Surfactants for Oil Recovery[1]

G. P. AHEARN, Esso Production Research Company, P.O. Box 2189, Houston, Texas 77001

Abstract

There is estimated to be about 250 billion barrels of oil in this country that are currently deemed economically unrecoverable. With conventional recovery techniques it is possible to recover about 47% of the estimated total oil in place, and steady improvement in technology may eventually bring crude oil recovery up to 65% of the oil in place. It is apparent that oil recovery is a relatively inefficient process. Therefore, in light of the increasing costs of finding and drilling for new oil, there is an enormous economic incentive to recover even a fraction of the vast amount of oil left behind in our existing reservoirs. Water injection has been the most successful additional recovery process developed in the last century. It is estimated that by 1975, 41% of the nation's crude output will be recovered by this technique. For years the idea of developing a chemical that could be added to the injected water to increase ultimate oil recovery has intrigued the entire industry. This paper deals with recent attempts by the industry to develop surfactants to recover the oil that remains after conventional recovery operations. The requirements for developing an effective surfactant are discussed in detail and the chemist's role in assisting in this development is highlighted.

Introduction

For some time, the oil industry has recognized that the addition of oil and gas reserves during the next 10 years, even with a strong exploration effort, will probably fall short of that needed to supply the forecasted future demands of petroleum products in the United States. In view of this situation, the industry supports a costly research program to develop new oil recovery techniques. The objective of this research is to recover a fraction of the 250 billion barrels of oil from existing reservoirs currently deemed economically unrecoverable. In addition, supplemental synthetic sources of hydrocarbon raw materials such as coal and shale oil are also being developed.

Long Range Energy Outlook

Figure 1 shows the projected industry crude oil supply and product demand outlook through 1985 (1). Demand will be satisfied primarily by domestic petroleum, secondly by oil imports and finally the remaining volume by synthetic sources of petroleum. A fundamental assumption in this projection is that the United States as a world power will not become overly dependent on foreign sources of crude oil. Included in this forecast for domestic supply are crude oil, condensate and natural gas liquids. The data show that the domestic supply is expected to decline after 1975. Although there may be some variation in the assumptions underlying this forecast, it seems clear that a supply gap will emerge in the mid-'70s and could increase to approximately four million barrels a day by 1985. Since this forecast was made, Humble and Atlantic Richfield announced a significant oil strike on the north slope of Alaska. This find could delay the onset of synthetic fuels by five or six years. If three or four additional fields are discovered on the slope, the entry of synthetic fuels could be delayed as long as 15 years (2). In addition, accelerated offshore exploration activity could result in significant finds that will further delay synthetics. It appears, therefore, that the additional recovery of oil from so-called depleted fields will be a factor in supplementing our crude supply even before synthetic sources of fuel arrive on the scene.

New Recovery Processes

Improved recovery techniques encompass processes for the recovery of low- and high-viscosity oils. At present it is usually profitable to waterflood reservoirs containing oil having viscosities of less than 10 cp. On the average, about one half of the oil originally in place will remain after conventional waterflooding. Methods are needed to reduce this waterflood residual oil or to economically recover more oil after the waterflood is terminated.

One of the major problems associated with all oil recovery techniques is the tendency of the injected fluids to contact only a portion of the entire reservoir volume. The overall sweep efficiency or conformance is defined as the fraction of the accessible reservoir volume that is actually swept by the injected fluids. Although it is not my purpose to discuss this problem in detail, it is sufficient to say that the sweep efficiency or conformance is primarily related to the viscosity of the injected fluids and the resident crude oil, the relative permeabilities of the injected fluids and resident crude oil, and the permeability distribution or degree of heterogeneity existing in the particular reservoir. In the ensuing discussion it will become apparent that the sweep efficiency is exceedingly important to the success of all new recovery processes.

New recovery methods can be divided into three categories. First are the miscible displacement processes, which on some occasions have been effective in recovering low-viscosity oils. The theory behind these processes is to inject fluids that are completely soluble in the reservoir oil and are therefore capable of displacing all of the oil from the contacted regions of the reservoir. The injection of high pressure gas, enriched gas, gas driven LPG (liquified petroleum gas) slugs, and alcohol solvent banks into the reservoir typify this kind of process. The major problem with most miscible processes is that they tend to contact only a small portion of the reservoir.

Thermal processes are mainly used to recover viscous crude oils. These reduce the viscosity of the oil and increase productivity and recovery. The injection of hot water, steam and underground or in situ burning are the more commonly used techniques. Although these processes are in a preliminary stage of development, some have been used successfully in the field.

Improved waterflood processes are techniques which have been used with either low- or high-viscosity oils. These processes generally use additives in the flood water or banks of fluids driven by water. Examples of such processes are carbonated water injection, carbon dioxide banks, viscous water and surface-active agents. Thus far, these processes have enjoyed little success in actual field application. Exotic and sometimes highly sophisticated techniques have less appeal to the practical oil field operator than simple injection schemes. Consequently, the idea of developing a cheap material that can simply be added to the flood water to increase recovery has intrigued the entire oil industry. Thus, the use of surfactants for oil recovery has received wide interest in recent years.

Forces That Trap Oil

The nature of the reservoir rock that holds crude oil is highly complex and difficult to predict. One method of studying the pore structure of a reservoir rock sample is to impregnate it at a high pressure with a low-melting alloy such as Woods metal. After the metal has been allowed to cool, the solid can be dissolved or broken away. A photomicrograph of the metallic cast bears the structure of typical pore spaces in a consolidated sandstone, as shown in Figure 2. Note the tortuous and interwoven pores. Obviously the flow channels in such a medium will vary continuously in direction, size and shape. The move-

---

[1] Presented at the AOCS Meeting, San Francisco, April 1969.

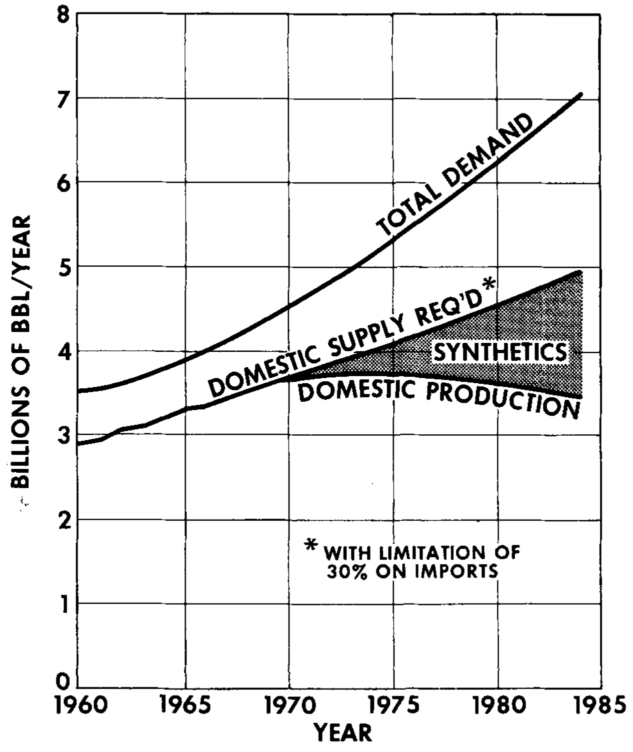


FIG. 1. U.S. supply and demand forecast.

ment and distribution of crude oil in this medium are governed by factors such as surface and interfacial tension, viscosity, pore size configuration and the wetting characteristics of the rock. When two immiscible fluids such as water and oil flow simultaneously through this porous medium, each fluid establishes its own channels of flow. As the saturation of oil is reduced, such as occurs during a waterflood, the channels for this fluid tend to break down until isolated islands of residual oil remain (Fig. 3) (3). In some cases this residual oil saturation may be as high as 50% of the original oil in place.

When this discontinuity of phase exists within a capillary network, there is a pressure drop at the oil-water phase boundary. When the oil phase in the reservoir is continuous, this force does not hinder oil production. However, when the oil phase becomes discontinuous as shown in Figure 3, the pressure gradient across this oil mass is higher than the hydrodynamic pressure gradient of the flowing water. This situation is analogous to the case where an oil droplet is wedged at a small capillary opening (Fig. 4). Gardescu (4) found that the pressure required to move this oil droplet through the opening could be calculated from the following equation:

$$\Delta P = 2\gamma\,(1/r_1 - 1/r_2)$$

where ΔP is the pressure drop between the forward and rear surface of the droplet; γ, the interfacial tension between the oil and water; r_1, the radius of curvature at the forward and smaller end of the deformed droplet; and r_2, the larger radius at the rear end of the droplet.

It follows from this relationship that a reduction in crude oil-water interfacial tension will allow this droplet to be squeezed through the constriction. In view of the capillary dimensions in porous reservoir rock and the hydrodynamic pressure gradients that are obtainable in the reservoir, the interfacial tension must be reduced from 30 dynes/cm (the approximate crude oil-water interfacial tension) to about .01 dynes/cm. This reduction is not achievable with most commercially available surfactants.

Aside from oil displacement by purely an interfacial tension reduction mechanism, surfactants may operate in a fashion similar to a typical detergent. That is, they may preferentially wet the rock surface and dislodge droplets of oil that adhere to oil-wet portions of a pore. Although oil reservoirs are generally preferentially water-wet, this does not negate the existance of oil trapped in oil-wet regions of the reservoir. This displacement mechanism along with others not readily apparent can also be operable during a surfactant flood.

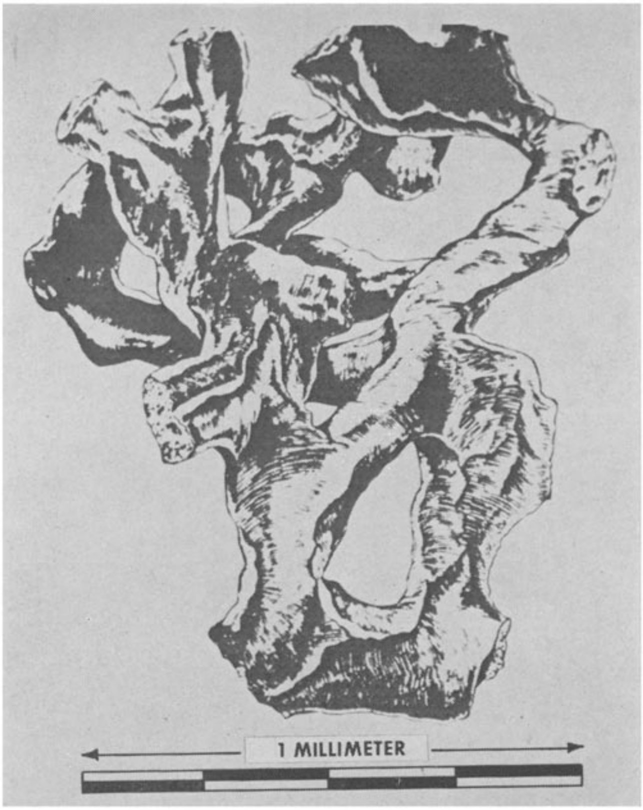


FIG. 2. Metallic cast of pore spaces in a consolidated sand.

Requirements For Efficient Oil Recovery

The idea to use surfactants for oil recovery was discussed in the patent literature as far back as 1927 (5), however, the process has not received a great deal of interest until recent years. Because of the competitive nature of this type of research, little has been published (except for the patent literature) from industrial sources. The complexity of the problem is illustrated by the fact that after many years of research a practical and economic surfactant flooding technique is not yet in commercial use.

In addition, there appears to be no unanimity of opinion regarding the mechanism by which surfactants displace oil from porous rock. As a matter of fact, some of the research results appear to be quite contradictory (6,7). However, most workers feel that the crude oil and brine composition, rock type and wettability, flooding rate and pressure gradient, interfacial tension, adsorption and surfactant type are important parameters. A consensus of results from the published literature can be summarized as follows: (a) Because of excessive adsorption on reservoir rock surfaces, surfactants are rapidly depleted as they travel through the reservoir and hence lose their ability to lower crude oil-water interfacial tension. (b) Concentrated slugs of surfactants are more effective; however, they are usually too expensive to be economically feasible. (c) The crude oil-water interfacial tension must be reduced to exceedingly low values for long periods of time, over long distances. (d) A critical flowing pressure gradient must be exceeded before oil can be mobilized by surfactants.

On the basis of these and other findings it has been concluded that an effective surfactant should have the following general properties: (a) It should lower the interfacial tension between crude oil and water to exceedingly low values (.01–.001 dynes/cm). (b) Its adsorption on reservoir rock should not be excessive. (c) It should be physically and chemically stable in reservoir brines and at reservoir temperatures. (d) It should be capable

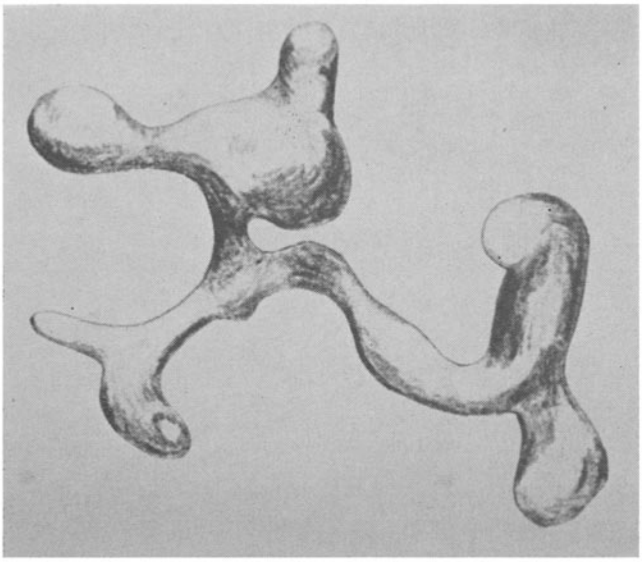


FIG. 3. Residual oil globule.

of contacting a large fraction of the reservoir. (e) It should be inexpensive.

Importance of Surfactant Type

Surfactants are generally classified into three types according to their ionization products: cationics, anionics and nonionics. In recent years, nonionic and anionic surfactants have received most attention as potential additives for oil recovery. Cationics adsorb strongly on reservoir rock and this adsorption is usually irreversible. Also, they tend to oil-wet the reservoir rock surface in a way that is detrimental to oil recovery.

Nonionics, particularly polyoxyethylated alkyl phenols, have received a considerable amount of attention (8). It has been observed that these materials are effective in recovering crude oil in laboratory tests and are usually compatible with the high salinity and divalent ions commonly present in oil field water. Ethyoxylated phenols are also somewhat more effective when their ethylene oxide content is optimized (9,10). However, when applied at elevated temperatures they become less soluble and less potent at temperatures that approach their cloud points. One of the most exhaustive studies performed to relate surfactant type to oil recovery was made by Dunning et al. (11). In this study 165 detergents were tested for oil displacement efficiency. These included 18 cationic, 40 anionic and 107 nonionic detergents. The results indicated no clear-cut correlation between the detergent's surface activity and its displacement efficiency, and that, except for certain formulations, cationic and anionic detergents were generally ineffective for oil displacement. The main conclusion was that nonionic detergents, because of their high displacement efficiency, appeared to be the most promising waterflooding additives.

In more recent years, research has been concentrated on anionic surfactants (12). One important advantage that these materials apparently have over other types of surfactants is lower cost. Regardless of chemical type, however, it appears from the literature that current research is being concentrated on optimizing the behavior of particular surfactants rather than using the screening techniques typified by Dunning's study. Considerable effort, for example, is now being directed at improving means of applying surfactants in the reservoir. Typical techniques range from the injection of emulsions or microemulsions to the use of various additives that enhance surfactant potency, reduce adsorption and improve conformance. Also, novel methods of injecting surfactant banks and generating surfactants in situ have been suggested in recent years.

In summary, the anionics and the nonionics are considered to be the most promising surfactants for oil recovery, however, their efficiency may depend on a number of parameters that are specific for a given crude oil, rock, brine and method of application.

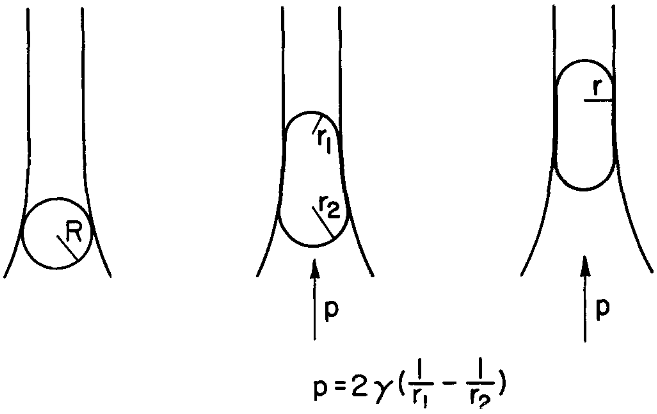


FIG. 4. Droplet distortion in a capillary opening.

Surfactant Flooding Techniques

Direct Surfactant Injection

Over the past 10 years the patent literature has recorded a multitude of ideas regarding novel surfactant flooding techniques. The most simple technique discussed is the direct injection of a surfactant or a mixture of surfactants in an aqueous solution. The surfactant is dissolved in concentrations that may range from 0.1 to greater than 10.0 weight per cent. If high concentrations are used, the surfactant is usually injected in the form of a concentrated slug or bank, since it would be economically prohibitive to inject it continuously at a high concentration. Adsorption of the surfactant will cause it to lag behind the floodwater as it moves through the reservoir. Chromatographic theory suggests that high concentrations of surfactant will not lag as much (13,14); it has been shown, for example, that a 10% detergent slug injected into a sandstone core moved 78–95% as fast as the water rate. A 0.0025% slug moved at a rate less than one fourth that of the water (15). In these studies surfactant slugs were also shown to be more effective for oil recovery than the continuous injection of dilute solutions. The surfactant slug injection technique is one of the more popular methods of applying this process.

Another technique is the injection of a slug of oil treated with surfactant (16). This batch of treated oil will miscibly displace the oil present in the reservoir. The injected water following the oil slug should displace the treated oil more efficiently than the original oil because of the reduced interfacial tension. Also, adsorption is minimized since the surfactant is present in the nonwetting phase. Tests have shown, however, that this technique does not always improve recovery. In fact, recovery is sometimes lessened when an emulsion is formed which plugs the formation and prevents water injection. In some instances the treated oil becomes dispersed into separate droplets and is trapped in the pore spaces, permitting the flood water to finger past it into the formation.

Additives With Surfactants

Many people have suggested the use of various additives to enhance the oil recovery efficiency of surfactants. However, economics usually restrict us to a small number of extremely cheap materials. If the additive can greatly increase the oil recovery over that obtained with surfactant alone, it may well be economically feasible to apply in the field. Some of the more promising additives to emerge in recent years are the various water thickening agents that have proven to be applicable in reservoir rock. These include such materials as partially hydrolized polyacrylamides; biopolymers formed by the fermentation action of Xanthomonad bacteria, currently being developed by a number of companies; and polyethylene oxide polymers.

(Continued on page 576A)

(Continued from page 544A)

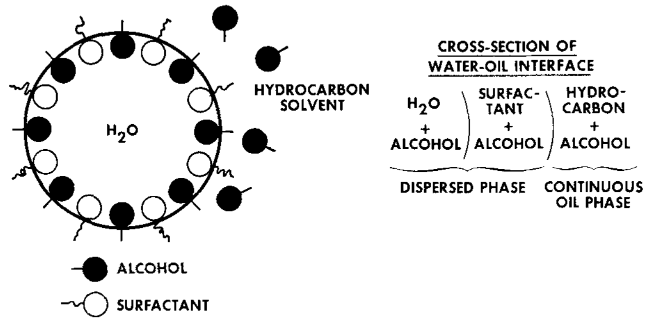


FIG. 5. Typical microemulsion structure.

These polymers provide a viscosity-building component to the surfactant solutions that minimizes the tendency of surfactants to conform only to a small fraction of the area under flood. Also, when added to the drive water, they will reduce the tendency of the water to finger or channel through the preceding detergent slug. The additional oil recovered by the improved conformance could easily justify the use of these additives.

Other additives, including various surfactant builders such as sulfates, silicates, phosphates, polyphosphates and chelating agents, have been suggested for enhancing surfactant potency, reducing adsorption and improving surfactant tolerance to reservoir brine. Also, various alcohols have been suggested to improve the miscibility of the surfactant-crude oil system. These additives may be useful in specific applications of the surfactant process.

Generating Surfactants In Situ

A popular idea is to generate the surfactant in the reservoir and thereby deliver it directly to the crude oil-water interface. The surfactant is propagated as the reactants move through the reservoir, and the adsorption problem is minimized. One method that has received some attention is the injection of a hydrocarbon solution containing an organic acid, e.g., stearic or oleic acid, and subsequent injection of a caustic solution which will react at the hydrocarbon-water interface to form a soap (17). This reaction will lower interfacial tension and promote partial miscibility between the hydrocarbon and water. The possible formation of a water-in-oil emulsion having low interfacial tension and increased viscosity is an added benefit that may aid in improving conformance. The method could also be applied without the hydrocarbon-acid precursor if the resident crude oil contained a high enough concentration of naturally occurring organic acids.

Another related idea calls for the injection of an ester of the acid, subsequent injection of caustic, and a delayed in situ saponification reaction which releases the soap and an alcohol (18). The alcohol creates a region of miscibility between the aqueous and hydrocarbon phases.

The injection of reactive materials such as SO_3, oleum and sulfuric acid has also been discussed (19). These reagents would react with the aromatic constituents in the resident crude oil to form surface-active organic sulfonates in situ and thereby lower the interfacial tension.

TABLE I
Surface Activity of Anionic Surfactant Used in Texas Test

Concentration, sulfonate in reservoir water (per cent by wt.)	Interfacial tension (dynes/cm)
10.0	4.3
5.0	2.8
1.0	1.6
0.5	1.3
0.1	4.3
0.01	19.5
0.001	29.7
0	33.3

TABLE II
Activity of Nonionic Surfactant Used in Kansas Test

Concentration (ppm)	Interfacial tension, γ (dynes/cm)
25	10.1
50	9.3
250	5.7

In summary, the in situ idea is intriguing, however, the heterogeneous reservoir is not ideally suited to be a chemical reactor for selectively generating surfactants for oil recovery. Most of the ideas suggested include reagents that are continuously being depleted by the oil and other reservoir constituents, and therefore would be economically prohibitive. It now appears that generating surfactants at the surface is a cheaper and more efficient means of operation.

Emulsion and Foam Flooding

One of the most interesting developments in recent years has been the concept of injecting micellar solutions (also known as microemulsions or soluble oils) into the reservoir. Several oil companies have conducted research on these systems, and one such oil recovery process has been described in the literature by Gogarty and Fosch (20). Because the process has received some publicity in the past year, it merits more detailed discussion. The micellar solutions contain surfactant (usually an organic sulfonate) in high concentrations, a hydrocarbon and water. After the viscous micellar slug is injected into the reservoir, it is driven by water containing a polymer. Mechanistically, the process is closely related to the miscible processes described earlier, however, it can also be considered a surfactant recovery technique.

Unlike macroemulsions, which are translucent and have particle sizes greater than 10^{-4} mm in diameter, microemulsions are transparent or translucent water-in-oil or oil-in-water dispersions that are thermodynamically stable and have micellar sizes of 10^{-6}–10^{-4} mm. These systems have been studied in depth by Shulman (21). A schematic picture of a typical microemulsion of water dispersed in a hydrocarbon is shown in Figure 5. Usually, surfactant concentrations of 10–20% are required and an alcohol (e.g., isopropyl) is added to increase the amount of water than can be solubilized in the hydrocarbon. These systems can solubilize as much as 70–80% water, however, increasing amounts will cause the system to invert from an oil-external to a water-external state. The inversion is marked by a significant viscosity build-up, caused by a change in the physical structure of the micelles, as illustrated in Figure 6. The figure also shows that salt water can be added to the system to control the viscosity, permitting a lower viscosity at higher water concentrations. Since water contamination of the micellar slug is highly likely in flow through the reservoir, it is important to prevent this inversion from occurring; the resulting viscosity increase would cause severe fingering and bypassing of fluids and possible reservoir plugging. Also, once the phase inversion has occurred the slug will no longer be miscible with the crude oil and its displacement efficiency will be reduced. Gogarty and Fosch (20) claim to have overcome most of the problems associated with the process and tests are under way to evaluate its economic feasibility.

The use of emulsifying agents for oil recovery has been studied periodically and the injection of oil-in-water and water-in-oil macroemulsions has been suggested. Because of the problems observed with emulsion stability and propagation in the reservoir, this process has not received much attention in recent years.

As mentioned earlier, the injection of high-pressure gas into the reservoir for oil recovery has been successful on specific occasions. The sweep efficiency or conformance

(Continued on page 578A)

(Continued from page 576A)

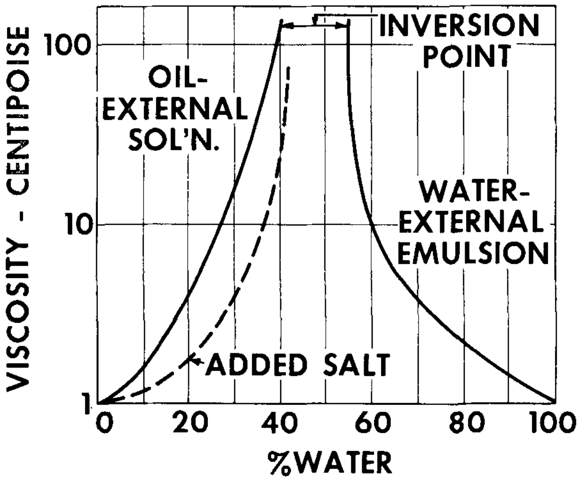


FIG. 6. Effect of water concentration on microemulsion viscosity.

of this process is usually poor because of the high mobility (low viscosity) of the gas, which tends to channel through the residual oil. Various combinations of gas and water have been suggested to improve sweep since water has a lower mobility than gas. It has also been proposed to inject a foaming agent into the partially depleted oil reservoir and follow this with a gas drive (22). A stable gas-in-water dispersion or foam is formed in the reservoir ahead of the driving gas flood. The foam front greatly reduces the mobility of the gas and allows it to contact a larger portion of the reservoir. Several workers are actively studying the foam flooding technique, but a practical method of applying this technique in the field is currently not available. The major problem appears to be the inability to maintain a stable foam for a long period of time in the reservoir environment.

Field Trials of the Surfactant Process

Few reports of field trials of the surfactant process have been published, since such trials are usually conducted under strict security measures. Usually, if there is no attempt to expand a small pilot test into a larger operation, it can be inferred that the economics are not attractive. Three notable field tests of the surfactant process have been conducted in recent years.

Field Test Of An Anionic Surfactant

An interesting test of an anionic surfactant was conducted during 1961–63 in Texas (23). The process involved injecting a small slug of a low molecular weight sulfonate. The concentration of sulfonate in the aqueous solution was 30 weight per cent. The reservoir was partially depleted and therefore still producing oil in the later stages of the waterflood. Significant injectivity improvement was observed in all wells that were treated with the surfactant. In addition, the oil production rate, shown in Figure 7, was increased over the predicted waterflood decline rate for the test area. At the normal decline rate the predicted production would be about 250 bbl/month in November 1962, compared with 450 bbl/month observed as a result of surfactant injection. It is not known how long this increased production was sustained; this information is important for any economic evaluation of the process. Field data also indicated that the additive was transported through the formation without substantial adsorption on the reservoir rock.

The surfactants recommended for use in this process include a wide range of low molecular weight sulfonates which have a solubility of at least 5000 ppm in water. The equivalent weights of these surfactants range from about 120 to 320. The alkylates range from simple C_8–C_{10} alkylated benzenes to highly complex mixtures of light oil distillates or gas oils, produced in the petroleum refining process. These low molecular weight sulfonates will not adsorb significantly on reservoir rock. However, they usually are not very effective at reducing crude oil-water interfacial tension. Table I shows the typical surface activity of one of these sulfonate surfactants measured against an Oklahoma crude oil.

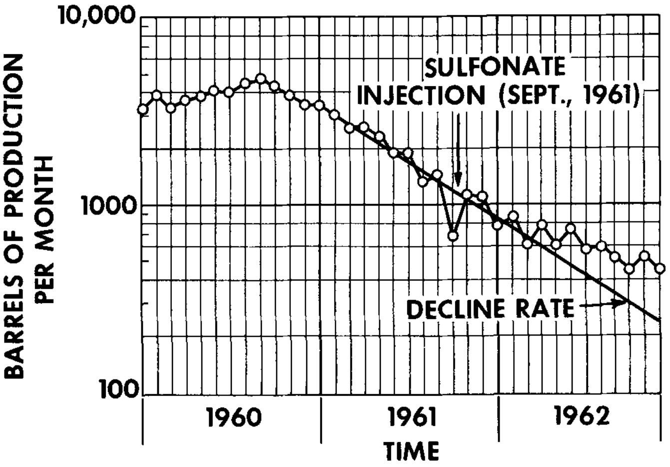
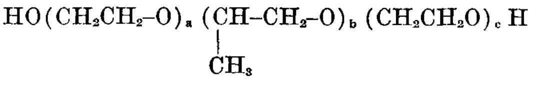


FIG. 7. Oil production rate in anionic surfactant test.

Although specific details of the Texas test have not been given, the published data indicate that surfactant injection increased oil recovery over that obtainable by water injection. It also appears that some side benefits such as improved fluid injectivity were observed. Surfactant adsorption does not appear to have been an insurmountable problem in the test, and this problem therefore may not be as serious a deterrent as has generally been believed.

Test of a Commercially Available Nonionic Surfactant

Another test was performed by a surfactant manufacturer in conjunction with an independent oil field operator in Kansas (24). The surfactant was a nonionic having the general structure:



$$HO(CH_2CH_2{-}O)_a\,(\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2{-}O)_b\,(CH_2CH_2O)_c\,H$$

It is a block copolymer based on ethylene and propylene oxide. The decision to use this particular surfactant was primarily based on past studies which indicated that its adsorption was less than one tenth that of other nonionics evaluated (25,26). Surfactant injection was started in 1956. A rather unusual injection schedule was followed; the initial concentration was very low, 250 ppm, and was cut back to 25 ppm after a few weeks and maintained at that level for three years. A production response was noted as late as 1959 and the field was slugged again with a 250 ppm solution for a short time. Injection was continued at a level of 25 ppm until 1966. The oil production history is shown in Figure 8; note that the predicted normal waterflood decline would have continued until the flood reached its economic limit in 1962. As a result of surfactant injection, the flood life was extended and it reached the economic limit in 1966. Approximately 147,000 extra barrels of oil were attributed to the injection of 50,675 lb of surfactant over this period of time. Thus, the extra oil was obtained for a cost of about 10¢/bbl. The additional oil, however, did not represent a very large fraction of the oil remaining after waterflooding, approximately 0.9% of a pore volume. Usually recoveries of at least 10–15% pore volume of additional oil are considered necessary to make a surfactant process look economically attractive.

It is interesting to note that, as was the case with the

(Continued on page 580A)

(Continued from page 578A)

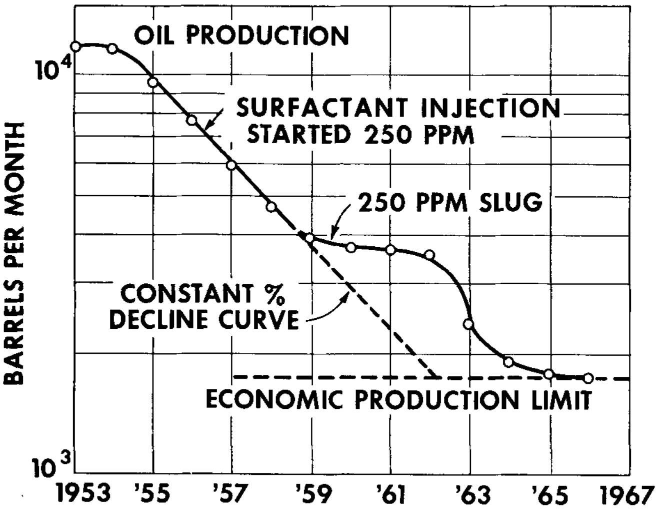


FIG. 8. Oil production history of a surfactant test in Kansas.

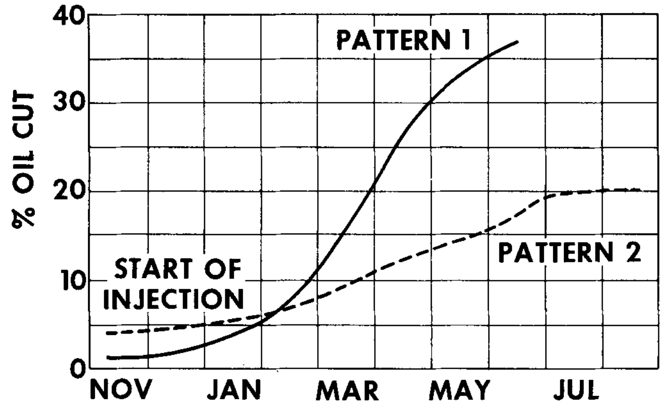


FIG. 9. Production behavior during microemulsion test in Illinois.

anionic surfactant, the nonionic material does not appear to have the interfacial tension lowering ability that is necessary to displace significant quantities of residual oil. Table II illustrates this point with the crude oil produced in the Kansas test.

It is also significant that the produced water contained surfactant concentrations as high as 10–15 ppm, illustrating that the surfactant passed through the formation without being extensively adsorbed. In summary, the test did not indicate that this process could recover large quantities of oil, although it could perhaps be profitable in limited applications.

Microemulsion Pilot Test

Probably one of the most ambitious field-testing programs in recent years has been described by Gogarty and Fosch (20). Tests of the microemulsion process (discussed earlier) have been under way since 1962. Thus far the results have demonstrated the technical feasibility of the process, but little has been published on its economic potential. Three tests in the eastern Illinois area have been completed and a larger-scale project is now under way in the same area to determine commercial feasibility. In addition, a test is in progress in the Bradford area of Pennsylvania, as a joint oil industry venture.

The production behavior of the most recently completed test is shown in Figure 9 (20). Two isolated patterns were used in this test; in both, the injection of the micellar solution was followed by thickened water. Both patterns were producing at a very high water-oil ratio, characteristic of the late stages of a commercial waterflood. As the producing wells began to respond, the per cent oil cut went from 1.0% to 36.0% in Pattern 1 and 4.0% to 19.0% in Pattern 2. Flow data indicated that Pattern 1 had apparently received a larger volume of the micellar slug than Pattern 2. Actual core samples taken from the reservoir at a point 40 ft from the injection well were completely devoid of oil. This result, although not surprising for a miscible process, indicates that the slug was behaving as anticipated in the reservoir environment. Also, core samples taken behind the slug front contained no adsorbed surfactant. Analysis of the produced oil showed that surfactant had passed through the reservoir, illustrating that adsorption was not a severe problem in this test.

Although the tests appear to be encouraging, one must remember that the cost of the micellar solution is a significant factor. Success depends upon the ability to transport a small slug through the reservoir in such a manner that it maintains its integrity. Additional large-scale tests over the next few years using smaller and more economic slugs will be more conclusive. Right now industry observers are taking a wait-and-see attitude before they consider this process to be a commercial reality.

From these results it can be concluded that surfactants offer great potential for improved oil recovery over that achievable with conventional techniques. Although an economic surfactant flooding process is not yet in commercial use, recent field trials are encouraging. However, they point to a need for further improvements before the process achieves widespread application.

The chemist and chemical engineer in the surfactant industry can provide additional technology to aid in the development of a workable surfactant process. The economic incentive for the industry is very high since a single average-size oil field may require as much as 100–200 million lb/year of surfactant in a commercial operation. Success depends upon a better understanding of the basic surfactant requirements and an increased dialogue between the oil and surfactant industries.

REFERENCES

1. Cameron, R. J., J. Petrol Technol. *21*, 253 (1969).
2. Oil Gas J. *66*, No. 43, 50 (1968).
3. Jordan, J. K., W. M. McCardell and C. R. Hocott, Ibid. *55*, No. 19, 98 (1957).
4. Gardescu, I. I., "Behavior of Gas Bubbles in Capillary Spaces," AIME Tech. Pub. 306, 1930.
5. Atkinson, H., U.S. Patent 1,651,311 (1927).
6. Kennedy, H. T., and E. T. Guerrero, Trans. AIME *201*, 124 (1954).
7. Mungan, N., Soc. Petrol. Engrs. J. *115* (1964).
8. Guereca, R. A., and H. S. Butler, Producers Monthly *19*, 21 (1955).
9. Dunning, H. N., H. J. Gustafson and R. T. Johansen, Ind. Eng. Chem. *46*, 591 (1954).
10. Stratton, C. A., U.S. Patent 3,401,748 (1968).
11. Dunning, H. N., and R. T. Johansen, "Laboratory Evaluation of Water Additives for Petroleum Displacement," Bureau of Mines Report 5352, July, 1957.
12. Ahearn, G. P., and W. W. Gale, U.S. Patent 3,302,713 (1967); J. Reisberg, U.S. Patent 3,348,611 (1967); J. C. Kirk, U.S. Patent 2,808,109 (1957).
13. Preston, F. W., and J. C. Calhoun, Jr., Producers Monthly *16*, 22 (1952).
14. DeVault, D., J. Am. Chem. Soc. *65*, 532 (1943).
15. Taber, J. J., Trans. AIME *213*, 186–213 (1958).
16. Jones, L. W., U.S. Patent 3,126,952 (1964).
17. Brown, W. O., C. E. Cooke and P. H. Monaghan, U.S. Patent 3,330,347 (1967).
18. Holmes, B. G., U.S. Patent 3,358,757 (1967).
19. Meadors, V. G., U.S. Patent 3,167,119 (1965).
20. Gogarty, W. B., and W. C. Fosch, J. Petrol. Technol. *20*, 1415 (1968).
21. Schulman, J. H., Ann. Rev. Phys. Chem. *11*, 169 (1960).
22. Felsenthal, M., J. W. Quinn and C. I. Jacocks, U.S. Patent 3,376,924 (1968).
23. Ferrell, H. H., and G. J. Heuer, Jr., Canadian Patent 789,323 (1968).
24. Inks, C. G., and R. I. Lahring, J. Petrol. Technol. *20*, 1320 (1968).
25. Heydigger, H. R., and H. N. Dunning, J. Phys. Chem. *63*, 1613 (1959).
26. Hsiao, Lun, and H. N. Dunning, Ibid. *59*, 362 (1955).

[Received May 14, 1969]