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The heat-resistant gas-generating energetic composite materials for needs of the oil industry

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Abstract. The article shows the development prospects for the producing of the heat-resistant gas-generating energetic composite materials (ECM) recommended as propellant of the downhole devices intended for increase in oil recovery of oil wells. The operational characteristics of series of the versatile heat-resistant propellants for downhole devices of different purpose and the mechanism of action are provided. These versatile propellants are recommended for use in wells with any geothermal conditions and allowing increasing significantly in oil recovery of wells.

1. Introduction

According to officially published data, the average coefficient of oil recovery in the oil industry of Russia is only 0.2-0.4. It should be noted that in USA, for example, the share of secondary and tertiary treatment of oil wells, which increase their efficiency (oil recovery ratio), accounts for more than 80% of the total volume of oil produced [1]. In Russia, unfortunately, despite the efforts of the profile scientific research institutes [2-5], necessary attention was not paid to these methods, and huge number of the so-called "wasted" wells have accumulated, the resources of which are not exhausted. From the positions of the rational use of natural resources and the economic feasibility the depreservation and "revival" of such wells is very perspective direction in the oil industry.

In this regard, the development of new efficient methods for the secondary and tertiary treatment of "wasted" and other low-yield wells is very relevant task, and in recent years, these developments in Russia found "second wind" and, finally, receive due attention of oil producers.

In the oil industry, different methods of increase in efficiency of oil wells are applied [6]:

- treatment with liquids: hydraulic fracturing (HF), hydrochloric acid treatment (HAT), treatment with gas heat-generating solutions (GHGS) and combustible-oxidative mixtures (COM);
- mechanical drainage using cumulative, jet, bullet perforators;
- timely locking of exploration and production wells using sealing devices;
- method of filtration blast waves (MFBW)
- thermobaro-gas-chemical effect (TBGCE) on the well bottom-hole zone using downhole devices (DD) of the different mechanism of action.

The choice of method is largely defined by the composition and structure of the rock in which the oil layer is located. In some cases, it is advisable to use more simple methods, in others - the combined use of the different methods providing different mechanisms of action.



The implementation of these methods of influence on the bottom-hole zone is carried out using special downhole devices of the different mechanisms of action:

- devices of thermobaro-gas-chemical effect on the bottom-hole zone, which include the powder pressure generators (PPG), generators with an adjustable pressure impulse (GAPI), downhole pressure accumulators (DPA), etc.;
- devices for mechanical drainage of the well and near-wellbore zone: bullet (BP), cumulative and jet perforators;
- devices of combined (perforation and TGHV) action of type GD, GDK, PG;
- devices of complex action of AKV, MAC;
- well sealing devices (WSD) preventing emergencies and environmental pollution.

It is considered that the methods of thermobaro-gas-chemical effect (TBGCE) are most effective, because they provide a complex effect of several working factors – the baric (pressure), thermal (temperature) and chemical (chemical activity of gaseous combustion products of propellant charge of DD).

2. The baric factor

When burning the powder charge in the range of the productive layer, the pressurized fluid of the formed gases that is there, is displaced into the structure of the layer, expands the natural cracks, pores and channels and creates new cracks of greater length and degree of openness. The increase in the layer structure of similar cracks leads to repeated increase in the conductivity of the layer and, consequently, the productivity of the well.

3. The thermal factor

During the combustion of 1 kg of TN type propellants offered by us for increase the efficiency of the DD, 3344-5434 J of thermal energy is released. The maximum temperature of gases emitted during charge combustion of the downhole device can reach 3500 °C, but due to the relatively good thermal conductivity of the well column, liquid and rock, the medium temperature at the level of the downhole wall does not exceed 350 °C. The heated powder gases, penetrating deep into the layer through the cracks, melt the heavy components of oil (resins, asphaltenes and paraffins) which have dropped out in use. After charge combustion, the pressure in the well decreases, and the powder gases in the layer displace the formation fluids and the melted deposits in the wellbore.

4. The chemical factor

During the propellant combustion in the well occurs chemical effects of aggressive gaseous combustion products on the rock structure and formation fluid. For example, the effect of hydrogen chloride released during the propellant combustion causes the fluidization of hard deposits and fluids due to their partial or complete decomposition. Sometimes, to enhance the effect of chemical factor, for example in carbonate collectors, the powder charge is burned in the medium of hydrochloric acid which is previously pumped to the well that leads to repeated increase in productivity of wells.

The effectiveness of the above factors largely depends on the performance properties of the propellants used in DD as propulsive mass.

The Research Institute of Polymeric Materials (now JSC “NIIPM”) is leading enterprise in the Russian Federation in the field of producing of the heat-resistant gas-generating solid propellants. In addition, JSC “NIIPM” is one of the first DD developers for thermobaro-gas-chemical effect (TBGCE) on the bottom-hole zone, which include the powder pressure generators (PPG), generators with an adjustable pressure impulse (GAPI), downhole pressure accumulators (DPA), etc.

The experimental work in this area began at the institute in the early 70s of the twentieth century. The serial production of the powder pressure generators for oil wells was developed by “NIIPM” in 1979. Industrial application under the trade name "DPA - downhole pressure accumulators" found three modifications of the powder generators: DPA-5; DPA-6; DPA-200U.

DPA are intended for processing the bottom-hole zone of oil wells with the dismantled operating

equipment. The temperature-time resource of operation of DPA-5, DPA-6 is 3 hours at 100 °C; and DPA-200U is not less than 12 hours at 200 °C and not less than 24 hours at 150 °C. The DPA consists of one igniter, several burning elements (5-7) and the device for assembly, collected in the set on piece of geophysical cable.

The main technical characteristics of serially produced DPA are given in Table 1.

The main difference and advantage of DPA-200U is that the burning elements of DPA-200U are made of high-heat-resistant energy-intensive composite material (propellant).

The heat resistance of combustible composite materials is provided by the use of heat-resistant polymers such as ethylene-propylene, divinyl-styrene copolymers, compounds containing α -oxide cycles in their chain, etc.

The range of the heat-resistant propellants developed in NIIPM is rather wide, which increases possibilities of the choice of propellant in relation to specific DD and conditions of specific wells. Depending on the purpose and application conditions for DD in addition to heat resistance, impose whole range of different requirements (Table 2, 3) to propellants.

For impact on bottom-hole zone of producing wells, it is advisable to use slow-burning propellants in PPG and DPA devices, which provide the long and deepest heating of the zone.

The fast-burning propellants apply in bullet perforators for well drainage, as well as in PPG and DPA for thermobaric-gas-chemical effect on the bottom-hole zone of both the forcing and producing wells. At the same time, the productivity of wells increases, not only due to temperature and gas chemical effects, but also due to the baric influence of shock character (the sharp pressure jump exceeding the ground pressure), creating a system of cracks in zone of the forcing and producing wells and also pressure shock in zone of the forcing wells.

For providing the alternating effect of working pressures from low to high shock pressures, including impulse, in order to build up the thermodynamic system of the oil layer, it is advisable to combine slow and fast-burning elements in one DD.

It is also possible to increase the efficiency of propellants by increasing the role of the chemical influence of the gaseous products of their decomposition, increasing the share of reactive gases and liquids such as chloride and fluoride hydrogen. The use of so-called "acid-forming" propellants is much more effective than the currently used acid treatment of wells, as it provides the complex effect on the bottom-hole layer zone of the different factors (temperature, pressure, gases and acid). For example, hydrogen chloride is the active chemical agent that effectively decomposes different deposits that prevent the outflow of oil from the oil layer. In flooded wells, the hydrogen chloride interacting with the well fluid forms hydrochloric acid. In addition, the thermo-gas-chemical impact apparatus, equipped with propellant, works directly in the productive zone of the oil layer, and the hot hydrochloric acid produced during the combustion process affects the structure of the rock directly in the layer treatment zone, increasing its porosity and permeability. The high temperature, pressure and gases provide deep penetration of the reactive hydrogen chloride into the layer and its effective cleaning.

A large range of the propellants with the wide range of performance characteristics (energy, ballistic, heat resistance, etc) provides the possibility of targeted regulation of the DA operating mode depending on the application conditions. For providing of universal use in the different geothermal conditions, including in deep and ultra-deep wells and in wells with the complicated geothermal conditions, for example, at the Tyumen, Kamchatka, Tajikistan, Uzbekistan, and Ukraine fields, the special requirements are imposed on the thermal stability of propellants (up to 100-300 °C).

The studies carried out in JSC "NIIPM" allowed us to create the series of the heat-resistant, up to 200-300 °C, gas-generating acid-forming propellants of the TN series for downhole devices with an increased (more than 2 times) content of hydrogen chloride in the combustion products. The acid-forming propellants are more expedient to use in downhole devices for processing of carbonate and terrigenous collectors in wells with the increased water content. In addition, taking into account their high heat resistance, they can be successfully used in wells with the complicated geothermal conditions.

The latest studies of JSC "NIIPM" are directed to development of the new more effective, universal and low-price propellants. As a result, in production are implemented the several new brands of solid

propellants like TN-15/5E with the improved operational characteristics for production of the wide nomenclature of charges for equipment of the modern downhole devices.

These propellants have the following advantages:

- increased amount of the hydrochloric acid emitted during the charge operation;
- high, up to 150-200 °C heat resistance;
- possibility of long stay of charges in the well without changing the performance characteristics: at 150 °C - not less than 24 hours; at 200 °C - not less than 12 hours;
- large gassing;
- low sensitivity to mechanical influences and electric spark;
- simple and low-price technology that provides the rapid transition of mass production to any standard sizes of charges.

The main operational properties of the new composite propellants are given in Table 4. The developed heat-resistant propellants are universal and can be recommended as propulsive mass of the most different downhole devices (accumulators and powder pressure generators of wells, bullet perforators, soil intake devices and soil samplers such as DPA, PPG etc.) for operation practically in any geothermal conditions.

5. Conclusion.

The actuality and development prospects for the producing of the heat-resistant gas-generating propellants for needs of the oil industry are shown.

The series of compositions of the versatile heat-resistant propellants for downhole devices for various purposes and the mechanism of action that meets all the requirements defined by their operating conditions is developed.

The performance characteristics of the various heat-resistant propellants developed at JSC «NIIPM», which increase the versatility of the use of downhole devices and their efficiency are presented.

Table 1. The main characteristics of DPA produced by JSC «NIIPM».

Designation	Serial			New modifications	
	DPA-5	DPA-6	DPA-200U	DPA-5	DPA-6
Outside diameter, mm	110	110	65-110	70-110	102
Passage diameter, mm	-	22	20	-	24
Length of powder charge, mm	1200	1200	1000	900	1060
Mass of powder charge, kg	16	14	7	5	14
Quantity of charges in one set, pcs.	6	6	6	5	6
Mass of the pressure accumulator, kg	94	84	42	25	84
Ignition method	Electric minimum current of operation 1,5A				
Maximum application temperature, °C	100	100	200	100	100
Permissible time of stay in the well at the maximum temperature, h	3	3	12	3	3
Minimum hydrostatic pressure in the well treatment interval, MPa	3	3	3	3	3

Table 2. Apparatus and heat-resistant propellants to increase the productivity of oil wells using the TBGCE method.

THERMOBARO-GAS-CHEMICAL EFFECT (TBGCE) ON THE BOTTOM-HOLE ZONE											
DOWNHOLE PRESSURE ACCUMULATORS (DPA) AND PRESSURE GENERATORS (PPG)											
SLOW-BURNING SOLID PROPELLANT			FAST – BURNING SOLID PROPELLANT			PULSING SOLID PROPELLANT			ACID-FORMING PROPELLANTS		
For production wells			For forcing and production wells			For forcing wells					
Provide the heating and gas-chemical fluidization of high-viscosity oils, deposits and formation fluids in zone of production wells			Provide the physical effect of shock character for creating: - system of cracks in zone of the forcing and producing wells - pressure shock in zone of the forcing wells			Provide the alternating effect of slow- and fast-burning propellants in order to build up the thermodynamic system of the oil layer around the well and its driving			Provide the fluidization of high-viscosity oils, decomposition of oil deposits and formation fluids in structure of cracks and macropores of layer		
Requirements	It is reached	It is perspective	Requirements	It is reached	It is perspective	Requirements	It is reached	It is perspective	Requirements	It is reached	It is perspective
Heat resistance ↑	100...200°C	150...270°C	Heat resistance ↑	200...250°C	270°C	Heat resistance ↑	100...200°C	270°C	Volume of gases, l/kg ↑	900...1000	1100
Burning velocity mm/s ↓	1,5...10	<1,5	Burning velocity mm/s ↓	10...25	>30	Burning velocity mm/s ↓	2...25	2...30	Amount of 12% acid (HCl and HF), kg/kg	2,0	3,1

Table 3. Apparatus and heat-resistant powders and propellants to increase the productivity of oil wells by methods of mechanical drainage of the bottom zone and timely blocking of wells.

MECHANICAL DRAINAGE OF DOWNHOLE ZONE			TIMELY LOCKING OF EXPLORATION AND PRODUCTION WELLS		
CUMULATIVE, JET, BULLET PERFORATORS			WELL SEALING DEVICES (WSD)		
HEAT-RESISTANT FINE-GRAINED POWDERS			HEAT-RESISTANT LOW-GAS SOLID PROPELLANTS		
Provide the drainage of an upsetting column and creation of network of cracks in structure of layer for increase in its permeability			Provide the rational use of minerals, prevent emergencies and environmental pollution		
Requirements	It is reached	It is perspective	Requirements	It is reached	It is perspective
Heat resistance ↑	290°C	300...500°C	Heat resistance ↑	200°C	270°C
Force ↑	80-115	>115	Burning velocity 5...10 mm/s	5	10...20

Table 4. The main operational properties of propellants of the TN series.

Composition brand	Characteristics with P = 50 MPa, V = const				Density, g/cm ³	Characteristics with P = 50 MPa, V = const	
	Energy-capacity, kgf · m/kg	Volume of gases, l/kg	Temperature of gases, K	Amount of 12% acid (HCl), kg/kg		Temperature of the beginning of decomposition, T _{nir} , °C	Temperature and time of operation resource
TN-15/5	106400	1029	2790	1.9	1.68	≥240	200° C ≥ 12 h
TN-18/5K	80200	735	2860	0.2	1.84	≥300	200° C ≥ 24 h 250° C ≥ 12 h
TN-15/5E.1	110670	979	2576	1.9	1.74	≥240	150° C ≥ 24 h
TN-15/5E.2	109500	1028	2814	2.0	1.64	≥240	160° C ≥ 24 h
TN-15/5E.2V	93647	872	2845	0.9	1.77	≥300	180° C ≥ 6 h
TN-15/5E.2G	72215	687	2930	0.2	1.92	≥300	180° C ≥ 6 h
TN-15/5E.2D	76100	8326	2176	1.4	1.71	≥300	180° C ≥ 6 h
TN-15/5E.2E	64630	739	2300	0.6	1.83	≥300	180° C ≥ 6 h
TN-15/5E/4	102880	904	3009	3.1	1.87	≥300	150° C ≥ 24 h

Notes:

1. The velocity of the gas input can be adjusted over the wide range by the surface of the charge burning.

2. The experimental testing of the high-heat-resistant propellants is carried out (up to 250-300 °C and above).

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