. Modifying of fine grained concrete by micro- and nanosize particles of shungite and titanium dioxide. Bulletin of Belgorod State Techno-logical University named after V.G. Shukhov. 2010. 2. P. 66 – 70.
[40] Shilin A.D. Investigation of fine grained concretes developed with te use of mechanoactivated shungite. Materials of reports of the 52d International Science and Technology Conference of teachers and students: in 2 v. 2019. P. 326 – 328.

[41] Rubanik V.V., Shilin A.D., Belous N.Kh., Rodtsevich S.P., Rubanik V.V.Mr., Shilina M.V. The influence of shungite additives on the properties of fine grained plasticized portland cement concretes. Advanced materials and technologies. Materials of international symposium. 2017. P. 301 – 303.

[42] Shablinsky G.E., Lukutsova N.P., Pykin A.A., Tsvetkov K.A. Investigation of dynamic strength and rigidity of products made of fine grained concrete modified by nanostructural shungite filler. Bulletin of MGSU. 2010. 2. P. 231 – 236.

[43] Lukuttsova N.P., Pykin A.A., Shirko S.V., Matsaenko A.A. Techno-environmental feasibility study of getting nanomodifier for concrete. Construction and reconstruction. 2012. 41 (3). P. 42 – 47.

[44] GOST 10060-2012 Concrete. Methods for determining frost resistance. M.: Standartinform. 2014. P. 18.

[45] Lukutcova N.P., Pykin A.A. Theoretical and technological aspects of getting micro- and nanodispersed additives based on shungite contained rocks for concrete. 2013. 223 p.

[46] Urhanova L.A., Savel’eva M.A. Investigation of microstructure and properties of cement stone modified by sulfur sol. Novel technologies in science and education. Materials of the V Russian national Research-to-Practice Conference with international participation. 2017. P. 103 – 112.

[47] Mukhametrahimov, R.Kh. Galautdinov A.R., Garafiev A.M. Electrode concrete heating with the use of electrically condactive mineral. Proceedings of KGASU. 2019. 4 (50). P. 418 – 426.

[48] Urkhanova L.A., Lkhasaranov S.A., Buyantuev S.L., Fedyuk R.S., Taskin A.V. Reducing alkaline corrosion of basalt fiber in concrete. Magazine of Civil Engineering. 2019. 91 (7). P. 112 – 120.

[49] Mukhametrahimov R.K., Galautdinov A.R., Potapova L.I., Garafiev A.M. Investigation of structure formation of modified shungite contained cement stone by means of IR spectroscopy method. Proceedings of KGASU. 2021. 58 (4). P. 70 – 81.

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