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Review / Обзор

Thermochemical Technologies for Cleaning Production Wells

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Термохимические технологии очистки добывающих скважин

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As a result of oil and gas well operations, they are regularly clogged with asphalt-resin-paraffin sediments (ARPD) and gas hydrates, which significantly complicates the oil and gas production up to the complete well shutdown. The paper presents a new promising technology, and the special developed equipment for cleaning oil-well tubing and annular space of oil and gas wells. The process principle is to initiate an exothermic process inside the oil-well tubing by a chemical reaction of alkali or alkaline earth metals (groups I, II of the periodic table of Mendeleev's Periodic Table) with water or acid, as a result of which a large amount of heat is generated, leading to the effective decomposition of asphalt-resin-paraffin sediments and gas hydrates both inside the oil-well tubing and in the annular space. Metallic sodium and metallic calcium were tested as heat-transfer metals, their effectiveness was compared. The results of pilot industrial tests in oil fields are presented. Techniques for eliminating sediments with thermochemical devices in situations often occurring in the process of oil production are proposed: cleaning the annular space from gas hydrate sediments, eliminating wax and gas hydrate sediments inside the oil-well tubing, cleaning when the bottomhole communicates with the wellhead through the pipe channel.

Ключевые слова:
газогидраты, гидраты, насосно-компрессорные трубы, насосно-компрессорная труба, термохимическое устройство, термохимический процесс, затрубное пространство, сообщение забоя с устьем, парафиновые отложения, ликвидация отложений, удаление отложений, асфальтосмолопарафиновые отложения, несквозная перфорация, спецворонка, перфорированный контейнер, обечайка, корпусное устройство.

В результате эксплуатации нефтяных и газовых скважин регулярно происходит их засорение асфальтосмолопарафиновыми отложениями и газогидратами, что значительно затрудняет добычу нефти и газа вплоть до полного прекращения работы скважины. В работе представлена новая перспективная технология и разработано специальное оборудование по очистке насосно-компрессорных труб и затрубного пространства нефтяных и газовых скважин. Принцип технологического процесса заключается в инициировании экзотермического процесса внутри насосно-компрессорных труб в результате химической реакции щелочных или щелочноземельных металлов (I, II группа периодической таблицы Д.И. Менделеева) с водой или кислотой, в результате чего выделяется большое количество тепла, приводящее к эффективному разложению асфальтосмолопарафиновых отложений и газогидратов как внутри насосно-компрессорных труб, так и в затрубном пространстве. В качестве металлов-теплоносителей испытаны металлический натрий и металлический кальций, сопоставлена их эффективность. Приведены результаты опытно-промышленных испытаний на нефтяных месторождениях. Предлагаются приемы ликвидации отложений с помощью термохимических устройств в ситуациях, часто имеющих место в процессе нефтедобычи: очистка затрубного пространства от отложений газогидратов, ликвидация отложений парафина и газогидратных отложений внутри насосно-компрессорных труб, очистка при сообщении забоя скважины с устьем по трубному каналу.

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Introduction

Operating costs of the oil companies are constantly on the rise as hydrocarbon extraction increasingly strives for the polar latitudes and moves to the northeast. One of the main reasons for the decrease in the efficiency of oil and gas extraction can be attributed to a decrease in the variability of the application of methods for enhanced oil recovery [1–26], as well as the search and implementation of innovative technologies for the intensification of hydrocarbon extraction. One of the pressing issues in oil production is the fight against deposits of paraffin, tar, asphaltenes and gas hydrates inside the oil well tubing, through which the oil rises from the bottomhole to the surface. As a result, the useful pipe section decreases, the flow rate drops, and without taking certain measures, the tubing is completely clogged [27–31] (Fig. 1).

Fig. 1. Tubing with paraffin deposits on the inner surface

There are many technologies for cleaning the tubing [32–37], but basically they come down to the use of thermal, chemical and mechanical methods. Thermal methods include: heating the tubing with water vapor using a mobile steam generator (MSG) or with hot oil using a mobile advanced hot oiler (MAHO). At the same time, the treatment of wells with hot oil is unproductive due to the fact that the oil has a low heat capacity, cools down quickly, and, moreover, it is required to involve the additional vehicles (tank trucks) to transport oil supplied for flushing and attract the commercial oil volumes, and this is the oil that has already been purified from water and gas. In addition, there is a danger of "dead" plug formation during the circulation and solidification of a saturated paraffin solution in the well, as well as the accumulation of refractory paraffins on the tubing walls, the removal of which is very difficult and does not lend itself to the above cleaning methods to a sufficient extent.

Chemical methods (flushing with solvents) are currently used on a limited scale due to the fact that they do not contribute to the complete dissolution of asphalt-resin-paraffin deposits (ARPDs) and gas hydrates in them, have a high cost, and are also highly toxic and explosive.

Mechanical methods for cleaning wells (with scrapers) are unreliable due to the frequent breaks of the wire on which they are attached, in addition, a detached scraper can itself be the cause of well clogging [38, 39].

A more effective solution to the problem of removing ARPD and gas hydrate deposits can be the use of special equipment for the implementation of thermochemical treatment technology, which is being developed by the Department of Oil and Gas Field Development and Operation, Oil and Gas Institute of the Siberian Federal University. This technology originally emerged in the 1990s, at the junction of Chemistry and Physics. This happened when Vladimir Belyaev, an engineer from Krasnoyarsk, suggested Yuri Belyaev, who was then the Head of Oil and Gas Production Stimulation Department at the Moscow Institute of Oil and Gas, to use active metals as a coolant. The main components of reagents are chemical compounds of groups I and II according to Mendeleev's Table. The first device implemented this technology was a solid metal bar (coolant) with a diameter of 16 mm and a length of 300 mm, wrapped in aluminum foil. Metallic sodium was used as a coolant. The manufacture of these devices was merged into the Krasnoyarsk Chemical and Metallurgical Plant. The Krasnoyarsk company "Sibres" was engaged in the dissemination of the technology of thermochemical exposure of ARPDs and gas hydrates in the tubing using the manufactured devices. The geography of technology application was wide enough, it included the oil fields of Tyumen, Nizhnevartovsk, Lyantor Purpe, Nyagan, Almetyevsk, Saratov, Bashkiria, Tatarstan and Yakutia.

Metallic Sodium as a Coolant

The technology consisted in carrying out a thermochemical reaction in tube side of the tubing, which leads to the melting of paraffin deposits and ejection of liquid reaction products and paraffin at the wellhead by formation pressure or an electric driven centrifugal pump (ECP). For this purpose, devices containing a coolant with perforation applied to the lateral surface are fed into the well tubing through a standard lubricator. By gravity, the devices drop down to the level of deposit formation, while the water present in the oil (more than 10 %) intensively reacts with the coolant composition, releasing a large amount of gas and heat. With a lower water cut in the well fluid, water is supplied through the lubricator from the wellhead. Heat and gas melt the ARPDs and gas hydrates, and bridging elements are removed from the tubing surface. In this case, molten paraffins are mixed with the reaction products, as a result of which they lose their adhesive properties to the tubing metal. Moreover, the aluminum compounds produced during the processing, interacting with iron oxides on the inner tubing surface, clad the pipe surfaces with an oxide film. At the same time, the pipe metal corrosion, ARPD and gas hydrate deposition rates and hydraulic resistance decrease, the production rate of wells increases, and also, even after a single treatment, the time between overhauls (TBO) increases approximately twice. This is confirmed by laboratory and numerous field tests carried out by the authors of this method.

The thermochemical equation for the reaction of sodium metal with water under standard IUPAC conditions (P = 101325, Pa = 1 atm, t = 25 °C) is written as:

$$2\text{Na(t)} + 2\text{H}_2\text{O(fluid)} \rightarrow 2\text{NaOH(t)} + \text{H}_2\text{(gas)}$$
$$\Delta\text{H} = -68 \text{ kcal},$$

where: ΔH – change in the standard enthalpy of reaction calculated according to the rules and on the basis of values borrowed from the literature [40, 41], that is, in this reaction, as a result of the interaction of 1 mol of sodium with 1 mol of water, $-\Delta H/2 = 34$ kcal of heat is released.

Despite their widespread use, these devices had a number of disadvantages. First, the issue of connecting the elements into a single whole was not resolved, the devices were fed into the tubing one by one and operated inside separately. This disadvantage significantly affected their efficacy. Second, the sodium density of 0.96 g/cm^3 is less than the borehole fluid density, so different types of weighting agents had to be used in order to "drown" the devices in the borehole fluid and force them to sink down to the level of deposits. Third, sodium is an active metal with the ability to spontaneously ignite in the open air, which added the fire hazard at oil handling.

Metallic Calcium as a Coolant for Cleaning the Annulus

After years of oblivion, the technology was revived and brought to a new technical and technological level. Metallic calcium started to be used as a coolant, which made it possible to manufacture devices that were more technically advanced and safe to use. This choice was due to the physical and chemical properties of the reagent. With a calcium density of 1.56 g/cm^3, there is no need to use various weighting agents in the device design for immersion in the well fluid and tubing. Metallic calcium is not fire hazardous, because in the open air it is gradually saturated with moisture and turns into calcium hydroxide – slaked lime. Moreover, calcium is a metal that lends itself well to machining. That is what made it possible using a thread to solve the problem of connecting a large number

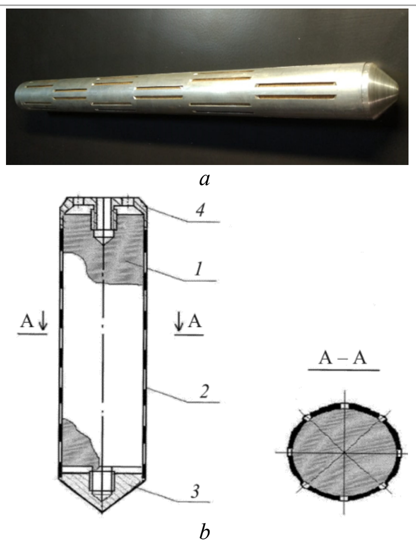

Fig. 2. Device: *a* – photo; *b* – diagram; *1* – coolant; *2* – shell; *3* – top cap; *4* – end cap

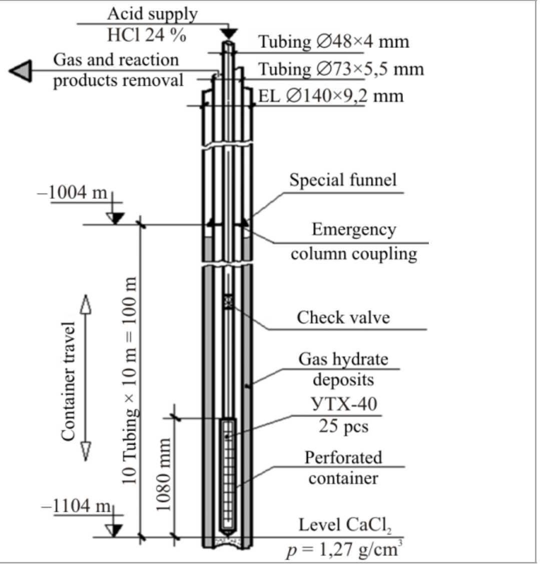

Fig. 3. Diagram of pilot testing at well No. 24

of elements into a single whole, which was embodied in the new device design.

In January 2011, the first calcium coolant was produced, which marked the transition to a new type of device. The coolant is a solid metal bar obtained by extrusion from calcium granules on original equipment designed and manufactured by V.P. Ulyanov. The new device was devoid of the negative properties of previous samples. In it, the cylindrical metal plays a double role: first, the coolant, and second, the tightening element of the entire structure, which made it possible to connect a certain number of cylinders into a single structure. Another innovation in this device design is the perforated aluminum shell, which gives rigidity to this structure and additional heat during the reaction (Fig. 2). The technology of using the devices has also undergone changes, now the second reagent in the reaction with the devices is not the water of the well fluid, but 24 % inhibited hydrochloric acid, the calculated volume of which was supplied from the wellhead.

The device was granted a patent of the Russian Federation for the utility model No. 97165 [42]. Another patent of the Russian Federation for the utility model No. 99059 [43] was granted to a device wherein the coolant is made in the form of tablets pressed from calcium granules with a central hole through which a tube pulling together the end caps passes.

A pilot test (PT) of these devices was carried out at wells No. 24 and No. 7 of the Yurubcheno-Tokhomskoye field (YTF) in the Krasnoyarsk Territory in December 2017. These wells have a powerful gas release: for example, at well No. 24 the gas-oil ratio was 191 m^3/m^3. For the first time, the devices were used to decompose gas hydrate deposits in the tubing annulus.

The thermochemical equation for the reaction of metallic calcium with hydrochloric acid under standard conditions is written as:

$$\mathrm{Ca(t)} + 2\mathrm{HCl(gas)} \rightarrow \mathrm{CaCl_2(t)} + \mathrm{H_2(gas)}$$
$$\Delta H = -145.5\ \mathrm{kcal},$$

where: ΔH – change in the standard enthalpy of reaction [40, 41], that is, in this reaction, as a result of the interaction of 1 mol of calcium with 2 mol of hydrochloric acid, a heat equivalent to $-\Delta H = 145.5$ kcal is released. It can be seen from the above equation that, theoretically, the amount of heat released as a result of the chemical reaction between calcium and hydrochloric acid is approximately 4 times greater than the heat released during the reaction between sodium and water. Thus, the use of calcium as a coolant is energetically much more profitable.

The essence of this new method for liquidating gas hydrate deposits in the tubing annulus is reduced to carrying out a thermochemical reaction in the tubing space and decomposing gas hydrates while transferring a large amount of heat through the pipe wall. This technology is shown below step-by-step (Fig. 3). After unscrewing and lifting the tubing section with a diameter (∅) of 48 mm that is not stuck with gas hydrate, a special funnel designed by V.P. Ulyanov is installed, after which the structure is lowered back onto the sleeve connection. Thus, a single channel is formed for feeding thermochemical devices into the interval of gas hydrate formation. Thermochemical devices [42] in the amount of 25 pieces are loaded into a perforated container and using the tubing lift pipes ∅48 mm they are lowered 100 m below the collar connection of the emergency tubing through blowout preventers. Then, the calculated volume of inhibited 24 % hydrochloric acid is pumped through this tubing. The displacement mud volume is calculated in such a way as to place the fed acid in an equilibrium position – both in the ∅48 mm lift pipe and in the small tubing annulus of ∅73 mm.

With the beginning of calcium chloride and hydrogen production in the tubing as a result of the chemical reaction between hydrochloric acid solution 24 % and metallic calcium during the gas hydrate decomposition in the space of a large tubing annulus or production string (PS), the process-based holding is performed in the lower container position. Then, the container is raised to the point of tubing joint, held, lowered onto one pipe and held again. This operation shall be repeated twice, which contributes to uniform heating of the tubing surface and the most complete gas hydrate decomposition in the PS space into its constituent gases and water, which are subsequently displaced from the PS by a high-density calcium chloride solution, which is independently supplied from the wellhead. After two cycles in the lower container position, the reaction products are also washed out with a calcium chloride solution supplied from the wellhead independently and rise through a small annulus (space between ∅48 mm and ∅73 mm tubing) to the wellhead into the collecting tank. Lift pipes are risen to the wellhead and disassembled. Further, a string of ∅48 mm tubing is lifted using a special funnel with a constant filling with killing fluid. At the final stage, fishing operations are carried out by an overshot with a turn-up and lifting of emergency pipes.

This technology has shown its high efficacy. Thanks to the thermal calculation by a production engineer V.A. Belyaev, it allows to melt and lift up to 10 emergency tubing at the wellhead in one run of a container loaded with devices. The process of gas hydrate deposit decomposition in the annular space of well No. 24 continued up to –1284 m, where the gas hydrate deposits with inclusions of metal residues trapped in the pipe after drilling blocked the passage in the ∅73 mm tubing space – at this mark the PT of produced thermochemical devices was completed (Fig. 4).

In the process of PT of thermochemical devices (UTKh-40G) [42], the following advantages were revealed:

1. Even partial destruction of the emergency tubing string is completely absent, as in the mechanical method of gas hydrate deposit destruction in the well annulus (drilling in tubing). Overall accident rate of the emergency tubing extraction process is reduced, the extracted emergency suspension pipes are suitable for further use.
2. Well workover time reduced by 30 %. The time spent on the repair of the Yur-24 well in the period from 17/08/2016 to 04/11/2016 was 79 days, 16 emergency tubing with ∅73 mm were removed from the well. Time spent on PT at the Yur-24 well in the period from 08/12/2017 to 02/02/2018 was 56 days. 25 emergency tubing with ∅73 mm were removed from the well.
3. Efficacy of the emergency tubing removal from the well increased by 36 %.
4. Delivery of the coolant in the interval when the gas hydrate deposits are located below 1000 m.

The authors positioned the devices manufactured by them as universal, i.e. allowing them to be used both for cleaning the tubing space from paraffin, and the annular space from gas hydrate, but the PT carried out at the Yurubcheno-Tomsk field showed that this is far from the case. The results obtained during the PT at wells No. 24 and No. 7 allow us to draw the following conclusions:

1. The proposed technology for gas hydrate deposit decomposition in the well annular space, according to the diagram provided above, gives an effect and can be applied only in the absence of communication between the bottomhole and the wellhead through the tubing string. This is exactly the situation that took place during the operations at well No. 24.
2. The devices used for PT at wells No. 24 and No. 7 and produced under the patent [42], are ineffective. The presence of through perforations on the shell promotes the device start-up at the descent stage, which leads to the loss of a part of thermal energy before reaching the interval of deposits.
3. The above technology cannot be used in the well when the bottomhole communicates with the wellhead through the tubing string and the well fluid is lost. This situation took place at the well No. 7, where there was a passage through the tube, and the heated acid was absorbed by the bottomhole; therefore, the gas hydrate decomposition did not occur in the annulus. The result at well No. 7 on gas hydrate liquidation is negative.

The above arguments suggest that for stable operation to eliminate sediments, you need to have different technologies and types of equipment to work in each specific situation.

After careful analysis, the devices were designed and manufactured that were devoid of the above disadvantages. New devices for gas hydrate decomposition in the annular space were called "shell-based devices for thermochemical treatment of wells", they were granted a patent of the Russian Federation for the utility model No. 194665 [44]. The device appearance is shown in Fig. 5.

The main part of this advanced device is an aluminum shell (Fig. 6) with grooves on both ends. On the cylindrical surface of the shell along the axis, grooves with blind perforations are made, located in a row, and each subsequent row of these grooves is radially displaced relative to the previous one by 45°. Metal thickness in the place of blind perforation is 0.4–0.6 mm. After inserting the shell of the coolant in the form of one or several cylinders obtained by extrusion, the head and tail caps are inserted into the end grooves, followed by rolling of the shell metal beads. Additional tightness of the joint is provided by applying a sealant to the perimeter before rolling, which contributes to the conservation of thermal energy at the flushing stage and its full release in the interval of thermochemical reaction.

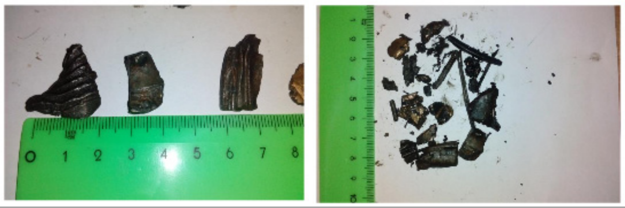

Fig. 4. Photo of metal fragments from the well No. 24 of the Yurubcheno-Tokhomskoye field, raised to the surface during flushing

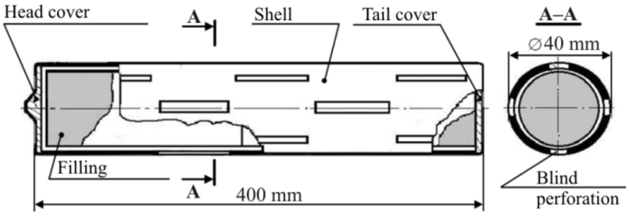

Fig. 5. Shell-based device for thermochemical treatment of wells

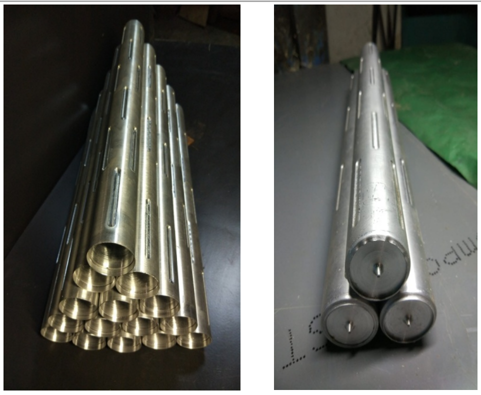
a *b*

Fig. 6. Photo of shells (*a*) and shell-based devices assembled (*b*)

Shell-Less Thermochemical Devices for Removing Paraffin Deposits Inside the Tubing

To eliminate paraffin deposits inside the tubing, shell-less devices were developed, for which a patent of the Russian Federation for the utility model No. 198341 was granted [45]. In this case, the design looks as follows: device components, its head and many of the tail parts are combined into a single whole (Fig. 7). The surface of each component is coated with a multilayer polymer that protects the active metal of the coolant against environmental influences (rain, snow), as well as against water that is part of the well fluid during the run.

The device coating composition was developed by the authors of this technology. The connection takes place due to the external and internal threads available at the end of each component.

The number of components connected together can be any random, the limiting factor is a height of the lubricator – the well parts, where the device assembly is placed, and after opening the central valve it enters the tubing and then descends under its own weight to the sediment interval, where the movement stops. Further, after the volume of hydrochloric acid is fed into the tubing, the tubing is run down to the beginning of deposits, where the well fluid is replaced by an acid having a higher density. The acid completely flushes the device assembly,

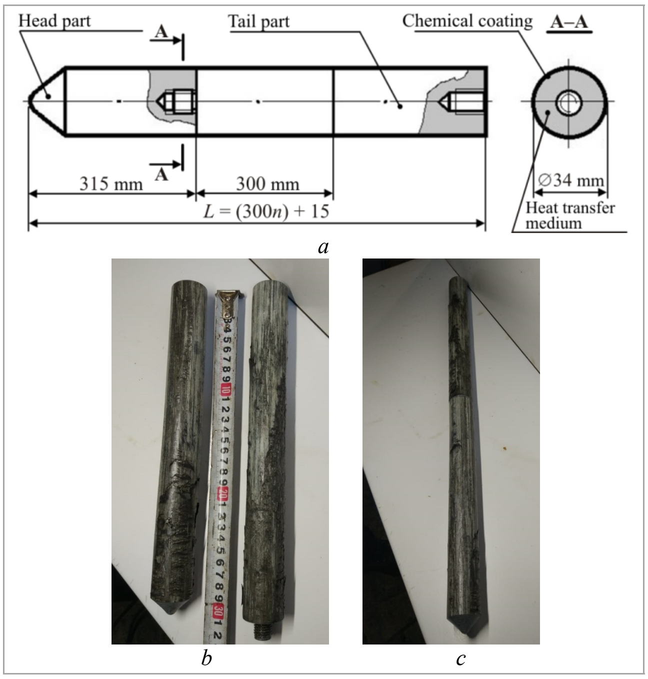

Fig. 7. Shell-less device for thermochemical treatment of wells: *a* – layout; *b, c* – photos of the head and tail end of caseless devices and their connection

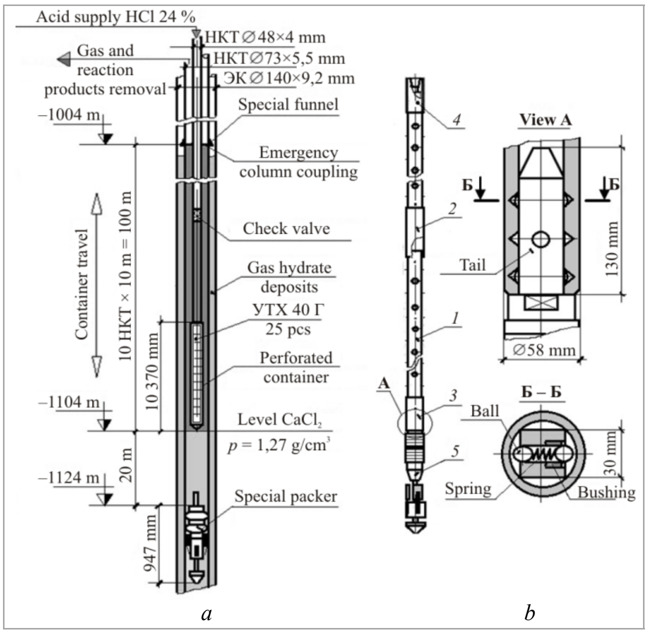

Fig. 8. The proposed technology and device: *a* – the technology of gas hydrate deposit liquidation in the annular space of wells when the bottomhole is connected with the wellhead through a tubing string; *b* – a diagram of a perforated container bundle with a packer; *1* – section; *2* – coupling; *3* – plug; *4* – cross over; *5* – special packer

while a reaction occurs with the coating, as a result of which its thickness tends to zero, and a reaction with active metal of the coolant begins.

The reaction proceeds violently, with a large release of heat and gas, which contributes to the heating of acid, tubing metal walls and the melting of sediment products that rise upward at the wellhead. The flow rate of device elements during the chemical reaction is complete, the tubing is not contaminated with solid residues, its internal space is not clogged. After complete melting of paraffin deposits in the treated interval, paraffin compounds and reaction products are pushed out of the tubing by formation pressure or ECP. At the wellhead, the paraffin reaction products are collected in a receiving tank for further disposal.

The Deposit Elimination in the Tubing Annulus when the Bottomhole Communicates with the Wellhead through the Tubing String

To eliminate gas hydrate deposits in the annular space of oil wells when the bottomhole communicates with the wellhead through a tubing string, as at the well No. 7 of YUTM, the authors proposed the following technology (Fig. 8, *b*). The plug design (Fig. 8, *3*) was changed, a square hole for the packer stem installation was added in the lower part. Grooves for the spring-loaded balls are used to securely fix the packer stem at the container end. Fig. 8, *a,* shows a bundle of a perforated container and a packer. Functionally, the container is now not only a vehicle for UTKh 40G devices delivery to the required depth interval, but also a unit for installing (removing) a special packer.

The proposed technology is very promising and flexible, as it allows the following:

1) to eliminate gas hydrate deposits in the annular space using a string with a special funnel that covers the emergency string, followed by turning and lifting the treated tubes to the wellhead;

2) to operate in the interval of gas hydrate deposition without lifting the tubing string.

The proposed application technology is as follows. The bundle of the container with the packer on the ∅48 mm tubing is lowered to the lower mark of the specified interval, where, after its fixation, the calcium chloride solution with a density of 1.27 g/cm^3 is pumped through the lift pipes. After filling the entire volume of small annulus with the process fluid, the loaded container rises two pipes higher, where, from this mark of the interval, a thermochemical reaction begins with heating and decomposition of gas hydrates into gas and water behind the tubing wall. Once processing of the upper interval completed, the container with devices is lifted to the wellhead. Then, the perforated container is loaded with a new batch of devices, lowered 10 pipes (100 m) below the previously treated tubing interval, and the process is repeated.

The decomposition of gas hydrate deposits in the annular space continues until the pressure rises therein, which indicates its connection with the bottomhole. After that, the packer is connected to the container and lifted to the wellhead on the lift pipes. Then, the direct well flushing with calcium chloride solution, which is the most common inhibitor of gas hydrates, is switched on, and during this process the annular space is freed from deposits, and then the well is put into operation.

Conclusion

Oil production is an important branch of the national economy, therefore, before being used in production, the devices and equipment shall undergo approbation, which will confirm their claimed properties. Before the equipment goes into commercial operation, the comprehensive industrial testing of each piece of the equipment developed by the authors hereof shall be conducted on a larger number of wells – it is the task of the next stage. Thus, the implementation of new advanced equipment samples will provide a significant saving in time spent on the well workover, which ultimately will affect the final product cost.

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