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Research of cement stone degradability in difficult mining and geological conditions of Ukraine

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The features and prospects of hydrocarbon potential of Ukraine are analyzed. It is established that the basic resource of oil and gas deposits is concentrated in difficult mining and geological conditions, where the larger share of reserves belongs to the category of deposits with hard-to-recover reserves. In such conditions, additional requirements should be set for the casing and cementing systems, in particular for cementing productive deposits.

The formulations of basic plugging materials were researched and their sedimentation stability destruction was established. The influence of technological processes during well completion on the casing and cementing system is assessed and the impact of these operations on the state of the insulating ring in the well is characterized. Using the example of complications during well casing and cementing, attention is focused on the technological and operational requirements for plugging materials.

The degradability of cement stone based on base cements PCT I-100 was assessed by visual research and X-ray phase analysis (XPA). The deformation of stone samples under the influence of aggressive medium and the almost complete absence of binding crystalline hydrates in the samples at XPA were established. The results obtained indicate the need to use degradation-resistant plugging materials. The advantages of plugging systems based on composite cements are characterized and typical modifiers that can be used to regulate the properties of plugging mud and cement stone are presented. The influence of aggressive environment on cement stone based on composite material DRCT was researched. Quantitative analysis of the elemental composition and XPA of the researched samples of DRCT cement stone in aggressive mediums of magnesium chloride and sulfuric acid, as well as in formation water of the chlor-calcium type, confirm the corrosion resistance of the stone made of material DRCT. The research results allow us to recommend the cementing material DRCT for cementing oil and gas wells in difficult mining and geological conditions.

Keywords: well, casing and cementing system, cement stone, cement stone corrosion.

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Statement of the research problem

Hydrocarbons remain a key source of energy security for many countries, despite the level of development of the economic sector. The work of Ukrainian geological scientists confirms the extremely powerful potential of oil and gas deposits in Ukraine. Research have confirmed the prospects for oil and gas in the deep-seated lower Carboniferous deposits of the Dnieper-Donets Basin (DDB), where about 70% of the forecast reserves are concentrated [1]. At depths of more than 5,000 m, there are deposits with hydrocarbon accumulations in the main oil and gas bearing areas of the DDB, which are confined to the central axial and marginal graben zones [2]. The direction of deep wells construction is associated with the expectation of discovering large gas condensate deposits in heterogeneous carbonate-terrigenous reservoirs on large anticline structures [3].

The construction of deep wells in the Carpathian region and in the DDB requires drilling a complex geological section. Increasing thermobaric conditions of fluid-saturated reservoirs location, development of fields with hard-to-recover reserves, including the presence of closely spaced differently saturated and differently pressurized horizons, and thick layers of chemogenic sediments alternating with layers of mudstones, anhydrite, dolomite and clay carbonates, set additional requirements for the well as an engineering structure. Construction of wells in such conditions will require the use of modern technological solutions and materials for both well drilling and high-quality casing. Reliability of the well casing system at all stages is the main guarantee of its construction and further operation for a long time.

I. Analysis of modern foreign and domestic research and publications

During the construction of wells, the issue of reliable casing and cementing and high-quality delineation of formations is an important task, and the main condition for its solution is the tightness of the wellbore space to prevent uncontrolled impact of rock mass and formation fluids that may impact the operational reliability of the well for the entire period of its exploitation.

Careful attention should be focused on ensuring high-quality and reliable delineation of hydrocarbon horizons, especially for drilling oil and gas wells in fields that are classified as hard-to-recover. Currently, according to research of Ukrnafta's specialists, about 20% of the fields ensure for 80% of hydrocarbon production, while the remaining 80% ensure for only 20% of production [4]. At the same time, the share of fields with hard-to-recover reserves in this company is about 70% [5]. Additional challenges in such conditions include the creation of a high-quality isolation ring, the main task of which is not only to delineation differently saturated and differently pressurized horizons [6], but also minimizing the negative impact of plugging systems on the filtration and capacitive characteristics of reservoirs.

It is well known that significant repression during well construction, which can be more than 150% during initial opening and sometimes more than 200% during cementing, can lead to deterioration of reservoir properties of oil and gas saturated horizons. Research of the impact of cement slurry on the phase gas permeability of reservoirs on the example of the Semyrenkivske field confirmed its reduction from 1.3 to 10 times [7].

It should be noted that both the dispersion medium of the plugging systems, forming complex and insoluble emulsions, and the dispersed phase, which can block further fluid movement, can have a negative impact on the reservoir properties.

The quality of well casing is directly affected by technological operations caused by certain processes under thermobaric conditions [8].

The quality of the well casing and its durability is determined by the condition of the cement stone that forms the insulation screen. At the same time, the condition of the isolation screen determines the precondition for reliable delineation of fluid-saturated horizons and protection of the casing from aggressive fluid impact [9, 10], which will have a direct impact on further hydrocarbon production [11].

The composition of the cementing material, the technological properties of the plugging mud and the operating characteristics of the cement stone will form the base of oil and gas wells casing and cementing [12, 13, 14]. To improve the quality of casing and cementing, it is necessary to use special buffer systems that minimize mixing zones and increase the degree of adhesion of cement stone to the bounding surfaces [15].

Damage of homogeneity of the insulation screen contributes to the deterioration of stone adhesion and can intensify the destruction process [16].

The requirement to ensure high-quality well casing and cementing in conditions of small annular gaps and when casing sidetracks during well workovers requires the use of stabilized plugging materials with increased elastic and deformation properties [17].

It is known that the negative impact of poor-quality casing and cementing can be reflected not only on the development system of field, but also on the environment and safety at work [18].

Damage of the reliability of productive horizons delineation can lead to uncontrolled fluid flow to the daylight surface [19], as well as to be a precondition for extra-colonial flows and fluid migration [20]. Unfortunately, the damage of the casing and cementing system also led to complex industrial accidents [21].

Research carried out by a number of scientific schools in the direction of well casing and cementing confirms that it is possible to increase the bearing capacity of the casing system with high-quality cement stone at the casing-pipe-cement stone-rock interface by 20-28% compared to uncemented pipes.

II. Results of research and discussion

In most cases, Portland cements with certain admixtures and fillers are usually used for cementing casing in Ukrainian fields, depending on temperature conditions. However, such materials and established approaches do not always meet the cementing conditions. Table 1 shows basic formulations of plugging materials and their parameters.

An example of a research of increased water separation and damage of sedimentary stability is shown in Fig. 1.

The example of the formulation shown in Table 1 and Fig. 1 confirms that the requirements for sedimentation stability of plugging systems remain within the lower limits of the requirements of the regulated regulatory documents. However, additional research, for example, an increase in the time of water separation research from 2 h to 3.5 h confirms a significant increase in this indicator, almost more than twofold. Under such conditions, the casing system will be exposed to significant risks of quality damage of horizon delineation with further consequences depending on the mining and geological conditions.

It should be noted that, in addition to the use of unstabilised plugging materials with appropriate technological and operational properties, a fairly thin insulating ring can be subjected to significant loads [22]: as a static impact – casing pressing after waiting on cement (WOC), where, according to the results of the cement acoustic logging research, the greatest decrease in cementing quality was obtained during casing pressing with a pressure of more than 15 MPa [23], and dynamic operation due to the complex movement of the drill string. It should also be noted that the complex dynamic movement of the drill string can also lead to significant casing deterioration [24] and sometimes to damage its integrity.

In addition, significant loads will be transferred to the casing and cementing system during perforation [25]. In some cases, in the presence of a complex geological section due to the presence of closely spaced horizons of different pressures and different saturations, perforation is one of the causes of casing fluid flows. Since casing perforation causes a damage of the cement stone contact density with the casing and rock [26]. It is known that during cumulative perforation in a well, the internal pressure can reach 300 MPa on the casing. At a cumulative perforation density of more than 10 holes per 1 m, the cement ring's contact with the casing is disrupted up to ten meters due to the increase in the energy field caused from triggering charges.

Significant loads can be transferred to the casing and cement stone during fluid stimulation operations [27], including during hydraulic fracturing [28].

All of the above processes have a significant impact on the condition of the insulation screen. The impact of these technological operations will depend on many factors, among which the type of plugging material used for cementing, the condition of the insulation screen and the age of the cement stone are important. However, it is also needing attention on the negative impact on the insulation ring if aggressive fluids are present in the section [29].

Special attention to the localization of water belts and the lack of durable and corrosion-resistant stone is relevant for the well casing and cementing in aggressive chemogenic deposits conditions, and cuts with thick water-saturated formations or aggressive fluids.

During well cementing, the cement can be in contact with a number of systems:

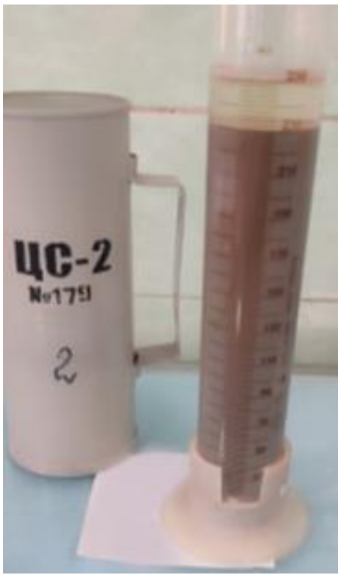
– formation water saturated with salts of polyvalent

Table 1.

Parameters of the plugging mud

Type of cement	Formulation of plugging mud, mass share						Density of plugging mud, g/cm^3	Flowability of plugging mud, mm	Time of research				Research conditions		Strength of stone in bending after 24/48 h,
	quantity of cement	additive		water					2 hour		3.5 hour		temperature, °C	pressure, MPa	
		name	quantity	density, g/cm^3	pH	quantity			*$K_{sed.\ stab.}$	**W, ml	*$K_{sed.\ stab.}$	**W, ml			
Lightweight plugging material	100	NTFK	0.057	1.0	7.5	85	1.54	250	0.93	9	0.88	20	48	30	0.8/1.1
PCT I-100	100	NTFK	0.025	1.0	7.5	48	1.82	230	0.96	7.5	0.9	14	52	35	5.2/–

Note. *$K_{sed.\ stab.}$ – sedimentation stability coefficient
**W – water separation



a) water separation of the plugging mud

b) sedimentation channels in water separation

Fig. 1. Water separation and sedimentation channels.

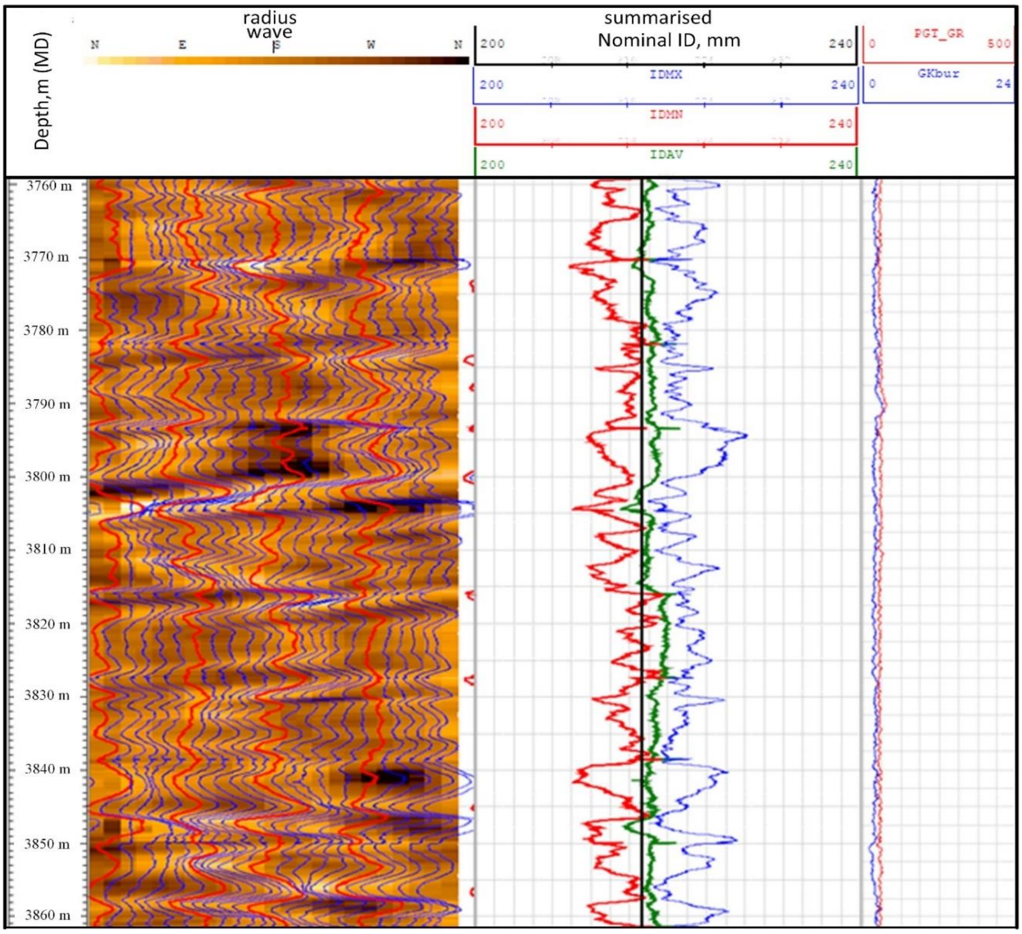


Fig. 2. Results of MFC well research.

metals;

– drilling mud, the dispersion medium of which contains salts;

– rock.

As a rule, saline sediments are characterized by increased cavernousness. During wells cementing using process water or mineralized water as a spacer, some of it may remain in the cavity area. Due to gravitational replacement, part of the buffer spacer or drilling mud will be located in the upper part of the cavity area. This will result in an increase in salt saturation of these process liquids and further potential dissolution of chemogenic deposits. A similar situation may arise when using unstabilised plugging muds. As a result, in such cases, the corrosion rate will be more intense, and the cement stone can be quickly destroyed. At the same time, the vector load of the rock mass will be transferred to the casing only. Similar situations can arise when casings are cemented with unstabilised plugging systems that provoke the forming of 'water belts' along the wellbore, especially under the ledges and in the upper part of the cavity. In addition, there are cases when permeable interlayers are present in the lithological section of saline sediments. In such cases, during cementing with unstabilised plugging muds, the dispersion medium of the plugging systems may be lost and, as a result, their pumpability may be completely stopped. Such a situation occurred in well 55-Jaroshivka, where the non-productive time was more than 319 days, while the duration of well construction before the complication occurred was 151 days.

The impact of chemogenic deposits on the stability destruction of the casing and cementing systems is shown on the example of well No. C of the DDB field. For this well, a casing string diameter 244.5 mm was run down to a depth of 4273 m, and in the interval 2944-4273 m, the casing string was completed with pipes P-100 with a wall thickness of 13.84 mm to cover unstable chemogenic sediments subject to plastic deformation processes. However, within four days of completing the casing, the casing lost its passability for 215.9 mm bits.

For example, Fig. 2 shows the results of the deformation analysis of the intermediate casing in the interval 3750-3860 m based on the data of the microprofilemetry evaluation with a 24-lever MFC device.

The results of the MFC research with a multi-lever microprofiler (Fig. 2) confirm the deformation of casing. At the same time, electromagnetic flaw detection MTD in the interval of 3750-3860 m confirms a decrease in the casing wall thickness in some places and up to 15%, which may indicate the impact of external deformation processes on the casing and the operation of a special tool in eliminating process damage that led to metal loss. Quite often, during the construction of deep wells, cases of casing integrity destruction are recorded due to their rubbing. The research results of the parameters of the intermediate casing of well No. C are shown in Table 2.

As can be seen from the results of the carried-out research in Fig. 2 and Table 2 was found destruction of the casing string condition and its internal diameter was

Table 2.

Parameters of casing diameter 244.5 mm according to data MFC24C-J

Bottom of pipe, m	Length of pipe, m	Maximum internal diameter, mm	Maximum penetration, %	The depth of maximum penetration, m	Column internal diameter, mm	Minimal internal diameter, mm	Depth of maximum narrowing, m
3644.1	10.5	222.1	17.3	3640.3	217.3	216.2	3640.7
3655.4	10.3	221.1	13.5	3648.7	217.3	212.6	3648.6
3666.9	10.5	224.9	27.4	3664.8	217.3	214.6	3657.3
3678.2	10.4	225.5	29.7	3673.9	217.3	211.8	3674.0
3689.8	10.5	224.5	26.0	3687.4	217.3	212.1	3687.6
3701.4	10.6	227.2	35.7	3695.6	217.3	211.9	3694.1
3712.5	10.2	224.0	24.3	3704.4	217.3	212.5	3704.2
3723.7	10.1	224.7	26.7	3716.9	217.3	211.8	3716.9
3735.2	10.5	226.0	31.5	3727.6	217.3	210.2	3727.2
3746.7	10.6	225.4	29.1	3736.4	217.3	212.7	3745.9
3758.3	10.5	223.9	23.9	3751.6	217.3	214.0	3751.6
3769.8	10.5	225.3	29.0	3760.4	217.3	211.5	3768.2
3781.4	10.6	225.1	28.1	3774.9	217.3	206.8	3774.7
3792.8	10.4	224.7	26.6	3785.2	217.3	212.6	3785.2
3804.0	10.2	228.3	39.6	3794.3	217.3	206.5	3796.6
3815.4	10.4	225.4	29.1	3812.5	217.3	211.7	3812.3
3826.9	10.4	224.5	26.0	3824.9	217.3	214.1	3825.3
3838.0	10.1	225.9	31.1	3830.5	217.3	212.2	3830.3
3849.4	10.4	226.9	34.7	3849.4	217.3	210.2	3841.6
3860.8	10.4	226.3	32.6	3859.3	217.3	211.7	3858.5
3872.2	10.4	225.3	28.7	3862.1	217.3	212.5	3861.9

reduced from the baseline value of 216.9 mm to the actual 206 mm. This technical condition of the intermediate casing made it impossible to further construct the well in accordance with the design decisions.

One of the reasons for the loss of stability of the mountain massif in the pre-bore zone, according to the research of V. Luban and G. Strilets, is a change in the energy state of rocks, which is caused by a decrease in elastic and an increase in plastic deformation. Not adhering to a certain extent with the necessary requirements for well casing and cementing in such conditions, technological factors activate the deterioration of natural equilibrium, creating prerequisites for the intensification of plastic deformation.

The processes of ion exchange at the boundary of the formed mediums (an array of chemogenic deposits and the dispersion medium of plugging systems) intensify the destruction of the stability of chemogenic deposits. It should also be noted that the volume of liquids in the bischofite-water system increases by about 3.5 %. In a saturated NaC1 solution, the increase in the volume of bischofite-mineralized water is greater than in fresh water. The increase in the medium temperature provokes an increase in solubility and an increase in the volume of the bischofite-water liquids, which in some cases can cause the transfer of these forces to the casing. Therefore, it is important to use sedimentation-stable plugging systems.

During constructing deep wells, due to the circulation of process liquids, the temperature in the pre-bore zone near unstable chemogenic deposits can provoke their additional dissolution. It is also necessary to take into account heat generation during the structure formation of plugging mud. Temperature changes in the pre-bore zone have a direct impact on the stability of the rock mass and the condition of the insulation screen [30].

Under certain circumstances, the well casing and cementing system can be subjected to extremely high external pressures. As an example, in well No. 71 of the Kobzivske field, the casing string was equipped with pipes diameter 168 mm of P-110 strength group with a wall thickness of 12.06 mm and a permissible compressive pressure of 91 MPa for casing and cementing in chemogenic deposits conditions. That is, taking into account the back pressure from the drilling slurry, the casing string had to withstand an external overpressure of 117 MPa, which is almost 2.3 times higher than the calculated rock pressure at a depth of 2220 m. However, during the well drilling, the drilling tool's passability was lost due to a destruction of the casing integrity.

It should also be taken into account that under thermobaric conditions of the well, the impact of chemogenic deposits on the technological properties of plugging systems cannot be fully predicted in advance. Such peculiarities are caused by the influence of salt-saturated deposits on the change in the kinetics of structure forming and their subsequent impact on the operational properties of cement stone. The main technical measures to prevent the damage of the casing and cementing systems under the influence of chemogenic sediments prone to plastic deformation are the use of high-strength pipes and special plugging systems adapted to these conditions.

It is well known that the use of mineralized water as a mixing liquid for plugging cement is a necessary requirement for wells cementing in conditions of chemogenic deposits. Both in Ukraine and in global practice, sodium chloride is generally used, due to the following factors

– salt deposits are represented by 50-90% halite;

– cement stone formed on the basis of plugging material prepared with mineralized water containing sodium chloride provides good adhesion to calcium chlorides and sulphates, the share of which is up to 19% in salt deposits;

– under thermobaric conditions and when using stabilized plugging systems with sodium chloride, satisfactory adhesion can be obtained with potassium chloride, which is up to 4%, and other salts.

The expediency of using NaCl-based mineralized water as a dispersion medium for plugging mud helps to improve the rheological characteristics and increase the density of the plugging mud, and is a prerequisite for increasing the adhesion of cement stone to bounding surfaces. These technological solutions provide increased corrosion resistance of cement stone and improved quality of sediment separation.

The impact of salt deposits or formation water on the technological parameters of the can be quite unpredictable in terms of the thickening of plugging mud, as well as the kinetics of structure formation and physical and mechanical properties of cement stone.

The absence of an insulating screen in the intervals of chemogenic deposits often leads to a damage of the stability of the casing and cementing systems.

In addition, in the absence of an insulating screen made of cement stone, corrosion processes actively spread to the casing.

To eliminate such risks during well cementing and to ensure comprehensive loading of the rock mass on the casing, the off-casing space should be filled as much as possible with high-quality cement stone formed based on a stabilized dispersed-armoring plugging mud with zero water separation and minimal water loss.

Defects in the casing and cementing system can spread both in the cement stone and in the contact areas (casing-insulation ring-rock) [31]. The absence of a high-quality insulating screen can be as a channel for the movement of formation fluids along with aggressive components.

One of the most important factors that determine the unsatisfactory quality of well casing is the factors associated with the technological and operational properties of the plugging materials.

Providing reliable protection of a rather thin insulating ring from the impact of aggressive formation water is a challenging task. One of the methods to solve this problem may be the use of plugging materials with increased corrosion resistance.

Chemical corrosion of cement stone occurs when it interacts with an aggressive medium both at the initial stage of structure formation and during well operation.

The ability of cement stone to withstand exposure to aggressive medium for a long time will characterize its corrosion resistance.

The most aggressive corrosion on cement stone in the well is the influence of magnesium salts. The aggression of these salts is especially relevant for Ukrainian DDB fields, where it is necessary well casing and cementing in conditions of a thick layer of chemogenic deposits. In the lithological section of DDB chemogenic deposits, the most commonly found saline rocks are halite, as well as potassium and magnesium salts, such as carnallite and bischofite. Magnesium salts in excess of 4.5-5.0 g/l in terms of Mg have a negative impact on the physical and mechanical properties of cement stone. In such cases, the degradation of cement stone can take place until the complete decomposition of calcium hydrosilicates and the destruction of cement stone.

Corrosion of cement stone under the influence of halite is insignificant compared to other salts, since in the presence of magnesium salts, cement stone quickly corrodes and destructed.

It should be noted the importance of the influence of corrosion products on the intensity and duration of the corrosion process on cement stone. In the case of forming of well-soluble corrosion products that can be carried out of the drained pores of cement stone, the physical and mechanical properties of cement stone will deteriorate (decrease in strength, increase in porosity and permeability, etc.). At the same time, the rate of corrosion will increase in proportion to the rate of removal of curing products to the outside. Otherwise, if the structure of the cement stone is dense and the stone is poorly soluble, and corrosion products accumulate in the pores of the stone, then at first there will be an increase in the strength characteristics of the stone and self-sealing of the microstructure. However, at a later stage, when the cement stone is about one year old, the strength characteristics may decrease due to an increase in internal stresses as a result of an increase in crystallization pressure.

The impact of magnesium aggression on cement stone is caused by the interaction of magnesium ions with hydroxide groups of cement stone to form magnesium hydroxide, which is poorly soluble in water.

According to the results of the carried-out research and analysis, it can be stated that magnesium sulphate has the greatest depth of penetration into the structure of cement stone, forming gypsum and magnesium hydroxide crystals with calcium compounds in the cement stone. The presence of magnesium sulphate salts causes chemical reactions with calcium hydroxide, hydroaluminates and hydrosilicates. These reactions continue until the calcium hydrosilicates are completely decomposed, causing the cement stone being destroyed. Reactions between $MgSO_4$ and hydrated compounds schematically (after V.M. Jung) [32] can be presented as follows:

$$Ca(OH)_2 + MgSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + Mg(OH)_2;$$

$$3CaO \cdot Al_2O_3 \cdot 6H_2O+3MgSO_4+6H_2O = 3(CaSO_4 \cdot 2H_2O)+2Al(OH)_3+Mg(OH)_2;$$

$$3CaO \cdot 2SiO_2 \cdot 3H_2O+3MgSO_4+nH_2O = 3(CaSO_4 \cdot 2H_2O)+2SiO_2 \cdot nH_2O+3Mg(OH)_2 .$$

During magnesium chloride reacts with calcium hydroxide, soluble calcium chloride is formed, which can be leached out, and slightly soluble magnesium hydroxide in the form of a brittle mass:

$$Ca(OH)_2+ MgCl_2= CaCl_2+Mg(OH)_2 .$$

It should be noted that magnesium hydroxide exhibits expanding properties, while having no binding properties [33]. Low-solubility gypsum that precipitates in the cement stone medium additionally causes its destruction.

Sulphate corrosion causes crystallization of new-forming, which additionally cause microcracks caused by the increase in internal stresses during crystal growth. During this corrosion, the permeability of the cement stone increases faster compared to the decrease in strength. This is due because microcracks form additional channels for filtration. Due to the increased cross-sectional area of the filtration channel, its capacity cannot be completely shielded by the corrosion products of the stone. When a continuous channel is formed from microcracks, the corrosive effect of formation water causes erosion of the stone and loss of strength characteristics due to the dissolution and removal of calcium hydroxide.

An important factor of impact the destructive processes of cement stone state under the influence of salt aggression is also an increase in the volume of salts during the phase transition from less hydrated forms to forms with large amounts of crystallization water. The forming of crystalline hydrates is accompanied by an increase in the volume of the solid phase, which can lead to stresses in the structure of the pore space of cement stone that can intensify its destruction. The structure of the cement stone has an important impact on the stability of the cement stone, which is due to the distribution of pores by size and porosity of the cement stone [34], and its permeability.

Cement stone undergoes changes in its physical and mechanical properties during the age cycle. At the age of two days, the strength of the stone will depend on the passage of primary hydration processes. It is known that the hardening process at the age of up to 28 days will contribute to the completion of the hydration of the β-form of dicalcium silicates. Subsequently, at the age of cement stone up to 180 days, thermodynamic equilibrium is established, since the hydration processes are basically completed. However, if the cement stone is exposed to an aggressive medium, the thermodynamic equilibrium can be shifted up to 360 days [35]. Research of corrosion resistance of plugging materials is carried out with an assessment of the strength of cement stone under the influence of an aggressive medium, considering the dynamics of its change over time. In addition, to research the impact of corrosion process on cement stone, it was evaluated at the age of eight and ten years.

The magnesia aggression on cement stone is quite active, which is due to the influence of both anionic and cationic components. Carried-out laboratory researches confirmed increased aggression in the medium of 5% $MgSO_4$ for cement stone samples based on cement PCT I-100 in the case of using both fresh technical mixing water (UN8) and mineralized water (UN9). The dimensions of the cement beams were (height × width × length) (mm) 20 × 20 × 45 (Fig. 3a) and 20 × 20 × 55 (Fig. 3b).

As can be seen in Fig. 3, sulfate-magnesium aggression causes changes in the geometric dimensions of cement stone samples with pronounced signs of deformation and breaking stresses. A decrease of the strength characteristics of the cement stone was already recorded at the age of 180 days, indicating the destructive processes of the cement stone. The corrosion processes of cement stone were confirmed by XPA results (Fig. 4), which showed the absence of the portlandite phase and a small content of the alite phase, which is difficult to identify.

In the research series of samples (Fig. 4) based on cement PCT I-100 (UN8) and (UN9), the sulfur content in terms of oxide is 9-11 wt.%. Both series are characterized by a complex phase composition with the presence of an amorphous component. The main phases for the group are gypsum $CaSO_4 \cdot 2(H_2O)$ at different degrees of dehydration (multiple phases), ferrous sulphate and its hydrated form, and calcium carbonate $CaCO_3$. There is a significant content of X-ray amorphous phase. The X-ray crystalline phase of portlandite $Ca(OH)_2$ lacks, and the X-ray crystalline phase of allite Ca_3SiO_5 is not unambiguously

a) mixing liquid process water

b) mixing liquid mineralized water

Fig. 3. Samples of cement stone based on cement PCT I-100 at the age of 10 years with magnesium sulfate corrosion.

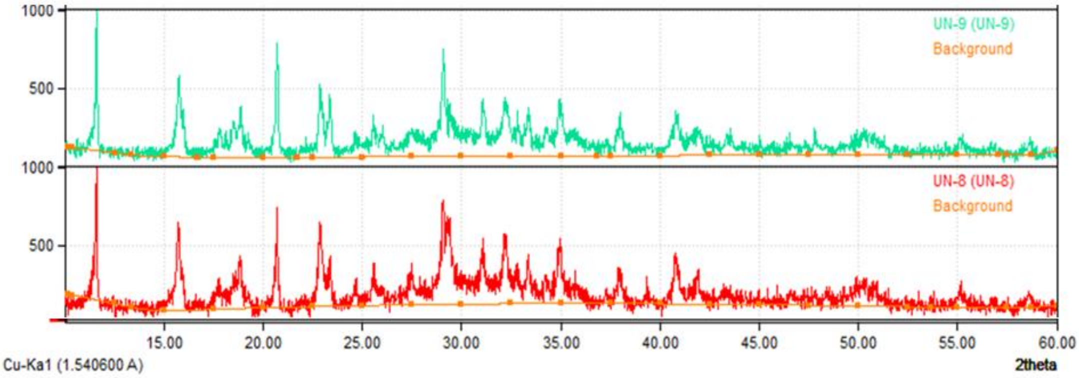


Fig. 4. XPA of cement stone samples based on cement PCT I-100 at the age of 10 years.

identified.

It should be noted that calcium hydroaluminates and hydrosilicates undergo almost complete decomposition under the influence of magnesium sulfate aggression. In addition, during this aggression, when gypsum interacts with calcium aluminates, the forming of highly insoluble calcium hydrosulfoaluminate occurs, which provides an increase in volume of up to 2.8 times. The crystallisation pressures of the formed ettringite contribute to the active growth of internal stresses, which increase the degradability of the stone.

One of the methods to increase the corrosion resistance of cement stone is based on the use of composite cements with hydraulically active additives. In this case, the use of hydraulically active additives allows to bind calcium hydroxide released during the hydrolysis of cement minerals, preventing the forming of ettringite, which can cause stone destruction [36, 37, 38].

In addition, in composite cement, during structure forming, the clinker component of the cement is hydrated with the simultaneous interaction of hydrate new forming with fillers and polyfunctional modifiers. Polyfunctional modifiers and active admixtures ensure optimization and improvement of the properties of the plugging mud and the operational properties of cement stone based on it [39, 40]. Carried-out scientific research have confirmed the possibility of self-armoring of the stone microstructure [41].

Composite cements are actively used in the construction industry [36].

The possibility of using composite plugging systems has been confirmed by carried-out research and industrial tests [42, 43, 44].

Composite cements are characterized by slower kinetics of structure forming. At an early age, the strength of admixture-free Portland cements may exceed that of stone based on composite cements. However, under thermobaric conditions, cement stone based on composite cements has improved operational characteristics: higher strength, increased crack resistance [45], which is important when casing and cementing production deposits, especially in conditions of their secondary opening, as well as resistance to aggressive medium [46].

Researches have confirmed the effectiveness of mineral additives in cements and the improvement of their performance properties [47, 48, 49].

To regulate the properties of the plugging mud certain additives can be used as modifiers, in particular, foam suppressants for deaeration of the mud, plasticizers to ensure the required rheological characteristics of the plugging mud [50, 51]. Cellulose ester modifiers are used to bind free water in plugging systems [52], especially under elevated thermobaric conditions [53]. The list of modifiers for different purposes is quite diverse, including dispersion-armoring additives [54] to improve the elastic and deformation properties of cement stone and expanding additives that increase the volume of cement stone. The feasibility of using polycomponent systems has been confirmed by a number of research [55]. However, the multicomponent composition of the plugging material requires a uniform distribution of the components in the overall system to obtain a homogeneous plugging mud and cement stone based on it.

Dry plugging compound of the type DRCT was used for the research [56] which is recommended for cementing wells at moderate temperatures.

The results of the quantitative analysis of the elemental composition are shown in Table 3.

The results of X-ray phase analysis of cement stone samples based on composite cement DRCT (prepared with 20% NaCl mineralized water) in different storage mediums are shown in Figure 5.

Based on the summarizing of the results of X-ray fluorescence spectroscopy (spectrometer-analyzer Expert 3L) and X-ray diffraction analysis (X-ray diffractometer Shimadzu XRD-7000), it was found that the material DRCT under study (laboratory marking C-HSC1) in the freshwater storage medium is a mixture of calcium hydroxide phases of portlandite $Ca(OH)_2$ and phyllosilicates of calcium silicates of varying degrees of hydration. A phase $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$ and a phase is isostructural with gyrolite are clearly identifiable, a phase with clinoptilotite is isostructural likely.

The researched material DRCT (marking C-HSC$_2$ – storage medium is chloralkali produced water with a density of 1.14 g/cm^3) is a mixture of phases of calcium hydroxide portlandite $Ca(OH)_2$, halite NaCl and calcium silicates of varying degrees of hydration. There is a clinoptilolite phase, a phase $Ca_2SiO_4{\cdot}xH_2O$ and a phase $2CaSiO_3{\cdot}H_2O$. The diffractogram shows a halo in the area of counter angles 20-40°, which implies an X-ray amorphous state of the phases with relatively small values of the characteristic interplanar distances – thus, mainly aluminosilicates with a relatively low degree of hydration

Table 3.

Oxide composition of cement stone samples at the age of eight years

Composition (in terms of oxides), wt.%	Storage medium for cement stone DRCT			
	C-HSC1 fresh water	C-HSC2 formation water	C-HSC3 magnesium chloride	C-HSC4 magnesium sulphate
Al_2O_3	3.40	2.40	3.60	3.35
MgO	–	1.41	–	3.34
SiO_2	16.15	13.59	14.86	16.68
SO_3	1.28	0.93	1.89	10.39
Cl	4.65	19.31	13.21	–
CaO	69.48	59.02	60.51	61.60
MnO_2	0.18	0.12	0.18	0.21
Fe_2O_3	4.29	2.93	4.46	3.54
SrO	0.06	0.27	–	0.14
TiO_2	0.44	0.11	0.42	0.44
Br	–	–	0.12	–

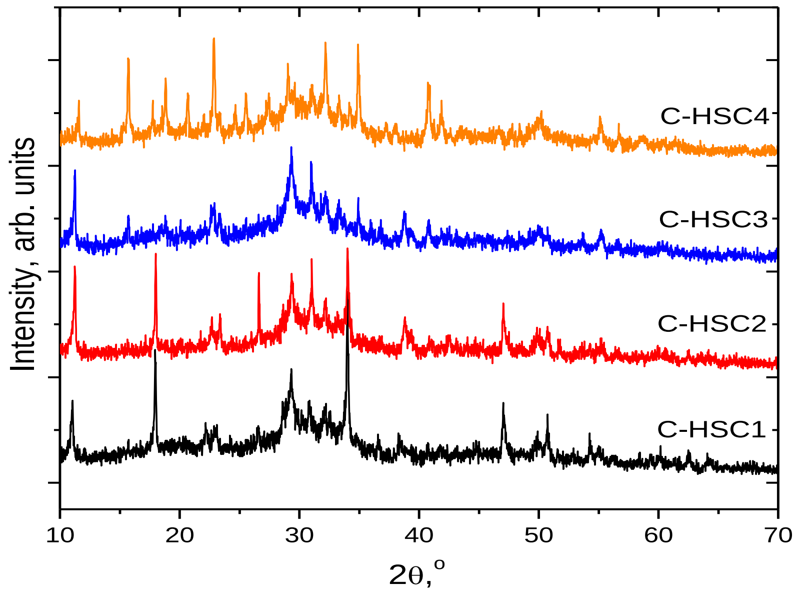


Fig. 5. Research and comparison of XPA analysis of cement stone samples at the age of eight years.

are amorphous.

The sample DRCT (laboratory marking C-HSC3) in the magnesium chloride storage medium is characterized by mixtures of phases of calcium silicate $2CaSiO_3 \cdot H_2O$ and calcium silicates of different degrees of hydration. A phase of clinoptilolite, a phase $Ca_2SiO_4 \cdot xH_2O$ and probably a phase with a tobermorite structure $xCaO \cdot ySiO_2 \cdot zH_2O$ are present.

The researched material DRCT (laboratory marking C-HSC4) in the magnesium sulfate storage medium is a complex mixture of phases of calcium silicate $2CaSiO_3 \cdot H_2O$, halite NaCl and calcium silicates of different degrees of hydration. Sulphur-containing phases – a phase $CaSO_4$ and calcium silicate sulphate $Ca_5(SiO_4)2SO_4$ are present. Clinoptilotite phase, a phase $Ca_2SiO_4 \cdot xH_2O$ and a phase with tobermorite structure $xCaO \cdot ySiO_2 \cdot zH_2O$ or $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ are present. Calcium carbonate and a phase of portlandite $Ca(OH)_2$ are present.

The kinetics of the strength characteristics of cement stone based on material DRCT in a chloralkali storage medium of produced water was also evaluated (Fig. 6).

It was found that the bending strength of the stone was 10.4 MN/m^2 over eight years. Such results indicate an increase in the strength of cement stone in the formation water medium over eight years by almost 80% compared to the baseline strength at the age of one day. Based on the results of XPA and the assessment of strength kinetics, it can be stated that the cement stone based on material DRCT has high operational properties. Earlier researches of the impact of basic acid systems used to treat the bottomhole zone on the state of cement stone confirm that composite plugging materials also form cement stone with increased acid resistance [57].

Carried-out laboratory researches have confirmed the increased corrosion resistance of cement stone based on composite cement of the plugging material DRCT. The obtained results allow us to recommend plugging materials DRCT for cementing oil and gas wells in difficult mining and geological conditions of Ukrainian fields.

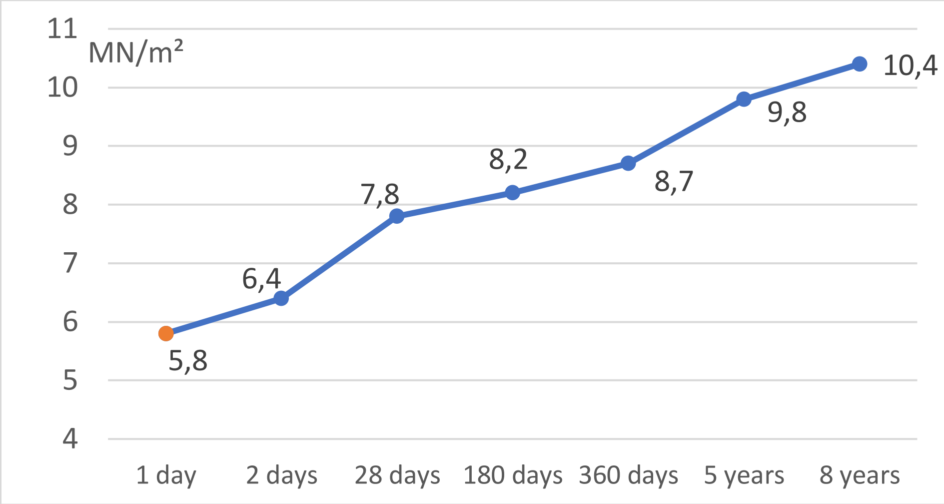


Fig. 6. Strength dynamics of cement stone based on material DRCT.

Conclusions

The complex geological section of Ukrainian fields requires the use of special plugging materials with the necessary technological and operational properties.

The sedimentation stability of basic plugging cements and materials based on them, as well as the degradability of cement stone under the influence of aggressive formation water medium, have been established.

Research have confirmed the advantage of using plugging materials based on composite cements.

X-ray phase analysis and research of the physical and mechanical properties of cement stone confirm the forming of corrosion-resistant cement stone with improved operational characteristics.

The results of analytical and laboratory researches make it possible to recommend plugging materials DRCT for cementing oil and gas wells in difficult mining and geological conditions of Ukrainian fields.

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Дослідження деградабельності цементного каменя в складних гірничо-геологічних умовах України

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Проаналізовано особливості та перспективи вуглеводневого потенціалу України. Встановлено, що базовий ресурс покладів нафти і газу зосереджений у складних гірничо-геологічних умовах, де левова частка запасів відноситься до категорії родовищ із важковидобувними запасами. В таких умовах повинні бути встановлені додаткові вимоги до системи кріплення, зокрема до цементування продуктивних відкладів.

Проведено дослідження рецептур базових тампонажних матеріалів та встановлено порушення їх седиментаційної стабільності. Оцінено вплив технологічних процесів під час закінчування свердловин на систему кріплення та охарактеризовано вплив даних операцій на стан ізоляційного кільця у свердловині. На прикладі ускладнень під час кріплення свердловин акцентовано увагу на технологічних та експлуатаційних вимогах до тампонажних матеріалів.

Визначено деградабельність цементного каменю на основі базових цементів ПЦТ I-100 за результатами візуальних досліджень та рентгено-фазового аналізу (РФА). Встановлено деформацію взірців каменю під дією агресивного середовища та майже повну відсутність в'яжучих кристалогідратів у взірцях при РФА. Отримані результати свідчать про необхідність використання деградабельно-стійких тампонажних матеріалів. Охарактеризовано переваги тампонажних систем на основі композиційних цементів та подано типові модифікатори, що можуть застосовуватись для регулювання властивостей тампонажного розчину і цементного каменю. Проведено дослідження впливу агресивних середовищ на цементний камінь на основі композиційного матеріалу DRCT. Кількісний аналіз елементного складу та РФА досліджуваних взірців цементного каменя DRCT в агресивних середовищах хлористого та сірчанокислого магнію, а також у пластовій воді хлоркальцієвого типу підтверджують корозійну стійкість каменю з матеріалу DRCT. Результати досліджень дозволяють рекомендувати тампонажний матеріал DRCT для цементування нафтових і газових свердловин у складних гірничо-геологічних умовах.

Ключові слова: свердловина, система кріплення, цементний камінь, корозія цементного каменя.