Research of technological properties of cement slurries based on cements with expanding additives, portland and magnesia cement

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Abstract. The boring log in the Eastern Siberia regions is characterized by the presence of frozen rocks, which causes a number of specific drilling problems. In such conditions, magnesia materials characterized by high expanding capacity are widely used for cementing wells. These materials improve well cementing quality by increasing the areas of complete contact at the rock-cement and cement-casing boundaries. For their effective use, it is important to evaluate the cementing parameters in comparison with the traditionally used Portland cement-based plugging materials. The high quality of the magnesia cement compositions in comparison with Portland cement was justified based on the data obtained from laboratory analysis.

Keywords. Rheological characteristics, rotational viscometer, grouting compositions, portland cement, magnesia cement.

Introduction
Well cementing is an important task in the process of well construction, especially in cryolithozone conditions. The quality of well cementing determines the duration of well operation and accident-free operation. Currently, about 68% of the country’s territory is permafrost. Well construction experience in the Eastern Siberia regions shows that the presence of frozen rocks in the geological section of the well affects a number of specific drilling-related problems and accidents, such as:

- borehole instability in cases of destruction (thawing) of the wellbore;
- partial and total lost-circulation of drilling fluid into pores and cracks of “dry permafrost” rocks;
- freezing of drilling, core and casing pipes to the walls of wells;
- freezing of the liquid column in the well;
- cement slurry failing to rise to the wellhead;
- casing collapse during reverse freezing, and the like.

In addition to the above reasons, a change in well temperature due to heat transfer from the drilling fluid and cement slurry to the rocks forming the well wall during the drilling period can threaten the sealing integrity of the cement sheath with the surrounding rocks and casing and later lead to borehole collapse and sticking of drilling equipment and tools [3,11].

Overwhelmingly, during drilling and well operations, there is a washout of conductor casings and surface casings due to the unsuccessful design of wellhead equipment in the zone of frozen rocks or unsatisfactory cementing of conductors and surface casing [4,19].

The low percentage ratio of the
cement sheath adhesion to the production casing can also be explained by the deformation of shrinkage during cement hardening, the value of which can reach up to 0.3%.

Well cementing experience in difficult geological conditions shows, that the use of conventional Portland cement clinker-based materials does not always provide quality cementing. Also, in permafrost intervals it does not set even when calcium chloride is added and the hydration rate at temperatures below 4°C is insignificant. The use of shrinking plugging materials does not allow to obtain a complete information about the state of the cement sheath – rock contact, due to the lack of close contact with the casing. The use of packers also does not provide a positive result due to intensive washouts (a factor of more than 2) of rocks composed of ice.

For high-quality cementing in the permafrost zone, quick-hardening, non-shrinking, sedimentation-resistant cements that form a frost-resistant stone and have strong adhesion to casing pipes, as well as a durable stone that can withstand cyclically varying temperatures are necessary [10,20].

Currently, improving the quality of casing oil and gas well casing is gaining more attention [18]. One of such measures is the use of expanding cement materials.

Materials with special additives that provide the effect of expansion, can improve well integrity by increasing the intervals of complete contact at the “rock - cement” and “cement - casing” boundaries, which increases the stress in the areas of contact of the cement sheath with the well casing and well wall, hence, reducing the likelihood of annular cross-flow. It should be borne in mind that in the case of a high dynamic of curing, internal stresses should ensure a small amount of volumetric deformation of the cement stone. And, on the contrary, with a slow set of strength, the structure of the cement stone is able, in the process of deformation, to fill the fractures that occur during expansion.

The main indicators of expanding additives in cement slurries that affect the quality of cementing are the amount of expansion of the cement slurry — stone in the solidification process and the amount of adhesion of the cement stone to the adjacent contacting surfaces [2]. The mechanism of expansion of the cement composition occurs by filling all, even microscopic, voids in the material, ensuring the strength and solidity of the structure. Due to its ability to expand, these compounds have an increased adhesion to almost any material. The advantages include relatively high durability and resistance to aggressive effects.

There are several expansion mechanisms for cement composition [21]. The first type is sulfoaluminate expansion. The increase in volume ensures the formation of an excessive amount of the three-sulfate form of calcium hydrosulfonic aluminum in the cement stone undergoing hardening. On expansion, an interaction between calcium hydroaluminates and calcium sulfate is manifested. This expansion mechanism is observed mainly in alumina types of cements, most of which are quick-setting. The second type is oxide expansion. Oxide expansion is ensured by the formation of calcium hydroxide or magnesium hydroxide, that have a larger volume compared to the initially taken oxides. The kinetics of hydration of calcium and magnesium oxides is regulated by the burning temperature, the degree of dispersion of limestone and magnesite, as well as the introduction of additional chemicals that serve as inhibitors of the hydration reaction [6]. The third type of expansion is the use of gas-releasing additives. In well construction practices, this expansion mechanism is used in a limited form, due to the fact that at high pressures, the resulting gas can be dissolved in the pore fluid of the cement stone. The negative consequence of gas expansion is the formation of a porous cement stone, which adversely affects its strength characteristics, especially in the conditions of the Far North. In addition, the presence of porous cement stone makes it difficult to determine the quality of well cementing using acoustic logging methods [9,15].

The most suitable of all the above described mechanisms for well conditions is the oxide type of expansion of the cement composition, as it provides the maximum amount of expansion with the minimum concentration of the expanding additive.

In addition, materials based on caustic dolomite and caustic magnesite also have bulk expansion properties during hardening, and the stone formed is characterized by high strength properties and corrosion resistance. When using compositions of magnesia cement materials, the cement slurry is
characterized by high sedimentation stability, zero water separation and technologically necessary setting time and thickening time [5,8].

Since most of the research work focuses on the technological and strength characteristics of cement stone, and the study of rheological characteristics is carried out much less frequently, the rheological characteristics of cement slurries will be studied. The degree of filling of the annular space with the cement slurry is largely determined by the rheological properties of the cement slurry, which is one of the most important factors in the prevention of annular flows.

The differences between the structural and mechanical properties of magnesian cement compositions intended for cement works in oil and gas wells, and Portland cement-based solutions, which are also often used in construction, are largely due to the requirements imposed on them. There are a number of requirements for cement compositions, which includes, ensuring a proper cementing job (preparation and mixing of the cement slurry, its injection and displacement to the designated height in technologically necessary time without the occurrence of lost circulation) effective replacement of drilling mud with cement, which is achieved by providing the necessary mode of movement of the cement slurry in the annular space and others. The assessment of the structural and mechanical properties of magnesian cement mortars that meet the above requirements, and the determination of the characteristics of their rheological properties that characterize the mobility of cement slurries, are flowability, plastic viscosity and dynamic shear stress (or consistency index and exponent, if the rheological model of the solution is exponential), static shear stress and consistency [14,15,16].

In this regard, it was decided to conduct a comparative laboratory analysis of cement materials to obtain the strength and rheological characteristics of Portland cement, cement with expanding additives, an oxide additive and magnesia cement composition [23]. In order to perform the laboratory analysis, it was necessary to:

1. obtain the strength characteristics of Portland cement, expanding and magnesia cement compositions;
2. obtain rheological characteristics of Portland cement and magnesia cement compositions;
3. assess the change in rheological properties over time in conditions of low temperatures;
4. determine the values of hydraulic resistance during the movement of cement slurries of the compositions under review in the annular and tube side of the cemented casing;
5. assess the possibility of ensuring the turbulent flow of the magnesia cement slurry without the occurrence of hydraulic fracturing of the section rocks in the process of its injection.

**Research methods**

The strength of cement during bending and compression of the samples is determined by its temporary resistance to bending and compression, respectively [7]. Cement strength is variable. Usually at the beginning of hardening, it quickly increases, then gradually stabilizes, and after a while it begins to decrease. Compressive strength (dimensions of cubes 4×4×4 cm) is determined by the destruction of samples on a hydraulic press. Bending strength is determined by the destruction of samples on a tensile machine. The dimensions of the prisms are 4×4 ×16 cm [11,12].

To determine the compressive strength, samples are first made (cement mortar is poured into molds of appropriate sizes, which are made of steel). At least 3 samples are made (from one batch), they are kept under the same conditions and for the same amount of time. Before pouring the solution into the molds, extensions with a height of 5 mm are installed to provide some excess solution. After an hour of hardening, this excess solution is cut off along the edges of the mold. After 24 ± 2 hours. The samples are freed from the forms and placed in water for storage until the time of testing.

Then, after 2.3 and 7 days, the samples are 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 second when determining the compressive strength. To determine the bending strength, samples are also made
(preparation procedure is the same as for samples for compression). The tensile strength of the cement in bending is determined using the testing machine MI-100.

A comparative assessment of the rheological characteristics is performed using a Fann 35 six-speed rotational viscometer [24,25].

The test fluid is in the annulus, or shear gap, between the two cylinders. The outer cylinder, or “rotor,” rotates at a known speed (shear rate). The viscosity of the liquid mud creates a moment on the internal measuring body and the torque is transmitted through the liquid to the internal cylinder associated with a precision spring, the magnitude of the shear stress is estimated from the angle of twist. The principle of work of such a viscometer allows you to simulate the most realistic conditions of technological processes encountered in the conditions of drilling wells [26].

To assess the features of the initial structure formation of magnesium solution, the values of the rheological characteristics for the cement slurries prepared with powders of magnesia binders (without taking into account chemical additives) were primarily determined.

### Laboratory research

In connection with the required properties, it was proposed to conduct experiments on the study of the strength properties of cement compositions [17]. The results of the study of the strength of various composition of cement materials measured in the course of laboratory work, are presented in Table 1.

| Type of cement material | Flexural strength, MPa | Compressive strength, MPa |
|-------------------------|------------------------|---------------------------|
|                         | After 2 days | After 3 days | After 7 days | After 2 days | After 3 days | After 7 days |
| Portland cement         | 4,20        | 4,88         | 5,68         | 10,25        | 15,65        | 17,25        |
| Cement with expanding   | 3,60        | 5,20         | 6,55         | 10,10        | 16,00        | 16,90        |
| additives               | Magnesia cement | 3,90        | 5,88         | 6,92         | 10,10        | 16,24        | 17,54        |

Research has established that magnesia cement possess the greatest strength. The results of this study are also related to the fact that, unlike Portland cement clinker-based materials, magnesia cement materials have positive volumetric deformations of cement sheath that are characterized in the absence of free access of moisture from the surrounding. Thus, we can conclude that magnesia cement slurry to the greatest extent meets the requirements for cement slurry/cement stone placed in the annular space of the wells [1].

Next, measurements of the rheological parameters of solutions based on Portland cement (water is used as the mixing fluid) and magnesia cement (mixing fluid — bischofite solution with a density of $\rho=1,26$ g / cm$^3$) were taken. The mixing fluid was chosen because of its property to regulate the process of structure formation and the formation of gypsum binder-based cement stone when entering into fresh water, thereby influencing the thickening and setting of the cement slurry.

The first measurement of the parameters of the produced solution was taken immediately after mixing the composition at its initial temperature. Further tests were carried out at a solution temperature of 15 °C.

Further, according to the formulas 1,2,3, the data obtained experimentally were processed [13].

To determine the dynamic shear stress $\tau_0$ through two adjacent test points with coordinates $(\gamma_1; \tau_1)$ and $(\gamma_2; \tau_2)$, where $\gamma$ – is the share rate in sec$^{-1}$ was held straight to the intersection with the y-axis and Formula 1 was used.

$$
\tau_0 = \frac{\tau_2 - \tau_1}{\gamma_2 - \gamma_1} \cdot \gamma \quad [dPa]
$$

Formula to determine the plastic viscosity $\eta$
The static shear stress \( \theta \) was determined after 10 s and 1 min using the following formula:

\[
\theta_{10\,sec/1\,min} = k_1 \cdot k_2 \cdot \varphi_{10\,sec/1\,min} \text{ [dPa]},
\]

where \( k_1 \) is the constant of the torsion spring; \( k_2 \) is the shear stress constant for the effective surface of the beam; \( \varphi_{10\,sec/1\,min} \) - limb readings determined after 10 sec and 1 min respectively.

Dependences of shear stress on rotational velocity are plotted. For greater clarity, the diagram (Figure 1) shows the curves obtained for different cements. The first is for a solution with Portland cement, the second is for a solution with magnesia cement.

Both of these materials fit the well-known fluid models. Moreover, the Portland cement slurry is well described by the Bingham-Shvedov model, and the magnesian slurry is close to the Newtonian fluid model. Dynamic shear stress for magnesia cements is close to zero [22]. For Portland cement, this characterizes the fact that the solution is sedimentation unstable. But for magnesia cements such dependence is not visible.

Figure 1. Dependence of dynamic shear stress on shear rate for solutions based on Portland cement and magnesia cement

The study found that over time at the same rotational speeds, the shear stresses increase with time, and the rheological models retain their appearance (Figure 2 and Figure 3).
Magnesia cements are characterized by increasing shear strengths (increase in value with time). This trend was not observed in portland cement slurries (Table 2). This can lead to the fact that short stops in the process of moving the solution can result in the formation of a difficult to pump slurry.

**Table 2.** Comparative results of laboratory studies of the rheological characteristics of Portland cement and magnesia cement slurries

| №  | Name of material and composition | \( \rho, \text{g/cm}^3 \) | \( \eta, \text{mPA*sec} \) | \( \tau_0, \text{dPa} \) | Shear strength, \( \text{dPa} \) | Shear strength, \( \text{dPa} \) | Shear strength, \( \text{dPa} \) | Shear strength, \( \text{dPa} \) | Shear strength, \( \text{dPa} \) |
|----|----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1  | Portland cement slurry           | 1,83 | 36,8 | 154,4 | 61,2 | 61,2 | 43,5 | 160,4 | 56,1 | 56,1 | 41,3 | 156,8 | 61,2 | 61,2 | 46,1 | 162,2 | 61,2 | 68,8 |
| 2  | Magnesia cement slurry           | 1,68 | 105  | 9,58  | 2,5  | 2,5  | 154,5 | 5  | 2,5  | 7,6  | 154,5 | 5  | 2,5  | 7,6  | 160,5 | 0  | 5,1  | 30,6 |
It is well known that the best replacement of drilling mud with plugging occurs in the turbulent flow regime. Using known formulas, the minimum velocity (denoted as Vkr) required to create a turbulent flow in the annular and tubular space during well cementing, and the hydraulic resistances were calculated. It is seen in Table 3 that for magnesian compositions, the transition to the turbulent flow regime occurs at higher flow rates.

**Table 3.** Results of the hydraulic calculation of Portland cement and magnesia cement slurries

|                  | Portland cement slurry | Magnesia cement slurry |
|------------------|------------------------|------------------------|
|                  | ρ, g/cm³               | 1,83                   | 1,68                   |
| Vkr, m/s         | in the annular space   | 1,75                   | 0,59                   |
|                  | in pipe                | 1,73                   | 0,51                   |
| Pmin, MPa        | in the annular space   | 2,133                  | 0,237                  |
|                  | in pipe                | 1,910                  | 0,198                  |

The hydraulic resistances (Pmin) was calculated at this particular speed, thus, the minimum hydrodynamic resistances arising during the transition to turbulent regime were obtained.

**Conclusions**

Magnesia-based cement compositions have better technological properties than Portland-cement compositions, allowing them to be prepared, pumped and placed in the annulus. The use of magnesia plugging materials ensures annulus integrity space due to the qualitative replacement of drilling mud with cement slurry.

Nevertheless, a further study of cement slurries with different expansion mechanisms should be aimed at the development of compositions that provide high-quality cementing of the entire well interval. It is also advisable to study prospective components that had not been previously used in cement compositions. Owing to the cheapness of compositions with expansion additives in comparison with magnesia cements, they can be used also in conjunction with additives that influence the increase in strength of cement sheath. One of such additives is silica fume, which is formed by cleaning the ore-thermal furnaces at metallurgical enterprises.

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