Paper presented at Chem. Tech. '78 - International Congress of Chemical Technology, Bombay, India. January 18-25, 1978, in the Symposium on "Offshore Oil Prospects and Its Implications".

8

TERTIARY OIL RECOVERY AND THEIR IMPLICATIONS

Symposium I

Prof. DINESH O. SHAH

INTRODUCTION

Energy is a very important resource and a factor influencing the standard of living and economic health of nations of the world. It can be said that the standard of living of many nations correlates with per capita consumption of energy — of these nations. The commonly employed sources of energy are crude oil, coal, hydroelectric, nuclear, geothermal and solar energy. As of 1973, the United States of America used 32% natural gas, 33% domestic crude oil, 13% imported oil, 19% coal, and 3% hydroelectric, geothermal and nuclear energy. However, in 1977, almost half of the crude oil used in the U.S.A. was imported. The consumption of crude oil in the U.S.A. is about 20 million barrels per day or about 7 billion barrels per year. Of the total energy used in the U.S.A. 28% is used by industry, 25% in transportation, 21% for residential and commercial purposes, and 26% for generation of electricity.

As of January 1975, the crude oil discovered in the U.S.A. was 441 billion barrels. If we take this as 100%, about 24% of oil-in-place has been already produced, 8.8% is considered to be reserves, additional 13.6% is considered to be tertiary oil target. Another 13.6% additional recovery would require future developments in teartiary oil recovery process. Thus 40% of original oil is considered unrecoverable. Hence, about 60 billion barrels is the estimated amount of oil that may be recovered by tertiary oil recovery processes.

The production of oil from reservoirs can be divided in three stages, namely, primary, secondary and tertiary oil production. In the primary production, the oil is pushed out by the forces such as entrapped gases, or gas caps. The secondary oil recovery is usually carried out by water flooding of the petroleum reservoirs. In recent years, polymers have been added into injected water to improve the efficiency of the water flooding, the tertiary oil recovery involves the use of several processes such as thermal or chemical flooding methods. Most of the tertiary oil recovery processes attempts to decrease the interfacial forces or viscous forces of the entrapped oil droplets.

The thermal processes include (a) steam injection, (b) in-situ combustion, and (c) wet combustion. Carbon dioxide flooding is also found to be promising because of its significant miscibility with oil and brine, although several phases do appear upon equilibration of crude oil-brine-Co2 systems depending upon the composition, pressure and temperature. Injection of liquified petroleum gas (LPG) is also considered to be a promising process. For crude oils containing high proportions of acids (high acid number), caustic flooding can also produce additional oil. Caustic solutions containing appro-

THE AUTHOR

Dr. Dinesh O. Shah(39), is a Professor of Chem. Engg., Anesthesiology and Bio-physics at the University of Florida (USA). He received his undergraduate training at Bombay University and subsequently his doctoral degree from Columbia University (USA). He spent a year at NASA Ames Research Laboratory in California and later moved to the Biological Oceanography Division of Columbia University investigating the dispersion of oil-spills, retardation of evaporations and wave damping by thin films of surface active agents and surface chemical aspects of sea water.

priate ploymers for mobility control have exhibited promising oil recovery. However, in recent years, considerable emphasis has been placed on Enhanced Oil recovery by surfactant-Polymer Flooding process.

CONCEPTUAL ASPECTS OF SURFACTANT-POLYMER FLOODING PROCESS

One can use a "five-spot" or a "line-Drive" pattern for tertiary oil recovery process. In the first case, four wells are in rows and alternate rows can be used for injection or production of fluids. In this process, first a slug of surfactant solution is injected. which is followed by a polymer solution The concentration of polymer is gradually decreased such that no hydrodynamic instability results.

It can be visualized that oil present in pores is interconnected during primary and secondary production. However, at the end of water flooding, it is likely that the bridges connecting oil in adjacent pores are snapped-off or broken. Hence, interfacial tension or capillary forces dominate the movement of oil ganglia in the porous media. The crude oil/brine interfacial tension can be 20-30 dynes/cm. In the presence of an appropriate surfactant, the interfacial tension can be reduced to $10^{-3} - 10^{-4}$ dynes/cm. Since lower interfacial tension facilitates the deformation of droplets, the oil ganglia can be mobilized in the porous media by such surfactant solutions. Hence, ultra-low interfacial tension $10^{-3} - 10^{-4}$ dynes/cm is needed for movement of oil ganglia through narrow necks of pores. The displaced oil ganglia must coalesce to form an oil bank. For this to happen, low interfacial viscosity is desirable. Hence, both interfacial tension and interfacial viscosity should be low for the formation of an oil bank in the porous media.

Polymer solutions are injected following the surfactant slug. Polyacrylamides or biopolymers are commonly used for this purpose. The polymer used should not be shear or temperature sensitive, should not plug the pores, and should not be susceptible to oxidation. Unfortunately, both these polymers have certain limitations in relation to these criteria. Since. the surfactant/polymer interface moves through porous media the interface is continuously ruputured and healed. This causes the mixing of surfactant and polymer and hence a concentration gradient across the interface. If there is a surfactant-polymer association, this may change the rheological properties of polymer solution and interfacial properties of surfactant solution.

The movement of oil ganglia in porous media involves rock/fluid and oil/brine interfaces The wettability of the rock surface is an important factor influencing the oil displacement efficiency. It has been reported that smaller the contact angle of brine on rock, be ter the oil displacement efficiency.

The major areas of research related to enhanced oil recovery are (1) Chemistry of injection fluids, (2) Chemistry of reservoir components, and (3) reservoir engineering. Two additional criteria for the process are economic feasibility and optimization. Since January 1975, we have initiated a broad multi-disciplinary research program on Enhanced Oil Recovery by Surfactant and Polymer Flooding at the University of Florida. The research program is divided in five major areas, namely. (1) Interfacial Phenomena (2) Surface Bulk and Porous Media Rheology, (3) Adsorption and Ion-Exchange Phenomena (4) Polymer Rheology and Fluid Mechanics, and (5) Thermodynamic Phenomena and Phase-Equilibria. A team of five professors, five post-doctoral associates, twelve graduate students and six undergraduate students are investigating various aspects of the surfactant-polymer flooding process. The main objective of the research program is to develop a broad frame-work of knowledge and information about the microstructure of injection fluids and the complex interactions that would occur between the injection fluids and the reservoir components such as clays, minerals, brine and oil. The research will be directed towards developing predictive relationships between parameters such as interfacial tension, Critical Micelle Concentration (CMC), Optimal Salinity and variables such as surfactant concentration, salt concentration and temperature. This research program is jointly supported by the Department of Energy and a consortium of twenty oil and chemical corporations. This research program will contribute about 0.5 million dollars to the total cost of the project.

Two quarterly newsletters and two semi-annual technical reports are sent to consortium members and to Department of Energy as well as to other academic institutions engaged in Enhanced Oil recovery research. A two-day progress review meeting is held annually at the University of Florida to discuss the results of the research and to determine the direction for the future research. This joint Government Industry-Academic Institution research program has contributed significantly towards developing a basic framework of knowledge required to design and to optimize oil recovery systems for reservoirs with different conditions

The following are a few recent publications which resulted from this research program.

1. "Improved Oil Recovery by Surfactant and Polymer Flooding", edited by D.O. Shah and R. S. Schechter, Academic Press, New York 1977.

2. "Micellar Solutions for Improved Oil Recovery" V. K. Bansal and D.O. Shah. In Micellization, solubilization and Microemulsions, Vol. 1, Edited by K. L. Mittal, Plenum Press, 1977, pp. 87-113.

3. "The effect of chain-length of oil and Alcohol Ratio on the solubilization, Phase Behavior and Interfacial Tension of Oil-Brine-Surfactant-Alcohol Systems". W. C. Hsieh and D.O. Shah.
SPE Paper No 6594. Presented at the SPE-AIME International Symposium on Oil field and Geothermal Chemistry, June 27-28, 1977.

4. "The use of High Resolution NMR spectroscopy for characterizing Petroleum sulfonates" W.C. Hsieh and D.O. Shah.
SPE Paper No. 600. Presented at the SPE-AIME International Symposium on Oil field and Geothermal Chemistry, June 27-28, 1977.

5. "Microemulsions and Tertiary Oil Recovery" V. K. Bansal and D.O. Shah In Microemulsions. ed. L.M. Prince Academic Press, New York. pp. 149-172 (1977).

6. "Some structural Aspects of Microemulsions and co-solubilized systems" D.O. Shah, R. D. Walker, W. C. Hsieh. N. J. Shah, S. Dwivedi, J. Nelander, R. Pepinsky and D. W. Deamer.