PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 3 (2024) pp. 664-674

Section: Technology

DOI: 10.15330/pcss.25.3.664-674

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 3 (2024) С. 664-674

Технічні науки

PACS: 33.20.Ea, 61.05.C-, 68.37.Hk, 73.63.Fg, 87.64.Je

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

Ye.M. Stavychnyi[1], S.M. Rudyi[1], Ya.M. Femiak[2], B.A. Tershak[3], S.A. Piatkivskyi[1],
M.M. Klymyuk[4], V.V. Kindrat[4]

Influence of acid systems on bottomhole zone decolmatization and set cement stability

[1]PJSC "Ukrnafta", Kyiv, Ukraine, Yevhen.Stavychnyi@ukrnafta.com
[2]Ivano-Frankivsk National Technical University of Oil and Gas, Ivano-Frankivsk,Ukraine
[3]LLC "EnergoComposit",Lviv, Ukraine
[4]Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine,

The state of the bottomhole zone during drilling was assessed on the example of well No. 47 Stynava. Based on the study of the impact of drilling fluid on the filtration and capacitance characteristics of the core material, it was found that the colmatation screen on the core material can be eliminated by acid treatment.

The studies and results of operations at wells of PJSC "Ukrnafta" have confirmed the effectiveness of oil recovery enhancement methods, among which the acid treatment of formations, whichare used both for cleaning of well bottomhole zone and forintensification.

The main technological parameters of a few cementing materials and mixtures, as well as the physical-and-mechanical properties of set cement based on them, were studied. The effect of acid treatment used during intensification on set cement was evaluated. It has been established that base cements and mixtures based on them are subjected to a significant aggressive effect of acids, which provokes the destruction of set cement.

The results of the study substantiate the expediency of using composite plugging cements for well cementing in difficult conditions where the set cement of the insulating ring can be exposed to acid exposure.

Keywords: well, acid treatment, plugging fluid, set cement, corrosion resistance.

Received 26 May 2024; Accepted 13 September 2024.

Introduction

Preserving the primary permeability of rocks in the well bottomhole zone (WBZ) during the opening of carbonate and terrigenous reservoirs, especially in the context of a single well, requires solving a complex problem: from the moment of initial opening to the end of well development. Repression on productive formations during well construction during initial opening and cementing ranges from 20% to 150%, and in some cases reaches much higher values. As an example, during well construction at the Hnidyntsy field of PJSC "Ukrnafta", the repression applied to productive intervals during drilling ranges from 3.1-7.0 MPa, and during cementing, it ranges from 11 MPa to 16 MPa, that is exceeds reservoir pressures by 65% to 120%. It is well known that the maximum preservation of natural permeability of formations in WBZ can be achieved by using modified drilling and plugging muds and improving a number of technological measures to prevent the penetration of dispersed systems and their filtrates into the formation (reducing the repression on the formation, reducing the time of exposure of the drilling mud to the formation, changing the casing bottom construction, etc.).

In case of reduced permeability of productive horizons or lack of expected flow rate, acid treatment of formations is carried out. The treatment on the pore and fracture space of productive formations in the WBZ with acid solutions ensures an increase in their filtration and capacitance parameters during the development or commissioning of oil, gas, gas-condensate and water injection wells. Acid treatment on formations also helps to dissolve introduced contaminants, formations and rock components during well operation caused by hydrocarbon production processes or other factors [1].

However, in the case of acid treatment on the formation, a significant impact is transmitted to the casing system, in particular to the set cement, which can lead to its degradation. Numerous works of scientists about of individual technological processes and the creation of new solutions to improve the quality and reliability of well construction and casing demonstrate the relevance of these research areas.

During carried out of different technological operations in the process of construction, production and work over of wells, complex processes can occur in the WBZ, which lead to reduction of the natural physical, mechanical and chemical state of the formation, including a decrease in filtration characteristics, which can significantly reduce well productivity.

Well surveys under stationary and non-stationary filtration modes have shown that after drilling and development, their productivity decreases by an average of two times, i.e. the well productivity factor is 50% of the productivity factor of a hydrodynamically perfect well [2].

In order to prevent the negative impact of colmatation processes during the initial opening of productive horizons when using water-based solutions, it is recommended to use low-clay or clay-free types of drilling fluids, in which the solid phase is represented by acid-soluble screening fillers with a selected fractional and component composition in accordance with mining and geological conditions. In such systems, solid insoluble sediment should not be formed during the destruction of components and the direct treatments of bottomhole formation zone clean [3]. Researches by Ya.B. Tarko has established that the deterioration of the energy state of deposits and their watering are the dominant factors in reducing well productivity. However, the analysis of the dynamics of well fluid flow rates showed that in many cases, the decrease in their flow rate occurs regardless of the energy state of the deposits. For example, at the Perekopivka oil field, the average well fluid flow rate decreased by 4.9 times over three years, while the average reservoir pressure in productive horizons decreased by only 9-11%. A similar situation was observed at the Artyukhy oil-gas-and-condensate field, where the average fluid flow rate decreased by 3.8 times over ten years, while the average reservoir pressure decreased by only 15%, and at the Korzhi oil-gas-and-condensate field, where the fluid flow rate decreased by 2.1 times over six years, while the reservoir pressure decreased by 4-9 % during this time. These data show that, by the side of above factors, one of the main reasons for the decline in oil and gas production rates is the colmatation of filtration channels in productive formations [4].

One of the ways to increase hydrocarbon production is to introduce methods to enhance oil recovery, among which acid treatment of formations, which form the basis of chemical well treatment methods and are most widely used not only for cleaning the WBZ but also for stimulation, occupies a significant place.

However, simultaneously with such processes, acid treatment also affects the set cement, which is the basis for the formation of the insulating screen. Calcium oxide, as the main oxide of all standard cement materials, has a particularly high affinity for organic and inorganic acids. During acid treatment at set cement destructive processes are taking place that lead to changes in its physical, mechanical and chemical properties. In the field of building, A.M. Neville [5] identified the interaction of cement alkalis with aggregate silica, volume changes due to differences in the thermal expansion of set cement and aggregate, and, above all, the permeability of the cement as one of the reasons for the degradation of set cement. The synthesis of set cementdurability as a composite is to "create an optimal microstructure of set cement, reduce macroporosity and increase crack resistance"[6].

During the preparation of the plugging mud, complex chemical reactions occur as a result of mixing the plugging material with water, including the processes of hydrolysis and hydration of cement clinker minerals, as well as the interaction of active aggregates. Submicrostructural stresses arise in the set cement matrix during the development of crystal hydrate neoplasms [7]. Researches of these stresses are significantly complicated because they are balanced in microscopic volumes of the set cement matrix. During structure formation, crystallization stresses improve the strength of growing neoplasms [8, 9]. It is not necessary to expect sharp differences in the stress state of the hardening gel under different conditions due to the possibility of stress relaxation during deformation of the material pores [10]. New formationsin the crystallization process are active in various aggressive environments, especially in acidic [11, 12].

I. Methodology

Presented in the paper researches are based on the analysis of the relevance of the problem of the state assessment of WBZ and ways of its cleaning, which based on the method of formations acid treatment, as one of the main directions of its solution; forming of the task and drawing up the main algorithm of studied object; scientific ideas for the evaluation and development of plugging systems for wells fastening in difficult mining and geological conditions; solution of the main mathematical dependencies with modelling of experimental data, analysis of the obtained results, grounded conclusions and main recommendations.

At the same time, the substantiation of the component composition and formulation of plugging systems was carried out on the basis of the use of modern methods of analytical and experimental researches by means of mathematical modelling, research methods, instruments and materials.

Evaluation of technological properties of plugging solutions and set cement was completed in accordance with the standards [13, 14, 15]. Researches of the set cement samples strength was carried out after their formation using the device PCK-1. The maximum working pressure was 100 MPa, and the temperature was 573.15 K. During the formation of set cement samples, the temperature regime was maintained using electric heaters operating in automatic mode with potentiometer registration. The required pressure was set by a hydraulic press and by heating the working fluid of the autoclave. The XRF analyser Expert 3L was used to determine the mass fraction of chemical elements in powdered materials and an X-ray diffractometer Shimadzu XRD-7000 was used to research the qualitative and quantitative phase composition and the X-ray diffraction analysis carried out. The estimation of acid resistance of the set cement was carried out in accordance with the methodology for determining the dissolution of rocks in acids, taking into account the technological requirements for cementing wells at PJSC “Ukrnafta” fields. This methodology provides for the determination of the main indicators for estimationofset cement acid resistance: speed, depth, volume, dissolution weight and acid resistance coefficient.

The dissolution rate of set cement R is determined by the formula:

$$\bar{R} = \frac{\Delta g}{S \cdot t}, \ \left(\frac{g}{cm^2 \cdot h}\right) \qquad (1)$$

where Δg – the difference in mass of the sample before and after acid treatment, g; S – surface area of the cement sample, cm^2; t – continuance of acid treatment on the sample, h.

The depth of set cementdissolution is determined by the formula:

$$\Delta l = \frac{\bar{R}}{\text{с}_{c.p.}} \cdot \text{t}, \quad \text{(cm/h)} \qquad (2)$$

where $\rho_{c.p.}$ – the density of cement powder, g/cm^3.

The volume of dissolved set cement is determined by the formula:

$$\Delta V = S \cdot \Delta l, \text{cm}^3 \qquad (3)$$

The mass of dissolved set cement is determined by the formula:

$$\Delta m = \Delta V \cdot \rho_{c.p.}, \text{ g} \qquad (4)$$

The relative weight loss of set cement is determined in percentage:

$$Lm = \frac{\Delta m}{m_i} \cdot 100, \% \qquad (5)$$

where m_i – the initial mass of the sample (before the acid treatment), g.

The relative volume loss of set cement is determined in percentage:

$$Lv = \frac{ДV}{V} \cdot 100 \qquad (6)$$

where V – the initial volume of the sample, cm^3.

The acid resistance coefficient K is determined by the formula:

$$К = \frac{m_f}{m_i}, \qquad (7)$$

where m_f – the final mass of the sample (after the acid treatment), g.

The aim of research is to evaluate the effect of acid treatment on WBZ, study their influence on set cement degradability, and search for and develop basic formulations of plugging materials with increased acid resistance.

II. Results of research and discussion

It is known that oil recovery using reservoir energy in most cases does not exceed 20 %. Methods of maintaining reservoir pressure can further increase the oil recovery factor by up to 25 %. However, in general, the overall oil recovery factor in the world experience ranges from 35 % to 45 % [16].

It should be noted, in particular, that oil production from fields classified as hard-to-recover is carried out at a low rate, with the final oil recovery in such cases not exceeding 30% of the initial balance sheet reserves [17].

One of the methods to increase hydrocarbon production is the introduction of enhanced oil recovery methods, among which acid treatment of formations takes a significant place. Acid treatment of reservoirs in the WBZ allows cleaning them from colmatation products and increasing current oil and gas production from specific wells.

Hydrocarbon production stimulation is especially relevant for fields that are at the final stage of development or are classified as hard-to-recover. Scientists of PJSC “Ukrnafta” [18] confirmed a significant increase of share of hard-to-recover reserves, which is about 70 %.

Thus, in 2005-2022, PJSC “Ukrnafta” performed 919 well operations with acid treatments. The additional oil production amounted to about 1265 thousand tons. The success rate of the operations is 82.5 %. Specific production per well operation amounted to 1.38 thousand tons of oil.

The increase of well flow rate during the implementation of acid treatment processes is achieved by increasing the permeability of formations in the WBZ, the formation of corrosion channels in the rock matrix, cleaning formations from various types of contaminants, restoring the previously reduced permeability of formations in the WBZ due to the influence of contamination [1].

At one time, sidetracking was carried out at well 47-Stynava. The research of the effect of clay-free biopolymer mud on the filtration and capacitance characteristics of a sample of core material (Table 1) of this well was carried out at the depth of 3544 m.

The analysis was carried out under simulated reservoir conditions:

– pressure of hydraulic core compression – 10 MPa;

– working zone temperature – 90 ℃;

– working pressure drop on the core – 1-0.5 MPa.

For core 15037. The drilling mud was pumped through the core during 3 hours. The volume of the filtrate was 2.3 cm^3. The crust, which washed on the working end of the core with a thickness of 0.5 mm, is loose. The recovery of core permeability was equal to β = 24 % after pumping 5.5 pore volumes of hydrocarbon fluid for one hour. The filtration rate decreased from 0.0127 cm/sec to zero. To determine the depth of colmatation, the method of cutting the working end of the

Table 1.

Characteristics of the core material

Number of core	Diameter, cm	Length, cm	Volume, cm^3	Porosity, %	Permeability, $mkm^2 \cdot 10^{-3}$
15037	2.70	5.70	32.62	13.80	5.0
11092	2.67	5.73	32.10	12.10	9.1

core with a length of 1 mm was used. In this case, no increase in the permeability recovery factor β was achieved. To determine the effective method of decolmatation, the hydrochloric acid treatment method was used. The core permeability was then restored to 98 % after pumping 22.2 pore volumes of hydrocarbon fluid in 40 minutes. The filtration rate was stable and equalled 0.05 cm/sec.

For core 11092. The drilling mud was pumped through the core during3 hours. The volume of filtrate was 3 cm^3. The crust, washed on the working end of the core with a thickness of 0.5 mm, is loose. The recovery of core permeability was equal to $\beta = 4.4$ % after pumping 2.5 pore volumes of hydrocarbon fluid in one hour. The filtration rate decreased from 0.004 cm/sec to zero. To determine the depth of colmatation, the method of cutting the working end of the core with a length of 1 mm was used. However, no increase in the permeability recovery factor β was achieved.

To determine the effective method of decolmatation, the hydrochloric acid treatment method was used. The recovery of core permeability was 82.3 % after pumping 15 pore volumes of hydrocarbon fluid in 19 minutes. The filtration rate decreased from 0.1 cm/s to 0.05 cm/sec. The research results confirm that the significant and deep colmatation caused by hydrochloric acid can be eliminated.

Thus, from this example, treatment of the core material by hydrochloric acid ensures its decolmatization. However, such methods of WBZ cleaning, and sometimes technological operations to stimulate hydrocarbon inflow create significant static and dynamic loads on the casing system, especially on the set cement. In well conditions, a rather thin insulating screen is constantly exposed to an aggressive environment. At the same time, the dynamics of corrosion processes will depend on the structural features of the set cement and the kinetics of aggressive agents. As is well known, the lack of a reliable cement ring behind the casing can lead to

– accelerated corrosion of casing by aggressive formation fluids;

– casing crushing of casing strings;

– destruction of the bottomhole zone;

– water breakthrough from neighbouring formations, pulling formation water from the bottom to the perforation holes;

– gas breakthrough from neighbouring formations and the "gas cap" to the perforation holes;

– oil and gas losses due to their flow into formations with low reservoir pressures;

– water flows in the intercolumnar space, formation of griffins, subsurface and environmental pollution.

One of the ways to ensure the durability of set cement is to use active mineral additives that ensure the binding of calcium hydroxide, which prevents the destruction of set cement [19, 20, 21].

Research by a group of scientists [19, 22, 23, 24] has established that all disperse and fine fillers are divided into two types according to their functions: reaction-active and rheologically active. The first type are characterized by an intense pozzolanic reaction of interaction of amorphous silica with portlandcement (quartz-containing fillers – microsilica, basalt, granite, quartz sand), which are reactive with lime, but are characterized by a slower, longer period of interaction with portlandite). The second type of dispersed aggregates (limestone, dolomite) is conditionally inactive, as they do not form strong products with calcium hydroxide [25, 26, 27].

The assortment of plugging materials for well cementing is quite wide, but the demand for such cements for oil and gas wells is rather low compared to cements for the construction industry. It is technologically and economically unprofitable for large cement assortment plants to produce a wide range of cement for oil and gas wells in small quantities. Therefore, the production of cement plugging, in compliance with all the strictly regulated requirements for the material composition, pluggingmud and set cement based on it, is unfortunately unprofitable for powerful cement producers. As a solution, it is more expedient to use a small range of basic cements, and to provide the necessary properties of the plugging material by introducing modifying additives (stabilizers, plasticizers, reinforcing composites, gas blockers, etc.) using special technologies. As an example, we consider the formulation of a plugging mud for cementing of the intermediate casing diameter 244.5 mm in well No. 99 of the Zakhidno-Sosnivka field in the interval 2430 – 2039 m in the conditions of chemogenic deposits. The formulation of the second portion of the plugging mud included the following composition: PCT I-50-100 (75%) + ground quartz (25%) + foaming agent "E" (0.1%) + retarder NTFK (0.025%). The research temperature was 40°C, the pressure was 46.3 MPa, and the test was stopped for 20 minutes after 1 hour of testing. The obtained parameters of the plugging mud and the strength of the set cement at a water-cement ratio of 0.53 (mixing liquid with a density of 1170 kg/m^3 NaCl) are as follows:

– density – 1870 kg/m^3

– flow ability – 245 mm

– water separation – 3.0mm

– thickening time up to 30Berden unit – 4 hours

– bending strength of set cement– 5 MPa

According to the results of laboratory researches and industrial applications (the confirmed example of the above-mentioned well No. 99) of the formulation during well cementing, it was found that the addition of 25% of ground quartz provides sufficient physical and mechanical properties of set cement and allows the use of plugging materials in combination with modifiers in difficult mining, geological and thermobaric conditions. In

Table 2.

Researches of the main parameters of plugging materials

№	Formulation of plugging mud, mass share		Main parameters of plugging mud			Set cement strength, age 1 day, MN/m^2		Fragility coefficient
	cement	water	density, g/cm^3	flowability, mm	water separation, ml	bending	compression	
1	PCT I-100 – 100	48	1.84	230	4.5	5.8	20.8	3.59
2	I-G –75 + MK – 25	48	1.85	240	6.0	6.5	24.2	3.72
3	TC-100	48	1.82	235	3.8	6.2	20.1	3.24
4	Cem-C100	48	1.83	245	3.2	6.7	20.0	2.99
5	DR-CT100	48	1.84	230	3.0	6.4	19.2	3.0

addition, the addition of ground quartz sand to cement contributes to a more complete utilization of the hydration activity of the binder. It should be noted that the presence of finely dispersed silicon hydroxide leads to the formation of new high-strength minerals, densification of the set cement structure, and significantly increases its deformation resistance during perforation operations, hydraulic fracturing and other mechanical stresses. It is possible to improve the quality and reliability of engineering structures during construction through the introduction of composite cements [19]. The conducted researches have confirmed the possibility and technical and economic feasibility of using composite materials also for cementing oil and gas wells [28, 29]. As you know, the peculiarity of using composite cements is that plugging mud based on them hardens more slowly. The slower kinetics of structure formation is fixed in the initial period, but later the set cement based on composite materials gains high strength. When set cement is formed under thermobaric conditions, the strength of composite samples eventually exceeds the strength of portlandcementin bending and compression. Set cement based on composite plugging mixtures has increased crack resistance and corrosion resistance [30].

The peculiarity and kinetics of the structure formation of composite cement lies in the hydration of the clinker component and the chemical interaction of hydrate neoplasms with active components and modifiers. The process of hydration of the composite material proceeds in the interaction with water of the cement components with hydraulic and pozzolanic additives. Components with different hydraulic activity participate in the reactions of structure formation of composite cements.

We have carried out researches a number of plugging materials and mixtures: PCT I-100, a mixture of I-G and microsilica (MS), TS-100, Cem-C100, and DR-CT100, which are used for cementing oil and gas wells at moderate temperatures. Table 2 shows the results of researches of the main parameters of the plugging mud and the strength of the set cement. Set cement samples for strength research were formed at a pressure of 0.1 MPa and a temperature of 75 °C.

Based on the researches, it was found that the set cement based on a mixture of I-G and silica materials is characterized by higher strength characteristics, but also has a higher value of water separation of the plugging mud. A decrease in the sedimentation resistance of the plugging mud for a mixture of I-G materials and silica indicates that its water separation rate is two times higher than for composite cement DR-CT100, 1.9 times higher than for cement Cem-C100, 1.57 times higher than for TS-100, and 1.33 times higher than for I-100 PCT. It should be added that in the event of a violation of sedimentation stability, gravitational migration of the dispersion medium may occur, which will cause a violation of the state of the insulation screen. At the same time, a system of pores and microcracks will form in the set cement matrix, which will form structural defects and which are an additional factor for the degradation of the set cement, which will increase under the influence of aggressive environment.

We would also like to draw attention to the fact that the set cement insulating ring, which is usually in the active kinetics of early strength gain, is subject to dynamic and static loads during pressurization and perforation operations. Such work on wells is carried out as soon as possible after their casing, due to minimizing the time for well construction and expectations of their rapid commissioning for hydrocarbon production. In order to minimize the integrity of the insulating screen and the cracking of the set cement under loads, the set cement must have a reduced brittleness, which can be physically expressed through the brittleness coefficient. The brittleness ratio characterizes the ratio of compressive strength to bending strength. If the brittleness coefficient is less than three, the set cement is characterized by satisfactory elastic and deformation properties. Based on the researches, it was confirmed that set cement based on composite cements is also characterized by improved elastic and deformation properties.

In addition, researches of the quantitative analysis of the elemental composition of composite cements Cem C100 and DR-CT was carried out. The results of researches are shown in Table 3 and indicate that the oxide compositions of Cem C100 and DR-CT are identical.

In addition, evaluation of Cem C100 and DR-CT were carried out based on X-ray phase analysis of Fig. 1 and Fig. 2, respectively.

Based on the generalization 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 main phases for the studied series of samples are portlandite $Ca(OH)_2$, alite $SiCa_3O_5$, and calcium carbonate $CaCO_3$. For the sample of Cem C100, the phases $Fe_2(SiO_4)$ and $Fe(SiO_3)$ are present. The phase of $Fe_2(SiO_4)$ is observed in the sample of DR-CT, although there is a tendency to increase the relative iron content in the series (up to about 9 weight % in terms of precipitate). The probable reason is that iron is in the form of ultrafine oxyhydroxides. The relative sulfur content tends to decrease from 2 to about 1.5 weight % (in terms of oxide). For samples of DR-CT, the presence of mica (potassium aluminosilicates) is observed. Quantitative Rietveld analysis of samples Cem C100 and DR-CT is not possible due to the presence of a significant content of the X-ray amorphous phase, the content of which is maximum for the sample DR-CT. The estimated values of the X-ray amorphous phase content for the sample Cem C100 are up to 54 (at least 46-48 molar %), and for the sample DR-CT – up to 57 (at least 50 molar %). According to the X-ray fluorescence spectroscopy data, the dominant component of the amorphous component is a calcium-containing phase, probably portlandite $Ca(OH)_2$. The targeted kinetics of the structure formation of the plugging material makes it possible to regulate the operational properties of set cement, in particular, to increase the set cement resistance to aggressive environments. The peculiarities of the hydration of the plugging material and the resulting structure of the set cement will have a direct impact on its corrosion resistance. The main parameters that have an impact on it are the water-mixture ratio, grinding fineness and fractional composition of the material, the type of

Table 3.

Comparative composition of plugging materials

Type of material	Composition (in terms of oxides), mass %									
	CaO	SiO_2	Fe_2O_3	Al_2O_3	SO_3	$K_2O + Na_2O$	MnO	TiO_2	SrO	ZnO
Cem C100	81.663	8.166	6.132	0.290	2.247	–	0.621	0.480	0.220	–
DR-CT	76.959	9.197	8.622	1.133	1.521	1.054	0.208	0.766	0.279	0.111

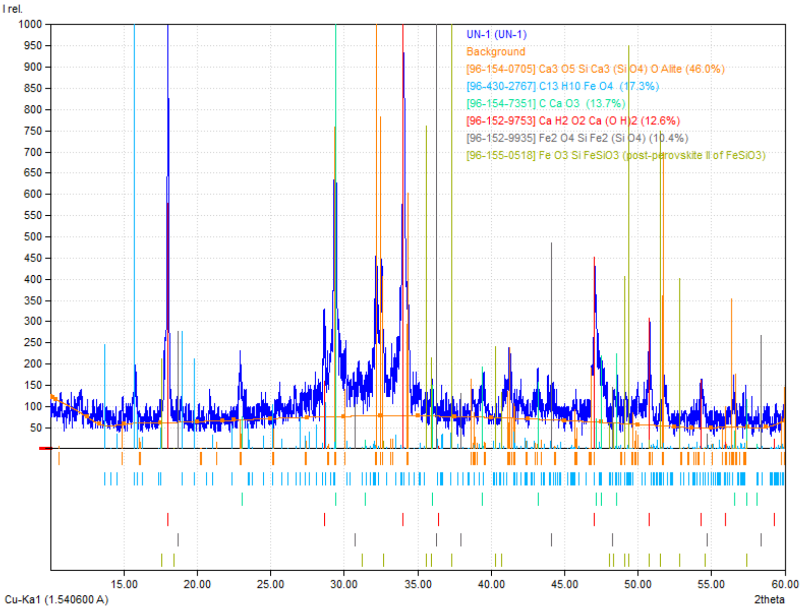

Fig.1. X-ray phase analysis of Cem C100.

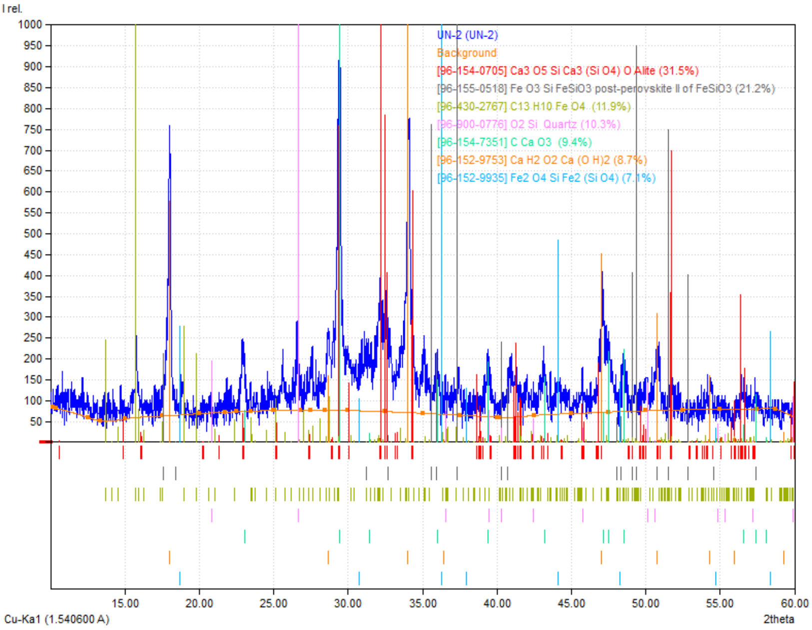

Fig.2. X-ray phase analysis of DR-CT.

Table 4.

Formation water of Rybaltsi field

Name of indicator	Units of measurement	Measurement result
Density	g/cm^3	1.1395
pH	units pH	5.52
Chlorides	mg/dm^3	134710.0
Sulfates	mg/dm^3	<50.0*
Hydrocarbonates	mg/dm^3	195.2
Carbonates	mg/dm^3	<3.5*
Calcium	mg/dm^3	18236.4
Magnesium	mg/dm^3	5350.4
Potassium + Sodium	mg/dm^3	58858.31
Mineralization	mg/dm^3	217360.18
Note: * – the content of the indicator is less than the minimum value of the measurement range of this methodology		

cement and modifiers used for the material, as well as the thermobaric conditions of formation and the structural features of the set cement.

Modifiers and additives to plugging materials of different genesis can improve the technological properties of the plugging slurry and the physical and mechanical properties of the set cement [31].

For the base materials, the acid resistance of set cement was evaluated. Research of acid resistance of set cement was carried out in the environment of the most widespread acids for stimulation of reservoir fluids inflows – hydrochloric 10% HCl and clay 10% HCl + 3% HF. The time of contact with acids is 3 hours, which is based on the results of laboratory researches and practical implementations at objectsof PJSC "Ukrnafta".

After evaluating the strength characteristics at an early age, the cement beams were transferred to the formation water of the calcium chloride type, chloride group, calcium subgroup with a density of 1139.5 kg/m^3. The water was changed every 30 days. The storage fluid for cement beams is the formation water of the Rybaltsi field (Table 4).

It should be noted that the acidic treatment on the formations will have a significant influence on the stability of set cement in oil and gas wells. When the set cement is up to two days old, its strength depends on the primary hydration. Subsequently, during the strength gain up to 28 days, the hydration of silicates of type β-C_2S ends. When the set cement is three to six months old, the thermodynamic equilibrium of the system is achieved in the process of structure formation. After the set cement samples reached the age of about six months, which is mainly due to the completion of hydration processes and stabilization of the dynamics of strength gain, their acid resistance was determined. When acids interact with set cement, they can create new formations that will dissolve in water and cause exposure of the inner layers of the set cement, as well as products that can block the newly formed gaps in the set cement structure. At the same time, acids can chemically interact with minerals present in set cement. Portlandite interacts with acids as follows:

$$Ca(OH)_2 + 2HC1 = CaC1_2 + 2H_2O$$

$$Ca(OH)_2 + 2HC1 + 2HF = CaC1_2 + CaF_2\downarrow + 2H_2O$$

Alite $SiCa_3O_5$ interacts with acids according to the following scheme:

$$Ca_3SiO_5 + 6HC1 = 3CaC1_2 + SiO_2\downarrow + 3H_2O$$

$$Ca_3SiO_5 + 4HC1 + 2HF = 2CaC1_2 + CaF_2\downarrow + SiO_2\downarrow + 3H_2O$$

The iron silicates Fe_2SiO_4 and $FeSiO_3$ interact with acids as follows:

$$FeSiO_3 + 2HC1 = FeC1_2 + SiO_2\downarrow + H_2O$$

$$2FeSiO_3 + 2HC1 + 2HF = 2FeC1_2 + FeF_2\downarrow + 2SiO_2\downarrow + 2H_2O$$

New formations that arise from such reactions have no binding or strength properties. The calcium chloride formed as a result of the reaction is a soluble compound that will be carried out of the set cement. As a result of further treatment to process fluids or cyclic treatment, the degradability of set cement will increase. Insoluble products such as calcium fluoride, iron fluoride and silicon oxide can block newly formed cracks in the set cement. However, this ability depends on many factors, and therefore blocking of cracks may not occur in all cases. Acids can also destroy hydrosilicates, hydroaluminates and calcium hydroferrites, turning into calcium salts and amorphous, unbound masses of $SiO_2 \cdot nH_2O$, $A1_2(OH)_3$, $Fe_2(OH)_3$.

When set cement interacts with an aggressive environment, colmatation screens can also be formed, which will help reduce the corrosion rate. In this case, the first mechanism of colmatation screening will consist of a silicic acid gel due to the interaction of the set cement silicate component with aggressive agents. The second screening mechanism can occur as a result of the interaction of aggressive agents with the calcium component of set cement.

The kinetics of acid aggression of set cement is more dynamic compared to the effects of salt aggression. These processes are caused by the intense penetration of hydrogen ions into the highly alkaline environment of set cement and are reduced slightly. At the same acid concentration, the rate of corrosion reduction of set cement in hydrochloric acid is lower than in hydrochloric acid, since the reaction processes produce the formation of easily soluble calcium chloride. At the same time, when sulfuric acid is applied to set cement, the reaction products, in addition to the silicic acid gel, are gypsum, which will further slowdown the corrosion processes. It is known that the initial rate of corrosion processes of set cement under the influence of hydrochloric acid is somewhat higher than that of sulfuric acid, which is justified by physical processes, since the chemical interaction of strong acids with calcium hydroxide is ionic, proceeding at a high speed and less sensitive to the composition of set cement.

To study the exposure of acid treatment on set cement, samples of set cement aged 180 days were selected. The degradation of set cement (formulations from Table 4) under the influence of hydrochloric (10 % HCl) and clay (10 % HCl + 3 % HF) acids, which are most widely used in the treatment of oil and gas wells' WBZ, was evaluated. The results of researches of acids exposure on set cement are shown in Table 5. The researches have established that set cement is subject to corrosion from acid exposure. At the same time, the corrosion resistance of set cement samples when modeling acid treatment for formulations based on PCT I-100 cement (No. 1) and a mixture (I-G-75 + MK-25) No. 2 is less than 0.85 and, according to the researches of V.S Danyushevsky, does not meet the criterion of corrosion resistance of set cement [32].

Figure 3 shows the characteristic formation of an amorphous mass on the research grouting mixture formulations after their acid treatment. The dimensions of the set cement sample based onPCT I-100 were 20 mm × 20 mm × 60 mm. Figure 4 visualizes the exposure of hydrochloric acid on set cement based on PCT I-100. The basic dimensions of the beam (width×height) are 20 mm × 20 mm, length 60 mm and 45 mm, respectively (Fig. 4). Splinters, longitudinal and transverse cracks were recorded on the samples, in some places with the destruction of scaly parts. Modeling the treatment of 10 % HCl on a sample of set cement based on TS-100 (formulation No. 3) provided a corrosion resistance coefficient (CRC) of 0.89, for Cem-C100 (formulation No. 4) – CRC = 0.91, and for DR-CT100 (formulation No. 5) – CRC = 0.92.

Fig. 3. Typical formation of amorphous mass on the research formulations based onPCT I-100.

Fig. 4. Acid corrosion of set cement.

Table 5.

Results of researches of acids exposure on set cement

Number of the formulation	Acid	Acid resistance coefficient, K	Relative mass loss, Lm, %	Relative volume lossLv,%	Dissolution rate, R, g/(cm^2·h)	Dissolution depth,Δl, cm/h	Volumeof dissolved set cement, ΔV, cm^3	Mass of dissolvedset cement, Δm, g	Sample age, days
1	Hydrochloric	0.85	15.44	8.77	0.06	0.02	1.823	5.65	180
	Clay	0.836	16.424	10.516	0.06	0.022	1.86	5.3	180
2	Hydrochloric	0.87	13.35	7.74	0.05	0.02	1.66	5.15	180
	Clay	0.84	16.06	9.43	0.06	0.02	1.622	5.03	180
3	Hydrochloric	0.89	11.21	7.09	0.04	0.01	1.18	3.4	180
	Clay	0.87	13.1	7.922	0.05	0.02	1.45	4.5	180
Cem-C100	Hydrochloric	0.91	9.2	5.439	0.037	0.012	1.12	3.58	180
	Clay	0.92	7.8	4.581	0.031	0.01	1.04	3.32	180
DR-CT100	Hydrochloric	0.92	8.2	5.135	0.035	0.011	1.06	3.38	180
	Clay	0.91	8.8	5.271	0.036	0.011	1.19	3.82	180

The treatment of acids (10 % HCl + 3 % HF) on a sample of set cement based on TS-100 grouting mixture resulted in a corrosion resistance coefficient of CRC = 0.87, for Cem-C100 –CRC = 0.92, and for DR-CT100 –CRC = 0.91.

As a result of the researches, it can be stated that cement based on composite cements (formulation No. 3, 4 and 5) is superior to the basic comparative materials in terms of the acid resistance coefficient. The degradation of set cement due to acid treatment, as well as the additional influence of aggressive reservoir fluids, can provoke the destruction of the well support system. Therefore, the durability and reliability of the insulation screen in the well will largely depend on the materials used (on the microstructure of the set cement, which is based on the granulometry and composition of the binder and fillers; water-cement ratio; efficiency and multifunctionality of modifiers), as well as the features and conditions of the work.

When choosing the type of grouting mixtures, it is necessary to use materials and set cement based on which, when interacting with an aggressive environment, it will form a colmatation screen that will minimize further diffusion of aggressive agents into the depths of the set cement.

It should be noted that defects in the crystal lattice of set cement, amorphous additives that are not involved in the process of structure formation, as well as the presence of open pore channels in the structure of set cement provoke an increase in the rate of corrosion processes.

Based on theanalysis carried out and a number of researches, we can state that one of the areas for creating the prerequisites for improving the quality of the insulation screen and its resistance to aggressive environments is as follows:

– use of composite grouting materials with controlled structure formation kinetics and resistance to aggressive environments;

– use of modifiers to regulate the sedimentation resistance and stability of the pluggingmud;

– creation of prerequisites for the formation of a homogeneous, low-porosity and low-permeability set cement structure.

Conclusions

1. Acid treatment of wells can, in some cases, increase the coefficient of core permeability recovery several times. Acid treatment of formations provides WBZ cleaning and hydrocarbon inflow stimulation.
2. Set cement based on basic Portland cements under the simulated conditions of acid treatment undergoes intensive degradation processes.
3. It has been established that composite plugging materials are capable of forming set cement with increased corrosion resistance to acids.
4. The introduction of active fillers and modifiers should ensure controlled structure formation and synthesis of set cement under well casing conditions.
5. The necessity for further research on the combined influence of aggressive waters and acidic treatment on the degradation processes of set cement

Stavychnyi Ye.M. – PhD;
Rudyi S.M. – PhD;
Femiak Ya.M. – Professor, Doctor of Technical Sciences;
Tershak B.A. – PhD;
Piatkivskyi S.A. – PhD student;
Klymyuk M.M. – PhD student;
Kindrat V.V. – PhD student.

[1] M.I. Rudyi, S.M. Rudyi, S.V. Naslednikov, *Acid treatment on an oil and gas reservoir*. Volume 1: Acids. Ivano-Frankivsk: Halytska drukarnya plus, 482 (2011).

[2] V.R.Voznyi, O.V. Dudra, *Analysis of methods of hydrocarbon inflow stimulation at the fields of OGPD "Boryslavnaftogaz" and estimation of oil-and-gas recovery factor.* Exploration and development of oil and gas fields, 1(46), 215 (2013).

[3] V.N. Koshelev, S.N. Shyshkov, *Ensuring qualitative opening of productive formations in conditions of abnormally low formation pressures*. Oil industry, 6, 38 (2007).

[4] Ya.B. Tarko, *Technology of thermochemical influence on the formations bottomhole zone*. Oil-and-gas energy, 1(6), 5 (2008).

[5] A.M. Neville Properties of concrete. Trans. M.: Stroyizdat, 344 (1972).

[6] V.R.Falikman, N.F. Bashlykov, *Low Water Demand Binder Technology for Environmental Friendly Cements with Low Clinker Conten*t. Proc. of the International RILEM Conference "Advances in Construction Materials through Science and Engineering", Hong Kong, China, RILEM Publications S.A.R.L., 150 (2011), CD.

[7] D.V. Rudenko, *Concrete based on a dispersed modified cement system*. Science and progress of transport, 4(64), 169 (2016); https://doi.com/10.15802/stp2016/78008.

[8] C.Y. Lee,H.K. Lee, K.M. Lee, *Strength and microstructural characteristics of chemically activated fly ash cement systems*. Cement and Concrete Research, 33 (3), 425 (2003); https://doi.org/10.1016/S0008-8846(02)00973-0.

[9] B. Middendorf, N.B. Singh, *Nanoscience and nanotechnology in cementitious materi*als. Cement International. 4, 80 (2006).

[10] A.M. Neville, Wlasciwoscibetonu. Crakow: Polski Cement, 874 (2000).

[11] J. Shtark Alkaline corrosion of concrete. Kiev: Profession, 144 (2010).

[12] R. Herdtl, M. Ditermann, K. Schmidt, *Durability of beton based on multicomponent cement*s. Cement and its application, 1, 76 (2011).

[13] *Plugging cements. Test methods*: DSTU B V.2.7-86-99. Valid from 2000-01-01. K.: State Committee for Construction, Architecture and Housing Policy, 18 (1999).

[14] Dry plugging mixtures. TU U 20.1-38821257-001:2014. Energo Composite LLC, Lviv, Ukraine.

[15] Dry plugging mixtures: TU U 23.5-3251045-001:2011. LLC "Spetsbudkonstruktsiya", Dnipropetrovs'k, Ukraine.

[16] P. Zitha, R. Felder, D. Zornes, K. Brown, K. Mohanty, *Increasing Hydrocarbon Recovery Factors*. Society of petroleum engineers. https://www.spe.org/en/industry/ increasinghydrocarbon-recovery-factors.

[17] M.P. Gnyp,V.Yo. Prokopiv, V.M. Doroshenko, *Principles of stabilization of oil production level at the late stage of field development. Problemy techniczne i technologiczne pozykiwania weglowodorow a zrownowazony rozwoj gospodarki.* Prace Instytutu Nafty I Gazu, 137, 801 (2006).

[18] V.M. Doroshenko, V.Yo.Prokopiv, M.I.Rudyi, R.B. Shcherbiy, *On the introduction of polymer flooding in oil fields of Ukraine*. Oil and gas industry, 3, 29 (2013).

[19] *M.A. Sanytsky, H.S. Sobol, T.Ye. Markiv, Modified* composite cements: a textbook. Lviv: Lviv Polytechnic Publishing House, 130 (2010).

[20] A. Hendi, H. Rahmani, D. Mostofinejad, A.Tavakolinia, M. Khosravi, *Simultaneous effects of micro silica and nano silica on self-consolidating Concrete in a sulfuric acid medium*. Construction and Building Materials. 152, 15 October 2017, 192 (2017).

[21] M. Amin, M.T. Bassuoni, *Response of concrete with blended binders and nanoparticles to sulfuric acid attack*. Magazine of Concrete Research. 70 (12), 1 June 2018, 617 (2018).

[22] V.I.Kalashnikov, O.V. Tarakanov, I.V. Yerofeeva, *Study of the rheological activity of limestone flour to obtain effective concrete*. Materials of the XI International scientific and practical conference "Actual achievements of European science": in 23 vol. Sofia, 13, 88-90 (2015).

[23] V.I. Kalashnikov, *Through rational rheology to the future of concrete*. Building materials of the XXI century. Concrete technologies, 5, 8 (2007).

[24] V.T.Yerofeev, A.P.Fedortsov, V.A. Fedortsov, *Increase of corrosion resistance of cement composites by active additives*. Construction and reconstruction, 2 (88), 51 (2020).

[25] V.V.Belov, S.L.Subbotin, P.V. Kulyaev, *Strength and deformation properties of concrete with carbonate microfillers*. Construction materials, 3, 25 (2015).

[26] Tarun R. Naik, FethullahCanpolat, Yoon-moon, *Chun Limestone powder use in cement and concrete*. Report No. CBU-2003-31 REP-525 // Department of Civil Engineering and Mechanics College of Engineering and Applied Science. The University of Wisconsin, Milwaukee. July (2003).

[27] Pieter Desnerck, Geert De Schutter, Luc Taerwe, *Stressstrain behavior of self-compacting concretes containing limestone fillers*. Structural Concrete, 13 (2), 95 (2012).

[28] B.A. Tershak, Ye.M. Stavychnyi, I.I. Ozarko, *Plugging materials of the new generation*. Scientific research – theory and experiment - 2012: materials of the VIII International scientific and practical conference, Poltava, 28-30 May 2012, Vol. 7,InterGraphics, 78 (2012).

[29] Ye.M.Stavychnyi, M.B. Kovalchuk, O. Hotsabina, *Composite plugging mixtures*. Actual problems of modern technologies: materials of the International scientific and technical conference of young scientists and students, Ternopil, 19-20 December 2012, Ternopil, 48 (2012).

[30] V.N. Vyrovoy, V.S. Dorofeev, S.B. Fitz, Concrete under impact conditions. *Odessa, 270 (2004).*

[31] A. Katz, H. Baum, Effect of high levels of fines content on concrete properties, ACI Materials Journal, 103(6), 474 (2006).

[32] Ye. M. Stavichnyi, B.A. Tershak, Ya.M.Femiak, A.O.Ignatov, S.A. Pyatkivsky, *Degradability of set cement under conditions of acid action in oil and gas wells*. International Oil Forum "Oil & gas energy", Ivano-Frankivsk, 12-14 October, 66 (2023).

Є.М.Ставичний[1], С.М.Рудий[1], Я.М.Фем'як[2], Б.А. Тершак[3], С.А. П'ятківський[2]
М.М. Клим'юк[4], В.В. Кіндрат[4]

Вплив кислотних систем на декольматацію привибійної зони свердловин та стійкість цементного каменю

[1]ПАТ "Укрнафта",Київ, Україна, Yevhen.Stavychnyi@ukrnafta.com
[2]Івано-Франківський національний технічний університет нафти і газу, Івано-Франківськ, Україна
[3]ТОВ "Енергокомпозит", Івано-Франківськ, Україна
[4]Прикарпатський національний університет імені Василя Стефаника, Івано-Франківськ, Україна

На прикладі свердловини № 47 Стинава проведено оцінку стану привибійної зони свердловини під час буріння. На основі досліджень впливу бурової промивальної рідини на фільтраційно-ємнісні характеристики кернового матеріалу встановлено, що кольматаційний екран на керновому матеріалі може бути усунений кислотним діянням.

Здійсненими дослідженнями та результатами робіт на свердловинах ПАТ «Укрнафта» підтверджено ефективність методів підвищення нафтовилучення, серед яких вагоме місце посідає напрям кислотного діяння на пласти, які використовуються як для очистки ПЗС, так і для інтенсифікації.

Проведено дослідження основних технологічних параметрів ряду тампонажних матеріалів та сумішей, а також фізико-механічні властивості цементного каменю на їх основі. Оцінено вплив кислотного діяння, що використовується під час інтенсифікації на цементний камінь. Встановлено, що базові цементи та суміші на їх основі зазнають значного агресивного впливу кислот, що провокує деструкцію цементного каменю.

За результатами досліджень обґрунтовано доцільність застосування композиційних тампонажних цементів для кріплення свердловин в складних умовах, де цементний камінь ізоляційного кільця може бути підданий кислотному впливу.

Ключові слова: свердловина, кислотне діяння, тампонажний розчин, цементний камінь, корозійна стійкість.