Bacteria in the Oil Field:

Petroleum engineers are nothing if not eclectic. In their quest for hydrocarbons, they exploit esoteric disciplines ranging from nuclear physics to satellite-assisted communications, from factor analysis to information theory. An area as far from home as any of these, but as pertinent, is microbiology.

Interactions of bacteria—both good and bad—with oil-field equipment and earth formations have been known for decades. As early as 1923, von Wolzogen Kühr discussed electrobiological corrosion downhole, and 11 years later he coauthored an electrochemical theory of bacterial corrosion. In 1946 Claude ZoBell of the American Petroleum Institute patented the first method for injecting bacteria into the formation to increase oil mobility. Today, entire disciplines are devoted to discouraging bacterial-related problems and to encouraging bacterial-related enhanced oil recovery (EOR). To understand how bacteria help and harm oil wells, first consider what bacteria are and how they work.

Bacteria belong to a group of organisms called procaryotes, whose cells have no compartmentalized nucleus (above right). Like all forms of life, bacteria use energy to carry on vital functions and to build new cells—that is, they have a metabolism. Bacterial metabolism is either anaerobic (without oxygen, called fermentation) or aerobic (with oxygen, called respiration).

In the oil field, the most common and troublesome organisms are anaerobic sulfate-reducing bacteria (SRB) of the genus *Desulfovibrio*. They obtain energy from organic compounds available in the well by the following reaction:

\[ 4H_2 + SO_{4}^{2-} + 2H^+ \rightarrow 4H_2O + H_2S + \text{Energy} \]

Although the details of anaerobic bacterial metabolism are still debated, specialists agree on its three main products (right): hydrogenase, an enzyme that catalyzes the oxidation of hydrogen even in anaerobic environments, converting iron from the metallic state to ionic state; acetic acid \([\text{CH}_3\text{CO}_2\text{H}]\), which forms pockets of corrosion, called concentration cells, at interfaces between iron sulfide \([\text{FeS}_2]\) and
Bad News, Good News

metallic iron; and hydrogen sulfide \([H_2S]\), which converts metallic iron to iron sulfide flocs (below right and right). Most bacterial corrosion detected by the Casing Evaluation (CET) tool is caused by anaerobes.

Aerobic bacteria are also present, but in smaller numbers and with less significant effects. Many aerobic bacteria oxidize iron from the ferrous \([Fe^{2+}]\) to the ferric state \([Fe^{3+}]\), with the precipitation of rust iron hydroxide, \(4Fe(OH)_3\):

\[
4FeCO_3 + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 4CO_2
\]

Corrosion is also hastened by oxygen concentrating beneath aerobic biofilms covering metal surfaces and promoting concentration cells.

Aerobic bacteria are most often found in fresh-water injection systems, but may grow in as little as a few tenths parts per million of oxygen. But if oxygen is not replenished they perish, leaving the field free to anaerobes. In some systems with limited oxygen, \(H_2S\) generated by SRB living in anaerobic microniches also contributes to the reduction of oxygen, which encourages SRB proliferation.

In addition to causing corrosion, bacteria can plug rock pores by liberating \(H_2S\), which causes precipitation of iron sulfide flocs, and by creation of bacterial slimes. These slimes consist mainly of an accumulation of bacterial cells and a glycocalyx,


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\[\text{Scanning-electron micrograph showing biofilm surrounding a corrosion pit. Enlargement, inside the pit, shows crystals of metal corrosion product, probably iron sulfide (planar objects), interspersed with bacteria (cylindrical objects).}\]

\[\text{Three-inch-diameter pit (left) caused by bacterial corrosion inside pipe removed from a recycle line in an oil-treating plant. The pipe has been cut longitudinally.}\]
population but not the more problematic sessile population. This may lead to the selection of a bactericide that kills planktonic bacteria but won’t penetrate the glycocalyx of sessile bacteria.

In laboratory experiments that permitted counting sessile bacteria separately, Ruseska and coworkers showed that of 10 bactericides, only isothiazolone controlled bacteria that had well-developed biofilms. They counted sessile bacteria with a Robbins Device, essentially a flow tube with a series of removable studs set into its wall. By following the buildup of bacteria on the studs as water flowed through the tube, they could segregate effects on sessile bacteria from those on planktonic.

Care must also be taken in selecting a medium for culturing the bacteria in the laboratory, called a nutrient substrate, since the medium can give misleading results. In one study of a West German oil well, investigators found that bacteria responsible for a rising H₂S level grew only on an acetate substrate. Cord-Ruwisch and colleagues note that a natural source of acetate nutrients is unknown, although they may be compounds of crude that are enriched in asphaltic and resin-like components that accumulate in treatment equipment, at the oil/water interface and at the well bottom. Routine culturing with lactate substrate, they note, would have significantly underestimated the number of SRB and might have masked the bacteria responsible for H₂S production.

The main concern in their study was that rising H₂S would cause the precipitation of iron-sulfide flocs that would plug the rock pores. To alleviate plugging, Cord-Ruwisch and coworkers could have used bactericides but opted not to because of economic and environmental concerns. Instead, they removed precipitates and particulates that carried SRB, added hydrochloric acid (HCl) to reduce the pH to about 5 and reduce iron sulfide precipitation, and maintained high salinity to inhibit SRB growth (150 g NaCl/liter [=150,000 parts per million] inhibited growth of most SRB). For at least three years following this treatment, no plugging or other SRB-induced problems appeared. These procedures concur with the recommendations of the (United States) National Association of Corrosion Engineers (NACE). The association recommends flushing and scraping all lines, backflowing injection wells where possible, and back-flushing filters—adding surfactants and bactericides where necessary.

Bactericide treatment requires careful pretesting and planning. The bactericide should include so-called bacteriostatic screening, or time-kill tests, that approximate the conditions expected in the reservoir or "plumbing." These tests indicate the effectiveness of potential bactericides. The bactericide may be applied continuously or once every few days to once a month or two. Continuous treatment is usually several times more expensive than periodic treatment, and the relatively high cost of the

Detecting and Controlling Bacterial Growth

Proper control of bacterial growth requires knowledge of the bacteria responsible for corrosion or plugging (or both), since treatment is bacteria-specific. One problem in selecting and monitoring the effectiveness of bactericides—chemicals that kill bacteria—is distinguishing sessile from planktonic bacteria, both of which can be sulfate-reducing (right). Sessile bacteria, which are responsible for most corrosion and plugging, adhere to surfaces with their glycocalyxes. Planktonic bacteria spend their lives floating freely, never attaching to a substrate. Although the concentration of sessile bacteria can be a few orders of magnitude higher than planktonic, their lack of mobility may make them scarce in samples taken from flowing fluids. Thus, bacterial counts from well fluids may reflect the planktonic.

Typical microbial consortium showing large variety of bacteria types. Although from the rumen of a cow, such a mixed population may equally be found in oil-field environments.
Increasing Oil Movability

The oil shortages of the 1970s sparked interest in extending the work Zobell started 30 years before—using bacteria to improve recovery. Some progress was made on Microbial Enhanced Oil Recovery (MEOR) but the ensuing oil glut halted most work. More recently, the low cost of MEOR has won it renewed attention.15

Current work modifies Zobell’s patent, which covered a method of injecting bacteria into a formation to increase oil mobility. Zobell isolated what he thought was a strain of Desulfovibrio that proliferated in salt solutions and tolerated relatively high temperature. These bacteria were thought to mobilize oil by producing biosurfactants or detergents that reduce interfacial tension and thereby increase the oil mobility. Later researchers suggested enhancing this process by adding nutrients, such as molasses, to feed the bacteria. Currently, a number of other microorganisms, including Clostriidium, are used in offshore applications. The graph (above right) shows the rapid decrease in sulfide ion and \( \text{H}_2\text{S} \) following aeration of water in the leg of an offshore platform. This aeration eventually reduced the SRB concentration in the water to 5 orders of magnitude and prevented further SRB growth. Unfortunately, Wilkinson found no way to prevent the formation of \( \text{H}_2\text{S} \) in the oil storage system and had to rely on avoiding uncontrolled discharge of contaminated water.

A comparative study of bactericides that focused on chemical, biological and toxicological properties, such as environmental pollution, rate of biodegradation, and carcinogenesis was carried out by E. Bessem of Akzo Chemie.13 Belchett concluded that the chemicals of choice belong to a class of compounds known as quaternary ammoniums, selected for their ability to inhibit or kill SRB. Rejected bactericides were chlorinated phenols (resistant to normal biodegradation), chlorine-releasing compounds (neutralized in the presence of organic, reducing material), and formaldehyde (potentially carcinogenic).

A different experience is reported by Cusack and coworkers.14 They successfully used sodium hypochlorite [NaOCl] (bleach) to clean injection wells plugged by bacterial growth. One of the problems now recognized in the application of bactericides is the necessity of penetrating the gleycoaly and getting to the bacteria. Bleach does this, breaking up the gleycoaly, killing the bacterium and loosening the biofilm enough for backflow to flush it from the formation. These authors show that, for reasons still unclear, bacterial growth in waterflooding is limited to within a few meters of injection and production wells. Thus, the resulting plugging is readily accessible to bactericide treatment. However, they also observe that the slimy biofilm, in addition to trapping floating nutrients for bacteria to consume, filters inorganic fines that can plug rock pores. Consequently, treatment by bactericide alone, however effectively it kills bacteria, may not satisfactorily unplug the damaged zone near the borehole. If the fines are susceptible to acid attack, the bactericide treatment must be followed by HCl injection to restore productivity. The sequence is important; if acid is injected first, it is not able to penetrate the bacterial biofilm to dissolve particulates.

1. A polysaccharide is a complex carbohydrate such as the starch of a potato or cellulose, which is the chief component of wood and cotton.
3. Acetate is an ester (a compound of alcohol and acid, usually without water) or a salt of acetic acid, \( \text{C}_2\text{H}_4\text{O}_2 \), the chief acid of vinegar. It is a significant nutrient for SRB. Lactate is an analogous compound related to lactic acid, \( \text{C}_3\text{H}_6\text{O}_3 \).
um, Enterobacter and Bacillus are being investigated. In the 1950s and 1960s, laboratory studies on cores were made in the United States, and successful single-well field tests were reported in Eastern Europe, but no field trials appeared in the US literature before 1972.16

In the last 15 years, researchers have identified many microorganisms that metabolize nutrients into products that can enhance the production of oil. By fermenting nutrients that can be easily injected into the formation (molasses, for example), certain anaerobic bacteria produce biosurfactants and detergents in place. Fermentation can also generate carbon dioxide, hydrogen, methane [CH₄], and nitrogen, thus contributing to oil mobilization by reducing viscosity (above). Viscosity is reduced also by solvents, such as acetones and alcohols, that are products of bacterial respiration. It has even been suggested that the gases produced could build up enough pressure to increase production from gas-depleted reservoirs. Although this effect has been observed in single wells, it has not been tried in tertiary recovery. Similarly, organic acids resulting from bacterial metabolism are thought to increase porosity and permeability by dissolving carbonate rock, but this is only now being tested on cores.

In addition to the salutary effects of bacterial metabolic by-products, the direct action of bacteria on petroleum may increase hydrocarbon production. Hydrocarbons with available hydrogen bonds (unsaturated hydrocarbons), strongly held on rock surfaces, appear to be attacked and released by SRB. Although some investigators believe that SRB can split saturated long-chain hydrocarbons into shorter ones, thereby increasing hydrocarbon mobility, the subject is controversial.17 A review of a number of field tests of microbial enhanced oil recovery in the US has been given by R.S. Bryant.18 Although many of these are single-well experiments, a few are true microbial floods. Oil production increased by 20 to 200 percent, depending on a variety of factors including initial oil saturation, temperature, salinity, permeability, bacteria and nutrients employed, and injection procedures. Bryant notes the need for studies of the transport of microorganisms in reservoirs. This may not only improve MEOR but also answer questions about the environmental safety of microorganisms, although the microorganisms typically injected do not cause disease.

An MEOR project requires the same foresight and planning as other oil-field projects. Reservoirs chosen must conform to a number of characteristics: temperature (<160°F [71°C]), salinity (<10 to 15 percent), permeability (>100 millidarcies since bacteria measure =1 micron), depth (<10,000 feet [3,000 meters]), and residual oil saturation (25 to 30 percent).15 The goal must be clear: waterflooding or permeability modification. Using core analysis or logs (such as the Geochemical [GLT*] log or the Litho-Density* log), as much information as possible should be collected on rock matrix mineralogy, clay mineralogy and distribution, and, from produced water samples, the nature of indigenous microorganisms. Temperature and salinity can adversely affect the project by increasing retention of the injected microbes through attachment or filtration, and clays may also adsorb surfactants and solvents produced by fermentation. Indigenous microbes may either help or hinder.

After injection, it is important to monitor produced fluids. The presence of nutrients, for example, suggests bacteria aren't growing well or that excess nutrient is being injected. Black water can indicate iron sulfide production by indigenous SRB. Microbial activity can also be assessed by examining samples of backflush water for foam or high turbidity, by smell (with certain microorganisms) or, more reliably, by lab culture and microscopic examination.

A field-wide test of MEOR was done in the Mink Unit of the Delaware-Childers field in northeast Oklahoma to determine whether MEOR could increase production in a mature waterflood.19 Four of 21 injection wells were each treated with 10 gallons [38 liters] of molasses before and after injection of 26 gallons [99 liters] of microbial formulation. After the wells were shut in for two weeks, backflush samples were drawn. The samples showed foam, indicating surfactant production and microbial viability. Thirty weeks later viability was further confirmed by the appearance of injected microorganisms in production wells about 1,000 feet [300 meters] from the injection sites. This is believed to be the first observed transport of microorganisms between injection and production wells. Output from the field's 15 producing wells increased 13 percent in the year after bacterial injection. Presumably, production might have been higher if all 21 injectors had received the same treatment. In addition, water/oil ratios at producing wells dropped nearly 35 percent.

Reducing Fluid Mobility/Permeability Microorganisms can also be used to reduce fluid mobility. Biologically produced polymers such as polysaccharide xanthan gum, a food additive, have been used for some time in EOR to thicken injection water and thereby increase sweep efficiency. Xanthan gum is especially attractive because of its
shear resistance, tolerance of temperature and salinity, and the convenience of manufacture within the formation, using a mixture of bacteria and nutrients. A similar approach has been suggested for selectively plugging high permeability channels and thief zones.\(^{16}\) Although this has worked in the laboratory, it has yet to be tested in the field. Plugging the borehole could be avoided, if necessary, by separate-stage injection of bacteria and nutrient; then a small amount of bactericide could stop growth at the face of the formation. Successful plugging would depend on choosing a microbial formulation that fosters creation of a glycolycol.

J.W. Costerton of the University of Calgary recently proposed an approach to plugging with a different application in mind.\(^{20}\) Costerton observes that certain starved bacteria shrink drastically then swell 500-fold after nutrients become available. He suggests that these bacteria be used to prevent coning. The cells would be injected into the formation at the level of the oil-water interface, where, because of their small size, they could penetrate as much as 15 feet (5 meters) radially. Then, after being fed an inexpensive diet of pulp and paper waste products, they would swell and clump, forming a plug that should prevent water from coming into the producing zone. This general method has been tried before, by injecting cement and polyacrylic, but these materials do not penetrate far enough into the formation and are more expensive than bacteria and nutrients. No field trials have been made, but laboratory simulations support Costerton’s hypothesis.

From the variety of field conditions studied and the observations of different investigators, it is clear that much remains to be learned of what could be called geomicrobiology and its engineering applications.


Letters

To the editor:

I enjoyed your October 1988 article “Archie II: Electrical Conduction in Hydrocarbon-Bearing Rocks” for very practical reasons which may be of interest.\(^{1}\)

Monitor Petroleum Co. was a nonoperating working interest owner in the drilling of the Wylee Petroleum #1 Quinn-Rushing, a Lower Tuscaloosa test in Lincoln County, Mississippi.

A dual-induction log showed a clean-looking zone with a very low resistivity of about 0.2 ohm-m. Despite the fact that sidewall cores showed up to 15% oil, the operator, with Monitor dissenting, chose to plug and abandon the well. No SEM analysis was attempted, but a visual inspection of the cores indicated several discrete units of upwardly coarsening grain-size deposition cycles and thus the possibility of differing clay mineralogy within each cycle.

Almost a year later, the operator and Monitor Petroleum re-drilled the well, and despite some mechanical difficulties, completed a pumping oil well. A dual-induction log run on reeceived showed a similar response—i.e., very low resistivity—to the initial log.

The work cited in your article, about how microporosity reduces resistivity, would lend credence to our original misgivings and prompt us to include SEM analyses when faced with similar anomalous log responses. It’s possible that the low resistivity was caused by micro-porous clays.

The producing streamline reservoirs of the Lower Tuscaloosa in southwestern Mississippi are notorious for their anomalously low resistivities, clay mineral contamination, and cyclic deposition histories. With relatively high well densities, log data from this area could supplement the ongoing theoretical work on the effects of clay microporosity on electrical conduction.

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November 3, 1988

[Ed: Watch for a future article on electrical conduction in shaly sands in The Technical Review.]

To the editor:

I enjoyed your lead article on Archie’s Law in the July issue of The Technical Review. I have always thought it curious that Archie chose a 0 (zero) for his subscript for R, the resistivity of brine-saturated rock. I guess there was no convention so he could certainly do anything he wanted, but it remains today virtually the only subscript in the formation evaluation business that is a number rather than a letter. Today’s convention probably would call it R\(^{w}\), (R-sub-w, saturated rock), or R\(^{o}\), (R-sub-o, brine saturated), or referring to the 1988 Schlumberger Log Interpretation Principles/Applications (p.122), we could go with R\(^{nw}\), (R-sub-nw, non-wetted formation rock) 100% salinaity with brine.

Several other oddities persist, however, even after setting aside the ‘numeral-rather than letter’ peculiarity. First of all, the saturation of the brine is not 0%, but 100%. One would think that R\(^{o}\) should be R\(^{o}\), to match the standard definition. Of course, I know (at least I think I know) that the zero comes from the saturation of oil, but so what...the saturating fluid is brine, not oil. Secondly, isn’t it odd that so many of us in the business refer to R\(^{w}\) as “R-sub-oh,” rather than “R-

sub-zero.” When I hear “R-sub-oh,” I will often ask the user what the “oh” stands for, and I invariably get a blank look that implies either “my gosh, I don’t know...I’ve never thought about it,” or “if you don’t know by now, you’ll never know, you idiot.” (This is the least odd of the oddities I’ve mentioned, since it is not uncommon to refer to zeros as “oh’s” in our daily conversation...telephone numbers, for instance.)

Please don’t think I am as disturbed by this subject as the length of this letter may imply. The real reason I am writing is that I just discovered how to use the subscripting capability of Microsoft Word on my Mac, and wanted to give it a whirl.

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Anadroll

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August 30, 1988

[Ed: We appreciate how you feel. With the October 1988 issue, we switched to Macintosh computers to produce The Technical Review.]

To the editor:

I would like to comment on part of Scott Broussard’s July 1988 article “High Resistivity in Oklahoma.”\(^{4}\)

For his first example, the question is how to explain the fact that the deep induction shows a high resistivity, the medium induction reads 6 to 7 times lower, and the SFL is somewhere in between. Bill Hoyle claimed that the response was caused by horizontal fractures. Scott Broussard later countered claimed there were no fractures. I agree with Scott, but do not agree with how he got there.

I disagree mainly with his statement: “The SFL, if it behaves anything like a laterolog (also a focussed resistivity measurement), would record less resistivity if the fractures were vertical.”

Horizontal fractures have a strong effect on laterolog-type measurements. This was established by Pierre Grimialdi at Etudes et Production Schlumberger in Clament, France using computer simulations, and published later by Alan Sibbit and Olivier Fairez.\(^{5}\)

A horizontal fracture with 100-micron aperture causes the shallow laterolog (equivalent in depth of investigation to the SFL) to drop in resistivity from 10,000 ohm-m (assumed matrix block resistivity) to around 900 ohm-m (assuming a mud resistivity of 0.1 ohm-m). A 100-micron vertical fracture, on the other hand, brings the shallow laterolog down to only 1,600 to 1,700 ohm-m.

I was therefore happy to see Scott verifying the various resistivity readings for “additional” effects and arriving at his conclusion: “probably no fractures then.”

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September 9, 1988


