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INCREASE IN THE EFFICIENCY OF WATER SHUT-OFF WITH THE APPLICATION OF POLYETYLENPOLYAMINE ADDED CEMENT

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Abstract: *As a result of intrastratal and interlayer flows of produced water of varying intensity, 25% of oil and gas wells are water-encroached in the world. Due to behind casing flow during the operation of oil and gas wells generally reduces the field's development efficiency. In the study, 1-6% (weight) polyethylene polyamine (PEPA) was added to the water in which the cement mixture will be prepared. The temperature dependence of the beginning and the end of the setting time of the obtained cement mortar was determined. Also, the adhesion properties of the cement mortar, the dependence of the strength to bending and compression on the dose of polymer were examined. It found that cement stone made of mixing cement with an aqueous solution containing 1-4% PEPA had high elastic properties. In addition, the presence of 2±1.5% PEPA in the specified amount of tampon solution increases the strength and to depressions of cement stone, improves adhesion properties.*
Keywords*: cement slurry; well productivity; polyethylene polyamine; wellbottom zone; cement stone; adhesion*
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Introduction

The rate of the products watercut in the wells under operation in the oil fields of Azneft PU varies depending on the life of the field and the stimulation methods. The water-encroachment rate of wells varies widely and is 30-40% in offshore fields and 85-99% in onshore fields. The analysis of the operation of flooded wells shows that for every ton of oil recovered more than 15 m3 of water is produced, which is economically and ecologically unacceptable.

One of the urgent problems is to increase the efficiency of technological processes to be applied in order to prevent the well product from being flooded. To do this, first of all, it is necessary to determine the source of water entering the well and to study the existing technological processes against it, to improve it taking into account its shortcomings, or to develop a new technological process [1-3].

In order to prevent or limit the flooding of oil well products, a mixture of various materials with cement, chemical agents and polymers are used. Water ingress into the well is possible both through filtration channels due to depletion of the formation, as well as the splash of the injected water, its flow from the productive horizon above or below the annular circulation, as well as the integrity of the layers [4].

The most common way to solve this problem is to fix with cement. However, due to insufficient adhesion of the cement mortar to the rock, insufficient elasticity and plasticity, the addition of a certain amount of polymeric substances to the composition results in enhancement these properties. The analysis of the references shows that despite some scientific research and applied work in this direction, researchers are focusing on the development of new cement-polymer compositions that retain their elastic properties for a long time or have similar qualities for both the oil industry and construction [5,6].

Min O.K. [7] determined the compressive strength, bending resistance, and adhesion of hardened cement at 7 and 28 days by adding up to 3% polyvinyl alcohol, butadiene-styrene rubber, polyacrylate, and ethylene-vinyl acetate (EVA) to portland cement. It was shown that after 7 and 28 days, the EVA-cement mixture is resistant to compression at 44 and 50 MPa, respectively, which in the control cement it has a price of 35-37 MPa.

In another study [8] using styrene-butadiene latex, acrylic and styrene-acrylic emulsion in the amount of 5; 10; 15 və 20%, cement-polymer mixtures were prepared and the mechanical parameters of the cement stone were determined. It revealed that the best water reduction effect occurred in SBL. As the amount of polymers in the cement increases, the permeability decreases. In all cases, the addition of polymer latex or emulsions increases the strength, plasticity and adhesion of the cement stone or the ability of the components to bond together.

As mentioned, low adhesion and penetration of the cement mortar, as well as high retraction and permeability lead to undesirable performance of cement stone. D.M P. Costa was able to prepare a highly elastic, durable cement stone that adheres well to low water-cement factors by adding polyacrylic acid as a plasticizer to the cement mortar and styrene-butadiene latex as an adhesion enhancer. It was shown that as the polymer / cement factor increases, the viscosity and spreading rate of the solution decreases. When the polymer/cement = 15%, the setting strength and shrinkage properties of the mixture were found to be effective [9].

In general, the analysis of the literature shows that by adding epoxy-acrylic emulsions [10], styrene-butadiene rubbers [11], latexes of various compositions [12,13], and even inorganic substances, it is possible to increase the plasticity and elasticity of concrete stone.It also eliminates the fragility of cement stone, which achieves economic benefits by prolonging its life.

The occurrence of formation and offshore flows during the operation of oil and gas wells generally reduces the development efficiency of the field. As a rule, flows occur in contact of the cement stone with the rock, and this is due to the lack of adhesion between the cement and the rock. The operational efficiency of oil and gas wells is largely dependent on the methods and materials used to secure the pipeline. Quality cementing ensures the longevity of well operation and, accordingly, the stability of oil and gas production. It is known that the strength of the cement stone in contact with the rock which provides the integrity of the casing, is one of the main features of the assessment of well reinforcement.

In the study, polyethylene-polyamine (PEPA) brand polymer was used in the preparation of cement solution from water-based solution in different percentages to determine the amount of cement slurry.

Experimental part

The cement used in the experiments is a special cement brand G-CC-1 (API Spec 10A Class G-HSR, Russia), the physical characteristics of which (Table 1) meet the standards required for the reinforcement of wellbore zones. PEPA, on the other hand, has a linear structure (Fig. 1), and is widely used as an epoxy resin binder. and is derived from Sigma Aldrich (CAS.No: 68131-73-7).

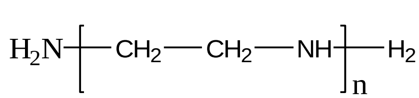

Fig. 1. Chemical structure of polyethylene polyamine

Water-based Portland cement slurry meets G-CC-1 (API Spec 10A Class G-HSR) standards.

Table 1. Physical and mechanical properties of cement slurry and PEPA

Special surface area, cm^2/gr	Setting time, hour-minute		Compression resistance, MPa						
	start	end	3 hours	6 hours	3 days	7 days		28 days	
4765	8-24	12-38	24.8	29.4	38.5	41.7		44.6	
Mineral and chemical composition of the element, % (mass)									
Al_2O_3	CaO	SO_3	SiO_2	Alkalinity, Na_2O	MgO	C_4AF+2C_3A	Tricalcium silicate	Tricalcium aluminate	
5.2	62.4	≤ 2.6	20.7	0.56	≤ 1.23	18.41	≥ 59.2	2.21	
Polyethylene polyamine									
M, gr/mol	Density, kg/m^3	Humidity, %	Solvent	Total nitrogen, %	Mineral mixtures, %	Color, odour, state of aggregation	Viscosity, mPa×s	Melting temperature, °C	
230-250	950-1050	2	H_2O, C_2H_5OH	30	0.2	Light yellow, NH_3 odorous, liquid	250	30	

$C_4AF + 2C_3A$ *- Tetracalciumaluminiumferrite +2 tricalciumaluminosilicate*
M *- average molecular weight*

Research to test the adhesion of G-CC-1 (API Spec 10A Class G-HSR) cement to rock in laboratory conditions at a water-cement ratio of 0.5 to 25 at temperatures of 50 and 75 □C on Adhesimeter ONIKS-1AP (Russian) (Figure 2,a) were carried out. A 20 mm diameter smooth steel rod was immersed 10 cm vertically into the cement slurry and let to set for 24 and 48 hours. In order to determine the initial and final setting time of the cement slurry, samples mixed with water containing 1-6% by weight of PEPA at a ratio of 0.5 water-cement factor were tested on a Vikatronic (Fig. 2, c) (Italy) device.

Fig. 2. Adhesion (a) properties of cement solutions, devices for determining the resistance to compression and bending (b) and setting times (c)

To determine the compressive and bending strength of the cement stone, concretes of 40×40×40 and 40×40×200 mm were prepared in a certain composition and tested on a Matest (Figure 2, b) (Italy) device. Their contains 1-6% PEPA in the liquid used to make concrete. The tests were compared comparatively at different temperature ranges.

Results and discussion

As is known, the time at which the solutions are prepared and the time at which they begin to set is an important parameter in cementing the wellbore or annulus. The fact that this period is too short is not conducive to applicationPremature setting process prevents the ideal injection of cement mortar, destroys equipment and can create undesirable rivets. The initial setting time of ordinary cement mortar is about 8 hours, which is technologically advantageous. The starting and ending points of cement setting mixed with 1-6% (mass) PEPA-added water at 25 °C were determined (Fig. 3).

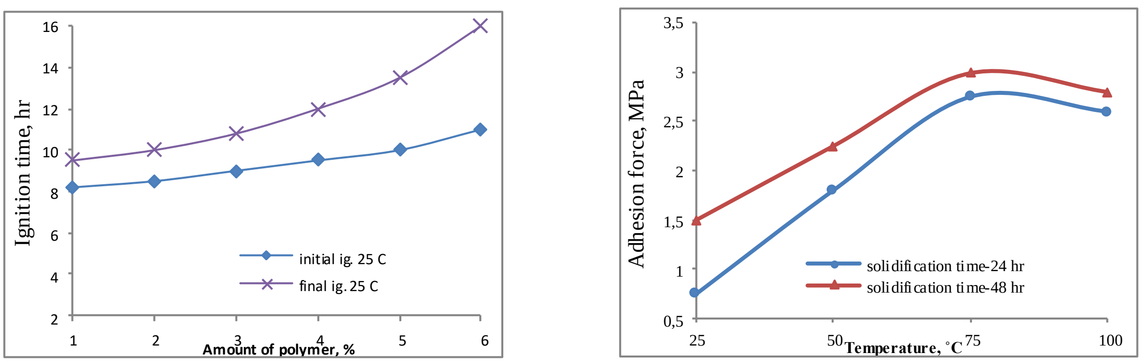

Fig. 3. Dependence of adherence of cement stone made of cement brand G-CC-1 to steel rod on setting time and temperature

As can be seen from Fig. 3, the beginning and the end of the setting time increase as the amount of polymer in the mixture increases. As the temperature increase, the beginning and the end of the setting time decreases. The initial setting time of the cement slurry prepared with 1% polymer solution is 8 hours and 15 minutes, and when the polymer content is 6%, it is 10 hours and 30 minutes at these temperatures. The final setting time of the cement slurry prepared with 1% polymer solution was 10 hours 30 minutes and 16 hours at the same temperature when the polymer content was 6%. For different temperature values, the beginning and end of setting time can be determined by the following equations:

$$\text{initial setting } (t = 25\ °C)\ t_{init} = 0.063C^2 + 0.11C + 8.1$$
$$\text{final setting } (t = 25\ °C)\ t_{fin} = 0.23C^2 - 0.34C + 9.7$$

It found that the initial cost of setting of the cement slurry in the amount of 1-3% of PEPA is observed with a slight increase. After 5%, this value increases to 1 hour which is effective in fixing the layer in the deeper parts. As can be seen, the end point of the setting increases from 9 to 15-16 hours. This makes perforation operations easier to manage and lower energy costs. The effect of increasing the amount of polymer on the setting time of the cement slurry is due to its chemical nature. Thus, the interaction between high-viscosity PEPA macromolecules and cement particles affects this process. The polymer chain limits the setting process of the cement slurry. This is due to the pre-accumulation of water molecules around PEPA which causes solidification. After the PEPA-water system is mixed with cement powder, the water molecules first move away from the polymer chain and then began to participate in the solidification process. Depending on the application process, the amount of PEPA may be be appropriate. The use of 3% polymer in the system we studied was accepted as the optimal amount, and this composition was used in subsequent studies.

As is known, their adhesion properties are an important parameter in the preparation of cement slurry. This affects their adhesion to the rock surface, in which case the adhesions of the prepared mass after 24 and 48 hours are maintained in the range of 25-100 °C with the retention of 0.5 water-cement factor containing 3% PEPA (Fig. 3). It is shown that the adhesion force increased depending on the temperature and curing time. The calculation of adhesion for different temperature values could be determined by the following equations:

Adhesion force after 24 hours $P_{adg} = -0.0005t^2 + 0.086t-1.15$

After 48 hours the adhesion force $P_{adg} =- 0.0004t^2 + 0.066t + 0.05$

When the heating temperature of cement stone increases from 25 °C to 50 °C, the adhesion force increases from 1.5 MPa to 2.4 MPa, from 50 °C to 75 °C from 2.4 MPa to 2.8 Mpa; from 75 °C to 100 °C from 2.8 MPa to 3 MPa. In both cases, the adhesion of the cement mass to 75 °C was found to increase from 0.75 MPa to 2.65 MPa. This is due to the increase in the flexibility of both cement particles and the polymer macromolecule as a result of the increase in temperature. The decrease in adhesion after 75 °C can be explained mainly by the release of water molecules in the composition and by the rupture of the physicochemical bonds between the polymer and the cement components. In addition, if the ambient temperature is above 75 °C, the increase in adhesion force decreases with both curing time and temperature. This can be explained by the fact that the coefficients of thermal expansion of cement stone and metal rods have different values.

Once the cement stone is fully cured, its resistance to compression and bending is an important factor in stabilizing the well bottom areas. From this point of view, the resistance of cement stone samples containing 1-6% PEPA to compressive and bending forces under pressure was measured (Fig. 4).

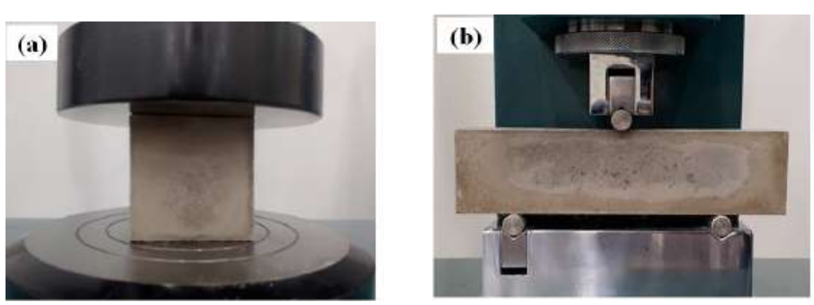

Fig. 4. Experimental test of compressive (a) and bending (b) resistance of cement stone containing 3% PEPA

Cube-shaped cement stones were used to limit the compressive strength, and rectangular prisms were used for bending resistance. Results of the dependence of compression and bending resistance on the amount of PEPA are given in Fig. 5.

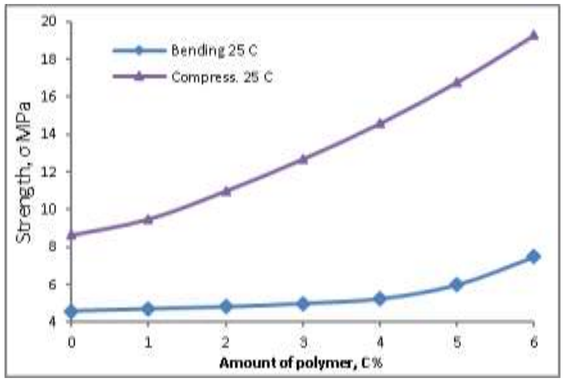

Fig. 5. Strength of G-CC-1 cement stone in the ratio of 0.5 water-cement to the amount of polymer

The values of compressive and bending resistance of cement stone at a temperature of 25 ℃ can be calculated by the following equations:

$$t = 25\ ℃\ \sigma_{bend.} = -0.086C^2 + 0.5C + 4.4$$
$$t = 25\ ℃\ \sigma_{compress.} = 0.144C^2 + 0.93C + 8.6$$

As can be seen from Fig. 5, when the polymer content in the mixture is up to 4%, the strength of the cement stone against bending and compression at 25 °C decreases by 7.1 and 2.6%, respectively, and by 10.5-11.5% when the polymer content is 5-6%. In accordance with this law, the ambient temperature is maintained. As the amount of PEPA in the composition increases, the resistance of the cement stone to compression and bending increases due to the plasticity and elasticity of the polymer. It is known that PEPA, because it consists of long macromolecular chains, provides interaction between particles. In addition, the elasticity characteristic of polymers is retained which is reflected in the cement stone.

During the study, the change in the conductivity of the cement-polymer stone after 48 hours following the curing depending on the amount and temperature of the polymer was studied and the results are given in Table 2.

Table 2. Changes in the performance of the cement slurry and cement stone depending on the amount of polymer and temperature

N	Amount of components, %			Setting time, hour-minute		Stone resistance after 48 hours, MPa		Stone permeability, k mkm^2
	cement	water	polymer	start	end	bending	compression	
1	2	3	4	5	6	7	8	9
$P = 0{,}1\ MPa, t = 25\ ℃$								
1	66	35	1	7-55	10-25	4.3	11.1	0.18
2	66	31	3	8-30	11-20	4.5	11.5	0.182
3	66	30	4	9-10	13-10	4.6	11.8	0.185

4	66	29	5	9-55	15-50	3.8	10.4	0.189
5	64	30	6	10-35	18-45	3.7	10	0.192

As can be seen from the Table, as the amount of polymer in the mixture increases, the permeability of the cement-polymer stone also increases. As the ambient temperature increases, the conductivity decreases as well. One of the main characteristics of the stone made by adding 4% of polymer PEPA to the cement is that it is more durable in terms of breaking strength. This feature is due to the relatively high elasticity of cement-polymer stone.

In laboratory studies, samples prepared by adding 4% (relative to water) of PEPA polymer to G-CC-1 cement were tested for durability after 48 hours of curing at 25°C. The procedure for comparative research, the scheme of studying the elastic properties of pure cement stone, and that obtained by adding 4% PEPA brand polymer to cement is given in Fig. 6.

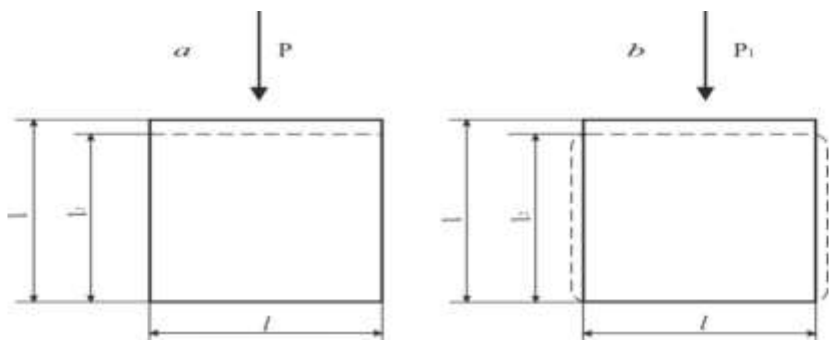

Fig. 6. Schematic description of the determination of elasticity of G-CC-1 cement stone and 4% PEPA-added mixture following 48 hours of curing, 25°C

Both samples are cubic and have dimensions $l = 40\times10^{-2}$ m. When force P (Fig. 6, a) was applied to samples made of pure cement, it collapsed after its height decreased from l to l_1. When the compressive pressure applied to the cement-polymer stone is P_1=P, the sample retains its integrity, and at a subsequent pressure increase, the sample collapses when the sample size reaches l_2 (Fig. 6, b). The coefficient of elasticity of cement-polymer stone is determined by the formula as follows:

$$\lambda_s = \frac{l-l_1}{l};\ \lambda_p = \frac{l-l_2}{l};$$

The ratio of the elasticity coefficients of cement and cement-polymer stones characterizes how the elastic properties change when a polymer is added to cement.

$$\frac{\lambda_p}{\lambda_s} = \frac{l-l_2}{l-l_1}$$

Samples made of pure cement with a water-cement ratio of 0.5 had a displacement pressure of 11.5 MPa at 25°C, while a stone with a 4% polymer added had a displacement pressure of 11.8 MPa.Thus, the compressive strength of cement-polymer stone is increased to 2.6% at the specified temperature, respectively.

When the cement sample was tested at a temperature of 25°C up to the compression (collapse) pressure, it was found that the sample begins to collapse when the pressure decreases to a height of 11.8 MPa at a height of l-l1 = 40-39 = 1 mm.

As a result of the research, it was determined that the performance of the mortar and cement stone was higher when G-CC-1 cement was mixed with PEPA polymer with 3-4% of the required water with a water-cement ratio of 0.5. Therefore, in order to prevent or limit the watering of the well product, it is possible to prepare concrete stone that can effectively adhere to the rock surface and is resistant to dynamic cracks by taking the components of the cement slurry to be injected into the reservoir in the following weight ratios: cement-100; liquid-cement ratio-0.5; polymer PEPA-3-4%; water-47-46.

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POLİETİLENPOLİAMİN ƏLAVƏ EDİLMİŞ SEMENTİN TƏTBİQİ İLƏ LAY SULARININ TƏCRİDİ ÜÇÜN EFFEKTİV TAMPONLAYICI TƏRKİBİN TƏDQİQİ

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Xülasə: *Dünyada neft və qaz quyularının 25%-i lay suların müxtəlif intensivlikli lay daxili və laylar arası axını nəticəsində sulaşmaya məruz qalır. Neft və qaz quyularının istismarı zamanı kəmərarxası axınların yaranması ümumilikdə yatağın işlənmə səmərəliliyini azaldır. Tədqiqatda sement qarışımı hazırlanacaq suya 1-6% (kütlə) polietilenpoliamin əlavə edilmişdir. Əldə olunmuş sement məhlulunun tutuşma vaxtının əvvəli və sonunun temperaturdan asılılığı müəyyən edilmişdir. Həmçinin sement məhlulunun adgeziya xassəsi, əyilməyə və sıxılmaya davamlılığınını polimerin miqdarından asılılığı tədqiq edilmişdir. Müəyyən olunmuşdur ki, sementin tərkibində 1-4% PEPA olan sulu məhlulu ilə qarışdırılmasından hazırlanmış sement daşı yüksək elastiki xassələrə malikdir. Bundan başqa göstərilən miqdarda tamponaj məhlulunun tərkibində 2±1.5% PEPA olduqda sement daşının möhkəmliyini artırması, adgeziya xüsusiyyətlərinin yaxşılaşdırması və depressiyalara qarşı müqavimətinin artırması baş verir.*

Açar sözlər: *tamponaj məhlulu, quyunun məhsuldarlığı, polietilenpoliamin, quyudibi ətrafi sahə,sement daşı, adgeziya*

ИССЛЕДОВАНИЕ ЭФФЕКТИВНОГО ТАМПОНАЖНОГО СОСТАВА ДЛЯ ИЗОЛЯЦИИ ПЛАСТОВОЙ ВОДЫ С ПРИМЕНЕНИЕМ ЦЕМЕНТА С ДОБАВКОЙ ПОЛИЭТИЛЕНПОЛИАМИНА

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Аннотация: *25 % нефтяных и газовых скважин в мире обводняются за счет внутренних и межпластовых перетоков пластовых вод различной интенсивности. Возникновение заколонных перетоков при эксплуатации нефтяных и газовых скважин в целом снижается эффективность разработки месторождений. В ходе исследования в воду затворения, в которой будет готовиться цементная смесь, добавляли 1-6% (масс.) полиэтиленполиамина (ПЭПА). Определена температурная зависимость начала и окончания времени схватывания полученного цементного раствора. Также были изучены адгезионные свойства цементного раствора, зависимость сопротивления изгибу и сжатию от количества полимера. Установлено, что цементный камень, затворенный водной основой, содержащей 1-4 % ПЭПА, обладает высокими упругими свойствами. Кроме того, наличие 2±1.5 % ПЭПА в указанном количестве тампонажного раствора повышает прочность цементного камня, улучшает адгезионные свойства и повышает устойчивость к депрессиям.*

Ключевые слова: *тампонажный раствор, производительность скважины, полимер, призабойная зона, цементный камень, адгезия, порода.*