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Research of cement stone permeability based on composite plugging material for oil and gas wells

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The article analyzes the state of hydrocarbon production potential of Ukrainian fields with a review of the past, present and future from the premise of oil and gas recovery in fields with hard-to-recover reserves. It has been established that significant volumes of hydrocarbons are classified as hard-to-recover deposits. Ensuring reliable delineation of horizons in such conditions needs the use of plugging materials capable of forming cement stone with appropriate operational characteristics.

The main factors affecting the tightness of the insulation screen are evaluated. The importance of forming a high-quality insulating screen for oil and gas wells is confirmed, both in terms of hydrocarbon production and in terms of labor safety and environmental impact.

The main technological parameters of the plugging mud based on material DRCT and cement PCT I-100, as well as their physical-and-mechanical properties of cement stone, were determined. According to the results of the research, both in terms of the parameters of the plugging mud and the physical-and-mechanical properties of the cement stone, an advantage and improved values of indicators were obtained for the plugging material based on composite cement DRCT compared to cement PCT I-100.

The research of X-ray phase analysis and quantitative analysis of the elemental composition for samples of cement stone based on plugging material DRCT were carried out under storage conditions in formation water of the chloralkali type and fresh water. It was found that the formed cement stone based on material DRCT has a densely packed structure. The permeability of cement stone samples based on DRCT in fresh and formation water storage was evaluated. The gas permeability for the researched samples is almost the same, which indicates the absence of a degrading effect on the cement stone. The obtained results of research of the technological properties of the plugging mud and the operational properties of the cement stone of the plugging material DRCT indicate that the material DRCT is suitable for cementing oil and gas well casing. The results of the introduction of the plugging material based on DRCT during the cementing of casing string diameter 127 mm in well No. 105 of the Verkhnyomaslovetske field confirmed the success of its application.

Keywords: well, casing, plugging mud, cement stone, permeability.

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Introduction

Hydrocarbons have been of key importance in the global economy and in the geopolitical context for a long

time, and will continue to be so in the near future. By the volume of natural gas reserves Ukraine is in the top three European countries.

Researches have shown that about a quarter of

primary hydrocarbon resources have been extracted from the Ukraine's subsoil, that are to about 360 million tons of oil and condensate and 1.8 trillion cubic meters of gas [1].

In 2024, gas production in Ukraine increased by 2.2 % to 19.12 bln cubic meters. In particular, JSC Ukrgasvydobuvannya produced 14.55 bln cubic meters of gross natural gas in 2024, which is 4.6 % more than in 2023 (over 13.9 bln cubic meters). In 2024, PJSC Ukrnafta produced 1.17 bln cubic meters of natural gas, 6.6 % more than last year (almost 1.1 bln cubic meters) [2].

Most hydrocarbon fields, given the long production process, are at the final stage of development or are classified as hard-to-recover reserves. The research results confirm that more than 72 % of oil reserves and 10% - 15% of natural gas reserves in Ukraine are considered hard-to-recover [3].

The importance of involvement resources for the development of fields with hard-to-recover reserves has been repeatedly established by leading scientists and oil and gas companies in Ukraine [4]. Scientific researches have established that the forecasted resource of heavy oil reservoir in Ukraine could be at least 50 bln cubic meters [1].

PJSC Ukrnafta has licenses for the development of oil and gas fields, where the share of fields with hard-to-recover reserves is about 70 % [5].

Given the long-term exploitation of oil and gas wells, which has led to a significant decrease in the formation energy of hydrocarbon horizons, while, as a rule, preserving the initial characteristics of water-saturated formations, the quality of primary cementing and the reliability of horizon delineation are extremely important for well casing process, especially in fields with hard-to-recover reserves.

I. State of Art

Ensuring the reliability and durability of a well as an engineering structure is to form a high-quality insulating screen as the main premise for reliable delineation of productive horizons.

It has been established that the leakage of the insulating cement ring tightness can occur due to the form of cavities/microgaps between the cement stone and the bounding surfaces, permeable channels in the cement stone, cracks/destructive deformations in the cement stone and degradation of the cement stone [6].

The technology of production the plugging material, the design of the component structure, the properties of the plugging mud and the technical-and-technological realization of the hydraulic program during cementing, as well as the characteristics of the formed cement stone are the basis for the tightness of the casing system for the quality of the insulation screen [7, 8, 9].

The inhomogeneity of the plugging mud causes heterogeneity of the cement stone in the well, which can affect the quality of the horizon delineation due to the deterioration of stone adhesion and, subsequently, its destruction [10].

The parameters of the hydrothermal synthesis of neoplasms in cement stone consisting of CaO and amorphous $SiO_2 \cdot nH_2O$ or quartz, and the sequence of

create of intermediate compounds, were determined by the researches at elevated temperatures [11], as well as the research of create of hydrate phases at high pressure and temperature [12]. The use of various kinds admixtures allows to improve the physical-and-mechanical properties of cement stone, and, as a result, to create the preconditions for the tightness of the insulation screen [13, 14, 15].

Researches emphasized the importance of understanding the influence of alkaline hydroxides in the synthesis of hydrate phases of cement stone and the course of hydrothermal reactions in the CaO-SiO₂-H₂O system [16].

The peculiarities of mining-and-geological conditions of well construction, in particular when drilling sidetracks, require an individual integrated approach to well casing, in particular with regard to the type of plugging material and the properties of the plugging mud and formed cement stone, which will determine the basis of the insulation screen condition [17].

One of the ways to form a durable and corrosion-resistant cement stone with a dense structure for oil and gas well casing is to use composite cement. For composite cement, hardening occurs as a result of the hydration of the clinker component, as well as the chemical interaction of hydrate neoplasms with active components in the cement that have different hydraulic activity [18].

The forming of a low-permeability cement stone is achieved by ensuring deep processes of cement hydration, as well as creating the preconditions for reducing intergranular and capillary porosity [19].

The forming of self-reinforcing composites during controlled crystal growth has been confirmed, where the matrix is formed by gel-like, submicrocrystalline, and isometric crystal hydration products, and the strengthening structure is filamentous (I/d>100) or needle-like crystals of neoplasms [20].

The kinetics of structure forming and the microstructure of cement stone have a basic influence on the preconditions for the tightness of the insulation screen [21].

Previous researches have shown that it is possible to control the structure forming processes of plugging systems based on composite cements by using modifiers, in particular, crents. Their use contributes to the controlled growth of strengthening crystals, providing a kind of synthesis of cement stone during hardening, which is capable of "self-healing" of the disturbed structure. In addition, the densely packed structure of the cement stone is ensured by the growth and stable existence of C-H-S and hexagonal AFm-phases and C-H, what colmatizing micropores [22]. In turn, the densely packed structure of cement stone is a precondition for its reduced permeability. Forming a cement stone with the required operational properties in the well conditions not only ensures effective delineation of differently saturated horizons, but also creates an additional protective shield for the casing [23, 24, 25].

The influence of the characteristics of cement stone and the peculiarity of its location on the equivalent stress of the casing string has been established, which makes it possible to increase the resistance of casing pipes to external forces [26, 27].

The non-availability of proper preparation of the wellbore for cementing, as well as the use of low-efficiency buffer systems, can lead to defects in the structure of the cement stone and in the cementing system. The content of drilling mud in cement stone not only reduces the physical-and-strength characteristics of the stone, but also is a precondition for the forming of migration channels for fluids [28].

The use of effective buffering fluids is a precondition for ensuring the forming of a strong, low-permeability cement stone in the well [29].

Regardless of the well design and geological conditions caused by a complex of factors, the cement stone must ensure the tightness of the insulation screen [30, 31].

In case of leakage of the casing system, spontaneous and uncontrolled migration of fluids can occur both during casing and during well operation [32, 33, 34]. In addition, poor-quality formation delineation will have a negative impact on hydrocarbon production from oil and gas wells. The failure of the tightness of isolation screen can also cause off-column fluid flows [35] and sometimes be a precondition for man-made accidents that have an irreparable impact on the safety of people and the environment [36].

The features of forming and quality of well casing process should provide for planned technological operations in the well, taking into consideration thermobaric conditions [37, 38, 39]. Since the condition and integrity of the production casing will have a direct impact on the safety of well operations [40].

Gas migration through the insulating cement ring is a long-term problem that requires repair and insulation work, with detailed design and testing of specialized materials [41]. However, in most cases, it is possible to eliminate inter-column pressures caused by a destruction of the casing and cementing system only partially or for a short period of time. Therefore, it is necessary to implement technological solutions in advance that will ensure the conditions for the high-quality forming of dense, low-permeability cement stone, thereby minimizing the risks of fluid migration.

II. Results and discussion

A problem during building and testing of wells is the disturbance of the tightness of the isolation screen, which is especially relevant for gas-saturated formations with abnormally high reservoir pressure, as well as in the conditions of well casing with closely spaced differently pressured and differently saturated formations. In such conditions, the most likely cause of fluid migration is a change in the hydraulic pressure in the well due to cement stone hardening, which leads a decrease in pressure to reservoir pressure or significantly lower. In addition, the system of well casing is adversely affected by the technological processes of casing leakage testing, which are often performed after cement stone hardening, particularly at an early age.

The above-mentioned processes, as some of the above, can cause a disturbance of the tightness of the insulation screen and cause fluid migration through the cement stone and through the contact and casing.

An important factor in increasing the tightness of the insulation screen is minimizing the permeability of the cement stone. In addition, the densely packed structure of cement stone creates the precondition for increasing the resistance to degradation of the stone under the influence of aggressive formation fluids and acidic action [42, 43, 44, 45].

We have tested the plugging material DRCT based on composite cement and cement PCT I-100 [46, 47, 48].

Carried-out researches have established (Table 1) that the technological parameters of the plugging mud based on DRCT have values that meet the established requirements for cementing oil and gas wells: at a plugging mud density of 1.84 g/cm³, a sedimentation-stable plugging mud was obtained, which, within the regulated period, taking into account the thickening time, ensures the forming of a cement stone strength of 5.6 MPa at bending at the age of one day.

In addition, samples of plugging material were formed to research the effect of formation/fresh water on cement stone and its characteristics based on X-ray phase analysis, as well as to estimation the physical-and-mechanical properties of cement stone, in particular its permeability. For the research, the formation water of the Rybalske field

Table 1.

Results of the research of the formulation of plugging mud and cement stone based on DRCT and PCT I-100

Type of plugging material	Formulation of plugging mud, mass share						; mnd,	ging	te, ml	Research condition s		Time of setting, hour-min		30 Bc,	bending Pa	ent e
	quantity of cement	name	quantity	density, g/cm ³	pH	quantity	Density of plugging g/cm ³	Flowability of plugging mud, mm	Water separation rate,	temperature, °C	pressure, MPa	beginning	ending	Thickening time to 3 hour-min	Strength of stone in be after 24 h, MPa	Fragility coefficient of cement stone
DRCT	100	NTFK	0.03	1.0	7.0	46	1.84	245	0.5	75	0.1	3-30	4-15	2-45	5.6	2.9
PCT I-100	100	NTFK	0.03	1.0	7.0	48	1.84	220	2.5	75	0.1	3-15	4-35	2-35	4.8	3.5

with a density of 1.1395 g/cm³ was used, which belongs to the calcium chloride type of water, chloride group, calcium subgroup, with a total mineralization of 217360.18 mg/dm³.

The markings of cement stone samples based on plugging material DRCT and storage conditions are shown in Table 2.

The cement stone samples were ground into a powdered state to the research of X-ray fluorescence spectroscopy and X-ray structural analysis.

The following instruments were used for the research: X-ray diffractometer Shimadzu XRD-7000 and precision analyzer Expert 3L.

The results of the researches of the quantitative analysis of the elemental composition of cement stone samples DRCT are shown in Table 3.

Based on the results of the generalization of the quantitative analysis, it was found that the researched samples of material DRCT (UN4) and (UN5) have an approximate quantitative elemental composition. The content of the element chlorine in the sample DRCT (UN5) indicates that the cement stone is in the formation water and may indicate partial crystallization of chlorides on the surface and in the structure of the stone. The generalized results of X-ray fluorescence spectroscopy (spectrometer-analyzer Expert 3L) and X-ray diffraction analysis (X-ray diffractometer Shimadzu XRD-7000) revealed that for the research series of samples UN4 and UN5 (Fig. 1 and Fig. 2) the main phases are portlandite Ca(OH)₂, allite SiCa₃O₅ and calcium carbonate CaCO₃. Iron is present in the composition of fayalite SiFe₂O₄ and clinopherosilite SiFeO₃. Iron is probably also present in the form of ultrafine oxyhydroxide particles. The relative sulfur content is similar for all samples, approximately 1.0-1.5 wt% in terms of oxide.

For sample UN5, the presence of a halite phase NaCl is observed, which is due to the reaction of hydrate phases

during storage of samples in formation water. Quantitative Rietveld analysis of samples UN4 and UN5 is very difficult due to the presence of an X-ray amorphous phase, the content of which is maximum for sample UN5. Estimated values of the X-ray amorphous phase content for the UN4 sample are up to 55-57 (no least 48-50 mol%), and for UN5 - up to 60 (no least 53-54 mol%).

Additionally, the permeability of cement stone samples was researches using the unit UIPK-1M based on the recommendations [49, 50]. To research the absolute permeability of cement stone samples to nitrogen, a cylindrical sample was formed. The ends of the obtained cylindrical samples were cut and polished on a facing machine. Then the geometric dimensions (diameter, length) were measured.

The prepared sample is placed in the core holder of the absolute permeability measuring unit and the specified reservoir pressure is created. After that, nitrogen is passed through it and the time of filtration of a fixed gas volume is determined at a constant fixed pressure drop at the inlet and outlet of the sample placed in the core holder (measurement in steady-state mode).

Record the measurement results (sample parameters, pressure drop (pressure)), gas flow and viscosity at the temperature of the test. The absolute permeability coefficient is determined by the formula:

$$K = \frac{2Q\mu L1000}{(\Delta P(2+\Delta P)F)},$$

where K – gas permeability coefficient, $\times 10^{-3} \ \mu m^2$ (mD); Q – gas flow rate measured at the sample outlet, cm³/s; μ – gas viscosity under filtration conditions, mPa/s or cP; ΔP – the pressure drop at the inlet and outlet of the sample, atm; L – sample length, cm; F – cross-sectional area of the sample, cm².

Marking of samples and storage conditions

Table 2.

Table 3.

Marking	Type of material	Medium of storage and research	Duration, years	Pressure, temperature, MPa/ deg. C	
UN4	DRCT	fresh water	0	0.1/22	
UN5	DRCT	formation water	8		

Quantitative analysis of the elemental composition of cement stone samples

	Quantitative analysis of the elemental composition of cement stone samples											
	Composition (in terms of	Number	of the anal	ysis UN4	Average value UN4	Number	Average					
(oxides), wt. %	1	2	3		1	2	3	value UN5			
	Al_2O_3	0.337	0.424	0.438	0.400	1.752	1.765	1.739	1.752			
	SiO ₂	9.736	9.650	9.631	9.672	8.241	8.231	8.141	8.204			
	SO_3	1.082	1.102	1.028	1.071	1.118	1.205	1.144	1.156			
	Cl	_	_	_	_	5.852	5.792	5.862	5.835			
	CaO	80.837	80.900	80.866	80.868	76.354	76.399	76.337	76.363			
	MnO_2	0.494	0.581	0.622	0.566	0.377	0.310	0.273	0.320			
	Fe ₂ O ₃	6.299	6.337	6.351	6.329	5.152	5.064	5.084	5.100			
	TiO ₂	0.723	0.749	0.726	0.733	0.583	0.517	0.453	0.518			
	SrO	0.394	0.393	0.475	0.421	0.383	0.408	0.312	0.368			
	BaO	_	_	_	_	0.091	0.090	0.156	0.112			

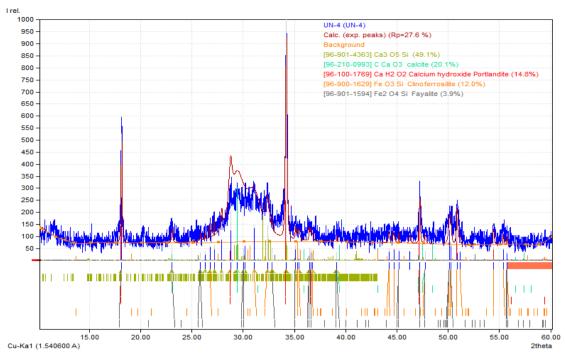


Fig. 1. Results of X-ray phase analysis researches of cement stone samples based on plugging material DRCT in medium of fresh water.

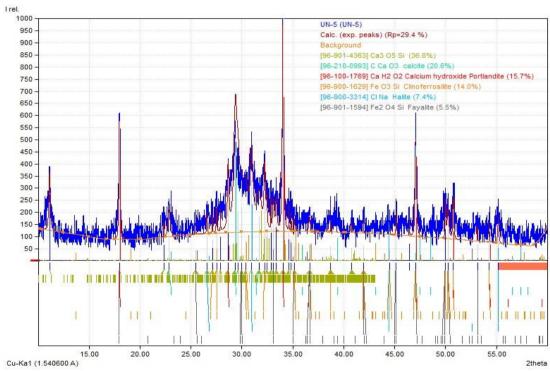


Fig. 2. Results of X-ray phase analysis researches of cement stone samples based on plugging material DRCT in medium of formation water.

Initially, the research of permeability of cement stone samples based on the plugging material DRCT by nitrogen, prepared at the age of one day, was carried out. After drying at a temperature of 105 °C until the sample weight stabilized, the absolute gas permeability was determined to be 0.42 mD. It should be noted that the basic permeability of the cement stone based on cement PCT I-100 after drying was 1.18 mD.

Then we researched the permeability of additional cement stone samples by nitrogen, which were stored in axicators under the influence of fresh and formation water, i.e., saturated with the corresponding waters. The obtained permeability index is very low due to the influence of capillary forces, as well as the presence of a blocking screen formed by corrosion processes (Table 4). Then the cement stone samples were dried to a fixed (constant) weight. The drying temperature of the samples was 105° C, and the drying time was 8 hours. After drying, the gas permeability was re-determined and the permeability of the cement stone was obtained without the possible influence of the aqueous phase.

Table 4.

The research of gas permeability

					8			
Material type and sample storage medium	Length of the sample, cm	Diameter of sample, cm	Pressure drop, atm	Nitrogen flow rate, cm ³ /sec	K, at saturation of samples with water, mD	Pressure drops, atm	Nitrogen flow rate, cm ³ /sec	K, after drying the samples, mD
DRCT (fresh water)	5.84	2.75	25	0.0724	0.0038	20.3	4.7169	0.37
DRCT (formation water)	6.26	2.72	24.9	0.096	0.0056	20.4	4.5045	0.384
K – gas permeability	coefficie	nt						

Based on the carried-out comparisons (Table 4), it was found that the permeability of cement stone for the sample in formation water exceeds the permeability for the sample in fresh water. The results obtained in absolute values indicate a very low permeability.

After drying, the gas permeability of the cement stone was obtained without the probable influence of the aqueous phase, which indicates a slight excess of permeability for the sample in formation water by 3.8 %.

Researches with the plugging material DRCT have resulted in the forming of a cement stone that significantly exceeds the basic requirements for cement stone based on research V.F. Gorskyi, where for a cement stone, in the absence of water saturation, gas permeability can be 0.5-1.3 mD, and when saturated with water, gas permeability is 7-10 times less [51].

The permeability of cement stone can be reduced by the use of expanding admixtures. In this case, the expansion of the cement stone improves not only the contact with the rock and casing, but also is a prerequisite for the forming of a dense structure due to curing under thermobaric conditions with bounding surfaces. However, in such cases, it should be taken into account that the well preparation for cementing should be properly performed, because the presence of a filtration crust on permeable layers can offset the positive effect of expansion or create preconditions for microdefects and the forming of microcracks in the stone structure.

Another way to reduce the permeability of cement stone is to use micro-admixtures or micro-cement admixtures that will provide a certain shielding of permeable channels by placing such admixtures between the grains of cement stone. An additional factor in reducing the permeability of the stone is the use of polymers that form blocking screens in the pore space of the stone matrix.

Based on the carried-out researches, a composite cement-based plugging mud formulation was developed and successfully implemented using plugging mixture DRCT-EA100-LF (expandable plugging material with reduced water loss of plugging mud) for cementing a

casing liner diameter 127 mm in the depth range of 1500-2070 m in well No 105 of the Verkhnyo-maslovetske field of PJSC Ukrnafta.

Conclusions

The article analyzes the hydrocarbon potential of Ukraine's subsoil, the peculiarities of forming the insulating cement ring in oil and gas wells and influence the mining and geological conditions on state of cement stone. Attention is drawn to the importance of using plugging materials that form a low-permeability corrosion-resistant cement stone, which is a precondition for ensuring high-quality delineation of productive horizons and reliable well casing.

The results of analytical and laboratory researches of the plugging material DRCT confirm required technological properties of the plugging mud based on DRCT and the proper exploitation properties of the cement stone. The X-ray phase analysis of cement stone samples based on the composite plugging material DRCT confirms the forming of a degradation-resistant cement stone.

It has been established that cement stone based on the composite plugging material DRCT forms a dense packed structure that accord the basic requirements for casing and cementing oil and gas wells.

The results of implementation of the plugging material based on the DRCT confirmed its compliance with the mining and geological conditions of well cementing.

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Дослідження проникності цементного каменя на основі композиційного тампонажного матеріалу для нафтогазових свердловин

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Проаналізовано стан видобувного потенціалу вуглеводнів родовищ України з оглядом минулого, сьогодення та подальшого майбутнього з передумови вилучення нафти і газу на родовищах з важковидобувними запасами. Встановлено, що значні обсяги вуглеводнів відноситься до категорії родовищ з важковидобувними запасами. Забезпечення надійного розмежування горизонтів в таких умовах потребує застосування тампонажних матеріалів, здатних формувати цементний камінь з відповідними експлуатаційними характеристиками.

Здійснено оцінку основних чинників, що впливають на герметичність ізоляційного екрану. Підтверджено важливість формування якісного ізоляційного екрану для нафтогазових свердловин, як з точки зору видобування вуглеводнів, так і з умов безпеки праці та впливу на довкілля.

Визначено основні технологічні параметри тампонажного розчину на основі матеріалу DRCT та ПЦТ I-100, а також їх фізико-механічні властивості цементного каменю. За результатами досліджень, як за параметрами тампонажного розчину, так і за фізико-механічними властивостями цементного каменю отримано перевагу та покращені значення показників для тампонажного матеріалу на основі композиційного цементу DRCT у порівнянні з ПЦТ I-100.

Дослідження РФА та кількісний аналіз елементного складу для взірців цементного каменю на основі тампонажного матеріалу DRCT проведено в умовах зберігання у пластовій воді хлоркальцієвого типу та прісній воді. Встановлено, що сформований цементний камінь на основі DRCT володіє щільно упакованою структурою. Оцінено проникність взірців цементного каменю для DRCT в умовах зберігання прісної та пластової води. Газопроникність для досліджуваних взірців є практично однаковою, що свідчить про відсутність деградабельного впливу на цементний камінь. Отримані результати досліджень технологічних властивостей тампонажного розчину та експлуатаційних властивостей цементного каменю тампонажного матеріалу DRCT свідчать про відповідність матеріалу DRCT для цементування обсадних колон нафтогазових свердловин. Результати впровадження тампонажного матеріалу на основі DRCT під час цементування 127 мм колони-хвостовика у свердловині №105 Верхньомасловецького родовища підтвердили успішність його застосування.

Ключові слова: свердловина, кріплення, тампонажний розчин, цементний камінь, проникність.