18 Application of Surface-Active Agents in Petroleum Production

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INTRODUCTION — ENHANCED OIL RECOVERY

About 45% of the world's energy consumption is supplied by petroleum and 20% by natural gas. The amount of reserves and the time these reserves may be used in the future have been appraised differently in the past. Though the estimated world-wide reserves of hydrocarbons are more or less a political subject, one fact is that only about 30% of the total oil in a reservoir may be recovered with conventional techniques. The improvement of oil recovery therefore may contribute to the energy supply in the future.

18.1 OIL RECOVERY MECHANISMS

The fact that most of the oil in a petroleum reservoir has to be left in the ground is due to two physical phenomena, the interfacial tension of the oil and its viscosity. In the following these are described for the case of porous sand-stone reservoirs. The same physical behavior in a slightly different way also applies to fissured reservoirs, which are often found in limestone deposits. Figure 1 shows a SEM-picture of a porous sandstone.

In Tables 1 to 3, typical examples of the composition of the three components — rock, water, and oil — that form a petroleum reservoir are given.

18.1.1 INTERFACIAL TENSION

Petroleum, which is generated over millions of years from organic matter that is buried deep in the earth, is usually trapped in underground structures formed by porous rocks. These rocks usually are sandstone or fissured limestone. The petroleum, which is produced in deep-lying source rocks,

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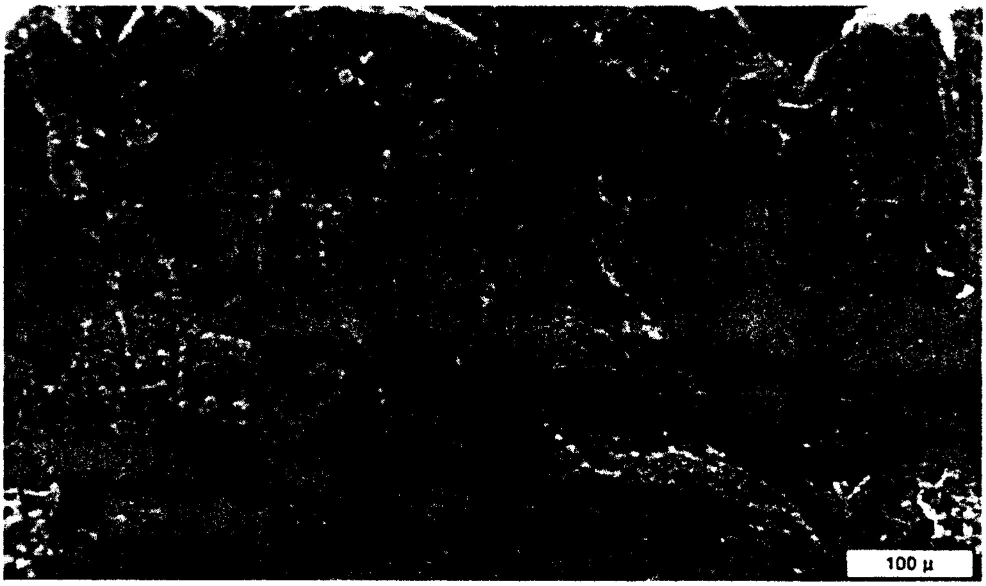


FIGURE 1 SEM picture of a typical sandstone, which is often found as an oil-bearing formation.

TABLE 1
Composition of Different Reservoir Rocks

Formation	Quartz (%)	Dolomite (%)	Mikroline (%)	K-Feldspar (%)	Kaolinite (%)	Muscovite/Illite (%)	Pyrite (%)	Chlorite (%)
Dogger-β	87	3		7	2	1		
Valanginian	82			8	5		2	3
Wealden	95		4	0.2	0.3	0.2		0.3

TABLE 2
Properties of Three Different Oils at Reservoir Conditions

Oilfield	Reservoir temperature (°C)	Density (g/cm³)	Viscosity (mPa)	Gas/Oil ratio ($m^3(V_n)/m^3$)	Isothermal compressibility (10^{-5} bar^{-1})
A	78	0.672	0.71	192	22.5
B	57	0.860	8.8	7	8.2
C	49	0.837	31	27	8.0

migrates to these structures and is trapped there, if these structures are sealed at the top. These structures then form what is called an oil field.

The production of a petroleum reservoir may be divided into different phases. The first, where oil is flowing freely from the reservoir to the production well, is the best known but in most cases also the shortest. Very early in the life of a reservoir, energy must usually be supplied to the porous medium which bears the crude oil so that it continues to flow to the producing wells. This energy is brought into the reservoir by injection of water or gas. With these secondary recovery methods, about 30 to 40% of the original oil in place may be recovered, while the rest must be left in the

TABLE 3
Analysis of Three Different Reservoir Waters

	Cations (mg/l)							Anions (mg/l)		
	Na	K	Mg	Ca	Sr	Ba	Fe	Cl	SO_4	HCO_3
A	75.800	284	1070	4910	217	5	47	126,800	204	n.a.
B	34,200	260	860	1990	28	2	18	58,700	6	n.a.
C	2300	61	5.3	48	n.a.	n.a.	2	2665	n.a.	1825

earth. In order to recover some of this oil as well, tertiary methods have been developed which are still the subject of research.

The force holding back the oil in the porous body of the reservoir rock is the interfacial tension between the different phases of oil, water, and gas flowing in the reservoir and the viscosity of the crude oil. In those cases where oil is being displaced by injected water, the interfacial tension between the oil and water and the wettability of the rock play important roles. In Figure 1, the pore space between sand grains is shown. If the rock is water wet, the flood water is imbibed into the rock and oil is displaced to producing wells. But, after a short time the situation is such that oil drops also have to displace water in order to allow the oil itself to move in the direction of the producing wells. In these cases, the capillary pressure between the oil and water has to be overcome. This means that oil has to drain water from the reservoir before it can move. As the pressure gradient in a reservoir often is smaller than the capillary pressure, these zones are bypassed by the displacing water.

As can be seen in Figure 1, the nonwetting phase (oil) has to pass small throats before it can leave the pore space. It is the diameter of these pore throats that determines the capillary pressure that has to be overcome to displace the nonwetting phase by the wetting phase.

The capillary pressure is

$$p_c = \frac{2\sigma \cdot \cos\theta}{r} \tag{1}$$

where σ = interfacial tension, θ = wetting angle, r = pore radius. If the diameter of the pores were uniform, capillary pressure differences would be zero, as is shown in Figure 2. In the case of an oil drop that is driven by water through a pore narrowing, the difference in capillary pressure is

$$\Delta p_c = 2\sigma \cdot \cos\theta \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \tag{2}$$

If we look at Figure 3, it is obvious that capillary pressure counteracts oil recovery. This means that the amount of oil that may be recovered is proportional to the pressure drop applied to the porous medium and inverse proportional to capillary pressure.

This may be expressed as:

$$1 - S_{or} \approx \frac{\Delta p}{l} \cdot \frac{r}{\sigma} \tag{3}$$

where S_{or} is the remaining oil or residual oil saturation, and r is the radius of the pore narrowing. If we want to express Equation 3 in terms of permeability and porosity, it becomes:

$$1 - S_{or} = \frac{\Delta p}{l\sigma} \sqrt{\frac{k}{\varepsilon}} \tag{4}$$

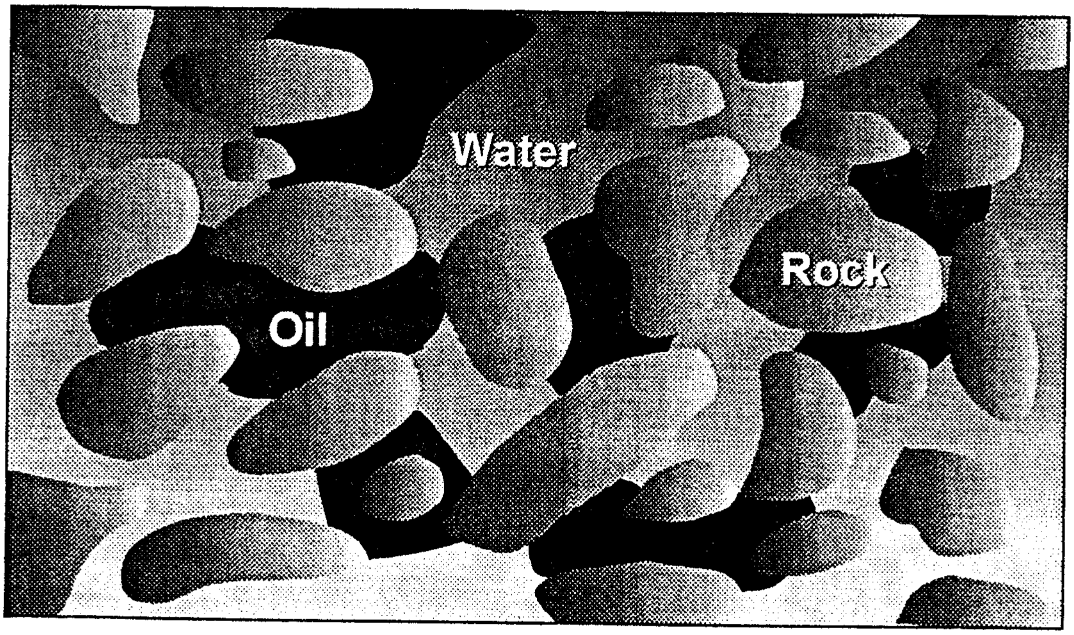
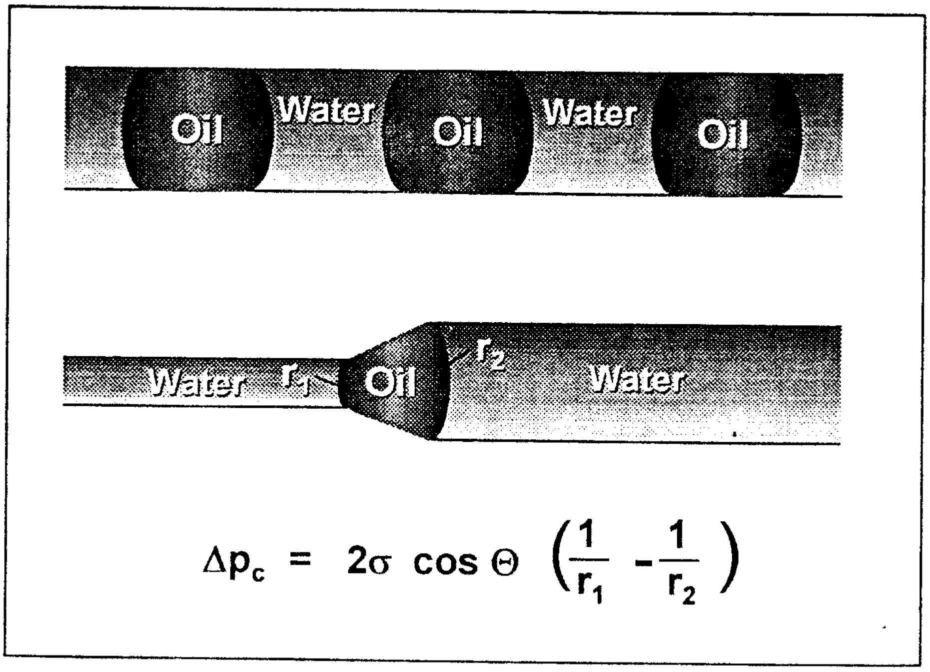


FIGURE 2 Porous medium with oil and water moving through a petroleum reservoir.



$$\Delta p_c = 2\sigma \cos\Theta \left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

FIGURE 3 Oil recovery and capillary pressure.

where k = permeability, and ε = porosity.

Taber (1968) investigated the influence of pressure drop and interfacial tension on residual oil saturation in laboratory experiments. He found that the oil recovery from a core of reservoir rock is proportional to the pressure drop across the core and capillary pressure. Some of his results are shown in Figure 4 together with results from our own experiments. Both experiments show the

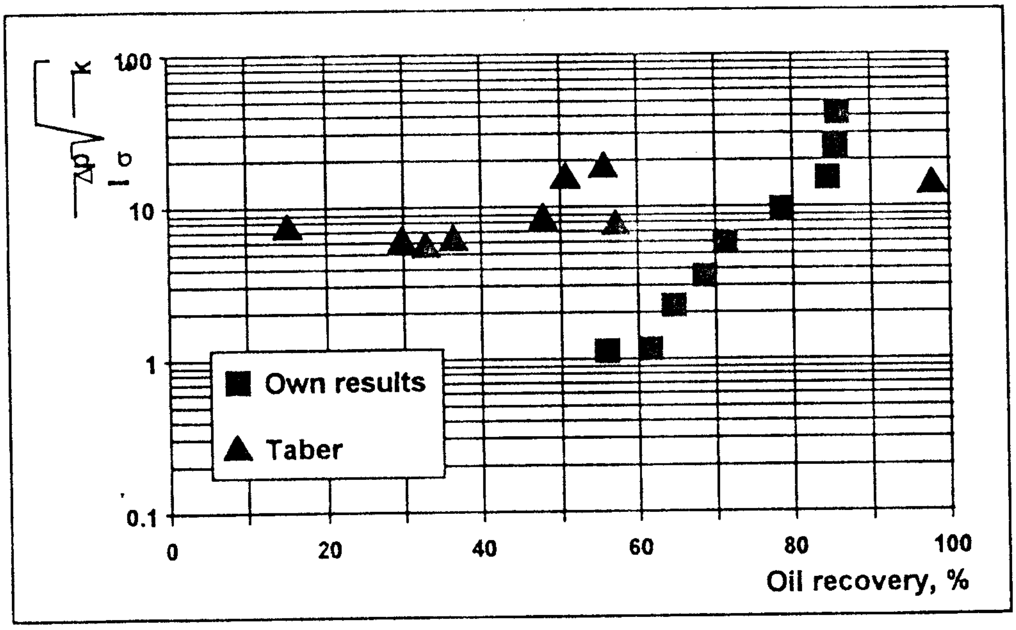


FIGURE 4 Pressure gradient reduced by σ and r vs. oil recovery.

above-described dependence of oil recovery on pressure drop. Taber's experiments were performed on a 420-mD Berea-sandstone, our own experiments on a 2000-mD sandpack. Though both series of experiments were performed on different materials and in different ways, they show similar results. As the pressure drop in an oil reservoir cannot be raised much more than is being done today, an alternative is to reduce interfacial tension in order to recover more oil by a method called surfactant flooding.

18.1.2 VISCOSITY

Another force that holds petroleum back in the pore space is viscosity. Viscosity of crude oil in a reservoir may vary between about 0.1 and 100,000 mPa·s, whereas the viscosity of water lies between 0.5 and 1.2 mPa·s, depending on temperature and salinity. Figure 5 shows the dependence of oil recovery on the viscosity ratio between oil and water. It is obvious that in the case of a high-viscosity oil the tendency of the water to bypass oil-filled zones is higher, the higher the viscosity of the oil is. In order to recover more oil from a reservoir, the viscosity of the oil must be reduced or the viscosity of the flood water increased.

Reduction of oil viscosity may be achieved by increasing temperature. This can be done by the injection of hot water or steam into the reservoir. This recovery method is usually applied in the case of heavy oils, for which primary and secondary oil recovery are very low (<10%). The viscosity of these oils is above 100 mPa·s and may reach values of several thousands and more. By steam injection, the viscosity of these oils may be brought to values of about 10 to 50 mPa·s, as shown in Figure 6.

Another method to increase recovery from a reservoir is to increase the viscosity of the flood water instead of decreasing the oil viscosity. This is done by a method called polymer flooding, which will be described below.

18.2 SURFACTANT FLOODING

Surfactant flooding means that surface-active agents are added to the oil/water system to reduce the interfacial tension. Oil/water interfacial tension may be reduced by these surfactants from 20

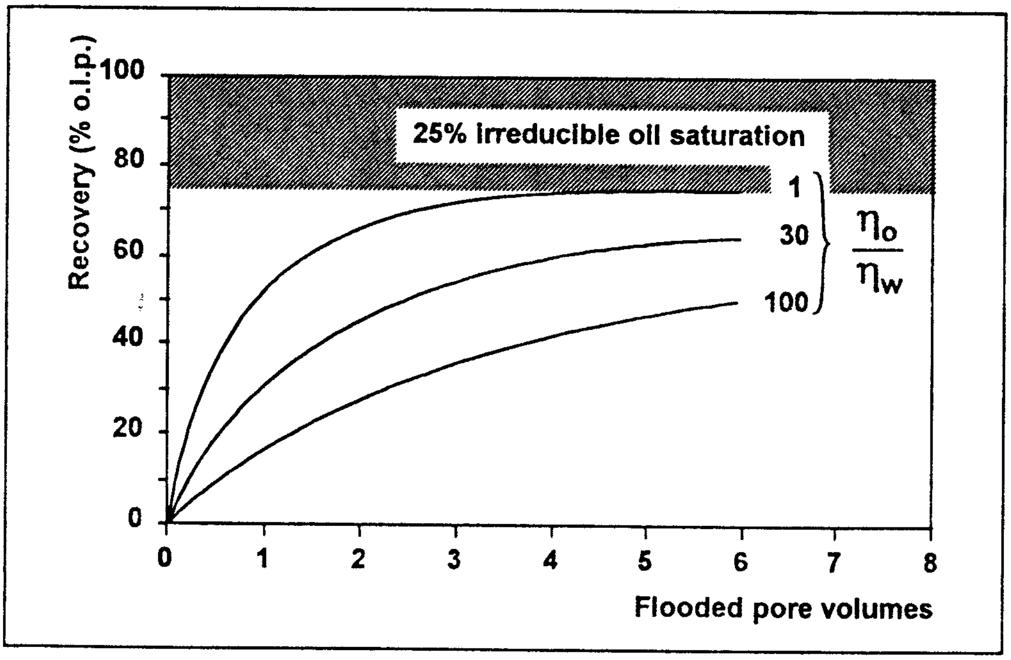


FIGURE 5 Influence of viscosity ratio on oil recovery process according to Tunn (1974).

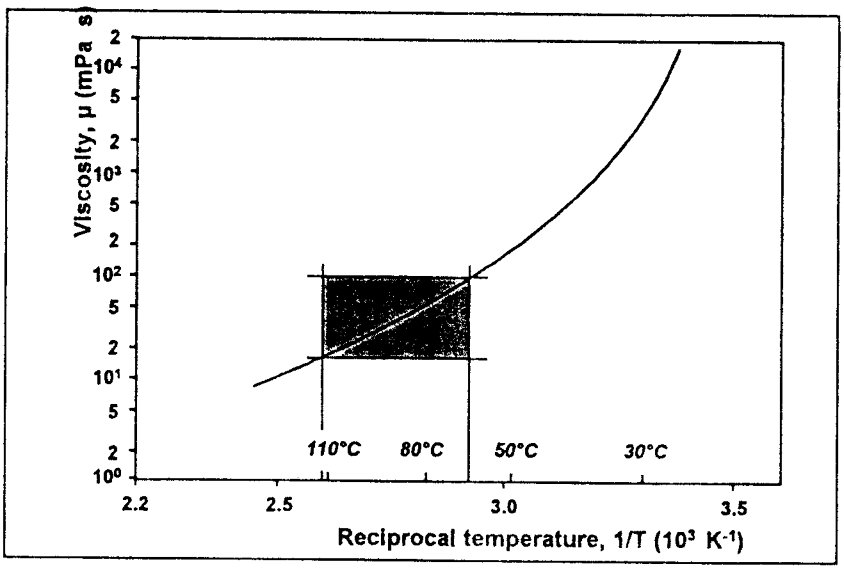


FIGURE 6 Viscosity of a heavy oil as a function of temperature.

to 10^{-4}–10^{-5} mN/m. This seems to be a very easy method to recover more oil from petroleum reservoirs. There are many chemicals that reduce interfacial tension between oil and water, and these chemicals can be produced in significant amounts at relatively low prices. But there are some adverse conditions that prevent this technique from being successful in practice. The environment in an oil reservoir is often such that surfactants cannot develop a reduction in interfacial tension as simply as described above.

TABLE 4
Surfactants Used in Enhanced Oil Recovery

Hydrophobic Part	Intermediate	Hydrophilic Part	Counter-ions
Isooctylphenolic	Ethyleneoxide	Carboxylate	Alcaline
Dodecylphenolic	Propylenoxide	Sulfate	Amine
Dinonylphenolic	Ethylene-propylenoxide	Sulfonate	Quartz
Naphten acid			
Fatty acid			

One aspect is that temperatures in oil reservoirs are relatively high (70 to 130°C), and the water in these reservoirs is very salty — salinities up to the solubility limit are often encountered. Also, reservoirs usually contain, besides quartz sand, significant amounts of clay minerals (Figure 1). As the name of these substances indicates, they are surface active, which means that they strongly adsorb at the rock surface.

18.2.1 SURFACTANTS PROPOSED FOR ENHANCED OIL RECOVERY

In order to reduce interfacial tension between water and oil, surfactants of various compositions have been tested, and additional surfactants have been developed. In Table 4 various surfactants are listed. Depending on the oil properties, the salinity of the reservoir brine, and the temperature, the surfactants are taylor-made using components as listed in Table 4.

18.2.2 APPLICATION OF SURFACTANTS

Many surfactants have been tested, and numerous laboratory experiments have been performed. The main reason why this recovery method is not applied at the moment is, besides some technical difficulties, the economics of the process. The amount of substance that has to be applied is quite high, as shown in Figure 7. In order to recover about 50% of the residual oil — i.e., 0.25 m^3 of oil — about 25 to 50 kg of surfactants are needed. This means that about 100 to 200 kg of chemicals are needed to recover 1 m^3 of oil. In oil field units, this means that at least 16 kg of chemicals are needed to recover 1 bbl of oil. If 1 kg of surfactant would cost about $3 (U.S.), the chemical cost for 1 bbl of oil would be $32, which is twice as much as today's oil price.

In a situation when oil prices are very low, no efforts are made to recover more oil from the resources, though technically it would be possible. So, about 70% of the oil will not be recovered and will probably be lost for the future.

18.3 POLYMER FLOODING

Flooding petroleum reservoirs with water-soluble polymers may be regarded as the most economic tertiary chemical oil recovery method, but this method also is hardly economic considering the current oil price situation. The polymers used and the main recovery mechanism of polymer flooding is described briefly in the following.

18.3.1 POLYMERS FOR ENHANCED OIL RECOVERY

Polymers for enhanced oil recovery should be water soluble, should develop high viscosity, and should not plug the reservoir during injection. Further, they should not be degraded by temperature or bacteria and should not precipitate in high-salinity reservoir waters. The water-soluble polyacrylamide can only be used in freshwater systems, whereas polysaccharides such as hydroxyethylcellulose or xanthan develop enough viscosity in high-salinity brines.

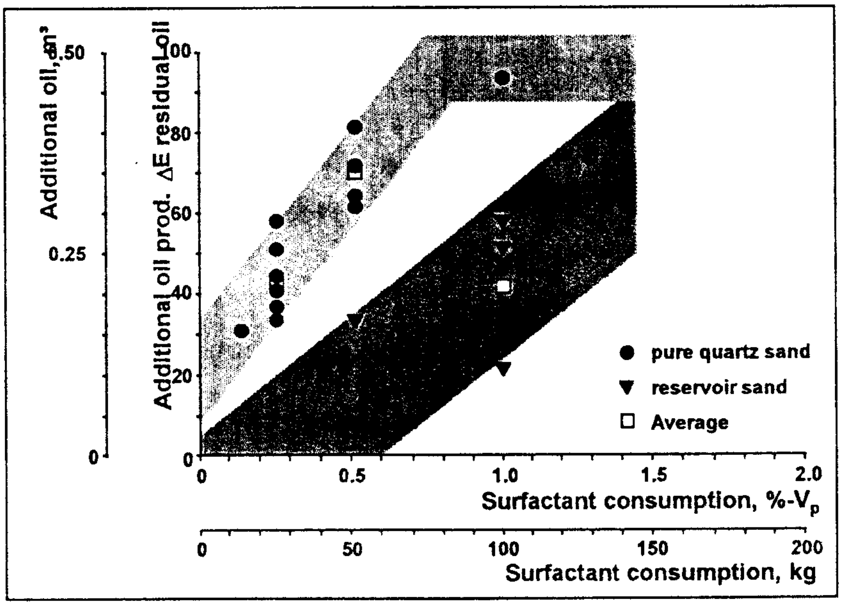


FIGURE 7 Amount of surfactant required for additional oil recovery, determined in various laboratory flood experiments.

The main problems of using these chemicals in enhanced oil recovery are the stability in the reservoir and the adsorption of the polymers on the reservoir rock. This means that the polymers should develop the desired viscosity throughout the entire flood process.

18.3.2 MECHANISM OF POLYMER FLOODING

As shown in Figure 5, in a linear displacement experiment the oil recovery depends on the viscosity ratio between the displaced and the displacing phase. This is due to capillary pressure, as described above, because the pressure drop during flow is proportional to viscosity.

In addition, it was found that in a heterogeneous medium, such as sandstone, the sweep efficiency, which represents the portion of the reservoir that is really influenced by the displacing fluid, depends on the viscosity ratio, too. According to Dyes, Caudle, and Ericson (1954), the mobility ratio:

$$M = \frac{k_w / \eta_w}{k_o / \eta_o} \tag{5}$$

(where $k_{w,o}$ is the effective permeability to water and oil, respectively, and $\eta_{w,o}$ is the viscosity of water and oil, respectively) influences the areal sweep efficiency as shown in Figure 9.

Apart from these two effects, the vertical sweep efficiency determines the performance of a flood. Before the mechanism that improves the vertical sweep efficiency during polymer flooding is discussed, some introductory remarks on the rheology of pseudo-plastic liquids are necessary.

For water and oil, the viscosity is, in most cases, a constant value. For polymer solutions, this is more or less not the case; the viscosity is a function of the rate of shear strain. Figure 10 shows flow curves of aqueous polymer solutions commonly employed in polymer flooding. The viscosity (or, more exactly, apparent viscosity) may vary as a function of shear strain within a wide range. This behavior in a well-determined range may be described by a power law.

In regard to viscous flow of a liquid, the rate of shear strain is a function of both flow geometry and flow velocity. For flow in porous media, this means that in narrow pores the rate of shear strain is higher than in larger pores, or, in terms of petroleum reservoir engineering, that at the same

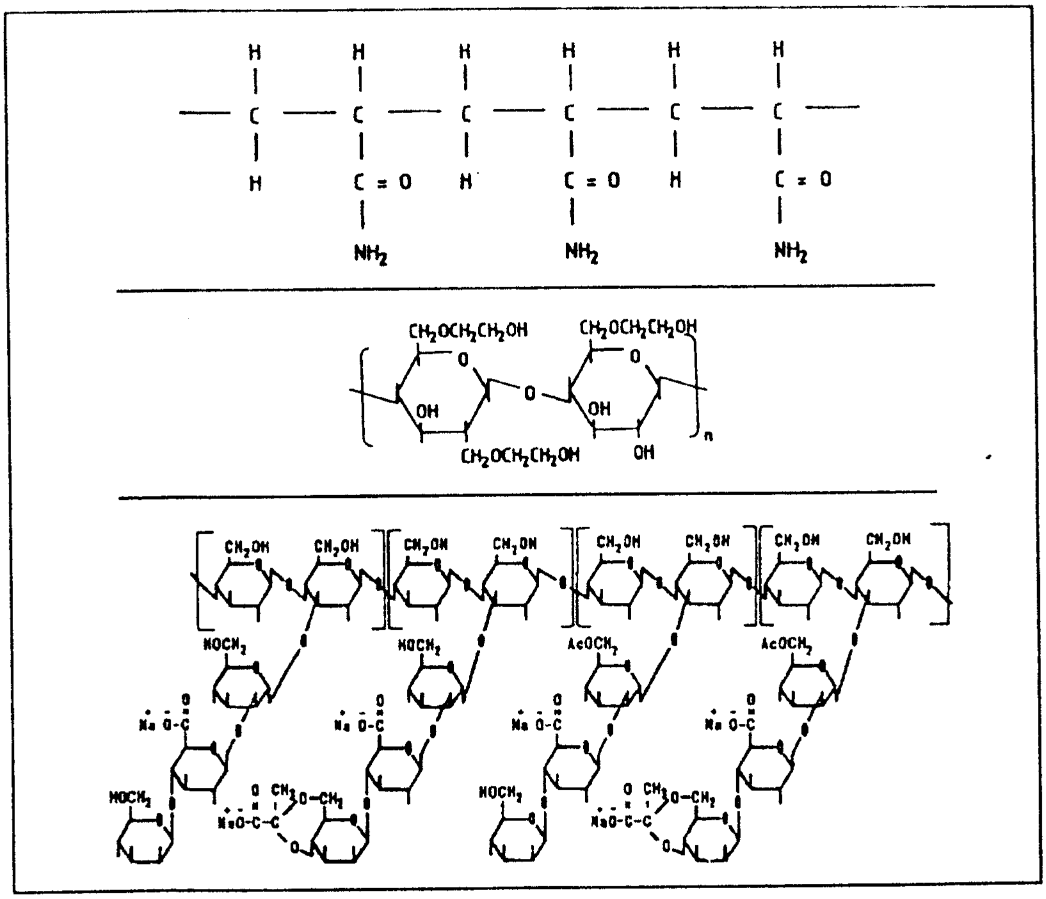
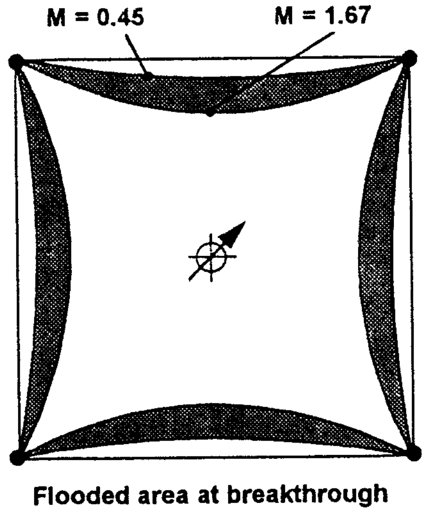


FIGURE 8 Molecular structure of water-soluble polymer used for enhanced oil recovery (polyacrylamide, hydroxyethyl-cellulose, xanthan).



Mobility ratio	Flooded area	
	at breakthrough	at f_w = 90%
10	0.51	0.83
2	0.60	0.88
1	0.70	0.98
0.5	0.82	0.99
0.25	0.87	0.995

FIGURE 9 Influence of mobility ratio on area sweep efficiency.

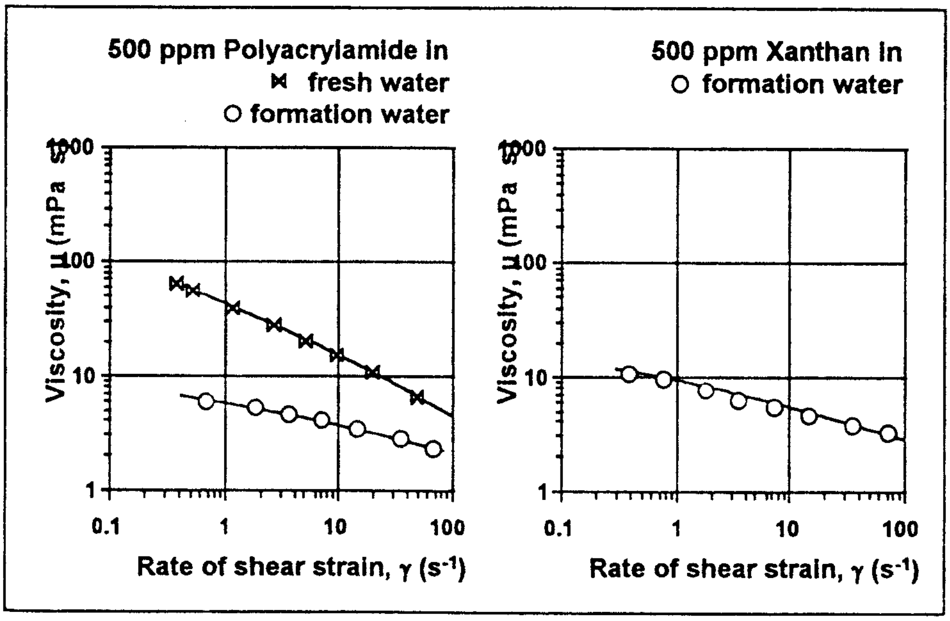


FIGURE 10 Typical flow curves of aqueous polymer solutions applied in polymer flooding.

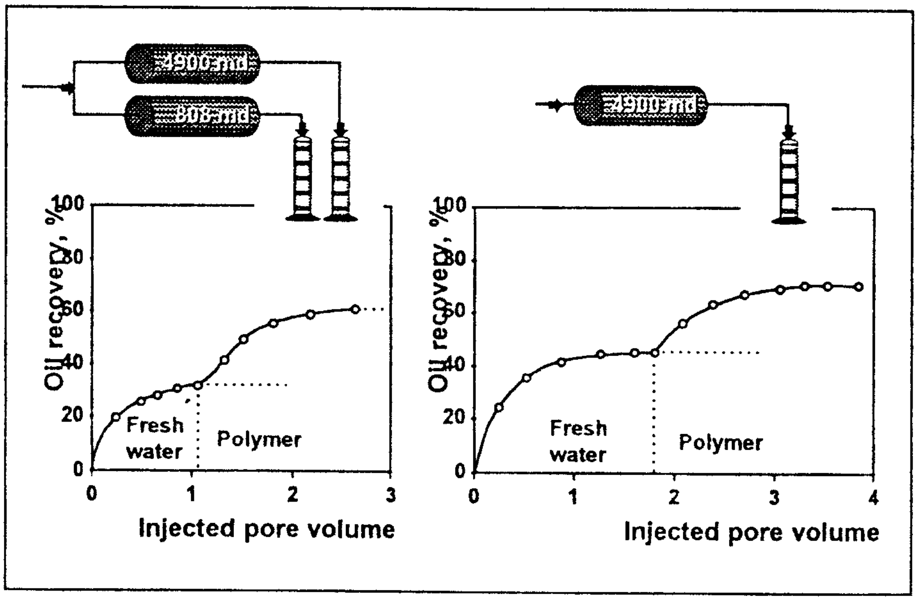


FIGURE 11 Improvement of vertical sweep efficiency according to Sandiford (1977).

Darcy velocities the shear rate in less permeable zones is higher than in zones having good permeabilities. Hence, for example, for a Darcy velocity of 0.2 m/day in a sandstone with a porosity of 25% and a permeability of 2000 mD, the rate of shear strain is 8.6 $\sec^{-1}$ for a polymer solution with $H = 40$ mPa^n ($n = 0.6$). For the same polymer solution at the same Darcy velocity in sandstone with a porosity of 20% and a permeability of 200 mD, the rate of shear strain is 30 $\sec^{-1}$. This means that the viscosity of the flowing polymer solution is higher in the sandstone with the high permeability (19.9 mPa·s) than in the sandstone with the low permeability (10.2 mPa·s).

Usually, highly permeable zones are preferentially invaded by the flood water during secondary operations or natural water drive, and low permeable zones are not flooded so that oil is left in these parts of a reservoir. During polymer flooding, a poor vertical sweep efficiency may be improved because the polymer solution, of course, first follows the paths prepared by water and then, because of its high viscosity, tends to block these parts of the reservoir, so that oil that was previously immobile starts flowing.

The pressure gradient in the reservoir and especially in those zones where oil was immobile becomes higher in a polymer flood than it was during the water drive. Figure 11 shows the results of flood experiments by Sandiford (1977). In a system of two parallel flooded cores of different permeabilities, the oil recovery due to polymer flooding is significantly higher than during a flood in one core of uniform permeability.

REFERENCES

Taber, J.J., Dynamic and Static Forces Required To Remove a Discontinous Oil Phase from Porous Media Containing Both Oil and Water, SPE 2098, SPE Reprint Ser. No. 24 (Surfactant/Polymer Flooding I), Society of Petroleum Engineers, Richardson, TX, 1968.

Dyes, A.B., Caudle, B.H., and Ericson, R.A., Oil Production after breakthrough — as influenced by mobility ratio, *Trans. AIME*, 201, 81–86, 1954.

Tunn, W., Gedanken über Einstzmöglichkeiten von Tensiden zur Erhöhung der Ausbeute von Erdöllagerstätten, *Erdöl - Erdgas - Zeitschrift*, 90, 50-53, 1974.

Sandiford, B.B., *Improved Oil Recovery by Surfactant and Polymer Flooding*, Shah, D.O. and Schechter, R.S. (Eds.) Academic Press, New York, 1977, 487–510.