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The development of energy-saving technologies of oil wells chemical treatment to prevent scale

L. Shangaraeva

Assistant Professor, Oil and gas department, National mineral resources university (Mining university) Russia, Saint-Petersburg, 21-st line, 2 mirabilissa@gmail.com

D. Tananykhin,

Assistant Professor, Oil and gas department, National mineral resources university (Mining university), Russia, Saint-Petersburg, 21-st line, 2 dmitryspmi@mail.ru

Abstract.
The buildup of inside wellbores is often a serious cause of energy losses, it reduce the productivity of the wells, leading to the current unplanned and costly workovers. Fight with scale in the well operation is one of the most important ways to increase the efficiency of oil production.
The research results show that active organic compounds of oil affect the kinetics of crystallization of scale. The technology for preventing scale in the downhole equipment is investigated in the paper.

Keywords: Scale, Inhibitor, Phosphonic acid, Adsorption-desorption characteristics.

Introduction

The main task in the oil industry is to increase the efficiency of oil production. One of the most important ways to solve this problem is to fight scale during wells exploitation. The scale in the downhole equipment leads to reduced productivity, premature failure of downhole equipment, current well remedial work and costly workover, additional energy and material costs.
The scale during the development and exploitation of oil fields is complex and multifactorial process that is most actively manifested in the later stages of development when increasing water cut wells [1-3]. Currently, most of the oil fields in Russia are under intense flooding, so the problem of increasing the efficiency of operation of such wells is relevant. This is typical for Romashkinskoye field which is currently in the later stage of the development.
In recent years, the problem of preventing the scale has been exacerbated by a sharp increase in the number of wells with scale with complex composition. The effectiveness of scale inhibitors decreases because of their use in the changed conditions.

Main part

The most commonly encountered in the process of development and exploitation of oil fields scale are deposits of calcite-$CaCO_3$, gypsum-$CaSO_4x2H_2O$, anhydrite-$CaSO_4$, barite-$BaSO_4$, barytocelestite-$Ba(Sr)SO_4$, halite-NaCl [4]. Composition of scaleon the surface of the downhole equipmentin those regions, where sedimentation mass contain saliferous beds and characterized by high salinitywaters, mainly includes salts of barium sulfate and calcium. Deposits of calcium carbonate predominate in formations with low salinity of formation waters, due to the lack of salt-bearing strata.
In general, scale has complex petrographic composition, which includes both mineral and organic part. The structure of scaleon the inner surface of oilfield equipment often have adsorbent bed of organic substances, which having high adhesion to metal and to the precipitation [5]. Thus, there is a suggestion that the process of crystal formation initially occurs in the liquid volume, and then there was their adsorption on the equipment surface by organic adsorbent bed [6].
The organic part, included in scale composition, represented mainly by aromatic hydrocarbons, asphaltenes, resins, paraffins, sulfur compounds.
Mixing of incompatible waters, leading to the scale formation, occurs during flooding for the implementation of the formation pressure maintenance system, when mixing formation waters from different interlayers on the bottom of the well, when the bringing the well on to stable production after the killing are carried out, etc.
Mixing of formation waters containing different amounts of salt-forming ions and dissolved carbon dioxide, can occur in the wellbore due to the different permeability of oil reservoirs interlayers, which often leads to formation of aqueous solutions supersaturated with calcium carbonate, and precipitation of carbonate scalein the wellbore. In the case of injection water breakthrough in the bottomhole formation zone, this factor may be decisive. The greatest instability in relation to the formation of calcium carbonate scaleshowa mixture of sodium bicarbonate water type with calcium chloride.
After killing the wellduringbringing it on to stable productionformation water, which comes from the reservoir, can be mixed with a well-killing fluid. As a result of mixing, for example, sodium bicarbonate typeof formation water with a well-killing fluidbased on calcium chloride may form an aqueous solution, which will be supersaturated with calcium carbonate, due to the increase in the number of calcium ions in the mixture and reducing the amount of carbon dioxide dissolved in the formation water. This in turn

leads to the precipitation of calcium carbonate in the wellbore and the downhole pumping equipment.

As a result mixing of incompatible waters leads to the formation of sulphate scale. This situation occurs when the formation water containing a large number of calcium ions, barium or strontium is mixed with water from overlying horizons, containing a significant amount of sulfate ions, which leads ultimately to the formation of scale of calcium, strontium and barium [7].

Study of the chemical composition of scale on Minnibaevskaya area of Romashkinskoye field have shown that in addition to inorganic salts, it is represented by the hydrocarbon components, mainly aromatic, unsaturated hydrocarbons, asphaltenes, resins, sulfur compounds (Table 1).

TABLE. 1. Mineral and component composition of scale from Minnibaevskaya area downhole equipment

Well	Composition	Descriptionofscale	Elementary composition,%
313	Barium sulphate,calcite	The sample is fully represented by barite-crustate particles about 1 mm thick,consists of a dense fine-grained unit light gray to white color. On the outside of particles there aresome thin powdery coating,which reacts well with hydrochloric acid. Judging by the reaction it is calcite.	AFS-3,7; $CaCO_3$-3,1; Fe_2O_3-19,2; $BaSO_4$-55; Al-2; S_2-4
950	Barium sulphate,cilex	Barite is 50%. It presented by powdery formations and dense secretions crustate folded fine-grained unit light gray color. Silex is present in small quantities.	AFS-14,6; $CaCO_3$-10,4; SiO_2-2; $MgCO_3$-1,0; Fe_2O_3-0,8; $BaSO_4$-48,3; NaCl-13,3
149	Barium sulphate,calcite	The sample is fully represented by crustate particles white color,black,consisting of splice parallel columnar microcrystals. On the outside of some particles there are small plaque of powderycalcium carbonate.	AFS-14,2; $CaCO_3$-3,1; Fe_2O_3-2,8; $BaSO_4$-75,4; SiO_2-4,5

These organic compounds hydrophobize surface of salt crystals formed in the flow that facilitates their adhesion to each other and to the hydrophobic surface of the tubes in the scheme of Fig. 1.

Surface-active compounds of oil adsorbed on the surface of the equipment 2, or solid mineral particles, precipitated crystals with the polar part 1 and hydrophobize them, as the hydrophobic part of the molecules 3 facing towards the environment (figure a). Hydrophobicity takes the place primarily due to the chemical adsorption of the active components of the oil. Adsorption layer 4 is formed, and polarity difference arises between the surface equipment or precipitated crystals and the adjacent liquid layer. The balancingoccurs due to the attraction to that surface the crystals and other solid particles, also having on its surface the adsorption layer of the active components (figure b). Each new particle has a hydrophobic oriented in the direction of the environment single layer of molecules of the active components 4, 5, 6,... n, between which there is always a difference between the polarities. Thus, during the balancing of this difference in the polarities occurs pulling and deposition of new solid particles from the liquid volume on the surface. The process of adhesion of solid particles has a continuous chaincharacter. According to this scheme, a double layer of adsorbed molecules of the active componentsis formed on the equipment surface and each stuck to it phase. And the surface, facing the hydrocarbon environment, takeagain the difference in polarities and attracts other phases [5].

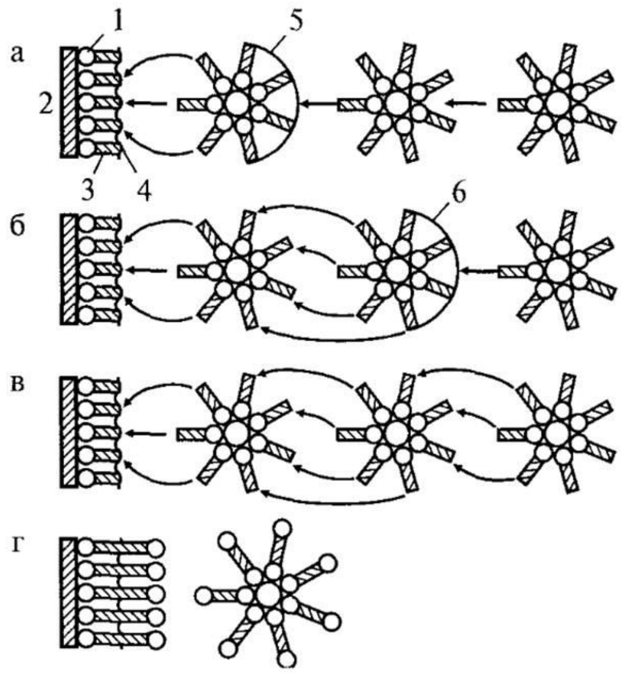

Fig. 1. The formation of scale: 1-polar part of the molecule; 2-solid surface; 3-non-polar part molecules; 4-6-adsorption layer, a, b, c-the process of deposition of particulate matter on the surface of the equipment; g-the existence of free particles in a volume liquids

The reliability of the mechanism is confirmed by the existence of oil emulsions, where on the surface of the water globules there is a double adsorption or multimolecular layer of natural active ingredients of oils and their salts. The interconnection of such particles and their adhesion to the surface of equipment, having the same double adsorption layer of the active components, is possible only if the appropriate conditions for the existence of the adhesive properties are met.

The organic components of the scale have excess free surface energy, which explains their fixing to the surface through physical adsorption.

Asphaltenes, resins and corrosion products, which are part of the scale, as colloids, possess surface activity and can adsorb a significant amount of salt ions, turning into the nucleus of crystal.

The analysis of the development of the Romashkinskoye field Minnibaevskii area and learning workover actions performed in the wells in order to enhanced oil recovery, showed that injection wells in Minnibaevskii area of Romashkinskoye field was used for the injection of aqueous solutions of sulfuric acid in the period from 1974 to 1994 to conformance control, which led to a significant increase the content of sulfate ions in formation waters. When comparing the locations of producing wells, complicated with barium scale and gypsum, and injection wells, where was held the sulfuric acidsolutions injection, it has been found that these regions are spatially the same. On this basis, it was concluded that injection of alkylated sulfuric acid in the reservoir of Romashkinskoye field subsequently influenced the processes of sulfates scale formation. Furthermore, it is known that sulfuric acid contributes to the change in oil properties. The technology of sulfuric acidapplicationare based on this effect.

Concentrated H_2SO_4 reacts with oil in the reservoir at the same time sulfonation of aromatic compounds, which are contained in the oil, and the formation of a whole range of surfactants: alkylarylsulfonic acids, alkylsulfonic acid esters, sulfones, asphaltene acids, asphalt-oxonium compounds, carbenes, etc. take place. According to laboratory data, the total yield of sulfonic acids by reaction of sulfonation of oil is from 4.6 to 9.1% by weight of the feed oil. Of these, water-soluble sulfonic acids are in 3.2% to 3.8%; and oil-soluble are 1, 5-5, 9% [8]. In addition, there is generation of acidic tar, which is a viscous resinous mass, which seals offflushed zones. Formed during the reaction between H_2SO_4 and oil substances are surface-active and can influence the kinetics of chemical reactions and processes of scale in the downhole equipment.

Organic substances can be divided into adsorbed and crystal by location in the structure of scale. Of particular interest is the water-soluble fraction of the organic component of scale. To study the effect of active acidic compounds of oil on the formation of scale have been extracted organic components from samples of scale, which are taken from oilfield equipment of Minnibaevskii area producingwells. Separating organic components can be divided into the neutral and active, which are natural surfactantsof oil. The latter are oil-soluble components-asphaltenes, resins and waxes and water-soluble-petroleum acids and their salts.

The composition of mentioned acidic compounds include about 25% phenol, 3% cycloartenol, 4% naphthols, 66% salts of naphthenic acids and other unidentified compounds.

The oil components in the process of scale play a role of oil wetting agents of salt crystals, which formed in the flow volume, due to the physical adsorption of water-soluble organic surfactant, mainly salts of petroleum acids.

On the one hand, water-soluble surface-active organic compounds, which adsorbed on salt crystals surface, inhibit the growth and the possibility of theirsalting-up, and the other-contribute to the aggregation of crystals and their adhesion to the pipe surface. Reducing the size of the crystals leads to the subsequent formation on pipes very dense sediments due to their high dispersion.

Surface-active properties of water-soluble organic components was established by determining the aqueous solutions of these components-air interfacial tension. Thus, aqueous solutions of organic active ingredients taken from scale of wells 1498 and 3133 of Minnibaevskii area reduced the surface tension to 49.6 and 58.2 mn/m respectively, compared to surface tension of distilled water-71.8 mn/m.

Active organic compounds affect the kinetics of crystallization of scale. The findings of this study show that in the presence of water-soluble organic components extracted from the scale the induction period of crystallization of barium sulfate from a supersaturated aqueous solution is slightly increased. However, by the end ofinduction period the scale precipitation occurs faster than without additives, i.e. the end time of the reaction decreases.

Organic salts having high adhesive properties, sticking to the equipment surface, can be nuclei for the scale on the surface of oilfield equipment. Thus, the formation and growth of scalefrom blended product offormation fluid on the surface of oil equipment take place under the influence of natural organic active ingredients of oil.

The explanation of the formation of scale on the basis of influence of active organic components of oilon the process, gives you the opportunity to consider it from the point of view of surface phenomena and allows you to divide this process into two stages:

1) a chemical process in which phase equilibrium is disturbedunder the influence of active organic (acid) compounds of oil, resulting in precipitation of insoluble salts of petroleum acids;
2) physical and chemical process by which precipitated insoluble compounds are deposited on the surface of the equipment. At this stage, active organic compounds of oil involved in the adsorption process and provide adhesion both to each other and to the surface of the equipment, i.e. cause the growth of crystals.

This separation makes it possible to develop recommendations and actions against the scale in oil-field equipment under the influence of acidic compounds of oil. The results show that the choice of scale inhibitors is not sufficient laboratory studies on the kinetics of crystallization of salts from supersaturated associated water in the presence of inhibitors. You must ensure that the surface activity of the inhibitors was higher than of oil in the field.

One of the most effective method is the injection of an aqueous solution of the scale inhibitor in the bottomhole formation zone for its subsequent long enough removal in

the wellbore during its operation (Shaidakov, V., 2012). Existing methods of selection reagent for specific conditions are based on the selection of the brand of the inhibitor and on its capacity. The adsorption-desorption characteristics of the inhibitor are not taken into account. However, the amount of inhibitors adsorption on the formation and its subsequent desorption depends on it.
As an inhibitor of the growth of salt crystals is widely known use of phosphonic acids(in particular, NTF and HEDP). However, an aqueous solution of these acids has a low adsorption-desorption ability and quickly taken out from the reservoir by fluid flow [9].
To improve the sorption properties of the inhibitors recommended their injection with weak acid solutions. So treatment of the bottomhole formation zone is carried out by the mixture of phosphonic acids with hydrochloric acid. Due to the acidic reagent there is rejection of oil film from the surface of the reservoir by reducing the interfacial tension in the system "formation-oil-inhibiting solution". Hydrochloric acid reacts with carbonate minerals and thus the adsorption area of the inhibitor on reservoir increases.
The major volume of oil is produced from sandstone reservoirs with carbonate concretion. Therefore, scale inhibitor should reduce the surface tension at the boundary of the “formation-inhibitor solution” and react with both silicate, aluminosilicate and carbonate concretions. It enhances the adsorption-desorption properties of the inhibitor.
Designed composition based on HEDP acid, ammonium bifluoride, hydrochloric acid is a multicomponent composition to obtain the highest inhibitory activity against inorganic salts.
The assessment of efficiency of the inhibitors by the ability to prevent the precipitation was carried out in the liquid solution of the averaged model of the formation water. Experiment results revealed that the developed chemical compositions have the necessary protective effect.
Laboratory studies to determine the oil-inhibiting solution interfacial tension at different concentrations of ammonium bifluoride, hydrochloric acid and HEDP in the inhibiting solution allowed us to determine the optimal concentration of the components included in the newly developed composition.
The use of chemicals to prevent scale in wells associated with the use of chemically aggressive fluids. Injection of corrosive agents in the bottomhole formation zone not only promotes downhole equipment failure, but also brings additional harm from the products which are formed as a result of exchange reactions and can worse the filtration properties of the bottomhole formation zone. All this leads to a significant increase in operating costs of oil and gas companies that have a negative impact on the oil production cost. Therefore it is necessary to consider the corrosiveness of injected compositions.
All considered chemical compositions showed acceptable corrosion rate in relation to the steel and these reagents can be considered as reagents to prevent scaling in the wells.
To determine the adsorption-desorption characteristics of inhibitory compositions was carried out filtration tests on core samples.
Efficiency of the developed composition is explained by the mechanism of influence on the reservoir of acid additives included in the composition.
The fluoric acid which is formed as a result of interaction of hydrochloric acid with bifluoride of ammonia reacts with the quartz and kaolin which are a part of terrigenousreservoir.
The resulting interaction of ammonium bifluoride with hydrochloric acid hydrofluoric acid reacts with the silicates of a reservoir and allows increasing the contact of the inhibitor with the surface, significantly reducingthe oil-inhibiting solutioninterfacial tension. Thus, the adsorption-desorption ability inhibitory compositionincrease. The developed method of preventing scale effectively and for a long time protect the downhole equipment and the reservoir from the scale. It is characterized by the ease and speed of application-the period well downtimein the processing does not exceed 24 hours.
The inhibiting composition will get into structure of silica sols, which cover the contact surface of the inhibitor with silicate minerals [10]. Due to this it will desorb slower from the reservoir, as films of silica sols being a part of inhibitor composition are more resistant to leaching. Which leads to the fact that the time of desorption raises, and from this we can conclude that effectiveness of the scale inhibitor increases

Conclusion

Conducted laboratory studies have shown that application of the developed inhibitor allows to increase desorption from formation in 1.6 times compared with the analogues. Wide range of effectiveness of the examined compounds is explained by the different mechanism of action on the formation of specific additives. Laboratory experiments have shown that desorption from the formation with the developed inhibitory compositions longer than the existing counterparts.
Besides development of the inhibitor compositions technological ways of their injection in a well are of great importance for the prevention of scale. One of the most effective methods is the intermittent injection of the chemical composition in the bottomhole formation zone.

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