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Investigating the influence of carbon nanotube-based additives on the phase composition of cement mortar during well cementation

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ANNOTATION: Introduction. This article presents the outcomes of research investigations examining the impact of carbon nanotube additives on the phase composition of cement mortars employed in well cementing operations. The quality of work on cementing and ensuring the impermeability of the casing string is quite important in terms of ecological compliance. **Research methods.** To solve this problem, heavy concrete was modified with a carbon nanoadditive. For research, a cement stone obtained by normal-moisture curing was chosen. Cement mortar CEM III/A32.5H was mixed with tap water for curing, preliminarily stirring a suspension of carbon nanotubes in water solution, a mixture of a water repellent and a hyperplasticizer. To ensure a homogeneous and highly dispersed structure of this suspension, its constituent components were subjected to preliminary dispersion in an ultrasonic field. **Results and their discussion.** The optimal ratio of carbon nanotubes in the composition of the cement mortar was determined, which amounted to 0.005% of the mass of cement for single-walled carbon nanotubes and 0.0005% for multilayer ones. The process of influence of the selected modifiers on the hydration products and the phase composition of the cement mortar was studied. An additive of complex action, including single-layer carbon nanotubes, was dispersed into solutions of a mixture of hydrophobic and hydrophilic surfactants, which made it possible to increase the strength of cement mortars up to 55%. **Conclusion.** In terms of modification, single-walled carbon nanotubes are the most efficient.

KEYWORDS: carbon nanotubes, cement mortar, hyperplasticizer, water repellent, nanomaterial.

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INTRODUCTION

In the Russian fuel and energy sector, nanotechnology has been extensively implemented since 2008, leading to increased energy efficiency and cost reductions through the adoption of nanomaterials. Currently, the integration of nanomaterials is a highly relevant and prioritized matter. Utilizing nanotechnology facilitates an interdisciplinary approach. This technology enables the design, description, production, and application of structures, tools, and systems by managing the shapes and sizes of objects at the nanoscale. Additionally, incorporating nanotechnologies and nanomodified materials can help decrease capital expenditures.

The oil industry remains the main branch of the Russian Federation's economy. There is a fairly close relationship between nanotechnology and the efficiency of oil and gas production processes [1–5]. Since the volume of oil production is increasing, the issue of building oil wells remains quite relevant. Construction of production wells can be conditionally divided into a number of the following stages: preparatory work, drilling, casing, testing, development, final work.

Of the above stages of well construction, we will consider such operations as fixing the wellbore and separating the formations. In turn, when performing well casing, it is required to do the following: prepare the wellbore, casing pipes and equipment for running the casing string, run and cement the casing string, perform quality control of cementing and casing string tightness. When using a cement slurry in oil wells, the requirements for it increase.

Cementing of oil wells is the final stage of well preparation for operation. A set of such works is aimed at the maximum life of the structure due to the following reasons:

- the requirement to isolate each oil and gas area in order to exclude the possibility of mixing water and raw materials from different reservoirs;
- the requirement to protect the metal surfaces of pipes to ensure high corrosion resistance (corrosion processes are accelerated when exposed to soil moisture on metal surfaces);
- the requirement to increase the strength of the entire structure (well), since the cementing process reduces the impact of soil movement on the well.

The quality of work on cementing and ensuring the tightness of the casing string is quite important in terms of meeting ecological requirements for the environment. When analyzing the total number of complications, it can be noted that leakage of casing strings is about 20%, and interlayer crossflows – more than 18%. Annular gas and oil manifestations occur due to significant damage to oil production and the environment, that is, the likely cross-flows between reservoirs may appear to be legal and environmental issues, as well as a loss in oil production. Therefore, the most important aspects in the construction of the wellbore remain integrity and zonal isolation of the wellbore.

To perform well cementing, it is important to prepare a high-quality backfill cement mixture with the required water-cement ratio and with special additives.

Currently known methods of protecting the casing from destruction and collapse are not always effective. To solve this problem, it is required to create an optimally strong well lining, in which the cement stone must be able to perceive the external load without destruction, while maintaining its solidity.

METHODS AND MATERIALS

When creating a cement mortar of good quality, various additives are used. To improve the performance properties of heavy concrete, it can be modified with chemical additives, namely carbon nanotubes.

There are several types of nanomaterials: nanoporous structures, nanotubes and nanofibers, nanoparticles, nanodispersions, nanocrystals and nanoclusters, nanostructured surfaces and films. Such a classification was recommended by the 7th International Conference on Nanotechnology, which was held in 2004 in Wiesbaden (Germany). The regulation of the nanoscale properties of the system leads to a change in its macroparameters. The nanometer range was initially determined in the range from 1 to 100 nm at least one of the coordinates. Carbon nanotubes can be represented as extended cylindrical structures with a diameter of one to several tens of nanometers and a length of up to several centimeters [2, 5–15]. They have the form of hexagonal graphite planes rolled into a tube. Carbon nanotubes impart specific physical and mechanical properties, act as an effective tool for improving the physical and mechanical properties of composite materials [6, 16–18]. They, having a large number of free chemical bonds, can change the consistency of the concrete solution, while ensuring the adhesion of aggregates of optimal quality, which in turn improves the reliability of the composition used in a guaranteed way. In 1991, carbon nanotubes were developed, having a diameter of 0.5–1.0 nm. From the point of view of the modern vision of material objects, the nanometer range ranges from 0.1 to 100 nm.

To improve the performance properties of heavy concrete, it can be modified with chemical additives. Carbon-containing structures, namely carbon nanotubes, can be used as a nanomodifying material [19–21].

The history of the appearance of nanotubes is interesting. For a long time it was believed that carbon has the ability to form only two crystalline structures – graphite and diamond. Everyone is well aware of diamond crystals, but less known is the fact that the structure of graphite is layered: carbon atoms are located in a plane with strong bonds between themselves, but at the same time, these planes themselves are at considerable distances from each other and from each other. loosely connected. Graphite itself exists in the form of flakes with dimensions of approximately 20 nm, however, carbon atoms have the ability to form single-layer sheets of rather large dimensions. As it turned out, such single-layer carbon sheets are twisted into one layer or several layers in the form of tubes. Due to the small size of carbon tubes (1 nm), they are called nanotubes. Carbon nanotubes have certain exceptional structural and functional properties, such as sufficiently high strength, durability, resistance to mechanical stress and temperature extremes, a high degree of inertness to both acids and alkalis. Nanotubes have the ability to increase the stability of cement mortars in many ways, reaching high values of elastic moduli, and contribute to the formation of a significant number of centers of concentrated crystallization. In general, carbon nanotubes exhibit a unique combination of resilience, strength and stiffness compared to, for example, fibrous materials that typically lack such properties. The thermal and electrical conductivity of carbon nanotubes is also characterized by high values and is comparable with other materials that conduct heat and electricity well. At the present level of development of nanotechnologies, the process of studying the properties of a concrete solution modified with carbon nanotubes is of great scientific and practical importance and interest [22–26].

Research in the field of nanotechnology implementation is a priority and is supported by the government of the Russian Federation (included in the list of the priority areas for the development of science and technology). This also applies to modified structural concretes with nanosized particles to improve the physical and mechanical characteristics and extend the service life of structures.

Experimentally determined the optimal dosage of carbon nanotubes in the composition of the cement slurry. When performing research work, it was found that when carbon nanotubes were added to the cement stone, a network structure was formed. This network structure, in turn, contributes to the emergence of new features, namely:

- the appearance of resistance to the formation of shrinkage nanosized cracks in the cement mortar;
- the appearance of neoplasms such as calcium hydrosilicates.

The appearance of calcium hydrosilicates in the initial period of hydration contributes to an increase in the concentration of calcium ions.

The process of modifying heavy concrete with nanoclusters contributes to a significant increase in the strength characteristics of cement mortars under such mechanical loads as compression and bending.

The modified structure of cement mortars with nanosized particles is achieved in two ways:

- growth of purposefully nanosized particles in a hardening binding medium;
- nanosized particles are preliminarily synthesized, which are subsequently introduced into the required mixture.

Currently, the second method is the most common. However, it is necessary to take into account the following feature: in the process of synthesizing nanosized tubes, due to their high surface activity, they are combined into conglomerates in the form of powdered granules, which in turn makes it difficult to uniformly distribute throughout the volume of the composite mixture. As a result of this feature, it is possible to obtain a material having a high heterogeneity in strength, density, and other properties.

When modifying heavy concrete with a nano-additive, its strength almost doubled compared to concrete without the presence of nano-additives.

It is interesting to analyze the effect of nanocarbon tubes on changes in the properties of a cement composition, which is a model of heavy concrete.

The cement-sand mixture includes cement and sand in a ratio of one to three, respectively. To ensure the process of hardening of inorganic binders in a cement mortar, it was closed using tap water. A suspension of carbon nanotubes was premixed in the solution. This mixture included such components as water, water repellent and a mixture of hyperplasticizer.

Numerous studies and experiments have confirmed that in order to improve the strength of a cement slurry, it is required to improve the efficiency of dispersion of carbon nanotubes in the composition. To achieve homogeneity of the mass of the suspension, all the main components of the solution were first dispersed by the ultrasonic method.

For research, a cement stone was selected, obtained by normal-moisture hardening of a cement mortar of normal density for more than 20 days.

Experimental work using cement was carried out in accordance with [27]. As a filler for a fine medium, sand with a fineness modulus of 2.7 from the Kamsko-Ustyevsky deposit was used. The dosage of nanoadditives was taken as a percentage of the volume of the cement composition.

The cement mortar was made on the basis of Portland cement produced by the CEMROS industrial holding. Portland cement clinker CEM III / A32.5H was mixed with tap water for hardening, a suspension of carbon nanotubes in an aqueous solution of a mixture of a water repellent (to reduce water absorption) and a hyperplasticizer (to increase strength) was previously mixed in it. To ensure a homogeneous and highly dispersed structure of this suspension in a volume of 100 ml, its constituent components were preliminarily dispersed in an ultrasonic field for 3.5 minutes. A 100W ultrasonic disperser was used. Hyperplasticizers made on the basis of polycarboxylates affect cement mortar due to the steric effect, namely, the forces of mutual repulsion of cement particles increase with the introduction of hyperplasticizers. The additive Remicrete SP60 (FM) was chosen as a hyperplasticizer based on polycarboxylate ether (this additive allows stripping for 4 hours, unlike traditional types of plasticizers), as a water repellent – the organosilicon additive Tiprom-S (based on potassium alkyl siliconate with 55% concentration).

As an additive with a combined action of a water repellent and a hyperplasticizer, a carbon nanotubular material was chosen – Tuball graphene nanotubes manufactured by OKSiAl.ru LLC with a specific geometric surface area of 90–130 m^2/g and multilayer CNTs with a specific geometric surface area of 180–200 m^2/g.

RESULTS

Microstructural analysis of a sample of the cement composition was carried out using a Merlin electron microscope manufactured by ZEISS (Germany) with a high resolution class and a scanning function. Using such a microscope, linear measurements of the microrelief parameters of solid structures are performed. Chips of cement mortar samples were sprayed with an alloy containing gold and palladium (Au/Pd) in a ratio of 80/20 on a Quorum 150 T ES universal vacuum deposition unit.

An important indicator that describes the adsorption properties of the test sample is the specific surface area. The specific surface area was determined by the most common multipoint Bruner-Emmett-Teller (BET) method.

There are single-walled and multi-walled carbon nanotubes. The simplest type is single-walled carbon nanotubes. Such carbon nanotubes have a thickness of about 1 nm, while their length can be much longer. If we consider the internal structure, the tubes look like wrapping graphite using a hexagonal grid. At the vertices of the grid are carbon atoms. It turns out that the nanotube has a geometric shape of a cylinder, and it has no seams. For single-walled carbon nanotubes, the minimum and maximum diameters are 0.3 nm and 5 nm, respectively. A characteristic feature of single-walled carbon nanotubes is the simplicity of their structure, a small number of defects, and improved mechanical and physical and technical properties. The next type is multilayer carbon nanotubes. Such nanotubes have in their composition several layers of graphite, which are folded into the shape of a cylinder. A distance of 0.34 nm is maintained between them. Multiwalled carbon nanotubes have greater thermal stability, thermal conductivity and electrical conductivity, in contrast to single-walled carbon nanotubes.

The optimal ratio of carbon nanotubes in the composition of the cement mortar was experimentally determined, which amounted to 0.005% of the mass of cement for single-walled carbon nanotubes and 0.0005% for multilayer ones.

The influence of the selected modifiers on the hydration products and the phase composition of the cement mortar was studied.

To determine the phase composition of cement stone hydration products with selected additives, specialists from the Technology Transfer Center were involved. The phase composition was studied using a SmartLab X-ray diffractometer manufactured by Rigaku Corporation.

In the studied samples of cement stone with a complex nano-containing additive, a process of deeper hydration of the silicate phase of the cement mortar was observed. This indicates an increase in the selected temperature range of the endothermic effect.

An additive of complex action, including single-layer carbon nanotubes, was dispersed into solutions of a mixture of hydrophobic and hydrophilic surfactants, which made it possible to increase the strength of cement mortars up to 55%. The increase in the strength of cement mortars is explained by the formation of microstructural elements of the optimal type in the cement stone. In the initial period of hardening of the cement stone, the process of formation of low-basic calcium hydrosilicates is accelerated, which was revealed by the results of optical and thermal studies, namely, X-ray phase analysis and differential thermal analysis.

When multilayer carbon nanotubes are added to the cement mortar, the microstructure of the cement stone is characterized by a looser and more inhomogeneous structure.

CONCLUSION

The research findings indicate that single-walled carbon nanotubes demonstrate the highest efficacy for modification purposes. It can be inferred that single-walled carbon nanotubes serve as primary crystallization centers, predominantly for low-basic calcium hydrosilicates. Furthermore, a faster rate of structure formation is observed in comparison to compositions lacking nanoadditives.

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Roza Il. Vakhitova – scientific management; research concept; methodology development; participation in development of curricula and their implementation; writing the draft; final conclusions.

Diana A. Saracheva – participation in development of curricula and their implementation; follow-on revision of the text; final conclusions.

Ilgam K. Kiyamov – scientific management; research concept; writing the draft; final conclusions.

Linar S. Sabitov – scientific management; research concept; writing the draft; final conclusions.

Vasily Iv. Oleinik – participation in development of curricula and their implementation; writing the draft; translation of a scientific article into technical English.

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