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Overview of emulsified viscosity reducer for enhancing heavy oil recovery

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Abstract. Chinese water flooding heavy oil reserves are abundant and the output is increasing year by year, but the heavy oil water flooding recovery rate is low. It is of great significance to improve the heavy oil water flooding recovery rate to improve the development level of heavy oil reservoirs. This paper reviews heavy oil emulsified viscosity reduction technology, emulsified viscosity reduction theory, viscosity reducer flooding microscopic mechanism and structural characteristics of surfactants for heavy oil emulsified viscosity reduction. Meanwhile, the research focus of emulsified viscosity reducer in the future is put forward.

1. Introduction

Global heavy oil accounts for over 70% of total remaining oil resources, China also has abundant heavy oil resources, onshore heavy oil accounts for over 20% of total oil resources, heavy oil production has accounts for over 10% of total crude oil production [1]. Due to its high content of colloid and asphaltene, heavy oil has the characteristics of high density, high viscosity and poor fluidity, which brings great difficulty to the exploitation and transportation of heavy oil [2].

At present, thermal recovery is the most common and successful method for heavy oil exploitation at domestic and abroad [3]. The application of heavy oil viscosity reducer is also very active [4-7], and it plays an important role in heavy oil exploitation and transportation. Thermal recovery is mainly to reduce the viscosity of heavy oil by heating to increase its fluidity. In the absence of bottom water and thick oil layer, thermal recovery technology is very effective, and the recovery rate is very high. However, after the thermal recovery, the remaining oil layer thickness is less than 10m or the depth is higher than 1km and the reservoir with bottom water in the oil layer, the heat will lose a lot during the process of transportation and heating the crude oil, and the heating will not reduce the viscosity. The application of thermal recovery technology in this case is limited [8], and it is generally considered to further improve the recovery of heavy oil reservoirs by means of cold recovery. Cold recovery is the use of physical or chemical methods that do not involve temperature rise (such as the addition of appropriate chemical reagents) to improve the fluidity of heavy oil, utilizing reservoir characteristics and appropriate process to achieve the purpose of viscosity reduction exploitation [9].

Chemical flooding is a common method for cold recovery of normal heavy oil. It refers to the ability to increase the oil displacement or sweep ability by injecting a solution containing chemical agents into the reservoir, so that the recovery rate can be further improved on the basis of water flooding. Common chemical flooding methods include: polymer flooding, alkali flooding, viscosity



reducer flooding and composite flooding [10]. Polymer flooding is the process of exploiting crude oil by utilizing their own viscoelasticity of the polymer solution to exploit crude oil during the flow process, thereby enhancing oil recovery. The viscosity of the polymer solution is high, which reduces the oil-water mobility ratio, thereby increasing the swept area and enhancing the oil recovery. Alkali flooding is achieved by injecting an alkaline agent into the reservoir, which reacts with acidic components of the crude oil, such as petroleum sulfonic acid, to form a petroleum sulfonate surfactant, which is then acted upon by the surfactant to enhance the recovery. Viscosity reducer flooding refers to the emulsification and deformation of heavy oil by reducing the interfacial tension and softening the interface film, and at the same time forming O/W emulsion, which reduces the viscosity and flow resistance of the heavy oil and achieves the purpose of enhancing oil recovery. However, a large amount of remaining oil may still exist after a single chemical flooding, and the recovery rate is not very ideal. In order to further improve oil recovery, it is hoped that the effects of various single drives can be integrated to develop a method of composite flooding.

Viscosity reducer flooding is one of the most effective methods for exploiting heavy oil at present, and screening out excellent viscosity reducer can greatly improve heavy oil recovery.

2. Outline of Heavy Oil Emulsified Viscosity Reduction Technology

Heavy oil emulsified viscosity reduction is to mix a certain concentration of surfactant solution with heavy oil at a certain temperature, making the high viscosity heavy oil is dispersed in the active water as oil droplets to form low viscosity O/W emulsion. This emulsion can fundamentally improve the rheological property of heavy oil and greatly reduce the flow resistance of crude oil.

Heavy oil emulsified viscosity reduction technology began in the 1960s, Simon and Poynter injected surfactant into the wellbore to convert high-viscosity crude oil from W/O to O/W emulsion, thereby improving oil recovery efficiency and reducing pipe resistance [11]. The technology is to inject a surfactant solution into the bottom of the well to form low viscosity O/W emulsion with heavy oil, thereby reducing the oil-water mobility ratio, changing the surface wettability of the formation rock, and also solving oil blockage in the near-well zone. It can be used for both cold recovery and thermal recovery at different stages of steam injection.

California had also established an industrial pipeline with surfactant to emulsify and transport high-viscosity crude oil [12]. The Orinoco zone in Venezuela is the largest heavy oil gathering belt in the world. Adding all the reserves of the Orinoco region in Venezuela, Venezuela become the second largest oil storage country in the world after Saudi Arabia. The Venezuelan heavy crude oil has a high content of colloid and asphaltene, and viscosity is very high. Reducing viscosity by adding light crude oil dilution and heating to the refinery, but the transportation costs is very high. Therefore, the subsequent processing and transportation of this heavy oil limits its development. In the mid-1980s, PDVSA abandoned its plan to supplied the heavy oil to the refinery, and in turn, the heavy oil was added to 30% water and surfactant (about 0.3%) to prepare to form stable O/W emulsion. This emulsion, known as Ormulson, was piped to coastal areas and sold worldwide as a boiler fuel [13]. The emulsification treatment of the heavy oil is simple and low in cost, the product is stable, and the transportation is easy, which promotes the development of the oil field. Its products are sold to Denmark, the United Kingdom, Canada, Japan and other countries. Since 1990, Bitor's Ormulson has been exported to more than 1000×10^4 t. The company plans to rise to 1200×10^4 t in 2000. They also saw great potential in the Chinese market [14]. Foreign countries have achieved great results in the exploitation and transportation of heavy oil by emulsification and reducing viscosity, which has produced good economic and social benefits.

Zhao Fulin believes that because crude oil contains natural emulsifiers (colloids, asphaltenes, naphthenic acids, porphyrins), water-containing crude oil is easy to form W/O emulsion, which makes the viscosity of crude oil increase sharply. However, the viscosity of the O/W emulsion is mainly determined by the viscosity of the external phase water. The viscosity of the water is very small, only 0.55 mPa·s at 50°C, which is much lower than the viscosity of the crude oil, and the higher the water

cut, the smaller the viscosity of the W/O emulsion is. Therefore, if we can try to convert the W/O emulsion into O/W emulsion, the viscosity of the heavy oil will be greatly reduced [15].

The exploitation of heavy oil in China had achieved remarkable achievements after more than ten years of development. At present, the scale of heavy oil exploitation is large, industrial production technology is becoming more and more mature, and emulsified viscosity reduction technology has been widely used in heavy oil exploitation, and becoming an important method for heavy oil exploitation.

3. Theoretical Analysis of Heavy Oil Emulsified Viscosity Reduction

The mechanism of heavy oil emulsified viscosity reduction can be understood from two aspects [16]: First, the contact of the surfactant solution with the heavy oil can reduce the interfacial tension between the oil and water, so after stirring at a certain temperature, the oil is dispersed in the surfactant solution as granule to form O/W emulsion. The surfactant molecules are adsorbed around the oil droplets to form directional monomolecular protective film, which prevents the oil droplets from re-polymerizing, and can reduce the friction of the liquid flow on the pipe wall and the intermolecular internal friction during the flow of the emulsion. Second, due to the wetting action of the surfactant solution, the flow resistance is significantly reduced, that is, a layer of surfactant solution water film is adsorbed on the pipe wall, so that the friction between the crude oil and the pipe wall becomes the friction between the surfactant solution and the pipe wall, and the flow resistance is significantly reduced. The two theories of heavy oil emulsified viscosity reduction are as follows.

3.1. Crude oil emulsion theory

Since the crude oil contains natural emulsifiers (colloids, asphaltenes, etc.) when the crude oil contains water, it is easy to form W/O emulsion, which causes the viscosity of the crude oil to increase sharply. The viscosity of the crude oil emulsion can be expressed by the Richardson formula [17]:

$$\mu = \mu_o e^{\kappa \psi} \quad (1)$$

Where : μ -- is the viscosity of the emulsion;

μ_o --the viscosity of the external phase;

ψ -- the volume fraction of the internal phase;

κ -- is a constant, depending on ψ , κ is 7 when $\psi \leq 0.74$, and κ is 8 when $\psi \geq 0.74$.

It can be seen from the above formula: (1) The viscosity of the O/W emulsion is only related to the viscosity of the water (very low, 0.55 mPa·s at 50°C), regardless of the viscosity of the oil. This is because the water is in a continuous state and the oil is in a dispersed state. And the viscosity of the emulsion increases in index as the volume fraction of the oil in the emulsion increases, that is, the viscosity of the emulsion is greatly affected by the volume fraction of the oil in the emulsion; (2) For W/O emulsions, the viscosity is proportional to the viscosity of the oil, and it index related to the volume fraction of water in the emulsion, that is, the higher the water cut, the higher the viscosity.

Since the viscosity of the external phase water is much smaller than the viscosity of the oil, the viscosity of the O/W emulsion is much smaller than the viscosity of the W/O emulsion, regardless of the viscosity of the crude oil itself. For the W/O emulsion that has already formed, try to break it down. For heavy oil that does not contain water, active water is added to form O/W emulsion.

3.2. Optimal density packing theory

According to optimal density packing principle for solid geometry [18]: For crude oil, stable W/O emulsion should be formed when the water content is less than 25.98%, and stable O/W emulsion should be formed when the water content is more than 74.02%, which is unstable in the range of 25.98%-74.02% can form W/O emulsion, can also form O/W emulsion. Zhou Fengshan of Peking University [19] called the unstable zone Similar to Emulsion. However, since the crude oil has natural W/O emulsifier, so W/O unilateral emulsion is generally formed, so that the viscosity of the crude oil is greatly increased. Emulsified viscosity reduction is adding a surfactant or using the surfactant formed by organic acid that contained in heavy oil and alkali. Its activity is greater than the activity of

the natural emulsifier in the crude oil, so that the W/O emulsion is converted into the O/W emulsion, thereby achieving the purpose of viscosity reduction. Yu Xiaoming [20] found the viscosity of O/W emulsion is very low by comparing the micrographs of heavy oil before and after emulsification, where the oil is the dispersed phase and the water is the continuous phase.

The heavy oil emulsified viscosity reducer not only forms stable O/W emulsion to reduce viscosity, but also penetrates and disperses into the colloidal and asphaltene flaky molecules by hydrogen bonding, and breaking up aggregates by plane overlap stacking. Forming lamellar molecules without random stacking, the degree of ordering is reduced, the spatial extension is reduced, the number of colloidal and asphaltene molecules contained in the aggregates is reduced, the cohesive force of the crude oil is reduced, which acts as viscosity reduction. Li Meirong's research [21] indicates that the main mechanism of viscosity reduction of heavy oil is the reduction of aggregate order.

4. Screening of Surfactants for Heavy Oil Emulsified Viscosity Reduction

On the one hand, a good performance emulsifier needs to have good viscosity reducing effect (emulsifying the oil-water mixed system into O/W emulsion), on the other hand, it needs better emulsion stability and demulsifiability [22]. Adaptation to the formation and economy are also factors to consider.

4.1. HLB value of the surfactant

In order to ensure the successful implementation of the heavy oil emulsified viscosity reduction exploitation, it is required to use emulsifier with larger HLB value. Generally, the HLB value is required to be between 7 and 18, which is more beneficial to form O/W emulsion.

4.2. Emulsion stability

The emulsion stability of the emulsion under different conditions and the easy demulsification of the crude oil in the dehydration treatment of the ground must be ensured. The so-called emulsion stability means that the emulsion is guaranteed not to break the emulsion during the exploiting process, and always keeps the water as the external phase and flows at a low viscosity. In the case of dehydration and demulsification, it is best not to add demulsifier, as long as heating can be broken.

4.3. Molecular structure of surfactant

It is required that the oleophilic chain of the emulsifier should not be too long and without branching, which is beneficial to form O/W emulsion and stabilize emulsion. And it is preferable to use homopolyether with polyoxyethylene chain in molecular structure or block copolyether type nonionic surfactant with polyoxypropylene chain and polyoxyethylene chain, but also consider the effect of the length of polyoxyethylene chain on its emulsion stability [23].

4.4. Good formation adaptability and compatibility

Adaptability mainly considers formation temperature and its adsorption loss. If polyoxyethylene type nonionic surfactant is used as emulsifier, its cloud point must be higher than the formation temperature, otherwise it will form W/O emulsion, but it will not form O/W emulsion, and it will also cause the addition of formation adsorption; If ionic surfactant is used, although the formation temperature (referring to the high temperature formation) is not as sensitive as the nonionic surfactant, it has poor water solubility at low temperatures and a large adsorption loss to the formation [24].

4.5. Low cost and good effect

In order to achieve this, two or more emulsifiers are often compounded to reduce the amount, reducing the cost and improving the efficiency.

Due to the differences in crude oil composition, characteristics, oil-water ratio, salinity and geological conditions in various regions, the emulsified viscosity reducer used is also different.

5. Microscopic mechanism of emulsified viscosity reducer flooding

5.1. Large oil droplet deformation re-transfer flooding

The viscosity reducer has a strong ability to lower the interfacial tension and the ability to soften the interface film. The oil droplets in the pores are pulled and deformed by the viscosity reducer, and flow along the narrower throat as the viscosity reducer flows.

5.2. Emulsification flooding

The emulsification of the viscosity reducer emulsifies the heavy oil into smaller oil droplets, forming a large amount of O/W emulsion, which can enter the small pores that could not be entered. The O/W emulsion formed with the viscosity reducer forward moves and reduces the flow resistance of large heavy oil.

5.3. Stripping heavy oil flooding

There are two main forms of stripping the remaining oil: First, the push-pull effect of the dispersed oil droplets will reduce the oil film, which is the main form. In addition, the viscosity reducer will also be driven by wire drawing. The emulsion moves forward under the driving of the viscosity reducer, which will promote the nearby oil film during the advancement. At the same time, under the emulsification, the oil film partially pushed will form small oil droplets, and the oil film will be stripped. This is repeated, and the viscosity reducer can effectively improve the oil displacement efficiency.

As the amount of viscosity reducer is gradually increased, the viscosity reducer concentration is also gradually increased. The oil-water interfacial tension is further reduced, and the oil film in the pores will continue to deform under the action of the viscosity reducer. Some oil film is pulled into a slender oil thread, and as the viscosity reducer flows and passes through the narrow throat to continue to move forward.

6. Conclusions

The content of colloid and asphaltene in heavy oil is relatively high and the viscosity is large, so the exploitation of heavy oil is much more difficult than ordinary oil. Under the situation of increasing global energy demand, it is particularly important to develop heavy oil resources and study scientific and economic heavy oil exploitation methods. The heavy oil emulsified viscosity reduction technology is technically feasible and economically reasonable, so this method can be used as one of the important methods for heavy oil exploitation. Although the development and application of heavy oil emulsified viscosity reducer have made great progress at domestic and abroad, the following aspects are still the focus of current and future attention.

(1) Study the effect of the composition of heavy oil on the emulsified viscosity reduction result and the relationship between the structure and properties of the emulsified viscosity reducer. The selectivity of viscosity reducer to heavy oil should be reduced, and the general adaptability of viscosity reducer should be enhanced.

(2) The development of emulsified viscosity reducer which is easy to break and dehydrate, and good in function and low in cost is still the main direction of future development.

(3) Always grasp the dose of the injecting viscosity reducer and the timing of the injection, controlling the damage of the viscosity reducer to the formation, and the effect of temperature and viscosity on the demulsification of the crude oil.

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