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RESULTS OF CEMENT-TO-ROCK CONTACT STUDY

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The paper focuses on the problems of oil and gas well cementation. It has been established that the main reason why formation fluids leak behind the casing is due to poor isolation of the annulus caused by incomplete cleaning of the filter cake, which results in weak or absent adhesion between the cement and the rock. The authors demonstrate that adding polymer modifier GM-II to the spacer fluid strengthens the cement-to-rock contact by several times. Moreover, mixing spacer with cement slurry does not degrade such important properties as spreadability and consistency of the latter. The paper contains investigation results on the content of polymer spacers that improve cementation quality of oil and gas wells. Spectral infrared and X-ray analysis allowed to define the impact of phase composition and mineral structure of the system «cement stone-filter cake-formation rock» on improving leak tightness of the annulus. Electron microscopic study showed that the use of polymer spacers facilitates formation of felted net-like structures between hydrated minerals. The composition of these structures, binding cement grains and clay minerals, has been studied by means of energy dispersive X-ray microanalysis. Obtained results allow to come to the conclusion that these structures mostly consist of hydrated calcium silicate (more than 77% by mass), which agrees well with the findings of infrared and X-ray analysis. Pilot tests, performed at the Shengli oil field in China, have confirmed efficiency of developed spacer fluids.

Key words: well cementation, spacer fluid, filter cake, cement stone, adhesion, clay and cement minerals

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Introduction. Casing and cementation belong to the key processes of wellbore construction, and are characterized by high technological complexity. Over 25% of oil and gas wells in the world have inter-reservoir communications of varying intensity, leading to great economic losses [14]. Behind-the-casing leakages usually follow the cement-to-rock contact, as in many cases complete removal of the filter cake is impossible. As a result, there is no adhesive connection between the cement stone and the formation rock. With this in mind, it is evidently a highly relevant task to develop new polymer spacers which will increase cement-to-rock adhesion.

Authors present results of experimental research on contact strength (adhesion) in the system «cement stone – filter cake – formation rock» with varying concentrations of polymer modified clay GM-II and on its changes in the cement setting process (temperature 90 °C) [6].

Research methods and analysis of obtained results. The impact that developed compositions of spacer fluids have on the filter cake and cement slurry can be divided into several stages [8]. At the first stage, loose clay particles decompose in the spacer solution and form active ions that implement into the filter cake; shattered clay particles bind together into stable polymer chains.

At the second stage, a part of spacer solution diffuses into cement slurry. Hydrate ions of the latter are absorbed by the polymer grains of the solution, cement slurry and filter cake exchange their ions. After the annulus is filled with grouting mortar, the system «cement stone – filter cake – formation rock» is established.

The third stage is marked with the setting of the above mentioned system. Binding substances, responsible for peculiar net-like structures between the filter cake and cement stone, form on the surface of polymer spacer grains. These minerals play an important role in the improvement of well cementation quality.

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It has been identified [5] that polymer spacer fluids with various concentrations of GM-II have significantly higher adhesion between the cement stone and rock formation. As GM-II concentration rises from 15 to 25 %, in two days adhesion increases by factor of 6-18, in 60 days – roughly by factor of 14.

In order to test the possibility of using polymer spacers in wellbore cementation, experimental research has been carried out, where drilling mud and cement slurry were mixed with spacer fluids [15].

Results of spreadability tests for clay and grouting mortars with varying content of polymer spacer are presented in Table 1. The data clearly demonstrates that the growth of spacer concentration directly correlates with increasing spreadability of the mixture.

Table 1

Results of spreadability tests for grouting mortar (water-to-cement ratio 0.5) and polymer spacer

Composition of the grouting mortar and polymer spacer (by volume)	Spreadability, cm	Composition of the grouting mortar and polymer spacer (by volume)	Spreadability, cm
Grouting mortar	17	Grouting mortar: polymer spacer = 4 : 1	> 25
Grouting mortar: polymer spacer = 9.5 : 0.5	18	Grouting mortar: polymer spacer = 7 : 2	> 25
Grouting mortar: polymer spacer = 9 : 1	21	Grouting mortar: polymer spacer = 5 : 5	> 25

Results of research on the consistency of clay and grouting mortars with varying content of polymer spacer are presented in Fig.1 [16]. The graphs demonstrate that the time needed to reach technological conditions that would satisfy regulatory requirements of the cementing process is limited to two hours.

At the next stage, the authors investigated the impact of phase composition and mineral structure of the system «cement stone-filter cake-formation rock» on improving leak tightness of the annulus [3, 4].

Infrared spectroscopy of samples with polymer spacer allowed to identify binding hydrosilicates C–H–S(I) and zeolites (Fig.2). Peaks on the infrared spectrum of the control sample in the area of 3623 and 718.48 cm^{-1} correspond to stretching vibrations of O–H and Si–O in montmorillonite [7]. Infrared spectrum of polymer spacer sample does not contain these peaks, which points to the fact that montmorillonites in the filter cake were modified as a result of interaction with the spacer fluid. The peaks, corresponding to stretching vibrations of H_2O, are displaced in the spacer sample (wavelength

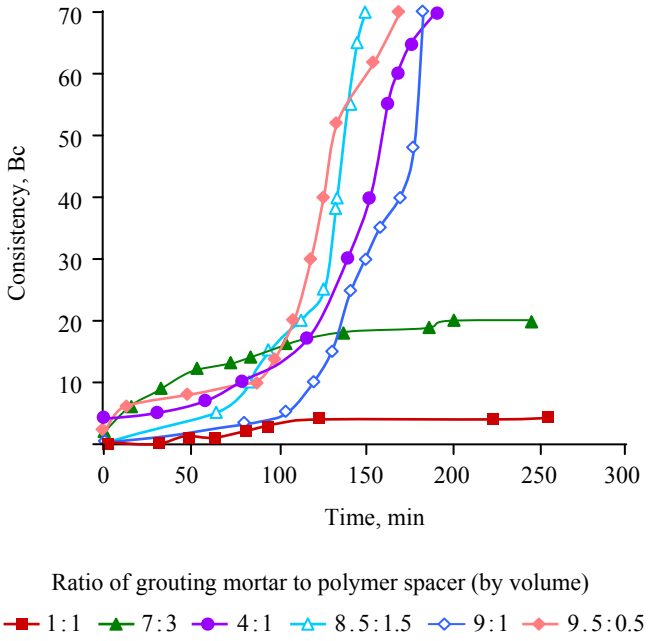


Fig.1. Dependency between grouting mortar consistency and polymer spacer composition by volume (t = 90 °C)

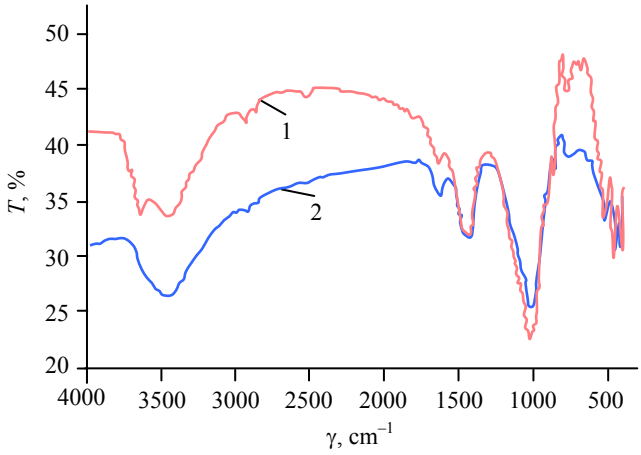


Fig.2. Infrared spectrogram of the cement-to-rock system composition
1 – control sample; 2 – polymer spacer sample

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3438.43 cm^{-1}) as compared to the control sample (wavelength 3438.45 cm^{-1}), which points to significant differences in their structures. The absorption spectrum at wavelength 3462.04 cm^{-1} corresponds to hydrosilicate C–H–S(I), and the band at 669.71 cm^{-1} is characteristic of zeolites [9].

It is an established fact [2, 13] that hydrosilicates C–H–S(I) and zeolites can bind grains of cement and clay minerals and reduce tension on their contact, which plays an important role in increasing adhesion on the boundary «cement stone – filter cake – formation rock».

Mineral composition of the filter cake can be examined by means of X-ray structural analysis, results of which are presented in Tables 2 and 3. X-ray structural analysis of filter cake composition revealed the prevalence of inert minerals (quartz, calcites, feldspars, montmorillonites, chlorides etc.) in control samples.

A the same time, polymer spacer samples were observed to contain binding materials: hydrated calcium silicate, ettringite, hydrated calcium alluminate, hydrosulphoaluminate, which increased cement-to-rock adhesion [1, 18].

Table 2

Results of X-ray structural analysis of the mineral composition for control samples

Characteristic peak $n \times 1000$	Hydration product	Characteristic peak $n \times 1000$	Hydration product
3.0945; 2.1167; 1.5330 etc.	Calcite	3.7593; 3.3089; 1.8540 etc.	Feldspar
2.8289; 2.4751; 1.4895 etc.	Quartz	4.4719; 2.1010; 1.6711 etc.	Montmorillonite
4.4240; 1.8170; 1.5334 etc.	Iddingsite	4.3207; 3.0945; 1.6370 etc.	Chloride

Table 3

Results of X-ray structural analysis of the mineral composition for polymer spacer samples

Characteristic peak $n \times 1000$	Hydration product	Characteristic peak $n \times 1000$	Hydration product
3.0292; 2.8303; 1.5261 etc.	Calcite	2.2792; 1.5330; 1.4562 etc.	$Mg(OH)_2$
3.8895; 3.3131; 1.8170 etc.	Quartz	3.6774; 2.4785; 1.9282 etc.	$Al_2SiO_4(OH)_2$
4.4313; 1.8170; 1.5334 etc.	Iddingsite	4.2455; 3.7619; 1.9284 etc.	Hydrated calcium silicate
3.7619; 3.2810; 1.8558 etc.	Feldspar	3.3601; 2.5281; 1.8558 etc.	Hydrosulphoaluminate
4.5907; 2.8303; 1.6354 etc.	Chloride	3.3601; 2.4785; 1.8558 etc.	$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot nH_2O$
4.3276; 3.3130; 1.5334 etc.	$CaSO_4 \cdot 2H_2O$		

Microphotographs demonstrate that the use of polymer spacer fluid facilitates formation of felted net-like structures between hydrated minerals. These structures bind cement grains and loose particles of clay minerals (Fig.3). The structure of the minerals is dense and solid. In con-

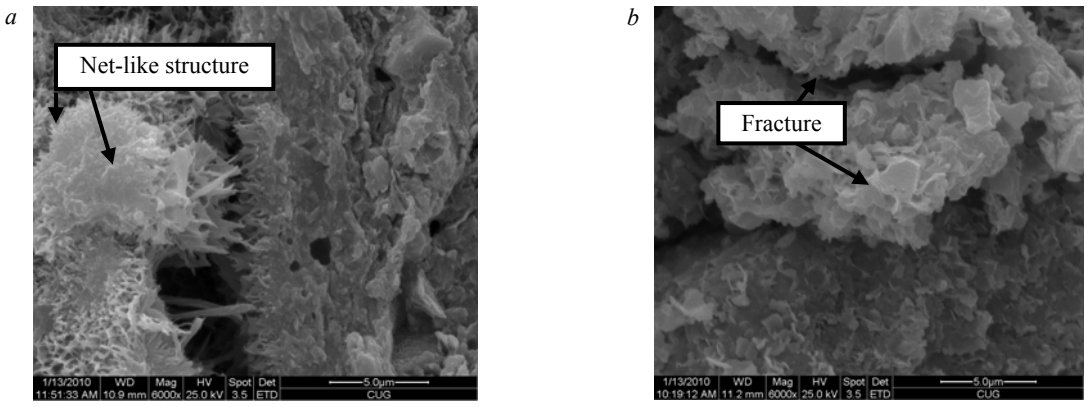


Fig.3. Microphotographs of the system «cement stone – filter cake – formation rock»:
a – polymer spacer samples; *b* – control samples. Magnification 6000^x

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trol samples, the intermediate zone between the cement and the filter cake has a lot of fractures and pores.

Analysis of the mechanism and process of interaction between the spacer fluid, grouting mortar and the filter cake revealed that polymer spacer is highly alkaline, which leads to degradation of filter cake particles. This process can be formulated as follows [11]: montmorillonite ((Ca, Na) (Mg, Al, Fe)$_2$[(Si, Al)$_4$O$_{10}$] (OH)$_2$·nH$_2$O)

$$Na_2SiO_3 = 2Na^+ + SiO_3^{2-};$$

$$Al_2O_3 + 2NaOH = 2NaAlO_2 + H_2O;$$

$$NaAlO_2 = Na^+ + AlO_2^-;$$

kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$)

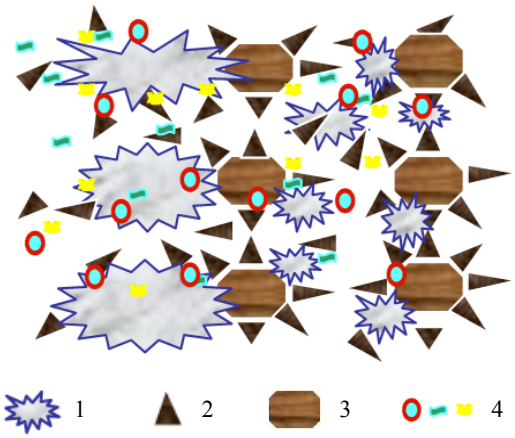


Fig.4. Pattern of interaction between polymer spacer and clay minerals

1 – polymer grain of spacer fluid; 2 – small mineral particles; 3 – clay minerals; 4 – active ions

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al(OH)_3 + 2 \cdot Si(OH)_4;$$

$$A1_2Si_2O_5(OH)_4 + 2Na^+ + 2OH^- + 4Si(OH)_4 = 2NaAlSi_3O_3 + 11H_2O;$$

$$A1_2Si_2O_5(OH)_4 + 2Na^+ + 2OH^- + 2Si(OH)_4 = 2NaA1Si_2O_6 \cdot H_2O + 5H_2O.$$

Illite, chlorite and hydromuscovite, as well as montmorillonite and kaolinite share similar oxides, hence the products of their reaction with polymer spacer are identical.

As a result of clay mineral degradation, the alkaline solution contains free anions SiO_3^{2-}, AlO_2^- and cations K^+, Na^+, Ca^{2+}, Mg^{2+}. This encourages their participation in consequent setting reaction and creates a possibility of their implantation into the filter cake through the destruction of clay particles in the alkaline media. Most polymer spacer minerals do not bind solely to the surface of the filter cake, but get implanted within its structure.

Apart from that, polymer spacer solution contains numerous hydroxyls R–OH and salts R–COO^+, which bind to negative surface charges of clay mineral particles. As a result, primary loose and shattered grains form integral polymer chains with solid bonds (Fig.4).

Due to the presence of latex in spacer composition, its ions get absorbed by hydrated formations of setting cement [10, 12]. Its negative charge and carboxyl bond –O–O– intensify interaction with cement ions, such as Ca^{2+}, Na^+, Fe^{3+}, Al^{3+}, Mg^{2+}, AlO_2^-, SiO_3^{2-}, OH^-, SiO_4^{2-} etc.

These active compositions, absorbed by the surface of polymer grains, react with each other in the following manner:

$$Ca^{2+} + SiO_3^{2-} + 2OH^- \rightarrow k CaO \cdot m SiO_2 \cdot n H_2O + H_2O;$$

$$x Ca^{2+} + y H_3SiO_4^- + zOH^- \rightarrow C\text{–}S\text{–}H;$$

$$5Ca^{2+} + 2H_3SiO_4^- + 8OH^- \rightarrow Ca_5(SiO_4)_2(OH)_2 + 6H_2O;$$

$$3Ca^{2+} + 2H_3SiO_4^- + 4OH^- \rightarrow Ca_3Si_2O_7 \cdot H_2O + 4H_2O;$$

$$Ca^{2+} + 2H_3AlO_4^{2-} + 6OH^- + 4H_2O \rightarrow CaAl_2O_4 \cdot 10H_2O;$$

$$1{,}74Na^+ + 2H_3AlO_4^{2-} + 3H_3SiO_4^- \rightarrow Na_{1,74}(Al_2Si_3O_{10})(H_2O)_{1,5} + 6H_2O.$$

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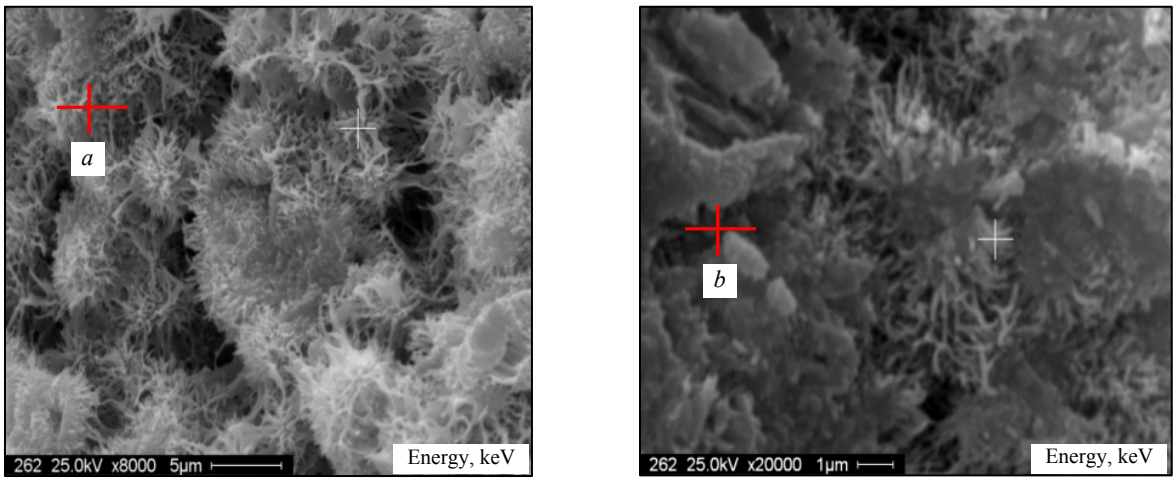


Fig.5. Results of energy dispersive X-ray microanalysis: light spots *a* and *b*

The reaction leads to formation of products observed in the mineral structure of the system «cement stone – filter cake – formation rock», including kCaO·mSiO$_2$·nH$_2$O and hydrated calcium silicate; wollastonite; oceanite; natrolite. These minerals have either strong binding properties, or high adhesion [15].

In the course of hydration process, solidification of cement slurry and concrete strength development, active ions produce a sufficient amount of binding and solid minerals (hydrated calcium silicate, wollastonite, oceanite etc.) on the polymer grain surface of spacer fluid. This process is accompanied by the formation of a net-like structure, which can be observed in the photographs.

By means of energy dispersive X-ray microanalysis [7], the composition of felted net-like structures has been studied (light spot positions *a* and *b* in Fig.5)

Table 4

Investigation results of the net-like structure mineral composition, %

Oxides	Light spot *a*		Light spot *b*	
	Mass fraction	Mole fraction	Mass fraction	Mole fraction
SiO_2	34.65	33.68	32.22	32.91
K_2O	4.13	2.56	3.12	2.03
CaO	61.22	63.76	45.06	49.32
Na_2O	–	–	4.75	4.70
MgO	–	–	3.88	5.91
Al_2O_3	–	–	4.20	2.53
Fe_2O_3	–	–	6.77	2.60

Numerical values for the results of energy dispersive X-ray microanalysis are presented in Table 4. Performed examinations allow to come to the conclusion that the structure mostly consists of hydrated calcium silicate (over 77 % by mass), which is in good agreement with the findings of performed infrared and X-ray structural analysis.

A part of this structure – white dendrite formation (Fig.5 and 6) – has a strong bond with the cement stone, another part is linked to filter cake particles. Furthermore, a contact between separate mineral particles has been observed in the filter cake (Fig.6).

As visible from Fig.5 and 6, mineral particles in the system «cement stone – filter cake – formation rock» bind together by means of solid net-like 3D-structures. These structures intertwine and form long polyanionic chains of high hydration, as well as strong crystallohydrate coating on the surface of clay and cement grains.

New formations, characterized by felted structure, high strength and adhesion to clay and cement grains, fill fractures and pores between the cement and the filter cake, facilitate cement setting, and provoke thickening of minerals in the intermediate zone, which enhances adhesion in the system «cement stone – filter cake – formation rock» [17].

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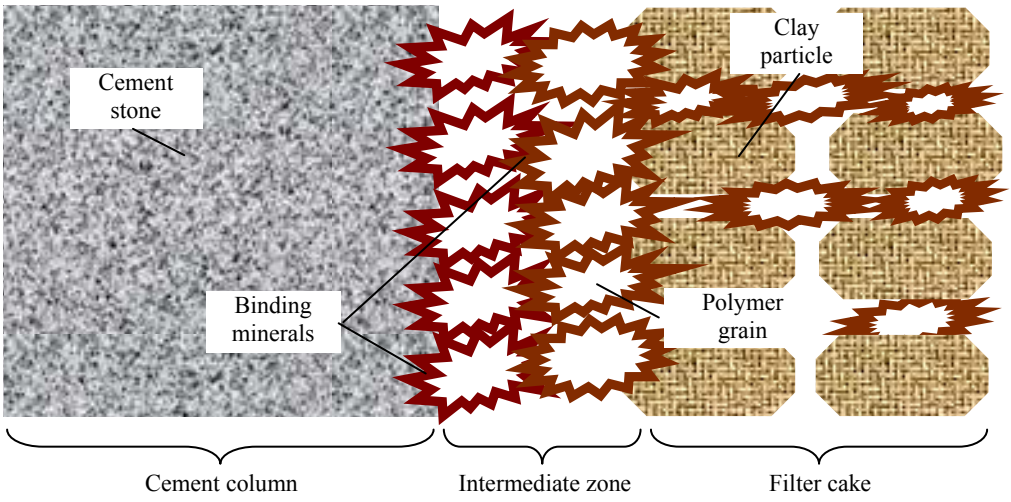


Fig.6. Binding pattern for the products of cement hydration and the filter cake

Industrial tests of the developed polymer spacer fluid were performed at the Shengli oil field in China, where vertical wells have been drilled to the depth of 3728 m (bottom-hole temperature 91.8 °C). Acoustic control of the cementation process and electrical logging have demonstrated high adhesion between the cement stone and the filter cake; the quality of well casing and cementation was 30 % higher than that in the neighbouring wellbores.

Conclusions

1. Review and analysis of modern methods and technological means have shown that development of new polymer spacers can enhance adhesion between the cement stone and the rock, which makes it a promising way to reduce behind-the-casing leakages.

2. Performed investigations of mineral composition changes in the system «cement stone – filter cake – formation rock» have confirmed the presence of binding hydrosilicates C–H–S(I) and zeolites in polymer spacer samples. Visual examination of microphotographs allowed to indentify that polymer spacer fluid facilitates formation of felted net-like structure between hydrated cement minerals and the filter cake; this structure binds the cement stone and the filter cake together.

3. Developed polymer spacer enhances adhesion between the cement and the filter cake: after 2 days – by factor of 20, after 30 days – by factor of 11, after 60 days – by factor of 15. Technological parameters of these mixtures satisfy regulatory requirements of the cementing process.

REFERENCES

1. Bobrov B.S., Lesun V.V. Hydration of Calcium Alumoferrite in Sodium and Magnesium Sulfate Solutions. Gidratatsiya i tverdenie tsementov. Chelyabinsk: UralNIIstromproekt, 1974, p. 46-54 (in Russian).

2. Budnikov P.P., Royak S.M., Malinin Yu.S., Mayants M.M. Research on the Kinetics of Mineral Hydration in Portland Cement Clinker under Hydrothermal Treatment. *DAN SSSR*. 1963. Vol. 148. Iss. 1, p. 59-62 (in Russian).

3. Litvinenko V.S., Nikolaev N.I. Mathematic Model of Well Cementation When Constructing and operating of Oil and Gas Wells. *Zapiski Gornogo instituta*. 2012. Vol. 197, p. 9-14 (in Russian).

4. Litvinenko V.S., Nikolaev N.I. Technological Fluids for Increasing Effectivity of Construction and Exploitation Oil and gas Wells. *Zapiski Gornogo instituta*. 2011. Vol. 194, p. 84-90 (in Russian).

5. Haoya L., Tabatabai Moradi Seied Shakhab, Nikolaev N.I. Study of the Filter Cake Impact on the Quality of Cement-to-Rock Adhesion. *Inzhener-neftyanik*. 2015. N 2, p. 22-25 (in Russian).

6. Haoya L., Nikolaev N.I., Kozhevnikov E.V. Research on the Properties of Polymer Spacer Fluid to Improve Quality of Well Casing and Cementation. *Stroitel'stvo neftyanykh i gazovykh skvazhin na sushe i na more*. 2015. N 6, p. 38-41 (in Russian).

7. Nakamoto K. Infrared and Raman Spectra of Inorganic and Coordination Compounds: Part B – Applications in Coordination, Organometallic, and Bioinorganic Chemistry. 6th Edition. New Jersey: Wiley, 2009, p. 416.

DOI: 10.25515/PMI.2017.4.428

8. Nikolaev N.I., Haoya L., Kozhevnikov E.V. Research on the Impact of Polymer Spacer Fluids on the Cement-to-Rock Contact Strength. *Vestnik PNIPU. Geologiya. Neftegazovoe i gornoe delo*. 2016. Vol. 15. N 18, p. 16-22 (in Russian).

9. Plyusnina I.I. Infrared Spectra of the Silicates. Moscow: Izd-vo Mosk. un-ta, 1976, p. 192 (in Russian).

10. Bezjak A. Kinetics Analysis of Cement Hydration Including Various Mechanistic Concepts. Theoretical development. *Cem. and Concr. Res*. 1983. N 3, p. 308-318.

11. Bish D.L. Rietveld Refinement of the Kaolinite Structure at 1.5 K. *Clays and Clay Minerals*. 1993. Vol. 41. Iss. 6, p. 738-744.

12. Cardno D.G., Riptey D.B., Crawford J.W. The Use of Silicate WBM Facilitates Successful Primary Cementation Operations on the BHP Petroleum Liverpool Bay Development. SPE/IADC Drilling Conference, 4-6 March, Amsterdam, Netherlands Publication Date. 1997, p. 32-37.

13. Haut R.C., Croot R.J. Laboratory Investigation of Light Weight, Low-Viscosity Cementing Spacer Fluids. *Journal of Petroleum Technology*. 1982, p. 1828-1834.

14. Nelson E.B., Guillot D. Well Cementing. Texas: Schlumberger, 2006, p. 773.

15. Tabatabaee Moradi S.S., Nikolaev N.I., Naseri Y. Developing High Resistant Cement Systems for High-Pressure, High-Temperature Applications. SPE Russian Petroleum Technology Conference, Moscow, Russia, 26-28 October 2015. N.Y.: Curran Associates, 2016. Vol. 1, p. 475-481.

16. Tabatabaee Moradi S.S., Nikolaev N.I. Considerations of Cementing Directional Wells in High-Pressure, High-Temperature Conditions. 7th EAGE Saint-Petersburg International Conference and Exhibition: Understanding the Harmony of the Earth's Resources through Integration of Geosciences, Saint-Petersburg, Russia, 11-14 April 2016. N.Y.: Curran Associates, 2016, p. 11-15.

17. Tabatabaee Moradi S.S., Nikolaev N.I. Optimization of Cement Spacer Rheology Model Using Genetic Algorithm. *International Journal of Engineering, Transactions* A: Basics. 2016. Vol. 29. N 1, p. 127-131.

18. Sweatman R.E., Nahm J.J., Loeb D.A., Porter D.S. First High-Temperature Applications of Anti-Gas Migration Slag Cement and Settable Oil-Mud Removal Spacers in Deep South Texas Gas Wells. SPE Annual Technical Conference and Exhibition, 22-25 October, Dallas, Texas. 1995, p. 45-48.

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