LECTURE 6
PHYSYCAL AND CHEMICAL EOR METHODS

Physico-chemical methods provide increasing displacement and sweep efficiency simultaneously or one of them. Among them there are two subgroups:

a) *methods that improve* water flooding based on reducing the interfacial tension and change in phases mobility ratios and providing an increase displacement and sweep efficiency;

b) *methods of residual oil recovery* from watered layers, that are based on full or partial change of working agents miscibility with oil and water.

PHYSICAL AND CHEMICAL EOR METHODS DURING FLOODING

This group of methods is based largely on changing mobility ratio of oil and water. As a result sweep efficiency increases simultaneously. The oil recovery factor increases slightly. Implementation of these methods has the greatest effect at the early stages of fields development as well as in the fields, where the high water cut combined with low oil recovery is observed.

The EOR methods during flooding include the methods that result in water mobility decreasing in the area of its motion, and the methods that are related to the change in the rock-oil-water system wettability and leads to a stimulation of the capillary imbibition process. These include:

- surfactant solutions flooding ;
- polymer flooding;
- alkaline and acid flooding.

Sometimes they include the use of foams, emulsions and gas-water mixtures.

1.*Oil displacement by aqueous surfactant solutions*

The method is based on the ability of surfactants to reduce the interfacial tension at the oil-water interface, change oil-water-rock surface wettability and properties of adsorption layers that are formed at the oil-water and oil-rock surface interfaces. It uses diluted non-ionic surfactant solutions.

It is recommend to use in heterogeneous reservoir, which can content bypassed oil.

Interfacial tension on the surface of the interface between the oil and aqueous surfactant solutions of this type at their concentration in them of 0.05 - 0.5% decreases from 25 - 45 to 4 – 7 mN/m.

Volumes of injected surfactants solution should be large (at least 2-3 pore volumes). Surfactants front moves through reservoir by 10 ... 20 times slower than the oil by water displacement front.

Surfactant aqueous solutions of concentration 0.05 - 0.1% at the initial oil saturation can displace up to 5 - 7% of oil.

One of the important properties of surfactants, which determine their low efficiency in oil displacement, is the ability to adsorb at the boundary of the phase separation. As a result, there is a backlog of the surfactant solution front with a working concentration below the displacement front, so that the surfactant solution actually acts on motinless residual oil. And bearing in mind that with the mentioned above (or even less) interfacial tension, the surfactant solution cannot transfer the residual oil to the mobile state, one should not expect a significant effect of the solutions of these surfactants on oil displacement efficiency in the homogeneous formation. However, in a non-homogeneous reservoir where by-pass oil can be revealed, a decrease in the interfacial tension can contribute to the displacement of oil.

The volumes of injected surfactant injection solutions should be very large (at least 2-3 pore volumes). The SAS front is moving 10 to 20 times slower than the oil displacement front with water.

Aqueous solutions of surfactants with a concentration of 0.05 - 0.1% at the initial oil saturation of the reservoirs can displace up to 5 - 7% of oil. The displacement of oil by surfactant solutions of the same concentration from the reservoirs, which have already been pumped water, reduces the efficiency of their application; reservoir models from fully flushed, only 2% of the oil could be displaced.

High temperatures and high content of salts with alkaline-earth element have a significant effect on the efficiency of oil displacement by surfactant solutions.

The future of the method mainly relates to the treatment of bottomhole areas of injection wells to increase their acceptability, by injecting low-concentrated (0.05-0.5%) and highly concentrated (1-5%) solutions for the development of dense clay reservoirs and injection pressure decrease, as well as the creation of surfactant compositions that provide a significant reduction in the interfacial tension to 0.01 ... 0.05 mN/m.

Proper selection of surfactants for the conditions of a particular field requires laborious laboratory studies. Along with the usual test of the compatibility of surfactants with formation and pumped water, turbidity temperatures, adsorption, the study of surfactant surface activity, more precisely, determination of conditions under which the achievement of a particular composite system of ultra-low phase tension is ensured.

As a result of studies with homologous series of surfactants it was found that the region of ultra-low tensions exists in a rather narrow range of water mineralization, the composition of the hydrocarbon phase (oil), equivalent weight - for anionic surfactants and the length of oxyethylene chains for nonionic oxygen surfactants or their derivatives at some fixed length of alkylradical.

In the USA, the concept of equivalent alkane hydrocarbon numbers (EAHNs) has been developed for the correct selection of surfactants. According to this concept, developed, as it is stated, on the basis of more than 100 thousand measurements, each oil should be assigned its EAHNs, that is, its behavior when measuring the interfacial tension can be accurately modeled by the pure normal hydrocarbon, the length of which is a hydrocarbon chain for any EAHNs oil. The EFSA of oil, in its turn, is calculated from the results of the measurement of the interfacial tension of mixtures of this oil with pure hydrocarbons, for which the EAHNs is known, at the border with a solution of well-studied surfactant, taken as a standard under strictly specified conditions. Thus, if the EAHNs of this oil is known, then the selection of surfactants can be limited to the results of measurements of the interfacial tension of their solutions at the border with the hydrocarbon that simulates the oil.

Another technique, which is considered simpler and does not require pre-determination of EAHNs oil, is the technique of determining the minimum of interfacial tension for an oil-reservoir system developed in Germany. This technique is based on the use of advanced spinning drop tensiometry, which allows you to quickly determine the dependence of the interfacial tension on the temperature and set the temperature at which the minimum tension is reached.

Both methods proceed from the fact that when selecting surfactants have a homologous series of surfactant samples, inside which is the product that is most suitable for a particular system of oil - water.

Studies conducted at the Institute of Deep Drilling and Oil Production of Germany by the displacement of tertiary oil by carboxymethylated oxyethylated alcohols have shown that even in low interfacial tension, good displacement of residual oil is achieved only at a temperature above a certain threshold. This temperature was slightly below the temperature at which the system exhibits a pronounced minimum of interfacial tension. The temperature at which the inversion of emulsions occurs is called the "Phase Inversion Temperature" (PIF). Further studies conducted in Germany on crude oil - reservoir water - surfactant systems showed a fairly clear correlation between the TIF of artificially prepared crude oil - reservoir water emulsions and the refractive power of the surfactants studied. The TIF of these emulsions was determined by their electrical conductivity.

2. *Polymer flooding*

World and domestic experience shows that gel-forming water-insulating formulations based on low-concentration aqueous solutions of various chemical products are highly effective in equalizing the profile of water injection wells and limiting the movement of water in highly permeable and well-washed layers. They are able to selectively filter in the flooded intervals of high-permeabl layers, flushed zone, creating artificial screens that resist the movement of the pumped water. Gel compositions can also be injected into the producing wells to create barriers to water filtration and limit the production of associated water. The radii of the created screens and barriers depend on the specific volumes of injected aqueous solutions of gel-forming reagents per unit thickness of the layer, as well as the technology of their injection. The volume of solutions and the technology of their injection should be chosen on the basis of a careful study of the nature of the heterogeneity of layers, their hydrodynamic interrelation and the degree of washing individual layers, etc.

The method is based on the ability of dissolved in water high chemicals polymers, even in small concentrations significantly increase water viscosity, reduce water mobility and thereby improve sweep efficiency.

When the concentration of the solution equal 0.01 - 0.1% its viscosity increases to 3 - 4 mPa*s. This leads to a significant reduction of oil and water viscosity ratio in the reservoir and the suppression of water breakthrough.

During polymer solutions flowing through porous media its viscosity can be reduced even more. That why, the polymer solution most suitable for using in heterogeneous layers and are applied in the case of high oil viscosity in order to increase sweep efficiency.

It is recommended to fringe polymer solution of 0,1 ... 0,5 pore volume with polymer concentration of 0.01 ... 0.1%.

Additional oil recovery after polymer flooding can grow in 7 - 8%, and the specific additional oil production is 200 - 300 t/t of polymer.

Polyacrylamide (PAA) gel is not technologically applicable (requires higher manual labor costs, higher transportation costs, freezes at freezing temperatures). A solution with a concentration of 0.6 ... 0.7% of such PAA can be obtained by recirculation with pumps, and metered supply to the drainage system is performed by plunger pumps. Preferred is a powdered polymer. UDPP-1,5; UDPP-5; UDPP-200 equipment was developed for the forming the powder solution.

This method is expensive, so the prospects for its use depend on the price of oil, the scope of cheap polymers production and the effective combination with other methods of increasing oil recovery.

In addition, polymer solutions with high viscosity better displace not only oil but also reservoir water, so they interact with the skeleton of the rock and the cementing substance. This causes the adsorption of polymer molecules that block the channels or worsen the filtration of water in them. But on the front of the displacement a shaft of inactive water is formed. These two factors lead to a decrease in the dynamic heterogeneity of fluid flows and, as a consequence, to an increase in the coverage of layers by flooding.

Polymer solutions are known to possess viscoplastic (non-Newtonian) properties, so that their filtration is only possible after overcoming the initial shear gradient and may improve or deteriorate depending on the filtration rate and molecular weight of the polymer.

One of the effective methods of exposure for deep treatment of the reservoir is the process of selective isolation of water channels by water-insulating compositions based on sodium silicate, tested and implemented on flooded oil reservoirs.

The mechanical strength of the gel is increased by the introduction of special additives in silicate solutions, which allows to maintain the tamping effect of the waterproofing layer in the flooded areas with very large depression (up to 20-25 MPa). Such additives include polymers, using which intermolecular bonds are formed between the pore walls and the surface of the sediment, which contributes to the stability of the layer and its strength.

3. *Alkaline water flooding*

The term *alkaline flooding* implies injection into the reservoir of reagents, solvents which are alkaline.

Concentration of solutions is preferably equal to 0.05 - 5%, and in some cases it can reach up to 25 - 30%.

The most strong alkaline reaction has the solutions *NaOH* and Na_2SiO_3 . These substances are recommended as basic reagents to enhance oil recovery. They both actively interact with acidic components of oil, heavy ions that water can contain (reservoir and injected), rock collector.

Application of alkaline action is based on the interaction of alkaline liquids (reservoir and injected) and the reservoir rock, which results in a change of the surface characteristics of the system oil-water-rock and consequently conditions of oil displacement by water.

The basis of these factors is the reaction of neutralization of the acid components of the oil with the formation of salts of alkali metals, which is surfactant. The formation of surfactants is accompanied by adsorption-desorption processes and mass transfer of the interaction products from the oil phase to the aqueous.

The decrease in interfacial tension occurs in a range of alkali concentrations, which is characteristic or each oil. Moreover, the presence of divalent in the water metals increases the minimum value of interfacial tension, and the presence of sodium chloride to 2% reduces it.

Any changes in the surface quantities (and especially the interfacial tension) over time are only caused by adsorption. The equilibrium time depends primarily on the size of the molecules or colloidal particles.

The best results are obtained by the use of alkaline flooding in the fields with highly active oils (organic acid content exceeds 2.5 mg KOH/g).

4. *Acids application*

The method of sulfuric acid injection (sulfuric acid flooding) is based on the formation of acid tar (viscous resinous mass) in watered zone (most significant factor) and surface active water-soluble sulfonic acids. As a result, water permeability of washed areas reduced, increases sweep efficiency and interfacial tension decreases (up to 3 ... 4 mN/m).

Either technical sulfuric acid with concentration of 96%, or so-called alkylated sulfuric acid (ASA) with concentration of 80 ... 85% (waste of sulfuric acid products of high gasoline) is used.

Use either technical sulfuric acid with a concentration of up to 96%, or so-called alkylated sulfuric acid (ASA) with a concentration of 80 ... 85% (sulfuric acid waste from the production of high-octane gasoline).

The technology of the method is to inject into the formation a small amount of sulfuric acid slug (about 0.15%) pore volume of the layer, which is pushed by water through the layer. For this purpose tanks with alkylated sulfiric acid (500…2000 m^3) are installed near an injection well. Then this acid is pumped into the reservoir and the well is connected to a common flooding system for further water injection.

The application of the method is accompanied by severe corrosion of the operating equipment and the well production string.

5. *Emulsions and foams application*

The usage of foams and emulsions during flooding reduces water mobility, which displaces the oil, thus changing the direction of water flow. The main result of foam injection in washed porous medium is a significant water permeability decrease. Only in the case of surfactants mixture usage, which lowe interfacial tension at the oil-water interface to very low values, foam injection in porous media can resulting residual oil displacement.

EOR by using oil emulsions in a solution of alkali or in diluted surfactant solution is also based on achieving uniformity promotion of displacement front through creation increased resistant in zones where water has the greatest mobility.

In recent decades abroad the widely used technology for the use of NAPAR in the form of microemulsions, which envisages "medium-phase" systems that can exist as a separate phase in contact with oil and water, while having a relatively low interfacial tension at the boundary with these phases. The type of emulsion is determined by the type of surfactant, with the predominance of the hydrophilic part leads to the formation of emulsions "oil in water", and with the predominance of the hydrophobic part - "water in oil". If the surfactant differs in its HLB value, the sodetergent - in its hydrophobic-hydrophilic character, then with the decrease of the hydrophilicity of the sodetergent the equilibrium is shifted to such extent that the type I system (according to Vincor) becomes a type II system (Vincor). In the formation of medium-phase microemulsions (type III according to Vinsor) when surfactants and sodetergent, the values of HLB and hydrophilicity which lie between the same values as for types I and III. If this is type I, then either the surfactant has too high a HLB value or the co-detergent is too hydrophilic. It should be noted that the real system has only three variables parameters of influence:

1 - type of surfactant;

2 - type of co-detergent;

3 - the ratio in the mixture of surfactants – co-detergent.

Determination of the stability of emulsions formed near the boundaries of the middle phase, showed that in HLB, slightly beyond the scope of medium-phase systems, stable microemulsions of the type "oil in water" are formed, with HLB above the values corresponding to the upper limit of the third phase, - water-in-oil emulsions.

Having obtained the optimum HLB value, it is possible to calculate the necessary degree of oxyethylation and also adjust the composition of the water phase (electrolytes and alcohol) for compensation for the deviation of the HLB surfactant from the required value. For example, the addition of isopentanol shifts the HLB towards greater hydrophobicity, which allows to achieve the optimal HLB at higher than necessary degrees of oxyethylation. Low molecular weight alcohols (isoprene-Pilov and secondary butyl) act in the opposite way, but the HLB shift in this case is an order of magnitude lower and can play a significant role only at high concentrations. Electrolytes act similarly to high molecular weight alcohols, shifting the balance toward greater hydrophobicity and thus necessitating the use of surfactants with a higher degree of oxyethylation to achieve the optimum HLB value.

More complicated is the effect of surfactant concentration. It was found that, in contrast to APAR, increasing the concentration on HLB of NAPAR leads to the hydrophobization of the system and, accordingly to, the need of increasing the degree of oxyethylation for achieving optimal HLB. The dependence of the HLB shift shift on the surfactant concentration is nonlinear, the greatest effect the change in the concentration has at small absolute values (less than 3%), and with increasing concentration its influence on the HLB decreases.

Thus, to ensure a strong reduction of the interfacial tension and high solubilization parameters, only the exact selection of the surfactant composition for the conditions of each particular object is required.

6. ***Application of biopolymers***

It is known that the world and domestic practice of oil field development in the mode of flooding indicates that all the variety of factors affecting the final oil extraction is reduced to two parameters:

- the rate of reserves production,
- prolongation waterless (or low water) production time.

In this connection, such aspect as the use of biopolymer technologies to extend the anhydrous period of oil wells operation deserves special attention. The calculations show that preventive injection of the thickening composition should prevent from the development of premature water break through.

Currently used chemically synthesized polymer polyacrylamide has a long history application, but in its production toxic compounds and the commercial form of the polymer may contain dangerous substances for human health. Therefore, the use of natural polymers obtained by biotechnological method (polysaccharides), helps to reduce the technogenic load on the environment, as during their natural decay they do not produce contaminants.

The main property that causes the use of biopolymers in oil production technologies is their high ability to thicken, while compared with chemically synthesized polymers, biopolymers have higher rheological properties. In addition, many biopolymers are able to form gel structures with high waterproofe ability.

After injection of biopolymer solutions (biopolymeric flooding) or its gel-forming compositions in the reservoir through the injection wells flooded intervals are blocked and redistribution of the pumped water into the oil-saturated zones, which ensures the further displacement of oil from the floodplain areas takes place.

The experience of using biopolymers to increase oil recovery by creating high volume fringes (5-35% of pore volume), as well as the results of mathematical modeling of the process of polymeric (biopolymer) flooding indicate the possibility of increasing RF (growth of extracted reserves) by 5-12 % and reduction of water-oil ratio by 2-4 times. The solution to the strategic problem is to increase the RF by 3-12% and to reduce the water-oil ratio when creating high-volume fringes of biopolymer solutions.

Control questions

1. What are the two main subgroups of physico-chemical methods used in practice?
2. What is the essence of physico-chemical methods during flooding?
3. What are the varieties of physico-chemical methods for increasing oil recovery?
4. What is the method of oil displacement by aqueous solutions of surfactants?
5. What is the reason for the increase of oil recovery when using surfactants?
6. What is polymer flooding?
7. What makes oil extraction higher when using polymers?
8. What is alkaline flooding?
9. What is the reason for oil extraction increase when using alkalis?
10. What is the essence of using acids for oil recovery increase?
11. What increases the amount of oil extraction when using acids?
12. What is the use of foams and emulsions to increase oil extraction of oil deposits?
13. Why does oil extraction increase with the use of foams and emulsions?
14. What is the use of biopolymers to increase the oil extraction of oil deposits?