DEVELOPMENT OF CEMENT STONE WITH ENHANCED STRENGTH PROPERTIES

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ABSTRACT. It is shown that cementing in conditions of permafrost is a complicated technical problem requiring the use of special technical means and technological methods. Well cementing experience in difficult conditions demonstrates that the use of traditional Portland cement clinker-based materials does not provide high quality well casing. The analysis of the main complications arising during well cementing at low temperature is presented. Quick-hardening and non-shrinking cements that form a strong stone and have high adhesion to casing pipes are necessary for high-quality cementing in difficult geological condition. The aim of the research was to study the additives that increase the strength of the cement stone. One such additive is silica fume, which is formed by cleaning the ore-thermal furnaces at metallurgical plants. The microsilica's properties improve concrete characteristics such as strength, wear hardness and frost resistance. The use of waste metallurgical production also makes the composition more environmentally friendly and reduces its cost.

Keywords: permafrost, microsilica, well cementing, strength properties

РАЗРАБОТВАНЕ НА ЦИМЕНТЕН КАМЪК С УВЕЛИЧЕНИ ЯКОСТНИ СВОЙСТВА

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РЕЗЮМЕ. Показано е, че циментирането в условията на вечно замръзнали почви е сложен технически проблем, който изисква използването на специални технически средства и технологични методи. Опитът при циментиране на сондажи при тежки условия показва, че използването на традиционен Портланд цимент на базата на клинкер не осигурява висококачествен циментов пояс на сондажа. Представен е анализ на основните усложнения, възникващи при циментирането на сондажа при ниска температура. За висококачествено циментиране в трудни геоложки условия са необходими бързо втвърдяващи се и не-свиващи се цименти, които образуват здрав камък и имат висока адхезия към обсадните тръби. Целта на работата е да се изследват добавки, които увеличават якостта на циментовия камък. Една от тези добавки е силициевият дим, който се образува чрез почистване на рудно-термичните пещи на металургичните предприятия. Свойствата на микросиликата подобряват характеристиките на бетона като якост, износване и устойчивост на замръзване. Използването на отпадъчна металургична продукция също прави състава му по-екологично чист и намалява цената му.

Ключови думи: вечно замръзване, микросилика, добре циментиращи, якостни свойства

Introduction

All cementing methods have one goal – to displace the cement slurry from the well annulus and raise it to a predetermined height. As a result, the possibility of movement of any liquid or gas from one layer to another through the annular space is prevented and the unstable, prone to collapses and scree rocks, are strengthened;

The importance of high-quality cementing is due to the fact that this is the final stage of well construction. Therefore, failures in its implementation can minimise the expected effect, cause an incorrect assessment of the prospect of explored areas, etc. The process of cementing wells (which is an irreversible operation), their repair and restoration are associated with significant costs and time.

Permafrost rocks are widespread throughout the world, occurring on all continents with the exception of Australia. In the northern hemisphere, the northern parts of Eurasia and North America are covered with permafrost. In Europe, permafrost is found in certain mountainous regions of the Caucasus, the Alps, Norway, the Kola Peninsula, and the Polar Urals.

Permafrost is currently about 25% of the total land area of the world, including 75% of Alaska's territory, 63% of Canada's territory and 47% of Russia's territory. The discoveries of large gas and gas condensate fields: Medvezhye, Urengoyskoye, Yamburgskoye, Kharasaveyskoye, Bovanenkovskoe and others in the north of the West Siberian Lowland attracted great attention to the study of the permafrost conditions in the region.

The presence of permafrost in the geological section and the poor quality of well casing can cause serious problems leading to such complications as inter-column flows, thawing of frozen rocks, low cement top, collapse of casing during reverse freezing, etc. In the permafrost interval a cement stone in the annulus of the well is formed with simultaneous exposure to a negative temperature — from the side of the borehole wall and positive — from the side of the casing string. A small amount of setting of cement stone, in addition to the presence of frozen rocks, is also due to the deformation of shrinkage during cement hardening. Sufficient operational reliability of well cementing in such conditions predetermines the use of special cement mixtures (Kozlov, Shepherds, 2014; Samsonenko et al., 2014).

In the studies devoted to this topic little attention was paid to the joint development of a non-shrinking cement mixture and the analysis of the dependence of porosity and permeability on the difference of thermal fields in the well, taking into account the additives introduced into the composition of the solution. In general, the problem of insufficient tightness of wells in the permafrost zone remains relevant, in accordance with which there is a need to develop effective compositions of sedimentation-resistant cement slurries that ensure trouble-free flow of frost-resistant processes in frozen rocks (Kozhevnikov et al., 2014).

The main task of the development of cement compositions for cementing wells in the interval of permafrost is to ensure their setting in a short time before freezing at a rapid rate of cement strength.

Hypothesis of the study

Analysis of theoretical studies in the field of hydration processes of hardening of mineral binders of chemical and morphological composition of minerals allowed recommending microsilica as the main additive to cement, as a component that increases the strength of cement stone (Ovchinnikov et al., 2013).

Currently, the great scientific and practical interest of researchers is associated with the possibility of using microsilica in various industries, since most metallurgical enterprises store the microsilica obtained on special dumps. In this regard, there are significant economic losses associated, firstly, with the cost of storing and storing waste, and, secondly, with lost profit from their industrial use. The utilisation and use of dust waste from silicon production (microsilica) should be considered as an important direction in saving material resources and improving the environmental safety of adjacent territories.

At present, it is known that microsilica is widely used mainly in the production of concrete for the manufacture of very strong mixtures for the production of durable cement stone. Practical use has shown that 1 kg of silica fume provides the same strength as 5 kg of ordinary Portland cement. The high properties of silica fume improve such characteristics of the stone as compressive and flexural strength, adhesion, wear resistance, frost and chemical resistance and significantly reduce the permeability and porosity of the cement stone. "The data are published by Munkhtuvshin, Balabanov and Putsenko (2017), as well as by Butakova et al. (2017)".

In the process of production of metallic silicon, as a rule, two types of products are obtained:

– metallic silicon (with a purity of at least 98%, used in aluminum, chemical and other industries);

– silicon dust (ultrafine material obtained in the gas cleaning process of ore-thermal furnaces).

According to European and American standards for the use of microsilica (EK 13263 and ASTM C 1240), the silica content (SiO_2) in microsilica should be at least 85%. From the table (Table 1) it can be seen that the largest mass fraction is SiO_2 (at least 98%).

Microsilica is a highly active pozzolan additive to cement with fine grain size distribution, and when it interacts with cement mortar, conditions are created for the conversion of fragile calcium hydroxide (formed by mixing cement mixture with water and hydrating clinker material) into crystalline calcium silicate hydrate, which creates conditions for increasing the strength of cement stone, and microspheres fill the space that is released by water. Accordingly, the density of the composition increases, which in turn also increases its strength, and hence, its durability.

Table 1. *The chemical composition of the nanostructure concentrate based on silicon dioxide*

Substance identification	Mass fraction, %
SiO_2	no less than 98.0
CaO	no more than 0.3
MgO	no more than 0.3
Fe_2O_3	no more than 0.1
Na_2O	no more than 0.1
Al_2O_3	no more than 0.3
K_2O	no more than 0.3

Microsilicates are conglomerates of solid particles, ranging in size from submicron to several tens of microns with complex chemical and phase composition. A photograph giving an idea of the diversity of the grain size distribution of silicon dust is presented in Figure 1.

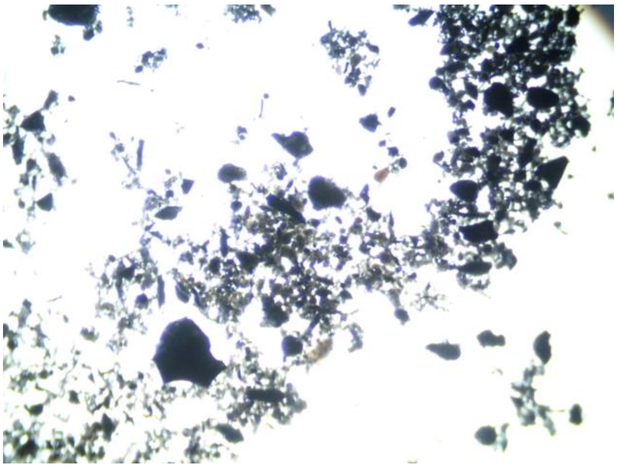

Fig. 1. Silicon dioxide nanostructures under the microscope

It should be noted that at present there are quite a few wells in which the permafrost interval is fixed by conventional pipes cemented by traditional cementing Portland cements. Therefore, for these conditions, it is important to estimate the probability of thawing of the near-wellbore zone during the operation of a well. This will solve the problem of reducing the intensity of thermal interaction in the "well-soil" system and substantiate the requirements for cement materials for securing wells in these conditions.

There is a vertical well passing through the permafrost. As a result of heat exchange between the fluid moving in the well and the frozen ground, it thaws.

We make the following assumptions: the rocks are uniform and isotropic; the density of the frozen rock is equal to the melted density; heat is transferred only by heat conduction; during the movement of the phase transition front in the permafrost, there is no mass transfer of liquid fluids.

The use of plugging materials with low thermal conductivity still leads to thawing of the near-wellbore zone of permafrost. The only question is the timing of the soil thawing around the well and the time when it loses stability. Therefore, the development of cement materials with low thermal conductivity or the use of other thermal insulation materials and technologies continue to be relevant.

In this case, another important factor affecting the strength of a cement stone is its porosity. With an increase in the total porosity of cement stone from 10 to 60%, its strength is very significantly reduced. Of all the types of pores, capillary and also pores containing trapped air have the greatest effect on porosity. With an increase in the number of such pores, the strength of the cement stone decreases. Finally, with the same degree of hydration and porosity, the strength of the cement stone depends on the nature of crystallisation of the hydrates as a filling (calcification) of large pores.

The studies were carried out with the help of computer microtomography - this is a reconstruction of three-dimensional models of x-ray images.

Methods

In accordance with the goal and objectives, the work included theoretical and experimental research. Cement samples were prepared in accordance with test standards. First, the dry components of the composition were mixed (Portland cement grouting PCT I-50, silica fume). The remaining components (amendment agent, stabiliser, plasticiser, and calcium oxide) were included in the mixing fluid. Then they were mixed in a paddle mixer with a rotation speed of 1500±100 rpm within 3 min. The water-cement ratio (W/C) for all samples was 0.5.

Low and negative temperatures slow down the setting of the cement stone, which increases the time of setting in the winter period of well construction. In this case, it is advisable to use additives that accelerate the setting. Under standard well conditions, at normal temperatures, the $CaCl_2$ electrolyte serves as a set accelerator. Calcium chloride is also often used in drilling at low temperatures; however, if the accelerator is used excessively in negative temperatures, thawing of frozen rocks during its exothermic reaction may be caused. When using 4% $CaCl_2$ solution, the solution has a high heat release rate at the beginning of the mixing (during hydration) with a minimum amount of heat generated in general.

In further studies, a 4% calcium chloride solution was used as a mixing fluid.

In addition to measuring the main properties of cement mortar, such as water-cement ratio, water separation, spreading, density, thickening time, setting time, expansion ability, adhesive strength of cement with metal, rheological properties, sedimentation stability, and permeability, significant attention was paid to measuring the strength characteristics

The temporary resistance to bending, compression and less tearing are characterised by the strength of the cement stone. Cement stone strength is variable. Usually at the beginning of hardening, it quickly increases, and then gradually stabilises, and after a while it begins to decrease. Strength is determined by the destruction of samples on a hydraulic press.

Compressive strength is determined by the destruction of samples on a hydraulic press. The prism size is 4x4x4 cm. Flexural strength is determined by the destruction of prism specimens on a tensile machine. The dimensions of the prisms are 4×4×16 cm.

To determine the compressive strength, samples are first made (cement mortar is poured into moulds of appropriate sizes, which are made of steel or plastic). At least 3 samples are made (from one batch), they are kept under the same conditions and the same amount of time. After 24±2 hours, the samples are freed from the moulds and subjected to testing on a hydraulic press. The strength is taken as the average of three dimensions. The loading rate should be no more than 2 MPa per 1 s when tested in compression.

To determine the bending strength, samples (Fig. 2) are also made (the preparation procedure is the same as for compression images). It was established that the final strength characteristics of the cement stone are acquired after 28 days of hardening. But after 2 days the strength of the cement stone is able to reach 90% or more of the maximum. Therefore, operational strength assessment is given after 2 days of hardening.

Fig. 2. Samples of cement stone under the influence of different temperatures

In this work, the samples were made and placed for a period of strength set-up (1 day) in a refrigeration chamber at temperatures of -5°C and -15°C. Further, to study the difference in the formation of cement stone with the same and different effects of thermal fields, the samples were placed in the refrigeration chamber simultaneously with the installation of the heating element (with a temperature of about 50–60°C) on the upper surface of the sample and were also left at rest for 1 day. The installation was filled with foam for thermal insulation of samples (Fig. 3).

Since the phase transformations of the components of the cement stone should be accompanied by its destruction, it is logical to assume that these changes will directly affect the structure of the pore space of the samples. In this regard, in accordance with the methodology described by Dvoynikov (2017), studies were carried out to assess changes in the structure of the pore space of samples obtained from cement slurry, which were stored at temperatures of -15, 5, 20°C at 2 and 28 days.

Studies were conducted at temperatures of 20, -5 and -15 °C with simultaneous exposure of the thermal field to the sample (heating element consisting of metal plates) and cold field (the sample was placed at negative temperatures). The time to build strength in specified modelled conditions is 2 day. Then the samples were tested for flexural strength and compression. The broken parts of the samples were checked on a microtomograph. Open, closed and total porosity, and the results of the study were divided into two “parts” – the upper side of the heat and the lower side of the cold.

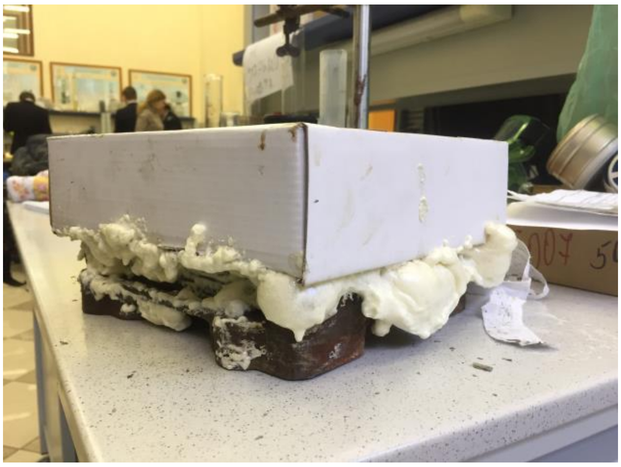

Fig. 3. Samples of cement paste in the form

Results

The table below (Table 2) presents the results of the measurement of the flexural and compressive strengths based on the average maximum value of the three samples in each experiment.

The table compares the samples prepared without the addition of microsilica and with a 10% addition to the dry mix. Samples were tested both at normal and at negative temperatures

Table 2. *The results of the study of strength characteristics of cement stone*

Temperature Max amount of strength	Standard composition (normal/negative)	Using microsilica (normal/negative)
Compressive (2 days)	10.2/8.0	19.1/14.3
Bending (7 days)	22.8/15.3	30.2/21.2
Compressive (2 days)	3.8/1.1	4.7/3.5
Bending (7 days)	9.4/3.5	12.6/5.5

According to the obtained results, it can be concluded that the addition of silicon production wastes to the cement slurry, together with the use of calcium chloride, was theoretically supposed to positively affect the properties of the cement stone and improve such indicators as strength, frost resistance, and permeability, provided that the cement content is low.

On the basis of the results in the table, we can build a graph of dependence of the amount of microsilica injected and the indicators of the strength of cement stone. The optimal percentage of microsilica is 10% of the dry mixture of the composition (Fig. 4).

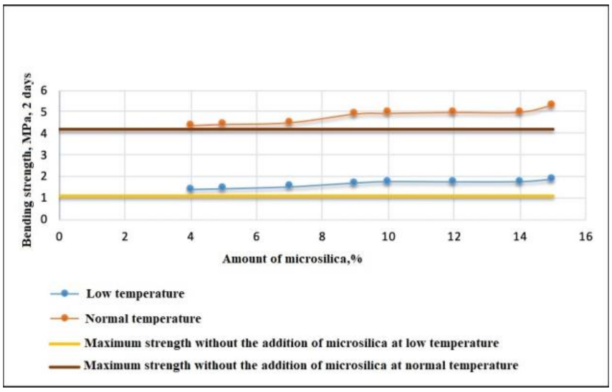

Fig. 4. Dependence of the influence of the amount of microsilica on the strength characteristics of cement stone

The analysis of the samples’ porosity shows that the total porosity has solidified for 2 days at normal temperatures and practically remains constant. For samples formed at lower temperatures, the total porosity is slightly lower. This is explained by the phase composition of the hardening products. Indeed, the cement stone obtained at these temperatures is mainly represented by hydroaluminates and calcium hydrocarboaluminates, the surface of which is blocked by the gel-like mass of partially reacted calcium hydrosilicates. Therefore, the fusion of these aggregates leads to the formation of a structure with a small pore volume and smaller size.

The confirmation is the data on the change in the integral porosity. It is noted that with increasing temperature there is an increase in pore sizes, and an increase in subcapillary pores (usually the cause of destruction processes) is not observed.

For samples hardened for 28 days, an increase in total porosity with increasing ambient temperature was observed.

However, for samples obtained and stored at the same temperature, the change in total porosity does not occur. Only redistribution of pores occurs, together with an increase in the volume of smaller pores. The result obtained is explained by the formation of the structure of the cement stone, mainly calcium hydrosilicates, which have a large specific surface, naturally a greater number of accretion contacts, and therefore a lower porosity. The redistribution of pores is caused by ongoing hydration processes. And since there is a reduction in size and there is no change in the total porosity, the results serve as another confirmation of heat resistance in the considered temperature range of stone formed from cement slurry using microspheres.

The results obtained by changing the pore structure at a temperature of -5°C for two days are quite interesting. Apparently, in this case, there are broken bonds between hydrosilicate compounds of high basicity. Since at these temperatures the solubility of the silica component is sufficiently small, the resulting low-base hydrosilicates do not have time to compensate for the negative effects of the phase transformations of the highly basic calcium silicate silicates.

For a stone made of cement-based Portland cement, without silica additives, in the study of its physical and mechanical properties a sharp drop in strength was found at temperatures of -5 and -15°C of the environment. The sample is marked by cracks. Therefore, they have not been subjected to research on changes in the pore structure.

Below (Fig. 5) a histogram is presented based on the generalised porosity data of cement stone samples.

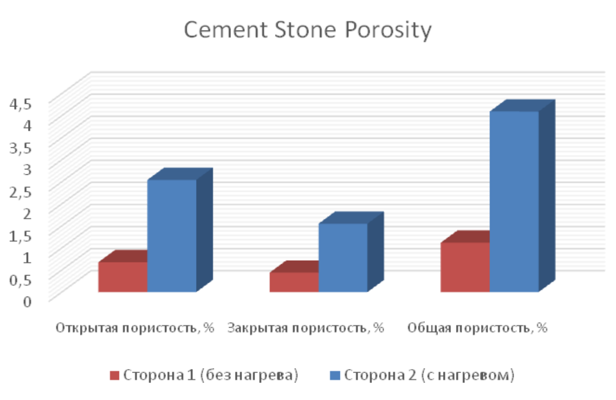

Fig. 5. Cement stone porosity

The heat side is red, the cold one is blue, respectively. As can be seen from the histogram, both open and closed (as well as total) porosity is more observed in the cold region of the sample, that is, from the frozen rocks in the well. In this regard, we can conclude that additional insulation material or technology is necessary to be added.

Conclusions

Based on the data obtained, we can draw the following conclusions: the material cracks when more than 15% of microsilica is added to the composition, so the further studies are not expedient. Adding 10% of microsilica to the solution increases the strength of the cement stone. By using it as a tempering fluid, the strength of 4% $CaCl_2$ solution is increased at negative and low temperatures. On the basis of the researches performed, it is possible to recommend the addition of calcium chloride to the composition of the cement mortar together with microsilica in order to increase the strength characteristics.

By analysing the data on the results of porosity studies, we can also conclude that at low and negative temperatures the number of pores increases, that is, an additional heating element is needed in the well.

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