PROSPECTS OF NANOTECHNOLOGY OF THE XXI CENTURY FOR CREATION OF CLIMATE-RESISTANT AND ENVIRONMENTALLY CLEAN TRANSPORT INFRASTRUCTURE

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ANNOTATION

The article presents the results of fundamental laser research, experimental work and long-term monitoring of highways built using concrete based on belite road cements. Belite cements, containing predominantly two-calcium silicates (C2S-belite 50-80%), ensure a service life of road concrete of up to 50 years without the need for repairs. Laser studies have revealed the structure of belite cement stone, formed by nano-sized new formations known as colloidal calcium hydrosilicates CSH, promoting almost complete hydration of cement grains.

АҢДАТПА

Мақалада Belite жол цементтері негізінде бетонмен салынған іргелі лазерлік зерттеулердің, эксперименттік жұмыстардың және автомобиль жолдарының ұзақ мерзімді мониторингінің нәтижелері келтірілген. Құрамында негізінен екі компонентті кальций силикаттары бар элиталық цементтер (C2S -билет 50-80%) жол бетонының қызмет ету мерзімін жөндеуді қажет етпестен 50 жылға дейін қамтамасыз етеді. Лазерлік зерттеулер цемент дәндерінің толық дерлік ылғалдануына ықпал ететін кальций коллоидты гидросиликаттары CSH деп аталатын наноөлшемді өсінділерден түзілген белит цемент тасының құрылымын анықтады.

АННОТАЦИЯ

В статье представлены результаты фундаментальных лазерных исследований, экспериментальных работ и долгосрочного мониторинга автомобильных дорог, построенных с использованием бетона на основе дорожных цементов белит. Белитовые цементы, содержащие преимущественно двухкомпонентные силикаты кальция (C2S-белит 50-80%), обеспечивают срок службы дорожного бетона до 50 лет без необходимости ремонта. Лазерные исследования выявили структуру цементного камня белит, образованную наноразмерными новообразованиями, известными как коллоидные гидросиликаты кальция (CSH), способствующими почти полной гидратации цементных зерен.

KEY WORDS

Highways, fundamental research, colloidal structure, cement belite concrete, asphalt belite concrete, ecology.

INTRODUCTION

Fundamental laser and experimental studies demonstrate that colloidal structures formed during the hydration of belite cements have unique properties, such as long-term thixotropy (self-healing upon destruction) and long-term rheopexy (strengthening under the influence of transport loads and seasonal temperature changes), exclusively under long-term conditions. operation of highways. The advantages of using belite cements in road construction, characterized by high manufacturability, allowing year-round construction of roads and their durable operation for up to 50 years in the sharply continental climate of Kazakhstan.

Monitoring of concrete roads based on belite cements confirms the long-term strengthening of concrete over 35- 46 years of road operation (within the limits of experience). For the first time in Kazakhstan, the scientific novelty and effectiveness of the theory put forward by the French scientist V. Michaelis was confirmed; on the strengthening of mineral binders with a predominant content of colloidal structures of cement stone, proposed 180 years ago and previously had no practical application. The novelty of the authors' development is confirmed by a number of patents, which may reveal the secrets of the durability of ancient Roman concrete.

Comparing the world's traditional long-term experience of road construction in Kazakhstan and abroad, it has been established that cement concrete road pavements based on quickly hardening (C3S - alite up to 65%) Portland cements with a crystalline hardening structure have a limited service life of road concrete up to 25-30 years between repairs. It has been established that this is due to the laws of physical and chemical strengthening processes, primarily with the rapidly hardening main mineral of Portland cement - tri-calcium silicate (C3S-

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alite), which is doomed to destruction within 20-25 years. For the first time in the world practice of road construction in Kazakhstan, it has been established that it is more effective to use road concrete based on belite cements, with a colloidal structure of long-term hardening, during long-term operation of roads, which prevents the possibility of premature deformations in concrete. -It has been established that the durability of belite cement structures is ensured by nano-sized colloidal calcium hydrosilicates CSH, due to the complete hydration of cement grains,in contrast to the crystalline structure of alitic Portland cements, with limited hydration of tri-calcium silicate C3S to 60%, leading to the formation of more than 40% «Young's micro-concrete» - the unhydrated interior of the cement grains. Subsequent hydration of which 15-20 years later leads to the destruction of the non-renewable crystalline structure of the outer shell of the cement stone, which explains the short service life of cement concrete road pavements traditionally used in the world up to 25-30 years.

If the motto of the previous 2012, Istanbul V Congress "Euroasphalt and Eurobitumen" was: "Asphalt concrete is a 100% regenerable material", then in 2016 at the Prague VI Congress it evolved into a new one: "The road layer can be built 100% from the old asphalt concrete».

The authors proposed and confirmed in practice a new theory of asphalt concrete, in which it was established that the service life of elastically plastic asphalt concrete depends on the duration of preservation (thixotropy) of a colloidal solution of asphalt binder based on an organic binder and the fineness of grinding the mineral powder. In traditional asphalt concrete, the colloidal structure of the asphalt binder depends on the limited aging period of bitumen, within 5-6 years. After this, the fragility of the bitumen films increases, which leads to exposure of the powder grains; under the influence of transport and temperature loads, the powder grains begin to stick together. The specific surface area of the inert mineral powder decreases, which leads to a decrease in the colloidal properties of the asphalt binder (thixotropy) and destruction of asphalt concrete.

The new technology has found a way to extend the life of a colloidal solution of asphalt binder by protecting the organic binder from aging and by long-term strengthening the colloidal structure of belite powder. In Kazakhstan, scientific research has proven the feasibility and development of highly wear-resistant asphalt concrete road surfaces.

The reliability of fundamental and experimental research is confirmed by effective nanotechnology of the 21st century in road construction and the results of long-term monitoring of roads, including tests of concrete samples subjected to various temperatures in laboratory conditions, and cores extracted from nanostructured concrete and asphalt concrete roads, operated for more than 35-46 years and 12 -19 years without repair. "Asphalt concrete is a 100% recyclable material," then in 2016 at the Prague VI Congress it evolved into a new one: "The road layer can be built 100% from old asphalt concrete." -The authors proposed and confirmed in practice a new theory of asphalt concrete, in which it was established that the service life of elastic-plastic asphalt concrete depends

RELEVANCE OF RESEARCH

At the end of the 20th century, traffic loads on highways increased by 2-3 times, the service life of cement concrete roads was reduced to 25-30 years, asphalt concrete roads on concrete bases to 10-12 years, with the restoration of the wear layer every 5-6 years. According to the global concepts of "eternal roads" in the USA and "roads with long life" in EU countries, it is believed that roads pay for themselves after 50 years of operation. To do this, it is necessary to increase the load-bearing capacity of the road structure layers from bottom to top, and the compressive strength of coatings to withstand heavy traffic loads. Kazakhstan has mastered alternative technologies with the operation of asphalt concrete and concrete roads with a colloidal hardening structure for up to 35-50 years or more. This ensures maximum resource and energy conservation of the environment.

Therefore, the development of belite cements based on industrial technogenic mineral wastes that have undergone

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heat treatment during the main production and have latent hydraulic activity is an urgent problem for research.

Recent research in the field of asphalt concrete has been devoted to the search and use of various polymers and additives in bitumen to improve the quality of asphalt concrete [3]. At the same time, it is well known that binders in asphalt concreteis not pure bitumen, but an asphalt binder consisting of bitumen and mineral powder [3]. Fine mineral powder with a specific surface area of up to 3000 cm2/g together with bitumen form a colloidal solution [3], which creates conditions for thixotropic colloidal hardening of asphalt concrete. The strength of purely bitumen bonds is tens of times lower than the bonds formed through joint interaction with mineral powder.

It is known that the colloidal system for strengthening mineral binders [4-6] has the properties of long-term preservation of thixotropy - reversible self-healing after destruction and rheopexy - strengthening under loads.

DISCUSSION OF RESEARCH RESULTS

The idea of creating a stronger base than a coating is not new [2-4]. The prospects for using industrial technogenic mineral waste (hereinafter referred to as TMR) in combination with cement or cement dust, lime and other activators have been repeatedly noted in the works of Kazakh and Russian scientists [4]. Below are the main results of research and testing of roads, confirming the durability of road concretes based on belite cements, their TMF, used in road construction in Kazakhstan, the strengthening of which has been going on for more than 35-40 years. (Picture 1.)

Figure 1. Kinetics of strength gain of self-healing concrete road pavements, with a wear layer of asphalt concrete onhighways built in 1976–1984: where 1, 2, 3respectively, on belite cements from TMF: fly ash from thermal power plants, bauxite sludge and granulated slag.

Table 1 provides a comparison of the chemical and mineralogical compositions of traditional Portland cements (hereinafter referred to as alite cements) and slow-hardening high-tech cements (hereinafter referred to as belite cements).

Table 1 - Chemical and mineralogical compositions of alite Portland cements and slow-hardening belite cements.

Note- conventional names of cements are given based on the predominant content of minerals: C3S - alit, C2S - belite.

Physicochemical studies have confirmed [4, 5,7] that the mineralogical composition of belite cement stone mainly consists of colloidal calcium hydrosilicates of the CSH type compared to crystalline new formations of Portland cement. The formation of the structure of slow-hardening cement stone during its hardening for 8 years is shown for clarity in photographs of fractures of cement beams tested in tension during bending, shown in Figure 2. The nature of the slow decomposition of cement grains and the occurrence of new formations is clearly visible in the photographs (Figure 2).

Figure 2. Photographs of fractures of samples hardened under normal conditions and tested after: a – 1 year; b – 3 years; c – 6 years; g – 8 years

In Figure 2a, undecomposed cement grains and grains with a formed peripheral shell are clearly observed, which gradually grows (see Figure 2b) and turns into amorphous gel-like new formations (see Figure 2c). The amorphism of these new formations is caused by the indistinctness and vagueness of their edges and their random growth in all directions. Along with amorphites, someprimordial crystals of C–S–H (see Figure 2b). In immersion, the gel is presented as a colorless isotropic mass with a refractive index of 1.330 – 1.567. The number of gel-like neoplasms in samples increases with increasing age of the samples. But even after 8 years of hardening under normal conditions, unhydrated grains are observed in cement samples, which indicates the potential of cement for further hardening. X-ray patterns of belite cement stone shown in Figure 3 confirm the data obtained.

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Curing time, months

Figure 3. X-ray images of belite cement stone samples, hardened for 3 months at temperatures +5; 0; -5; -10 oC. Where: a) – after 1 month of aging under normal conditions; b) – without aging under normal conditions

Thus, regardless of the temperature regimes of hardening of belite cement stone (within the limits of the experiment) and the holding time, the phase composition of the new formations does not undergo any significant changes. The slowing down of cement hydration processes with decreasing hardening temperature is evidenced by a decrease in the diffraction line corresponding to the interplanar distance of 3.027 Å, compared to 3.039 Å, during hardening at positive temperatures, described in detail by Kh.F. Taylor [6].

Figure 4 shows the results of testing a number of samples 5, 6, 7, 8 in comparison with samples that were constantly hardened under normal conditions-2.

Figure 4. Kinetics of changes in the strength of belite cement stone samples over time: 2 – constantly under normal conditions; 5,6,7,8 – pre-conditioned for 1 month under normal conditions, then respectively at +5°C; 0°C; -5°C, -10°C, then again under normal conditions: a- compressive strength; b – tensile strength in bending

Data indicate that low positive and negative temperatures slow down the hardening process of cement previously kept under normal conditions. Moreover, the lower the hardening temperature, the slower the strength gain occurs.

The greatest destruction in road concrete occurs during alternating freezing and thawing, with the temperature passing through 0 °C. Therefore, the main requirements for road concrete are their frost resistance during long-term operation of highways.

In July 2016, an examination of experimental sections of roads built using cinder concrete pavements with a wear

layer of cold asphalt concrete was carried out. It has been established that the roads are in good technical and operational condition, there are no potholes or subsidence, and there are temperature transverse cracks at a distance of 12-15 running meters. In some places the edge of the asphalt concrete pavement was destroyed. Slag concrete foundations, which have been in operation for 39-40 years, do not have any deformations, except for temperature cracks.

A visual inspection and testing of cores from the experimental site on the Fegolevo – Zhdanovo highway was carried out in the spring of 1989, i.e. 13 years after construction and a survey carried out in July 2016, i.e. after 39 years, it showed that the experimental site is in good operating condition. There are longitudinal and transverse cracks. The distance between transverse cracks, compared to 1989, was reduced to 12-15 pm, with an opening width of 2-3 mm. In some places the coating is a wear layer of asphalt concrete, there are potholes, but the cinder concrete is in good condition and there are no defects. We took a core sample and cut out concrete to test the beam for tensile bending. For 39 years of operation, no repair work has been carried out on this road.

Figure 5. Photo - 2016. Testing of samples of beams made from cutting out the lower layer of cinder concrete coating for bending strength (the structure of the beam is heterogeneous - the filler is a local gravel-sand mixture)

 Table 2 presents the results of testing cores drilled in 1989. from the bottom layer of concrete pavement and beams made from concrete cut in 2016 from the Fogolevka - Zhdanovo highway, built in December 1977.

Table 3 – Results of core testing in 1989 and beams 2005 from the bottom layer of concrete pavement of the Fogolevka - Zhdanovo highway

The results of a study of the technology for constructing slag concrete pavements with a wear layer of asphalt concrete in winter and monitoring of experimental sections of roads built in summer and winter are confirmed. This indicates that road slag concrete has the property of self-healing and long-term hardening, under the influence of constant dynamic vibration transport and climatic loads, during long-term operation of roads. Figure 1 interprets the results of testing cinder concrete foundations for a number of road sections built in 1976-1984. Strengthening of slag concrete has been taking place for 30-40 years during road operation.

The results we obtained from petrographic, X-ray diffraction (Fig. 2), differential thermal analyzes and observations using a scanning electron microscope showed that during the hardening of belite cements, the main structure-forming new formations in concrete are colloidal low-basic calcium hydrosilicates of the C-S-H type [7].

The experimental results obtained suggest that of all the theories of hardening of mineral binders, the colloid-chemical theory of V. Michaelis [6] can be distinguished, which, obviously, will be more justified for explaining the hardening processes of belite cements.

At normal temperatures, C–S–H hydrosilicates are formed in the form of lamellar colloidal submicrocrystals, the average length of which is close to 10,000 Ao (1 μ), and the width and thickness are, respectively, 360 - 560 Ao and 20 -30 Ao. Due to the very small size of hydrosilicates, as well as their ability to adsorb water on their surface, hydrosilicates have the properties of colloids. Loss or saturation of water is accompanied by a change in the distance between the layers of the crystal lattice of C–SH hydrosilicate, which leads to changes in the strength of the material. Further keeping the material in humid conditions ensures the adsorption of moisture by the gel, replenishment of the binding water films between the layers of the hydrosilicate lattice and restoration of the strength of the material. Therefore, belite road concretes have the property of self-healing, regardless of temperature and climatic changes and dynamic transport loads.

The main structure-forming component in belite cement stone is low-basic calcium hydrosilicates C–S–H, which are amorphous glue, nanosized [7-9], which have the property of long-term thixotropy. Concrete is the most common building material, being a nanostructured multiphase composite material that matures over time. It consists of an amorphous phase, nano- to micrometer-sized crystals, and bound water. The properties of concrete, as well as the destructive characteristics, exist in a multi-scale range (from nano- to micro- and macro-levels), when the properties of the material at each level are formed on the basis of the properties of the previous cell of a smaller size [9-10]. The amorphous phase of calcium hydrosilicate (C–S–H) is the "glue" that holds the components of concrete together [11,12]

Figure 6. Kinetics of changes in the amount of strongly bound water in belite cement stone during hardening at different temperatures: where 2 is constant under normal conditions, 5, 6, 7 and 8 – at the beginning one month under normal conditions, then three months at temperatures: + 5oC, 0oC, -5oC and -10oC and again for three months under normal conditions.

and is itself a nanomaterial. Recently, due to interest in the formation of stable concrete structures [9, 13, 14], much attention has been paid to nanoscale modification of the C–S–H structure to create hybrid, organic, cementitious nanocomposites. The layered structure and the tendency of silicon chains (except tetrahedral) to structural defects in C–S–H [9, 11] open up the possibility of introducing a variety of organic molecules into the basic structure of C–S–H. Three schemes have been proposed for hybridization or introduction of "guest molecules" into C–S–H. The first scheme interpolates organic molecules into the C–S–H layer [15].

We have studied properties of belite nanocements, such as self-healing, in order to develop technology for road construction work at different temperatures for yearround construction and operation of highways.

This is also confirmed by the change in the amount of strongly bound water in the cement stone of samples maintained at different temperature conditions (Figure 6).

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The results of changes in the amount of strongly bound water in cement stone (Figure 6), established by measuring the weight loss of samples after calcination at 1000 °C, previously held at 105 °C, confirm the following. The kinetics of changes in the strength (Figure 3) and the amount of strongly bound water (Figure 6) of cement stone, depending on the sample holding temperature, are similar, which confirms the reliability of the theoretical premises about the self-healing properties of belite cement. When the cement stone is kept at low temperatures (samples 5 - 8), the decrease in strength (Figure 3) is accompanied by the displacement of strongly bound water (Figure 6) from the fibrous

formations in the amount of 10–30% of the mass of the available moisture in their capillaries, and with further aging at Under normal conditions, their quantity and the strength of the cement stone are restored within one month. Further aging under normal conditions for three months, the strength and amount of strongly bound water exceeds normal hardening samples. This indicates a deepening of the hydration processes of cement grains and an increase in the dispersion of new formations at low temperatures, which also increases the strength of cement stone and concrete (Figure 3).

Figure 7 shows the results of tests of the strength of various compositions of road concrete depending on the amount of belite cement, which confirm the conclusion about a long-term increase in the strength of concrete over 2 years.

Figure 7. Kinetics of strength gain of road concrete over time depending on the amount of belitecement: 1, 2, 3, 4 5, – 7, 10, 12, 15 and 18wt.% cementrespectively

 When testing concrete samples aged 90 days for frost resistance, up to 200 freezing and thawing cycles were carried out. As can be seen from Figure 13, there is a slight decrease in strength due to the squeezing of moisture from the capillaries and a decrease in its quantity. With further conditioning of the samples under normal conditions, the strength of the concrete is completely restored and even exceeds the strength of the concrete of the 90-day samples (Figure 8).

(MRZ-200), depending on the quantitybelite cement: 1, 2, 3, 4, 5 – 7, 10, 12, 15 and 18wt.% cement containingС2S –75–80%

Road belite concretes harden slowly compared to traditional alite cements, but the strength indicators of concrete at the age of 180 days are practically comparable, and the deformation indicators of belite concrete even exceed those of alite concrete. At the same time, the tensile strength during bending is 31% higher, and the elastic modulus is lower by 5000 MPa (Table 4).

The high deformative properties of slowly hardening concrete indicate the high dispersion and tensile strength (cohesive bond) of the new formations of cement stone of belite cements (Figure 9).

Figure 9. Microstructure of cement stone: on the left – alite cement stone, after 28 days, E – ettringite crystals, CSH – C-SH fibers [6]; on the right – belite cement stone [7]: a – after 28 days; b – after 90 days, tube (*) CSH; c – after 180 days, C-SH fibers. Fiber sizes 0.3-0.5 nanometer. (Electroscope-magnification 25000)

X-ray phase, thermographic (not shown) and electron microscopic studies shown in the photo (Figure 9) confirm that in such concretes, the above technological and operational advantages are provided mainly by the gel-like hardening structure of belite cements.In the structure of traditional alite Portland cement stone, on the contrary, the insignificant content of gel-like two calcium hydrosilicates fills only the free space inside the main frame formed by the fusion of large crystalline hydrates.

No. Mixture composition	Materials used in the mixture, %						
	Asphalt concrete granulate	Crushed stone from blast furnace slag fr. 5-20	Crushed stone from blast furnace slag fr. 20-40	Belite powder	Activator cement M-400	Water	Bitumen
\mathcal{I}	40.0	10.0	30.0	20.0	2.0	5.0	2.0
2	40.0	10.0	30.0	20.0	2.0	5.0	O
3	30.0	20.0	30.0	20.0	2.0	5.0	2.0
$\overline{4}$	50.0	10.0	25.0	15.0	2.0	4.0	2.0
5	50.0	10.0	25.0	15.0	2.0	4.0	\overline{O}
6	60.0	10.0	20.0	10.0	2.0	3.0	2.0
$\overline{7}$	70.0	10.0	10.0	10.0	2.0	3.0	2.0
8	70.0	10.0	10.0	10.0	2.0	3.0	\overline{O}

Table 5 – Results of selection of compositions of asphalt-belite concrete mixtures for the construction of the Astana-Borovoye highway

Table 6 – Strength of samples of asphalt-mineral concrete cores cut from the base on the Astana-Borovoye highway (of various ages)

The test results given in tables 5 and 6 showed that the introduction of additional bitumen in an amount of 2% is unnecessary; Strength decreases and bitumen deposits appear on the road. Therefore, the road was built using composition No. 8, with a maximum amount of asphalt granulate up to 70%. The strength of asphalt concrete, the strength of which is strengthened during road operation up to M15-20 (within 3 years of experience) and exceeds the strength of traditional asphalt concrete by 3-5 times, depends on the core testing temperature (Table 7). This indicates that asphalt concrete retains the elastic-plastic properties of asphalt concrete at the microstructure level and bitumen molecules are embedded in the colloidal structures of calcium hydrosilicates C-SH, which is confirmed in the works of the USA, the Czech Republic, etc. [8-15].

Nanostructured asphalt-belite concretes and road concretes based on nanostructuring powders and cements meet the requirements of modern concepts of "eternal roads" and "roads with long life" in the USA and EU countries, which allow the construction of road structures with a service life of at least 50 years [2.5, 16-20].

The innovative concept for the construction of highways (road structures) provides for complete resource conservation at all stages of the "life activity" of the highway: during construction, repair and reconstruction, with complete recycling of all materials and their reuse.

RESEARCH RESULTS

- Belite cements, with a predominant content of two calcium silicates (C2S-belite up to 50-80%), demonstrate the high durability of concrete based on them in road construction, potentially up to 50 years or more, compared to alite (C3S up to 65%) Portland cements, having a shorter service life of 25-30 years for cement concrete roads.

- The uniqueness of belite cements, characterized by the formation of a colloidal structure with nano-sized calcium hydrosilicates CSH, ensures almost complete hydration of cement grains, due to which colloidal structures have the properties of long-term thixotropy (self-healing upon destruction) and long-term rheopexy (strengthening under the influence of transport loads and seasonal temperature changes), which ensures the elimination of premature destruction in concrete, exclusively under conditions of long-term operation of concrete roads.

- Research carried out for the first time in Kazakhstan confirms the effectiveness of the theory put forward by the French scientist V. Michaelis on the strengthening of mineral binders with a predominant content of colloidal structures, proposed 180 years ago, but which has not yet found practical application.

- Monitoring of roads built from belite nanostructured cement concrete and asphalt-belite concrete in real conditions, continuing the strengthening of concrete for 35-46 years, indicates their effectiveness and confirms the conclusions of the VI Prague International Forum: "The road layer can be built 100% from the old asphalt concrete.»

- Global concerns about environmental pollution can be reduced through the production of environmentally friendly belite cements, without the need to burn alite Portland cement clinker, by replacing heat-treated secondary products from large-scale industrial metallurgical and energy production. Global production of alite cements pollutes the planet's atmosphere by 7-10% with CO2 emissions.

- The transition of road construction to environmentally friendly cold nanostructured asphalt concrete, with the absence of toxic gases both during construction and during long-term operation from heating asphalt concrete road surfaces, will provide protection from air pollution in large cities.

- Research suggests that the use of belite cements and asphalt binders in road construction could lead to more durable infrastructure, reminiscent of the durability of ancient Roman concrete

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