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MICROBIAL ENHANCED OIL RECOVERY

WILLIAM R. FINNERTY — *Consultant*

FINNERTY ENTERPRISES, INC

160 CHINQUAPIN PLACE

ATHENS, GEORGIA 30605

INTRODUCTION

Energy in all its forms is the motive sustenance of modern, industrialized societies. Its use and availability determines social stability, economic viability, and power in terms of competing international economies and geopolitical affairs. The majority of the world's energy come from non-renewable fossil resources, with these resources and the energy derived from them representing the lifeblood of economies worldwide. Currently, crude oil reserves are estimated in excess of one trillion barrels of oil worldwide, with more than one-half of this fossil resource located in the Middle East.

Conventional oil production technologies recover only approximately one-third of the original known in-place oil following water flooding. Technologies to produce this remaining oil offer enormous economic potential through the development of new and cost-effective methods. For example, the total original in-place oil for the United States is estimated around 488 billion barrels of which 133 billion barrels have been produced with 28-30 billion barrels considered as recoverable reserves. The more than 300 billion barrels not recoverable by conventional technologies represent the

target of all enhanced oil recovery (EOR) research and development programs. Currently, EOR represents a relatively small percentage of total oil production (approximately 5% and 18% for the United States and Canada, respectively), with some analysts predicting that within 20 years 33% of total oil production will be through EOR technologies.

Microbial enhanced oil recovery (MEOR) has been a technology of interest for many years, with focused programmatic development by the U.S. Department of Energy beginning the late seventies and early eighties. The first international conference on MEOR occurred in 1982, the latest in 1990, where researchers discussed the latest information and advances. MEOR has progressed from a position of questionable efficacy to a status where well-documented field studies indicate beneficial effects for "new" oil production from the application of MEOR concepts and principles. A number of excellent reviews and treatises have appeared recently which serve to discuss the status of MEOR as well as address the advantages and limitations of this technology[1,2,3,4]

Microbial enhanced oil recovery is the application of microorganisms and the exploitation of their metabolic processes to increase the production of oil from reservoirs of marginal productivity. MEOR appears more feasible to tertiary oil recovery, although field situations are possible where the introduction of MEOR during secondary treatment is warranted for extended oil production.

OIL PRODUCTION AND MEOR.

Conventional oil production occurs in three stages: primary, secondary, and tertiary. Primary production is the result of natural internal reservoir pressures which exist within the formation. When this internal driving force diminishes to a point where oil production declines, then secondary treatment follows in the form of water flooding. Water flooding continues until the ratio of oil produced to water injected yields more water than oil and the economics of the treatment become non-sustaining in terms of oil production. At this point, tertiary methods are introduced to enhance further oil production. Tertiary EOR technologies include: 1) surfactant/polymer flooding; 2) solvent flooding; 3) miscible gas flooding; 4) in situ emulsification generating oil-in-water and water-in-oil emulsions; 5) steam flooding; and 6) in situ combustion, all designed for the microscopic displacement of trapped oil from the reservoir. Factors governing the microscopic displacement of oil include the geometry of the pore network within the formation, fluid-fluid properties, fluid-solid properties, pressure gradients and gravity, interphase mass transfer, interface aging effects, wettability changes, and emulsification [5]. All EOR procedures have shortcomings and constraints, basically relating to cost, amount of new oil recovered, and suitability of complex reservoirs for treatment. The efficiency of oil recovery from a reservoir is determined by various properties such as porosity, permeability, nature of rock surface, fluid properties relating to the bulk viscosity of the trapped oil, and the interfacial tension that exists between the

oil, water, and rock matrix within the formation. It is known that low oil viscosity and low oil-water interfacial tensions promote efficient displacement [6,7,8]. An understanding of the physics of multiphase fluid flow through porous media provides the basis for explaining how these various reservoir parameters influence oil production. The mobilization of oil trapped in rock matrices is determined by the relative magnitude of viscous forces allowing fluid flow and the capillary forces which inhibit oil movement in water-wet formations. A dimensionless parameter known as the capillary number, N_c , represents the ratio of viscous to capillary forces on oil trapped in pores [9]. Under reservoir conditions a N_c value of 10^{-2} corresponds to interfacial tension values in the order of 10^{-2} to 10^{-4} mN/m. Such ultralow interfacial tension values are achieved with synthetic surfactants and biosurfactants [10]. The introduction of surface active agents into oil-bearing formations has the potential for greatly increasing oil production when the surface properties of these agents are compatible to the physical and chemical properties of the reservoir such as brine concentration, pH, temperature, oil type and other critical factors. Do microorganisms and their associated metabolic processes have the potential to play a meaningful role as supplementary technologies in EOR programs?

MICROBIOLOGY AND EOR.

In view of the constraints and restraints associated with oil-bearing formations, what are the principles and concepts of MEOR that offer the promise of potentially new technologies for the

microscopic displacement of trapped oil from a multitude of formations worldwide. The MEOR strategies currently emphasized are

1. injection of microorganisms along with appropriate nutrients to support microbial growth for the production of metabolic products considered beneficial to trapped oil displacement. Metabolic products considered of value are: acids (acetic, propionic, and butyric acids) for reservoir rock modification, improved formation porosity and permeability, and carbonate rock dissolution; biomass accumulation for selective and nonselective plugging of channels and fractures, wetting of rock surfaces, oil emulsification through bacterial adherence; gas production (CO_2 , CH_4 , H_2) for reservoir repressurization, oil swelling, and viscosity reduction; solvents production (ethanol, propanols, butanols, acetone) for oil solubilization; in situ production of biosurfactants for lowering of interfacial tension and emulsification; and biopolymer production for plugging and mobility control.

2. The above-ground production of specific bioproducts (biosurfactants and biopolymers) and the subsequent application of these bioproducts as chemical enhanced oil recovery agents (CEOR), a technology not dissimilar to synthetic surfactant flooding programs under development for years. The central question is whether biosurfactants exhibit performance advantages in the reservoir over synthetic surfactants.

RESERVOIR MICROBIOLOGY.

Studies concerning the microbiology of oil-bearing formations

indicate the presence of a heterogeneous microflora consisting of aerobic, facultative, and anaerobic microorganisms. The taxonomic classification and cataloging of their physiological and biochemical properties remains to be accomplished. However, the realization has surfaced that oil reservoirs and, in general, deep subsurface environments are microbiologically-rich, metabolically-active ecosystems[2, 11]. The source of this indigenous microflora is undetermined, with possible point source contamination from surface origins or, alternatively, of subterranean origin.

The nature and quality of crude oil is highly variable, representing varying states of chemical maturation and alteration. Microbial degradation represents a potential major destructive phenomena affecting the quality of crude oil. The injection of microorganisms and/or nutrients to stimulate the growth of nascent microbial populations within the reservoir could result in the biotransformation of good oil to oil of poorer quality. The simpler hydrocarbons (paraffins, isoparaffins, simple 1,2, and 3 ring aromatic hydrocarbons) are rapidly metabolized by microorganisms [10]. Insights into the biodegradation of the heavy fractions of crude oil (the asphaltenes and resins) are essentially nonexistent, being largely considered biologically recalcitrant structures. Crude oil biodegradation, therefore, results in the disappearance of the light fractions of crude oil, a concentration of the heavy ends, an increased viscosity and density, and the enrichment of nitrogen, sulfur, and oxygen heteroatoms, yielding an oil of poorer quality than the original oil. Crude oils being susceptible to

significant biochemical alterations, biodegradation appears to represent one mechanism whereby vast heavy oil deposits are formed worldwide. It has generally been assumed that hydrocarbon oxidations occurs only in the presence of molecular oxygen. Recent studies have established irrefutably that anaerobic microorganisms can and do metabolize simple paraffinic(dodecane to eicosane) and aromatic hydrocarbons(benzene, toluene, xylene) [12, 13, 14]. These findings place new perspectives on the long term effects of injecting microorganisms and nutrients into oil-bearing formations and the short term gains to be realized from the application of such MEOR technologies. The introduction of microorganisms and nutrients can possibly result in the accelerated downgrading of oil quality.

RESERVOIRS AND MEOR.

The physical and chemical characteristics of oil reservoirs do present restrictions on the applications of MEOR processes. Collation of these physico-chemical properties has been assembled for specific areas of the United States which reportedly support MEOR options [2,15]. These citations provide the first comprehensive analysis of the limitations and potential applications of MEOR in select reservoirs. The factors identified in oil reservoirs for consideration of implementing MEOR options were porosity, permeability, pH, salinity, API gravity of the trapped oil, and temperature. Porosity being a measure of the total pore volume and permeability a measure of the ability of a porous matrix to transmit fluids, relate to the ability of microorganisms

to penetrate the formation. The pore entrance size becomes an important factor affecting the ability of bacteria to be transported through consolidated rock, due to the fact that the size of bacteria fall into the range of pore entrance sizes, causing the restriction of bacterial transport through the porous media. Jenneman et al [16] reports the injection of Pseudomonas species into Berea sandstone cores did not decrease permeability significantly; whereas, a 100% reduction of permeability resulted from the injection of a Bacillus species [17]. Therefore, filtration of bacteria from the injection fluid by the rock matrix restricts the penetration of bacteria into deeper regions of the formation, limiting the effects of any MEOR process. Approaches to counteracting this problem has been the injection of spores and ultramicrobacteria(UMB). UMB are bacteria which have much smaller diameters resulting from nutrient starvation [18] and appear to transport readily through porous media. The study of UMB for EOR processes has demonstrated their ability to penetrate throughout sandstone cores without significantly reducing injectivity or permeability [19, 20]. Accordingly, UMB appears to offer an attractive solution for the transport and dispersion of bacteria throughout the outer regions and depths of oil-bearing formations. It has also been observed that a greater depth of bacterial penetration occurs when the bacteria are allowed to grow through the porous media by the intermittent injection of nutrients [21]. Temperature and pressure will increase as the depth increases, averaging 1-2 C° per 100 ft and 0.43-1.0 psig per foot [2, 22].

Average reservoir temperatures range from 49-89° C, with the temperature-depth profile restricting microbial growth in reservoirs at depths of less than 3500 meters (<100° C). In general, most bacteria will be restricted to reservoirs with depths less than 2500 meters (<85° C). Pressure considerations seem of less importance in that temperature appears the most important parameter in determining any MEOR process.

Salinity and pH in oil reservoirs vary from 1% to 10% and from pH 3.0 to 9.9 [2, 22]. Thus salt tolerance is required of microorganisms used for MEOR as well as the ability to grow over wide pH ranges. Many microorganisms adapt easily to higher salt concentrations, although most microorganisms grow optimally between pH 6.0-8.0. Exceptions do exist, however, in the acidophilic, alkanophilic and halophilic groups of microorganisms. The type of oil present in a reservoir is an additional factor of importance. The toxicity of light volatile oil fractions to microorganisms and the density of heavy oils are generally considered unfavorable for the application of MEOR processes.

Accordingly, based on the limitations imposed by the reservoir, it is possible to identify certain conditions which appear to be most favorable for the application of MEOR processes. These reservoir conditions are: less than 10% brine, pH 4-9, permeability greater than 75 mD, API gravity of the oil above 18, and reservoir temperatures less than 75° C [2, 22]. Permeability and temperature appear to be the most restrictive parameters for MEOR processes.

MEOR FIELD TESTS.

Hitzman has reviewed the status of over 300 MEOR field tests conducted since 1953 [23], concluding that positive MEOR responses occurred in several reservoirs, that in situ microbial growth does result in chemical and petrophysical changes within the reservoir, and that the oil reservoir is not a totally biologically restrictive environment for microorganisms. Numerous field trials conducted in eastern Europe encompassed a wide range of reservoir parameters: temperatures ranging from 22° C to 97° C; depths from 50 to 1500 meters; porosities of 11% to 36%; permeabilities from 10 mD to 8100 mD, oil types from asphaltenic to light paraffinic oils; and treatment of limestone and sandstone formations [22]. Inocula generally consisted of mixed cultures (aerobic, facultative anaerobes, and anaerobic microorganisms) with molasses as the carbon source. Successes were highly variable with incremental oil production ranging from 0% to 200% after treatment. The classical studies conducted in 1953 involved the injection of Clostridium acetobutylicum and molasses into a loosely consolidated sand of high permeability. Significant changes began 3 months after the initial injection with incremental oil production increasing over 200% per month concomitant with large quantities of organic acids, CO₂, and CH₄ [24].

Recent studies of MEOR processes involve oil displacement from Berea sandstone cores injected with Bacillus licheniformis and a Clostridium species, resulting in alterations of the rock wettability, increased permeability, and oil displacement [25]. An investigation of oil displacement from cores using organisms

isolated from a proposed field site involving high salinities resulted in gas formation and incremental oil production [26]. The results were interpreted as resulting in a shift in the capillary number of the system as a function of gas formation in the pore spaces, reduction of interfacial tension, and plugging by the mixed culture. The Mink Unit field study of a microbially-augmented water flood conducted over 2.5 years involving the injection of a mixed culture consisting of 4 microorganisms resulted in a 13% increase in incremental oil without loss of injectivity or plugging [27]. The organisms traveled 100 meters to the production well through a 90 mD permeability formation. A successful MEOR process in Australia reported a 40% increase in incremental oil. An improved water-to-oil ratio, reduction of the interfacial tension, microbial growth, and repressurization were noted in a 260 mD sandstone formation at 76°C containing a light paraffin oil [28]. Successful MEOR field tests in Germany employed thermophilic halophiles growing on molasses [29]. Incremental oil production was observed in dolomitic formations at 15% salinity and 55°C. Gas formation was identified as the key mechanism for oil release. Interestingly, filtered culture broths injected into the formation released more oil. Oil release was attributed to the dissolution of carbonate rock by organic acids improving permeability and to gas and solvent effects acting to reduce oil viscosity, repressurization and modification of rock wettability. A comprehensive review by Tanner et al [3] discusses MEOR options in carbonate reservoirs, citing advantages such as acid production for the solubilization of

carbonate rock to CO₂, solvent production for miscible flooding, and biosurfactant production for altering matrix wettability and reduction of interfacial tension. Computer simulation of MEOR processes is a new developing tool for exploring various MEOR options [30, 31]. Further information is required, however, on the biological component of the models to obtain greater reliability and precision of computer-generated predictions.

BIOPOLYMER AND BIOSURFACTANT APPLICATIONS IN MEOR.

Selective plugging of high permeability zones by in situ biopolymer production has received interest as a potentially useful MEOR technology for improving sweep efficiencies of lower permeability zones. A field test designed for selective plugging and control of water flow in a Canadian heavy oil formation employed *Leuconostoc mesenteroides*, an extracellular slime producer [32, 33]. The organism was injected in a nutrient free medium, followed by the injection of molasses to induce in situ biopolymer production. Although the experiment failed to effectively block water flow, the organisms were transported more than 1 km into the formation, where they multiplied and produced biopolymer. *Pseudomonas* species and *Klebsiella pneumoniae* were injected as nutrient starved ultramicrobacteria into sand packs and revitalized by nutrient stimulation. These laboratory-based studies demonstrated uniform penetration and plugging of the sand pack by the bacteria and the ability of such systems to selectively plug high permeability zones having varying permeability characteristics [34, 35]. A number of Gram-positive bacteria have been isolated from oil brines which

grow anaerobically at temperatures up to 50° C and produce extracellular biopolymers [36]. The injection of these bacteria into the reservoir may not be required due to their existing presence as indigenous microflora. Nutrient stimulation may possibly induce biopolymer formation and desired plugging effects. The selective plugging of high permeability zones by in situ biopolymer production appears to offer potential opportunities for highly successful MEOR applications in improving sweep efficiencies and incremental oil recovery.

The use of synthetic surfactants in EOR technologies has been and continues to be an active area of development. The application of biosurfactants to EOR scenarios as CEOR agents is not a well-studied technology. The basic question concerning biosurfactants is whether they have surface active performance properties equal to existing synthetic surfactants systems used in EOR processes. A number of biosurfactant systems have been described in the literature and their properties and applications reviewed [37]. Many MEOR studies allude to and implicate the production of biosurfactants by diverse anaerobic microorganisms within the reservoir, mainly to explain some of the effects and mechanisms involved in oil displacement. However, little information is presented on chemical and physical properties of these biosurfactants produced by the anaerobic microflora. An exception is the extracellular synthesis of a cyclic lipopeptide by *B. licheniformis* JF-2, a facultative anaerobe [38]. Although biosurfactants are not currently in use or considered as CEOR

agents by the oil industry, potential applications are indicated for these surface active bioproducts in chemical flooding, in situ emulsification and deemulsification, viscosity reduction of heavy crude oils, and rock wetting properties. There are currently no examples of successful field applications of biosurfactants as CEOR agents. An extensive study has, however, developed a number of extracellular biosurfactant systems with physical properties commensurate to the effective displacement of oil [WR Finnerty, unpublished data]. These extracellular biosurfactants have been demonstrated to effect 60% to 80% microscopic oil displacement from sandstone cores containing a targeted oil. The physical properties supporting the application of these bioproducts as performance-effective CEOR agents are ultralow interfacial tension values (0.001 to 0.00007 mN/m, low critical micelle concentrations (100 to 300 micrograms/ ml), performance-effectiveness in 1% to 12% brine, broad pH range (pH 5.0-10.0), stable temperature profiles exceeding 200°C, surface activity insensitive to divalent cations, low adsorption to rock matrices with greater than 95% recovery in produced fluids, and are produced from cheap substrates. The success of these products in oil displacement is the targeting of biosurfactant surface properties to the oil type and reservoir characteristics. A matching of each biosurfactant to the oil type and the reservoir is a prerequisite for successful oil recovery. Also, the use of the spent culture broth as the surface active solution, following removal of microorganisms, has impacted significantly on the cost-effectiveness of the technology, since

there are no requirements for costly downstream product recovery. This surface active culture broth is formulated with respect to pH, salinity, and viscosity to match the physico-chemical properties of the oil and the reservoir. In many cases, culture broth dilutions ranging from 1:1,000 to 1:10,000 are possible, without the loss of performance effectiveness.

CONCLUSIONS.

MEOR represents a new and innovative technology which has progressed to a status of potential significance for recovering known in-place oil. The sophistication of MEOR studies has steadily advanced where controlled experimentation is demonstrating the effectiveness of MEOR options to stimulate and enhance oil recovery. A need continues for more and improved laboratory and field studies to better understand how microorganisms release oil. Adequate documentation exists that microorganisms can be injected into reservoirs, it is possible to stimulate their in situ growth and production of bioproducts considered of value to oil release, and such MEOR treatments do not uniformly result in such known deleterious effects as well souring or plugging. Most MEOR field studies to date have been limited to marginal reservoirs, to minimize possible economic losses. Future field studies will hopefully involve more favorable reservoir systems for treatment, rather than worst case formations. Many of the MEOR programs have been at or near the limits of biological applicability in terms of formation permeability, salinity, and temperature [39]. Future experimentation will be required to assess the long term effects

of MEOR packages on the in situ biodegradation of the lighter hydrocarbon fractions by anaerobic microorganisms. The rate and magnitude of alkane and simple aromatic hydrocarbon biodegradation is unknown, including biotransformations of the heavy fractions of crude oils. The future interface between the oil industry and the applications of MEOR programs appears most favorable and complementary in terms of developing performance- and cost-effective strategies for increased oil production. It may well develop that MEOR packages will become the only economically feasible option for viable EOR technologies in the near to mid term future.

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