

# BIOLOGICAL AGENTS IN OIL RECOVERY

## A STATUS REPORT

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### INTRODUCTION

The negative effects of microbial activity in oil production are well-known to the petroleum engineer.<sup>1-5</sup> Formation plugging problems or corrosion problems, especially in waterfloods, are undesirable characteristics of microbial metabolism which have been the subject of considerable expense to the industry. On the other hand, microbial activity has potential for enhanced oil recovery.

The use of microbial agents to improve oil recovery is not a new idea. It has long been noted that certain microbes are capable of attacking complex hydrocarbons and producing less complex molecules.<sup>6-8</sup> Bacterial strains have been shown to produce light hydrocarbons from crude while others can produce carbon dioxide as a part of their metabolic activity. More recent developments have shown that biopolymers capable of being used as viscosifiers may be produced by a fermentation process.<sup>9</sup> Potential exists to produce surfactants *in situ* by microbial activity.

It is the purpose of this presentation to review some of the basic requirements for microbial activity and how they relate to secondary oil recovery.

### MICROBIAL PROBLEMS

Problems in oil production associated with microbial activity are concentrated in the area of waterflooding. Here, water is injected into the producing formation which has a pore size range up to 15 microns. This means the rock matrix is a large filter capable of being plugged by suspended solids. Bacteria offer this plugging potential.

Although much work has been reported on the effect of bacterial population on reservoir plugging, no colonization level can be said to be capable of

reducing permeability by a certain amount. Each reservoir differs in physical properties so it is evident that some will tolerate more bacteria than others.

Slime: The *Pseudomonas* type of organism is capable of producing plugging problems in injection wells by creating a slime in water lines. Coupled with this are problems from algae which are frequently injected in water held in open pits or tanks. Algae can produce rapid plugging of injectors. However, they are susceptible to chemical preventative treatment by sterilizing agents or removal from the formation by injection of hypochlorite solutions.

Another source of slime is the iron bacteria frequently present in fresh water. These bacteria deposit gelatinous ferric hydrate on pipe walls. This deposit is capable of plugging pipe or the rock matrix. This slime source is not prevalent in oilfield brines as it requires a fresh water environment with 0.3 ppm oxygen and 0.1 ppm iron to support bacterial metabolism. Iron bacteria are prevalent in fresh waterfloods of the Illinois Basin where control must be rigidly practiced using biocides to maintain injectivity.

### CORROSION PROBLEMS

The sulfate-reducing bacteria are anaerobic microorganisms capable of reducing inorganic sulfates to sulfide. These bacteria cause enormous matrix plugging problems in waterfloods. The plugging action results as the bacteria produce large amounts of hydrogen sulfide. The  $H_2S$  then reacts with iron present in the injection water to produce insoluble iron sulfide. Sulfate reducers are prevalent in both fresh water and brine. They have been responsible for plugging in injection waters with temperatures ranging from 70 to 150°F.

In addition to the plugging action induced by sulfate reducers, they are frequently blamed for downhole corrosion. When steel pipe is in an aqueous environment, areas of the pipe develop different electrical potentials due to dissimilarities in the metallurgy. Ferrous iron goes into solution at the anode as electrons flow to the cathodic zone. The ferrous ions react with water to form hydrogen ions and ferrous hydroxide. The hydrogen ions then form free hydrogen at the cathode as the electrons are absorbed. Under anaerobic conditions the hydrogen will polarize the system and prevent further action. However, if a biological agent, such as sulfate-reducing bacteria is present in the water, the system will be depolarized and iron will continue to go into solution at the anode until a hole develops in the pipe. Sulfate-reducing bacteria require cathodic hydrogen for reduction of sulfates to  $H_2S$ , thus causing anaerobic corrosion in support of their metabolism.

#### MICROBIAL POTENTIALS

The fact that microbial activity may be used to "crack" petroleum makes it potentially feasible to treat entire reservoirs with inoculated water to increase oil production. One of the first advocates of microbial research to increase oil production was Dr. C. E. ZoBell, director of API Project 43a.<sup>10</sup> His work was accomplished between 1943 and 1952. ZoBell recommended injection of a salt requiring *Desulfovibrio* species which was capable of metabolizing hydrocarbons. His choice of bacteria was not a good one. Sulfate reducers, as previously noted, have corrosive effects on tubular goods and tend to plug formations.

Between 1945 and 1960, the patent literature contained many claims for bacterial processes. Much of this is unfounded and even now proved technically infeasible.

Laboratory studies by Updegraff and Wren<sup>11</sup> showed fermentation processes could be used to support biological metabolism. LaRiviere<sup>12</sup> expanded on the idea that hydrocarbon consumption was not necessary for bacterial growth. He proposed that a supporting substrate, such as molasses, be injected. This would "feed" the bacteria while they increased oil production by release of natural surfactants or dissolved surface-tension-reducing agents.

Dostalek<sup>13</sup> investigated the effects of *Pseudomonas* and *Desulfovibrio* cultures on oil production. Both cultures fared well in paraffinic oils, and the viscosity of the oil invaded by *Desulfovibrio* was decreased. Dostalek concluded that viscosity-lowering oil in anaerobic systems is due to the release of  $CO_2$  by bacterial action. Methane was also reported formed by strains capable of converting  $CO_2$  and by fermentation of fatty acids.

Field tests of bacterial oil release have been carried out in Poland, Hungary, Czechoslovakia, USSR and the U.S. These tests were generally conducted in high-permeability (1-3 darcies) sandstone where waterflooding had been well-documented.

Kuznetsov<sup>14</sup> (USSR) used a mixed strain capable of producing gaseous products ( $CO_2$ ,  $CH_4$ ) under anaerobic conditions. Ten thousand gallons of 4% molasses containing the mixed strain was injected and the well was shut-in for six months. The objective of the project was to lower oil viscosity, but the results indicated the reverse occurred. Oil viscosity increased 9.0 centistokes. Kuznetsov also reports:

1. Wellhead pressure increased 22.5 psi
2. Oil production increased by 12% for four months then dropped
3.  $CO_2$  and propane increased but methane actually decreased.

Yarbrough and Coty<sup>15</sup> conducted research for Mobil Oil which led to the most extensive field evaluation in the United States. The test was run in the 2000-ft deep Nacatoch sand of Union County, Arkansas. Sand permeability ran as high as 5700 md in an average 11-ft productive interval. The zone had been subjected to gas injection and waterflooding for five years prior to inoculation with a gas-producing *Clostridium*. The *Clostridium* was supported metabolically by injection of a 2% molasses solution at a rate of 100 BPD. As a result of the inoculation, water produced in the nearest offset produced ethanol, acetone, fatty acids and  $CO_2$ . The molasses began to appear in about 80 days. Over the next 11 months, fermentation products appeared in the offset and a second producer 665 ft from the injector, but no products were noted in wells located over 1000 ft from the injector. A temporary, slight production increase was noted, but more

importance was placed on the change in produced petroleum products. Results of the experiment are described by Davis.<sup>16</sup> "About 50% of the injected sugar could be accounted for as C<sub>1</sub>-C<sub>7</sub> acids." Additionally, CO<sub>2</sub> and methane were produced. About 80% of the methane came from petroleum while 20% was of bacterial origin. Hydrogen, an expected fermentation product, was not detected but may have been trapped in the formation and aided oil recovery.

Davis<sup>16</sup> described the results, "Although it is possible that the extensive subsurface bacterial fermentation of molasses resulted in the increased production of oil, the nearest offset produced oil contained no viable bacteria or fermentation products and had the same characteristics of oil produced from wells outside the test area."

The test was a scientific curiosity but results did not justify expansion of the project in the early 1960's. Microbiological activity showed signs of technical promise but nothing approaching commercialization was proven by the test.

More recent publication of work by Senuykov, et. al.,<sup>17</sup> emphasizes microbiological oil recovery is possible but there are no well-established criteria for the evaluation of oil-producing formations from the standpoint of carrying out bacterial treatment. Waterflooded reservoirs of suitable permeability, depth and temperature, salinity, pH and other ill-defined parameters should be good candidates for future work. Coty<sup>15</sup> further indicates the *Clostridium* used in his Arkansas test, "would appear to be the organisms of choice for microbial oil release rests".

In addition to confirming the results reported by Coty, Jaranyi<sup>18</sup> noted oil production increases of 30-140% with pressure increases of several folds in shut-in wells. There were cases where enhanced oil recovery was observed for five years in the test in Hungary.

## OTHER APPLICATIONS

### *Disaster Control*

The well-known problem of bacterial plugging has been considered as a means of controlling water distribution in the waterflood.<sup>19</sup> This mechanism for disaster control would allow injection of the microorganism and a spacer to carry it away from

the wellbore. The bacteria would follow the water injection profile and eventually plug thief zones. This would allow water injection into new, less permeable sections of the formation.

### *Surface Application*

A major use of microbiological process is the production of biopolymer which is subsequently used downhole as a mobility control agent in waterflooding.<sup>21</sup> Biopolymer is a polysaccharide complex produced by fermentation process in chemical plants. The polymer itself is a product of carefully controlled bacterial action. Once produced, the biopolymer acts as a viscosifier for water. Biopolymer is not a living organism-- it is the product of bacterial action.

One major problem with injecting biopolymers in a polymer flood is the viscous fluid tends to increase injection pressure by plugging the wellbore. In situ production of the biopolymer may some day be a feasible answer to this problem.<sup>20</sup> On the more practical side, research to produce new biopolymers for use as mobility control agents in surfactant flooding is the most important application of microbiology to the petroleum industry.

Another surface use of bioagents is in removal of oil pollution. Bacteria have long been known to degrade oil concentration in soil. Recent projects have developed salt-resistant bacterial strains capable of rapidly attacking oil slicks on fresh water and at sea.

## CONCLUSION

The use of bioagents to improve oil recovery by direct use in waterflooding appears impractical at this time. Future developments through research may improve feasibility of microbial oil recovery in the next 25 years. This will be expensive, high-risk research and will likely require governmental support to finance projects of the magnitude required.

On the other hand, research capabilities in industry today could be channelled to produce answers to pressing oil industry needs by using bioagents. The projects with the most chance of success will likely be those where surface treatment by microbial activity will produce a surfactant or polymer which is effective downhole. Success will come with control; and a major problem in

downhole application of bacteria is in controlling this metabolism. In situ chemical processes, such as matrix explosives and generated acid, have come and gone through the years. A major problem has always been lack of control downhole. This is doubly true with bioagents.

Listed below are several projects which may be of interest to the industry.

1. Microbiological improvement of biopolymers
2. Bioproduced surfactants
3. Diverting agents for thief zones
4. Permeability improvement agents - materials to act as deep penetrating, non-adsorbing surfactants to improve sweep efficiency
5. Technology to convert heavy oils to lighter ones
6. Stimulation of producing wells by destruction of wellbore damage.

The order of risk in research increases toward the bottom of the list. Possibly contained in this list is a project which will have major impact on secondary or tertiary oil recovery by the year 1990. In the meantime, we may have to be more concerned about investing in proper planning to prevent the undesirable effects of microbes on oil production.

#### REFERENCES

1. Bunker, J.J.: Microbiological Anaerobic Corrosion. *Jour. Soc. Chem. Ind.*, 59, (1940), pp. 412-414.
2. Kuznetsov, V.V. and Veryubitskaya, L.V.: Role of Microorganisms in Iron Corrosion in Water. *Mikrobiologiya*, 30, 1961, pp. 511-514.
3. Wanklyn, J.N. and Spruit, C.J.P.: Influence of Sulfate Reducing Bacteria on Corrosion Potential of Iron. *Nature*, 169 (4309), 1952, pp. 928-929.
4. Horvath, J.: Mechanism of Anaerobic Microbiological Corrosion. *Acta Chim. Acad. Sci. Hung.*, 25 (1960) pp. 65-78.
5. Anderson, K.E.: Bacteriological Testing. *World Oil*, 142 (4) 1956, pp. 176-182.
6. Kuznetsov, S. I. and Telegina, Z. P.: Physiology of Propane Oxidizing Bacteria. *Mikrobiologiya*, 26, 1957, pp. 512-518.
7. Ashirov, K.B. and Sazonova, I.V.: Biogenic

Sealing of Oil Deposits in Carbonate Reservoirs. *Mikrobiologiya*, 31, 1962, pp. 680-683.

8. Levenson, A. I.: 1954. "Geology of Petroleum". Freeman, San Francisco, 703 pp.
9. Lindblom, G.P. and Patton, J.T.: Substituted Heteropoly Saccharide. Can. Pat. No. 675,416, (1963).
10. ZoBell, C.E.: Bacterial Release of Oil from Sedimentary Materials. *Oil & Gas Jour.*, 46 (13) 1947, pp. 62-65.
11. Updegraff, D.M. and Wren, G.B.: (1954) The Release of Oil by Sulfate Reducing Bacteria. *Appl. Microbiol.* 2, (1954) pp. 309-322.
12. LaRiviere, J.W.M.: Release of Oil from Oil-Sand Mixture with Aid of Sulfate Reducing Bacteria. *Jour. Microbiol. Serol.*, 21, 1955 pp. 9-27.
13. Dostalek, M.; Spruny, M.; and Rosypalova, A.: Action of Bacteria on the Release of Oil. *Czech. Inst. Petrol. Res., Trans.*, 9, 1958, pp. 29-44.
14. Kuznetsov, S.I.: Formation of Methane in Gas-Petroleum Formations. *Mikrobiologiya*, 19, 1950, pp. 193-202.
15. Coty, V.F.: Microbial Oxidation of Aromatic Hydrocarbons. *Bacterial Proc.*, Abstr., 32, 1964, p. 6.
16. Davis J.B.: "Petroleum Microbiology." Elsevier Publishing Co., New York, 1967, pp. 276-279.
17. Senuykov, V.; Yulbarisov, E.; and Taldykina, N.: *Microbiology*, U.S.S.R. 39, 1970, pp. 612-616.
18. Dienes, M. and Jaranyi, S.: Increase of Oil Recovery by Introducing Anaerobic Bacteria into the Formation at Demjen Field, Hungary. *Koolaj Foldgaz*, 6, 106, 1973, pp. 205-208.
19. Crawford, P.G.: Possible Bacterial Correction of Stratification Problems. *Prod. Mon.*, 25 (12), pp. 10-11.
20. VanHeiningen, J.: Recovery of Petroleum from Rocks. Netherlands Patent 89, 580. (1958)
21. Frick, J.R., Jr.: Bacterial Processes in Oil Recovery. *Jour. Petr. Tech.*, 24, 1972, pp. 1469-1470.