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Research progress in oil-field scale prevention techniques

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The presence of scaling poses significant issues in the production and recovery benefits of oil fields. This article reviews the causes of oilfield scales and elaborates on common scale prevention methods, including chemical technique, ultrasonic technique, electromagnetic technique, and metal coating technique. The paper describes the existing techniques in detail, lists their respective advantages and disadvantages, and proposes a technology variation that can reduce the formation of scales. This work is expected to contribute guidance in normal oil field production.

Key words: Scaling causes; Scale prevention technique, Scale prevention mechanism

INTRODUCTION

Over recent years, various flooding techniques, including water flooding, polymer flooding [1,2], and three-component combination flooding [3-7], have been widely employed to enhance oil recovery in oil fields, which has caused increasingly serious scaling problems [8-10]. Scaling in formation can lead to formation plugging, which prevents water injection from reaching the injection allocation amount. Thus, oil well productivity is greatly reduced. Scaling in wellbores can increase the burden of underground maintenance operations. In addition, it can cause scrapping of water injection wells and oil wells. Scaling can also lead to blockage in pipelines, delivery pumps, and heat exchangers, which can affect the normal operation of crude oil treatment systems and sewage treatment systems, thereby increasing the costs associated with cleaning and replacing the equipment and pipelines. The deposition of scales can also result in local corrosion of the equipment and pipelines, leading to perforation in a short time and shortening of service life. Various scaling prevention measures have been proposed to solve these different scaling problems in oil fields. However, the complex and variable situations in oilfield production have produced higher demands for scale prevention and have also promoted the development of scale prevention techniques [11-14].

CAUSES OF OILFIELD SCALING

Incompatible chemical mixture

Mixtures between two liquids with incompatible chemical properties promote the interaction between scale-forming ions. Examples of this type of mixtures include the formation water with incompatible ions at different layers, formation water with surface water, clean water with waste water, and mixtures of different high-salinity liquids. Variations in formation pressure, temperature, flow velocity, and pH value can break the original chemical equilibrium; reduce the water’s capacity in mineral dissolution, cause oversaturation, and lead to depositions, thereby generating salt scales. Non-crystalline silicon dioxide and quartz are formed by the dehydration condensation reaction of silicic acid gels.

Defective pipelines

The flow line, flow velocity, pressure and density of the oil gas may change suddenly in some defective pipelines or at the turnings of pipelines, which readily leads to the aggregation of scales and subsequent passageway blockages.

Free sediments

The formation on the bottom of wells always contains a relatively high proportion of unstable and free sediments. These sediments can be carried to the well holes and pipelines during oil and gas production under certain conditions, which may result in scale formation and sand plugging.

Flooding agents

The flooding agents also corrode pipeline materials to a certain degree. Many dissolved gases, such as oxygen and carbon dioxide, are included in the pipeline fluids. These pipeline materials can undergo ionization, resulting in the formation of ferric hydroxide, ferric oxide, ferrous carbonate, ferrous sulfate and other corrosive materials. These can corrode the pipeline and also provide conditions for adhesion of other dirty materials, which promote scaling.

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External conditions variation

During the crude oil transport process in the pipelines, variations in external conditions, such as environment, temperature and pressure, can lead to the crystallization or decomposition of macromolecular hydrocarbons in the crude oil, such as coking materials, paraffins, and pitch. These materials adhere to the pipelines and combine with inorganic scales, such as sediments, leading to the formation of scale samples that are difficult to remove. Even crystals can be separated out from the high-solubility materials under certain external conditions, and they are then mixed with other scale samples.

Organic scale formation

Organic matter and bacteria contained in the crude oil are attached to the solid particles that are scattered in the crude oil or on the pipeline walls, and they react with the excretions from the microorganisms in the water to form slimes. The organic scales can adhere to the pipeline inwalls in a flocculent pattern. The existence of the organic scale can provide the conditions for the subsequent reproduction of dirt, resulting in thick dirt layers. In addition, defects in the pipeline inwalls or corrosions along the pipelines can also provide conditions for the formation of organic scales.

COMMON SCALE PREVENTION TECHNIQUES IN OIL FIELDS

Chemical scale prevention methods

Adding chemical anti-scaling agents is the most widely used method for inhibiting and slowing the formation of scales in both domestic and foreign oil fields. The chemical method involves the addition of anti-scaling agents to prevent or reduce the production of inorganic salt scales. The most popular chemical scale prevention mechanisms are described in detail below:

Solubilization

After being dissolved in water, the anti-scaling agent reacts with the scale-forming cations in the water to form stable soluble complexes. These complexes stabilize the scale-forming cations and thereby inhibit the deposition of salt scales. The anti-scaling agent added in small amounts, can react with many scale-forming ions to form chelates [16].

Crystal distortion and threshold effects

The anti-scaling agent is adsorbed onto the active growing points on the crystal and then reacts with the scale-forming cations to form chelates, which can inhibit the regular growth of the crystal lattice and can cause crystal distortion. Accordingly, the stress inside the large crystals increases, which makes the crystal more likely to rupture. However, it is not easy to inhibit the crystallization of scales. According to the spiral dislocation theory, during crystallization, crystal growth around the growing point is restricted when the finite active growing points are covered by molecules of the anti-scaling agent, which leads to inhibition of the crystallization and scale growth [17,18].

Electrostatic repulsion

The chain structure of the anti-scaling agent adsorbs several micro-crystals that have the same charge, and the electrostatic repulsion generated can hinder the collisions between the crystals, thereby hindering their growth. Meanwhile, polymers adsorb and wrap around the scale-forming micro-crystals, which allows the crystalline grains to achieve a favorable dispersion. The scale-forming micro-crystals can then be washed away by water [19].

Chemical anti-scaling agents

Dating back to the 1930s, anti-scaling has experienced a long development history, ranging from inorganic to organic matter, and from micromolecular to macromolecular polymers. Some anti-scaling agents have also been used for the preparation of nano-emulsions to improve scale prevention effects. Currently, the most commonly used anti-scaling agents in oil fields are organic phosphonate, low-molecular polymers, including homopolymers and copolymers, and modified polymers. Organic phosphonates are generally used for the prevention of calcium carbonate scale formation, while low-molecular polymers are used for the prevention of sulfate scale formation. Thus, these two types of anti-scaling agents can be combined for the prevention of mixed scale formation.

Organic phosphonate

Organic phosphonate anti-scaling agents in oil fields mainly include amino trimethylene phosphonic acid (ATMP), ethylenediamine tetra methylenephosphonic acid (EDTMP), diethylenetriamine pentamethylene phosphonic acid (DTPMP), hydroxyethylidene diphosphonic acid (HEDP), butane phosphate 1,2,4-tricarboxylic acid (PBTCA), 2-hydroxyphosphonoacetic acid (HPA), polyamino polyether methylene phosphonic acid (PAPEMP) and 3-hydroxy-3-phosphonobutyric acid (HPBA).

ATMP and HEDP were both developed in the 1960s and are still widely used in water treatment. In the 1980s, the organic phosphonic carboxylic acid was developed, in which PBTCA exhibited outstanding scale prevention performances under severe conditions, such as high temperatures, high hardness, and high pH values. Macromolecular organic phosphonic acid PAPEMP was prepared in the 1990s with a molecular mass of up to approximately 600 g/mol. Ether bonds were introduced into PAPEMP to increase calcium tolerance, scale-prevention ability, and dispersion performance.

Polymer-type

The most popular polymer-type anti-scaling agents used in oil fields include polyacrylic acid (PAA), polymethacrylic acid (PMA), hydrolyzed polymaleic acid (HPMA), maleic acid/acrylic acid (MA/AA), acrylic acid/hydroxypropyl acrylate (AA/HPA), sulfonated styrene/maleic acid (SS/MA), maleic acid/methyl acrylate/vinyl esters, acrylic acid/2-acrylamide-2-methyl propyl sulfonic acid (AA/AMPS), PPMA, phosphono-carboxylic acid (POCA), and polyaspartic acid (PASP). Among these polymer-type anti-scaling agents, PASP has the most favorable corrosion characteristics and scale inhibition effects and can replace phosphorous water treatment agents; PAA can disperse sediments and micro-crystals in salts, such as calcium carbonate and calcium sulfate without depositing them in the water, which allows the material to boast excellent scale inhibition performance; HPMA combines lattice distortion and threshold effects to effectively disperse calcium phosphate micro-crystals and to achieve favorable heat stability, which is useful for scale and corrosion inhibitions under high-temperature conditions; POCA can inhibit both scaling and corrosion and also has fairly high calcium tolerance, which allows this material to be referred to as a real multi-function agent.

Nano-emulsion-type

In low-water-content formation, soluble flooding agents can lead to slow oil production and can cause harms to reservoirs. The use of nano-emulsion to transport soluble flooding agents can effectively solve these problems. This method exhibits the following advantages: the emulsion droplets can be easily deformed and therefore do not readily block pore throats; the emulsion droplets can increase the sweep area and cannot lead to water coning; the emulsion droplets can be retained in the porous media and slow down demulsification and release with a long scale-prevention period; the anti-scaling agents cannot be released in great amounts before the oil well resumes production, and there is no waste, which is not comparable by the other squeeze methods; after the flooding operation is finished, the emulsion cannot retard oil production, which offers high operational benefits [20].

Physical scale prevention methods

Physical methods include the prevention of inorganic salts from depositing on the system walls through certain actions, during which inorganic salts can form crystal nuclei and even crystals in the solution. These crystals should be suspended in the solution without adhering to the system walls. Common physical scale prevention methods include ultrasonic scale prevention technique, magnetic scale prevention technique, and metal coating scale prevention technique, which are described in detail below.

Ultrasonic technique

Ultrasonic scale removal and prevention equipment is mainly composed of an ultrasonic generator, an ultrasonic energy converter, and pipeline assemblies for the installation of the ultrasonic energy converter. The equipment can be classified into three types according to installation method, including external equipment, embedded equipment, and built-in equipment. Ultrasonic scale removal and prevention equipment mainly uses a high-intensity acoustic field for the treatment of fluid by utilizing the ultrasonic wave’s cavitation effect, activation effect, shear effect, and inhibition effect. Therefore, the scale-forming materials in the fluid can exhibit a series of changes in physical configurations and chemical properties, as a result of which these scale-forming materials are dispersed, smashed, loosened, and ultimately not easily attached to the pipe walls to form scales. The various ultrasonic effects are described below:

(1) Cavitation effect. The energy of an ultrasonic wave can directly produce a large number of cavities and bubbles in the fluid medium. The rupturing of these cavities and bubbles generates a strong pressure peak within a certain range. Even some local pressure peaks can reach up to thousands of psi atmospheric pressure. These pressure peaks can smash the scale-forming materials and suspend them in water. Moreover, the scale layer that has already been formed will easily come off. The ultrasonic wave capitation effect is now widely applied in cleaning [21].

(2) Activation effect. Ultrasonic waves can enhance the activities of both flowing fluids and scale-forming materials, destroy scales' formation conditions, and diminish deposition conditions on the walls of the energy converter. Accordingly, the scale forming materials can form scattered sedimentary bodies rather than hard scales on the pipe walls.

(3) Shear effect. When the scale layer, pipe walls, and water are exposed to the radiation of ultrasonic waves, these three components can generate unsynchronized vibrations as a result of differing responses to the frequency of the ultrasonic wave. This generates relative movement at a high velocity. Differences in velocity result in a relative shear force between the scale layer and the interface of the pipe wall of the energy converter, leading to fatigue and loosening in the scale layer.

Inhibition effect of ultrasonic waves. The application of the ultrasonic waves results in changes in the fluid's physical and chemical properties, which effectively inhibits nucleation and growth of the ions in water on the pipe walls. Consequently, the number of scale-forming ions attached on the surface of the heat exchanger is reduced. Experimental results have shown that increasing the duration of the application of the ultrasonic wave results in increased scale prevention performance. When the ultrasonic wave is applied on the water, a sufficiently large ultrasonic energy can produce a transient, local, great, high-temperature, high-pressure, high-electric- field-intensity, and extreme physical environment in the transmission medium under normal-temperature and normal-pressure environmental conditions. The fluid can then produce the so-called acoustic cavitation effect and induce a series of mechanical, physical, chemical and biological effects. Accordingly, the goals of preventing and removing the scales in the fluids can be achieved.

The ultrasonic scale prevention technique exhibits several advantages, such as environmental protection, desirable performance, low costs, no corrosion, high quality, simple equipment, and ability to be easily controlled or remotely automated. These advantages have caused ultrasonic scale prevention to become a new high-efficiency technique in scale prevention applications. The equipment for ultrasonic scale prevention has the following characteristics:

(1) Synchronization of scale removal and prevention. The equipment can achieve the goals of scale removal and prevention simultaneously. It will remove the pre-existing scale and continuously prevent scale formation over a long period of time;

(2) Lower power consumption and low operating costs. A single device consumes only 1 KW/day at most. The output peak power of the power supply is continuously adjustable, and the device is maintenance-free;

(3) Triple automatic protection with favorable safety and reliability. The equipment combines intelligent function control with triple automatic protection, including overcurrent protection, overvoltage protection, and over-temperature protection;

(4) Humanization design and automatic control. The control instrument can automatically track frequency and monitor both the working conditions of the heat exchanger and the load conditions of the equipment in order to follow the responses in real time. When the equipment operates with no load, it can send an acoustic-optic alert and power off to protect the equipment's operation;

(5) Environmental protection. No chemical agents are used during the whole scale removal and prevention processes, with no corrosion, no interference, no pollution, no radiation, and no harm to operation staff and heat exchange devices;

(6) Energy conservation and consumption reduction. The average energy saving ratio exceeds 30%, excluding the benefits induced by prolonging the service life of the heat exchange devices and by halting the work and production associated with using other scale removal methods.

Electromagnetic technique

The electromagnetic scale prevention technique also has a series of advantages, such as small investment, easy operation, no toxicity, and no pollution. Moreover, this technique can combine many functions, such as scale prevention, scale removal, and sterilization. It is one of the most promising scale prevention methods. Although the electromagnetic scale prevention technique has been now widely applied in production practices, it still lacks the determination of a uniform theory regarding the phenomena observed experimentally. The existing proposed mechanisms can be classified into the following four types listed below:

(1) Intraatomic effect. Eliassen *et al*. stated that ion electron transfer required a considerable input of magnetic energy [22]. However, Ellingsen and Vik pointed out that this variation was quite transient and could not explain the magnetic memory effects [23].

(2) Effects of pollutants. Magnetism can enhance corrosion and dissolution, and it can

produce trace amounts of Fe^{2+} ions in the system. Fe^{2+} can inhibit the formation of hard scales and produce soft muds, which can be discharged with the pollutants to achieve scale removal and prevention. However, this mechanism cannot explain the experimental results in non-invasive magnetic processors and high-purity solutions.

(3) Molecule/ion interaction effect. According to the hydrogen bond rupture and deformation theory, magnetic treatment can strengthen the water's permeability, destroy the binding force between scales and walls, thereby causing peeling of limescales. Nevertheless, such explanations are typically qualitative. Srehrenik *et al*. [24] proposed a quantum mechanism based on magnetic fluid dynamics. This theory can explain the magnetic memory effect, but does not explain the behavior of cations in water besides Ca^{2+}.

(4) Interface effect. The double-electric- layer deformation theory assumes that the diffuse layers induced by the Lorentz force are isotropic. The Lorentz force can cause a substitution between synergistic ions and opposite ions, which can change the distribution of charges in double electric layers. Accordingly, the charges at the boundary of the stern layer and the potential can change transiently. This mechanism explains the flocculation and crystallization behaviors and also provides a quantitative performance parameter, potential. However, it cannot explain the flocculation under static conditions, as reported by Higashitani *et al*. [25].

Metal coating technique

In this technique, thermal spraying, electroplating, electroless plating, coating, or magnetron sputtering is used to coat the metal surface with hydrophobic substances [26]. The surface coating scale prevention technique exhibits certain characteristics, such as low surface energy, and a low and stable friction coefficient, which prevents the formed scales from becoming easily attached from the pipe walls to prevent scaling.

Technologies designed for scale prevention

Technologies have been put forward to either destroy or reduce scale-forming opportunities by varying the properties of flooding solutions, the equipment shapes, and some parameter ratios [13]. The specific scale prevention measures are described below:

(1) Small-interference screw pump, long-plunger, and short-pump-barrel pumping unit can be adopted to reduce friction between the produced liquid and the equipment.

(2) Underground choke can be adopted to form water-in-oil emulsions to reduce the flow velocity of oil wells and the production pressure difference.

Insoluble products can be deposited in the mixtures with incompatible water, leading to the formation of scales. Therefore, necessary chemical tests should be conducted on the formation water, the related property data should be mastered, and appropriate injection water should be selected in order to guarantee a favorable compatibility. The water exit layer and interlayer can be selectively blocked, and equipment and pipe columns with cover layers can be used to avoid mixing with the incompatible water.

CONCLUSIONS

Scale prevention in oil fields is a long-term, difficult task, and it is highly significant in practical production settings. The main development direction of chemical scale prevention agents is to develop novel low cost agents with excellent scale prevention performance, and high compounding stability. Moreover, these agents should be capable of both scale prevention and corrosion inhibition. Physical scale prevention exhibits a series of advantages, such as low cost, easy operation, and little environmental pollution. Physical methods can work quickly and have direct effects, which is desirable for scale prevention in severe scaling sites, such as oil wells and pipelines in the ground. Physical and chemical methods should be combined for scale prevention, while chemical methods alone are preferable for scale removal.

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