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This Technical Committee Report has been prepared by NACE International Task Group 075 on Biocides—Oil and Gas Industry*

Selection, Application, and Evaluation of Biocides in the Oil and Gas Industry

Foreword

The purpose of this technical committee report is to discuss the state-of-the-art considerations and methods for selecting, applying, and evaluating the use of biocides in oil and gas field operations. These field operations include stimulation, production, storage, transmission, hydrostatic testing, and water injection applications.

This report is intended to be a resource for oil and gas professionals. In addition to providing information on the selection, application, and evaluation of biocides, the report directs the reader to standard procedures, guidelines, textbooks, and regulatory documents for more in-depth information. This is achieved through the extensive use of references and an annotated bibliography.

This report was prepared by Task Group (TG) 075 on Oil Industry Biocides. TG 075 is administered by Specific Technology Group (STG) 31 on Oil and Gas Production—Corrosion and Scale Inhibition. It is published by NACE International under the auspices of STG 31.

NACE technical committee reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be recommendations for general application of this technology, and must not be construed as such.

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Contents

Section 1: Oil and Gas Field Microbiology

A detailed understanding and thorough evaluation of several issues are used in implementing an effective biocide program. This report is intended to provide oil and gas professionals with the background that can assist them in considering treatment alternatives, selecting the most cost-effective treatment program, applying the technology using practices that comply with governmental regulations, and continuously monitoring and optimizing the treatment program. Through the extensive use of references and an annotated bibliography, the reader is directed to standards, guideline documents, publications, and textbooks for additional information. A glossary of terms is also provided in Appendix A of this report. The use of biocides in refinery and other industrial applications is outside the scope of this report.

Types and Classes of Bacteria in Oil and Gas Field Systems

Identification and naming (taxonomy) of bacteria is an exhaustive science. To date, more than 5,000 species of bacteria have been identified, isolated, and named.[1,2] In virtually all oilfield systems, multiple strains of bacteria coexist in symbiotic relationships.[3-6] Classification of each strain of bacteria in a population is further complicated by the fact that no single test can be used to quantify all types of bacteria that might be present in oilfield populations. Different types of growth media, some with nonstandard formulations, are normally used to begin to quantify the numbers and types of bacteria in a single population.

For ease of discussion, microbiologists often group bacteria according to the organism's tolerance of oxygen, shape, optimum growth temperature, or metabolism. Bacteria that use oxygen in their metabolism are termed strict or obligate aerobic bacteria. In contrast, obligate anaerobic bacteria do not grow in the presence of oxygen. Facultative anaerobes function either in the presence or absence of oxygen, and microaerophiles use oxygen, but prefer low levels. It is common to find bacteria with different oxygen requirements coexisting in the same system and in the same deposits. In highly oxygenated systems, for example, anaerobic bacteria often survive in tiny crevices in pipe surfaces that are out of the direct flow of the oxygenated water. Furthermore, as populations of aerobic bacteria deposit on a system surface, oxygen diffusion to the surface is suppressed. This creates a reduced-oxygen environment in which microaerophiles and anaerobes can thrive, shielded from the oxygen in the system by the aerobic bacteria.[1,2]

Microbiologists typically group bacteria according to the shape of the bacterium's cell body (morphology). Bacteria are shaped as rods (bacillus), curved rods (vibrio), corkscrew curved rods (spirillum), and spheres (coccus). Shape alone, however, is not normally a good indicator of a bacterial type because a single strain of bacteria can take on different shapes depending on growth conditions, and many different species may have similar morphologies.

A third way that bacteria are grouped is by the optimum temperature at which they grow. Thermophilic bacteria have maximum growth rates at temperatures above 50°C (122°F). Mesophiles grow best in the middle temperature range of 20 to 37°C (68 to 99°F). Other organisms called psychrophiles only grow well near freezing temperatures of 4 to 10°C (39 to 50°F). While each species of bacteria grows at an optimum temperature, it can also adapt and grow at temperatures outside the ranges listed above. In fact, most species have the capacity to grow over a 40°C (72°F) range of temperatures. System parameters such as the availability of nutrients, pH, salinity, and pressure can also alter the optimum growth temperature for a particular strain of bacteria.

Finally, bacteria are often grouped according to the nutrients that the organism uses for growth and reproduction, the biochemical pathways where the organism obtains energy, or the end-product chemicals that the organism eliminates. Examples of this classification method are sulfate-reducing bacteria (SRB), acid-producing bacteria (APB), iron-oxidizing bacteria, sulfur-oxidizing bacteria (SOB), and manganese-fixing bacteria.

If bacteria are identified, they are typically given a genus and species name.[7-10] These names occur together as two words, the first referring to the genus and the second to the species. As an example, *Desulfovibrio desulfuricans* is a specific name of one type of SRB. Often, names of bacteria are intended to be descriptive of the main characteristic of the organism. Thus, the Desulfovibrio desulfuricans is a bacterium that is in the shape of a curved rod that acts to remove sulfate by reduction to sulfide.

Sulfate-Reducing Bacteria

SRB are one of the most common and problematic type of bacteria in oil and gas field systems.[11-16] Although strictly anaerobic, SRB can persist and survive in systems containing dissolved oxygen.[17] Typically, they are found in quiescent water in dead legs of pipes, ratholes of wells, and under deposits of scale and other bacteria. They are also found as free-floating (planktonic) bacteria in turbulent waters. SRB tolerate a wide pH range of 5 to 9.5, but some oilfield brines reportedly are too saline to be conducive to active growth.[18] Most strains of SRB grow best at temperatures between 25 and 35°C (77 and 95°F), but a few thermophilic strains function at temperatures higher than 60°C (140°F).[4,19,20] *Desulfovibrio*, *Desulfobacter*, and *Desulfotomaculum* are three common genera of SRB. Other genera have also been identified.[17]

While SRB often differ in appearance or in the substances they metabolize, they all oxidize organic compounds to organic acids or CO_2 by reducing sulfate ions to sulfide ions through anaerobic respiration. In the absence of sulfate ions, SRB can also respire through reduction of sulfite and other sulfur-containing ions. Sulfide ions that are produced during the respiration process can react with dissolved iron to produce black deposits of iron sulfide, or with hydrogen ions to form poisonous hydrogen sulfide (H_2S). The presence of either iron sulfide or H_2S in field systems causes operational problems (see section on Problems Caused by Oil and Gas Field Bacteria).

When steel corrodes, a layer of atomic hydrogen builds up on the cathodic surface. If the hydrogen is not removed, it polarizes the surface and causes the corrosion rate to decrease. Using hydrogen in their anaerobic respiration process, SRB remove the atomic hydrogen from the surface, causing the cathodic surface to depolarize and increasing the rate of corrosion.[1,21-23] As a result, pit formation is accelerated. This corrosion process has been termed microbiologically influenced corrosion (MIC) and is the subject of many excellent reviews (see annotated bibliography for further information).

Iron-Oxidizing Bacteria

Iron-oxidizing bacteria are also known as iron-depositing bacteria and iron-related bacteria (IRB). These microaerobic bacteria belong to one of the genera *Gallionella*, *Siderocapsa*, *Sphaerotilus*, *Crenothrix*, *Leptothrix*, or *Clonothrix*. Iron-oxidizing bacteria are filamentous bacteria, usually found in hemispherical mounds, termed tubercles, over pits on steel surfaces.[1,21] The presence of rust-colored water and yellow-orange slime deposits usually suggest the presence of oxygen or oxidizing chemicals; however, these symptoms are sometimes caused by iron-oxidizing bacteria. In oilfield systems, iron-oxidizing bacteria are reportedly found in open ponds, supply wells, filters, lines, equipment, and in injection wells.[24]

Iron-oxidizing bacteria derive their name from the fact that they respire by oxidizing iron(II) to iron(III). Many of these organisms can also derive energy by oxidizing manganese(II) ions to manganese(III) ions. In oilfield brines, the iron(III) forms ferric hydroxide and ferric chloride that accumulate in the tubercles (see Figure 1). In addition to being aggressively corrosive to austenitic stainless steel (SS) as well as carbon steel (CS), the ferric chloride deposits on the tubercle and establishes an anaerobic environment in which SRB can thrive.

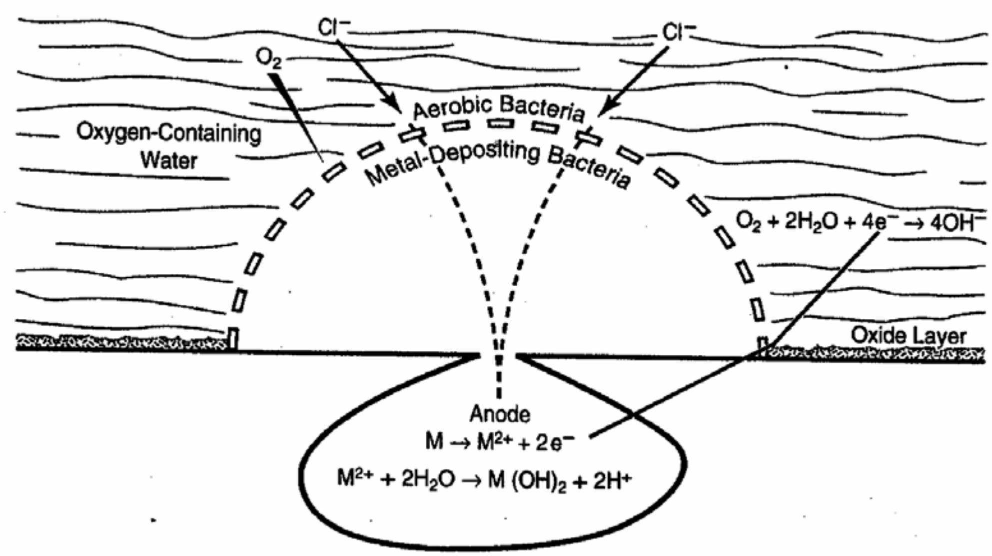

FIGURE 1: Reactions possible under tubercles created by iron-oxidizing bacteria.[1]

Acid-Producing Bacteria

Many bacteria produce organic and inorganic acids during their metabolism. Examples of APB are the anaerobic *Clostridium aceticum* that produces acetic acid and the obligate aerobic *Thiobacillus thiooxidans* that produces sulfuric acid.[1] *Thiobacillus* survive in acidic environments with pH between 0 and 4, but the optimum pH for growth is 2.5. It has been reported that *Thiobacillus* are most often found in storage tanks and platform legs.[25] The acids secreted by APB become trapped under the bacterial deposits and promote corrosion of a variety of metals by removing passivating oxide films from the surface.

Sulfur-Oxidizing Bacteria

The bacteria of the genus *Thiobacillus*, of which there are several types, belong to an unusual group of aerobic microorganisms called chemolithotrophs. These organisms obtain energy not by oxidation of organic compounds, but by oxidation of inorganic sulfur compounds (including sulfides) to sulfuric acid. The organisms build up their cell material by fixation of carbon dioxide.[1] The end product is sulfuric acid. *Thiobacillus* survive in acidic environments with pH between 0 and 4, but the optimum pH for growth is 2.5.

In addition to *Thiobacillus*, there exist a number of types of nonacid-producing SOB. *Beggiatoa*, one of the best known sulfur oxidizers, oxidizes H_2S to produce a characteristic gray slime containing elemental sulfur. Reportedly, *Beggiatoa* is frequently found where gathering lines dump into open pits.[25] The bacteria are difficult to culture in laboratory media and are usually detected by microscopic examination. *Chlorobium* and *Chromatium* are strains of anaerobic SOB that require sunlight to carry out photosynthesis.

Slime-Forming Bacteria

Bacteria produce a slimy coating called a capsule over the surface of their cell membranes. This capsular material, primarily comprised of polymeric starch-like substances called polysaccharides, assists the bacteria in filtering nutrients and resisting the effects of harsh environments and chemical treatments. This extracellular polymer (exopolymer or glycocalyx)[26] also facilitates sticking of bacteria to one another and to surfaces to make a cohesive matrix called a biofilm.

Some bacteria produce more exopolymer than others. Bacteria that produce copious quantities of exopolymer are called slime-forming bacteria. *Pseudomonas*, *Flavobacterium*, *Escherichia*, *Aerobacter*, and *Bacillus* are common genera of slime-forming bacteria. These bacteria are primarily aerobes, but some species are facultative anaerobes while others are obligate anaerobes. Slime formation in oil and gas field waters is a fairly common occurrence, and slime-forming bacteria are found in open ponds, supply wells, filters, lines, surface equipment, and storage tanks.[27] Because oxygen does not readily diffuse through the viscous exopolymer masses, the exopolymer deposits result in the establishment of oxygen concentration cells that lead to underdeposit corrosion and promote an ideal environment for SRB to thrive.

Biofilms

As individual bacteria cells excrete protective exopolymer, they become sticky and begin to adhere to surfaces. Debris, particulate matter, and other bacteria become embedded in the exopolymer film. If conditions in the film are conducive for growth, the embedded bacteria continue reproducing to form new microcolonies. The entire matrix of bacteria, exopolymer, debris, and particulate matter that adheres to a surface is termed a biofilm. Recent studies indicate that channels and void areas[28-32] separate the discrete microcolonies in a biofilm (Figure 2). The channels allow nutrients and other chemical species to diffuse into the biofilm. The void areas in the biofilm constitute 40 to 60% of the total biofilm volume.

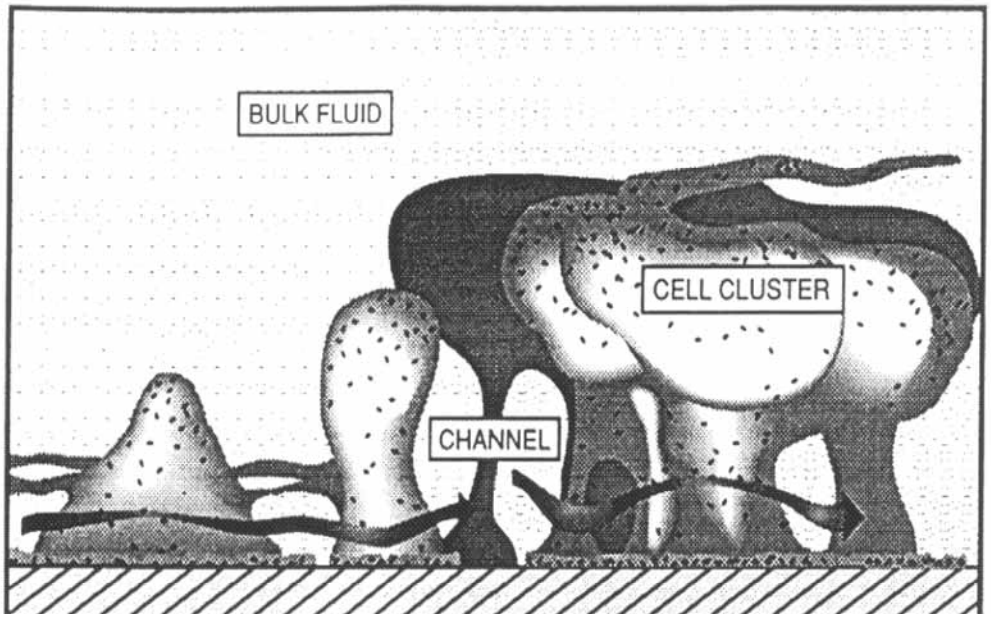

FIGURE 2: Model of a biofilm based on confocal scanning laser microscope images.[2,29]

As represented in Figure 3, many species of aerobic and anaerobic bacteria live in a symbiotic relationship within biofilms. Aerobic bacteria in the outer layers of the biofilm create an anaerobic environment at the base of the film where anaerobic bacteria can thrive. The aerobes also excrete metabolites that anaerobes use in their respiration processes. Thus, diverse consortia of bacteria can vigorously grow in biofilms.[1]

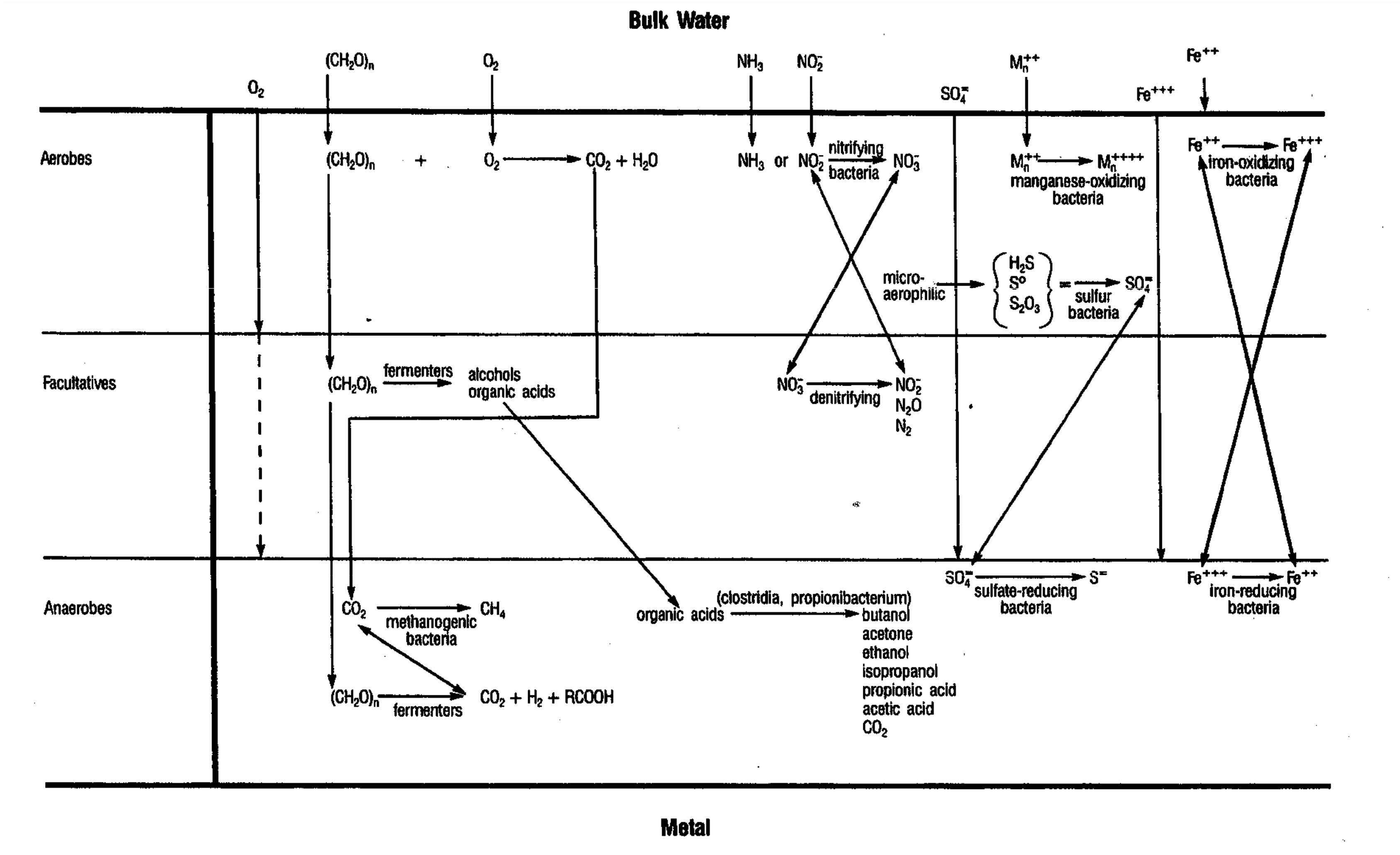

FIGURE 3: Strata within a typical biofilm and possible reactions within the strata.[1]

Surface-attached bacteria that live in biofilms are termed sessile bacteria. Because sessile bacteria are encased in exopolymer, they are more difficult to eradicate than free-floating planktonic bacteria. Yet it is the sessile populations that typically cause many operational problems in oil and gas fields. Although biocide selection tests for sessile populations are often more difficult to conduct than tests for planktonic bacteria, many microbiologists select biocides for their performance in controlling sessile populations.[33-37]

Factors Affecting Bacterial Growth Rate

Unlike green plants and a few species of photosynthetic bacteria, most oil and gas field bacteria obtain energy for growth and reproduction through bio-oxidation of various nutrients. Nutrients are food sources that provide the cell with carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, magnesium, iron, copper, sodium, potassium, and a few trace elements. The form of these nutritional constituents can vary widely, depending on the type of bacteria. However, regardless of their form, all nutrients are typically either dissolved in the brine or dissolved by exoenzymes secreted by the bacteria. Bacterial food sources include organic acids (such as lactic, ascorbic, and glutamic acids), sugars (such as dextrose and glucose), and hydrocarbons.[38,39]

Bio-oxidation of nutrients produces the energy that bacteria need to grow and reproduce. Different species of bacteria may use different series of bio-oxidation reactions (metabolic pathways), and a single strain of bacteria uses any of several alternate metabolic pathways. Aerobic bacteria carry out oxidation reactions using oxygen that is dissolved in water. Anaerobic bacteria carry out reduction reactions using molecular hydrogen that forms on corroding surfaces, as well as sulfate and nitrate.[1,17] The result of these metabolic pathways is the same: energy for the bacteria to grow and reproduce. The nutritional environment primarily controls the rate at which bacteria grow and reproduce. Under otherwise constant conditions, the growth rate of a culture of bacteria varies by more than tenfold, depending on the availability of nutrients in the growth medium.[40] Bacterial growth rate is also affected by temperature, pH, salinity, oxygen content, and, to a lesser extent, hydrostatic pressure.[41]

The number of bacteria in a water sample or operating system can change dramatically within only a few hours, in part because each bacterium reproduces through binary fission. Rates of reproduction vary depending on the growth conditions, but can be a matter of minutes. As an example of the dynamic growth of bacteria, if one bacterium was initially present and had a dividing rate of once every hour, in 24 hours there would be 2^{24} or 1.68×10^7 bacteria in the system if the system contained sufficient nutrients. Planktonic populations in oil and gas field systems typically reproduce at the maximum rate because the nutritional environment for free-floating bacteria is not diffusion-limited.

When system conditions change, the new conditions can significantly alter the bacterial populations in sessile deposits. The new conditions of nutrient availability, temperature, salinity, oxygen content, pH, and pressure retard the growth rate of one species while enhancing the growth rate of another species in the consortium. Because bacteria reproduce so rapidly, the consortium quickly adapts to the new environment. When laboratory tests are conducted, the nutritional environment, temperature, pH, salinity, and oxygen content of the culture media are normally matched to the system conditions.

Problems Caused by Oil and Gas Field Bacteria

Sessile bacteria accelerate corrosion processes in several ways.[1] They accelerate pitting corrosion by removing a corrosion byproduct—atomic hydrogen—from the cathode. In removing hydrogen, bacteria depolarize the surface and allow corrosion reactions to continue unabated. SRB also produce H_2S, increasing the corrosiveness of brine and causing metals to crack and blister. In addition, bacterially produced H_2S reacts with iron that is solubilized at the anode, thereby removing another corrosion byproduct to speed the corrosion process. APB produce acids that remove passivating oxide films from surfaces. The relationship between biological and inorganic corrosion processes is not completely understood and may be unique to each system.

Control of MIC is the most common reason for biocide treatment in oilfield systems.[34,42] However, MIC may only be a small part of the total corrosion mechanism in the system. When a potential biocide treatment program is evaluated, MIC is not normally considered alone, but as a portion of a total corrosion mechanism.

In addition to causing MIC, bacteria cause a number of other problems that increase the total cost of the production operations or devalue the production. A partial list of the operational problems that are typically caused by bacteria is shown in Table 1. Bacterially produced iron sulfide (FeS) causes plugging problems in production wells, downhole equipment, pumps, surface facilities, filters, and at sand faces in injection wells. As discussed above, SRB produce H_2S that can react with dissolved metals such as iron, zinc, and lead to produce insoluble metal sulfides. The metal sulfide particles collect throughout production facilities, but are notably responsible for failures of downhole pumps, frequent replacements of cartridge and sand filters in surface facilities, and loss of injectivity in injection and disposal wells.

Table 1: Examples of Operational Problems That May Be Caused by Bacteria

Increased frequency of corrosion failures
Increasing H_2S concentrations
Reservoir souring
Rapid production decline
Metal sulfide scales
Failure of downhole equipment due to metal sulfide deposits
Inefficient oil/water separation
Inefficient heat exchange
Black water
Black powder in gas transmission lines
Filter plugging
Loss of injectivity

Plugging of injection and disposal wells is a problem that is often underestimated by many production personnel. Planktonic bacteria are about 3 µm (0.003 mm) in diameter—approximately the same size as pores in reservoir rock. Bacterial cells, biofilm fragments, and metabolic by-products such as iron sulfide constitute a large percentage of the total suspended solids that are filtered or injected into a formation. At a sand face, bacterial solids act as a filter pad to trap other solids. The result is a solid mass of organic and inorganic matter that can significantly reduce injectivity.[43] The philosophy of most producers has traditionally been to acidize injection wells as needed. Although acidizing is an effective treatment for dissolving many inorganic deposits that may contribute to plugging, it is not typically effective in removing exopolymers and other bacterial solids.

Today, many producing wells and oil reservoirs are souring because water that was injected into either producing or injection wells was not effectively treated with biocide.[16,44] This practice has resulted in the development of sizable populations of SRB that are located either near the wellbore or in the formation. It is doubtful that any biocide can control bacterial populations that are established deep in a reservoir.

Bacteria and bacterial by-products sometimes cause operational problems in surface facilities, as well as in reservoirs. Biofilms can reduce the efficiency of heat exchangers. Metal sulfides, such as iron sulfide, which tend to be wetted by oil, accumulate at oil/water interfaces in separation equipment and storage tanks. These interface pads can cause ragged interfaces and inefficient oil-water separation processes.

Hydrogen sulfide (H_2S) is a poisonous, flammable gas. Not only is H_2S produced by bacteria, but it can also be produced from reaction of metal sulfides and acid. Rigorous safety precautions are followed when personnel are working in an area where H_2S gas is suspected.[45]

As a result of the numerous problems caused by bacteria in oil and gas production operations, aggressive measures have been taken to monitor and control bacterial populations. Measures to monitor bacteria, however, are not usually considered until after corrosion failures point to MIC. By the time that MIC is discovered, extensive and costly damage to the operating systems has often already occurred. Monitoring is often conducted in sweet systems with no hint of bacterial contamination to ensure that bacterial populations are under control and that operating costs and risks (health, safety, environmental, and mechanical failures) cannot be lowered by initiating an effective biocide program.[46] Ulman and Kretsinger[47] report a methodology that is often used to estimate the economic incentives for controlling oilfield bacteria and to establish the cost-effectiveness of various treatment options.

Section 2: Oil and Gas Field Biocides

Biocides are chemical products that are intended to kill or render harmless biological organisms. Bacteria are structurally and chemically complex organisms, and these complexities are targeted in several ways by modern biocides. Virtually every part of a bacterial cell and its metabolic pathway can be disrupted by biocides. In addition to acting on individual cells, biocides are designed to act on bacteria in biofilms. Biofilm parameters that influence biocide efficacy have been studied in well-characterized laboratory systems.[48,49,50] As a result, the various chemistries used for bacterial control in oilfield operations are often more varied than in any other group of treating compounds.

There are several ways to group biocides, but for oil and gas field applications, biocides are typically grouped into two chemical classes: oxidizers and nonoxidizers. The oxidizing biocides, such as chlorine (Cl_2), chlorine dioxide (ClO_2), and bleach (sodium hypochlorite [NaOCl]), generally provide much faster kill rates than nonoxidizing biocides. As a result, the oxidizing biocides are particularly useful in oil and gas field systems in which contact time with the bacteria is limited. However, oxidizers react with many different chemical species in the brine, including organic acids, soluble iron, and H_2S. Oxidation of these chemical species can produce copious amounts of solids that may need to be removed before the treated water can be reinjected. Another disadvantage of oxidizing biocides such as chlorine is that they react with oxygen scavengers and are therefore removed by the deaeration processes normally carried out in offshore seawater injection systems to prevent aerobic corrosion. In addition, oxidizers can be very corrosive to most metals; corrosion rates are especially high near the injection point in which the oxidizer concentration is highest. Thus, most produced water systems have a high chemical demand for oxidizing biocides. Oxidizing biocides are generally more cost-effective than nonoxidizing biocides in systems in which hydrocarbons are only present in low concentration (such as seawater injection and fresh make-up water systems).

Unlike oxidizing biocides, nonoxidizing biocides are generally less corrosive to metals and elastomers and do not form solids when appropriately applied. Within the nonoxidizer class, kill rates vary significantly from the relatively fast biocidal activity of 2,2-dibromo-3-nitrilopropionamide (DBNPA) to the slower isothiazolone.[51] Nonoxidizing biocides each have different advantages and limitations. Quaternary amines (quats), for example, are highly surface-active and may effectively penetrate biofilms; however, this surface activity may make it difficult for quats to propagate through high-surface-area systems and, as surfactants, they may also cause the treated fluids to foam. Other biocides function best over specific pH and salinity ranges.

Many of the chemicals discussed in this section are products that were originally used in water treating or preservative applications. As their utility in oil and gas field systems was discovered, the applications were extended. This section is designed to familiarize readers with some of the advantages and limitations of chemical biocides. Verifying that the biocide and treated water comply with prevailing governmental regulations is typical prior to using biocides.

<u>Oxidizing Biocides</u>

Oxidizing biocides are the most widely used biocides worldwide, and are the most common biocide used to treat seawater for injection. These biocides react with the cell wall and proteins in the cell membrane, altering the shape of the proteins and eventually causing the decomposition of the entire bacterial cell. Although oxidizers are inexpensive, they are notoriously corrosive (when free-halogen residuals are greater than 1 ppm as Cl_2) and can form a large amount of solid by-products.

Of the oxidizing biocides, chlorine and chlorine dioxide are the two most widely used biocides in oil and gas field systems. Other oxidizing biocides, such as halogenated hydantoin, chloramine, bromine, ozone, peroxide, and peracetic acid, have been successfully used in other industries to control bacteria, but have not been widely used in oil and gas field systems. The reader is referred to other texts[52,53,54] for further information on these oxidizing biocides.

Chlorine and Hypochlorite

When elemental chlorine (Cl_2) dissolves in water, it hydrolyzes in less than one second[55] into hydrogen ions (H^+), chloride ions (Cl^-), and hypochlorous acid (HOCl):

$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl$$

Hypochlorous acid is the active form of the biocide.

Hypochlorous acid is a weak acid that can dissociate into hydrogen ions and hypochlorite ions (OCl^-), depending on the pH and temperature of the system:

$$HOCl \rightleftharpoons H^+ + OCl$$

Hypochlorite is less effective than hypochlorous acid as a biocide. Below pH 7.5, the active biocide, hypochlorous acid, is the predominant species. However, above pH 7.5, the hypochlorous acid is predominantly ionized into hypochlorite ions. Based on ionization constants from Fair et al.,[56] Table 2 shows the percentage of nonionized hypochlorous acid in water as a function of the temperature and pH of the system. Figure 4 graphically shows the relationship at 20°C (68°F). The higher the percentage of hypochlorous acid, the more effective the product typically performs as a biocide.

At any given pH and temperature, the same relative concentrations of hypochlorous acid and hypochlorite are established, regardless of whether chlorine or hypochlorite is used to generate hypochlorous acid. Because the equilibrium concentration of hypochlorous acid is significantly higher below pH 7.5, chlorine and hypochlorite are often significantly more effective as biocides in acidic water.[57] The biocidal activity of chlorine and hypochlorite can be extended to alkaline pH for water that contains bromide ions (such as seawater). In this case, chlorine and hypochlorite oxidize bromide ions to hypobromous acid (HOBr), which is still an effective biocide in the pH 8 to pH 9 range.[58]

Table 2: Approximate Percentage of Nonionized Hypochlorous Acid in Water as a Function of pH and Temperature[56]

pH	Approximate Percentage of Hypochlorous Acid at Equilibrium					
	0°C (32°F)	5°C (41°F)	10°C (50°F)	15°C (59°F)	20°C (68°F)	25°C (77°F)
4.0	100.0	100.0	100.0	100.0	100.0	100.0
5.0	99.8	99.8	99.7	99.7	99.7	99.6
6.0	98.0	97.8	97.5	97.1	96.8	96.4
7.0	88.3	81.3	79.4	76.9	75.2	73.0
8.0	33.3	30.3	27.8	25.0	23.3	21.3
9.0	4.8	4.2	3.7	3.2	2.9	2.6
10.0	0.5	0.4	0.4	0.3	0.3	0.3
11.0	0.0	0.0	0.0	0.0	0.0	0.0

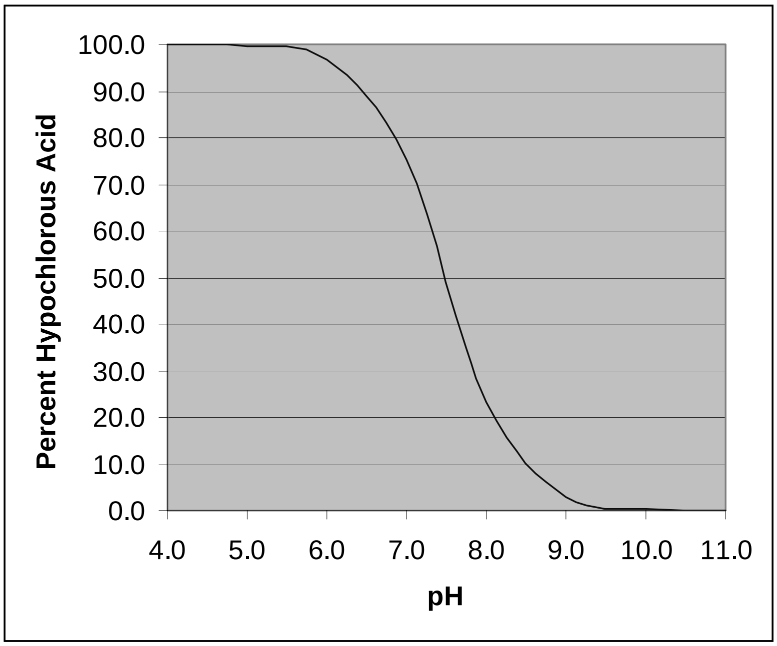

FIGURE 4: Approximate percentage of nonionized hypochlorous acid in water as a function of pH at 20°C (68°F)

Several different methods are available for forming hypochlorous acid in oilfield systems. Liquefied chlorine is often obtained in bulk containers and cylinders and fed through a chlorinator into the water.[59] Chlorine is a very hazardous chemical; special handling and equipment is typically used for safe and effective application of both gaseous and liquid chlorine.[59,60] Hypochlorite is often generated as a cost-effective alternative to chlorine. It is sometimes produced on site from water (such as seawater) that contains a sufficiently high concentration of chloride ions.[61] Hypochlorite is often added to systems as aqueous solutions of sodium hypochlorite (NaOCl, the active ingredient in bleach) and calcium hypochlorite ($Ca[OCl]_2$). For continuous biocide applications, aqueous hypochlorite solutions are seldom used because of their high cost compared to other sources of chlorine. However, bleach is sometimes used for batch cleanup operations in injection[62] and disposal wells or in produced water tanks.

The amount of hypochlorous acid typically used to control bacteria is dependent on the chlorine demand of the water and the contact time of the hypochlorous acid with the bacteria.[60] A free chlorine residual (the total concentration of chlorine, hypochlorous acid, and hypochlorite ions) of between 0.2 and 0.5 ppm is normally sufficient to control oilfield bacteria.[63] However, being strong oxidizing agents, chlorine, hypochlorous acid, and hypochlorite quickly react with many substances that are common in oilfield systems, including ferrous ions, iron sulfide, and H_2S. They also react with various treatment chemicals including oxygen scavengers, some corrosion inhibitors, and some scale inhibitors. The amount of chlorine, hypochlorous acid, and hypochlorite used in these reactions, thereby making them unavailable for bacterial control, is defined as the chlorine demand of the system. In order to achieve the 0.2 to 0.5 ppm free chlorine residual required to control bacteria, enough Cl_2 or hypochlorite to exceed the chlorine demand of the system is injected. Large injections of chlorine or hypochlorite are typically required to achieve a 0.2 ppm residual at the outlet. Therefore, chlorine and hypochlorite are not normally used in long uncoated steel lines or in produced water systems. Free chlorine residuals are often measured by an amperometric titration procedure immediately after sampling the water.[64]

There are many case histories that document the experiences of three operators in using hypochlorous acid to control bacteria.[65,66,67]

Chlorine Dioxide

Chlorine dioxide (ClO_2) is a gas that is soluble in water and generally applied in oilfield systems as a dilute aqueous solution. Unlike chlorine and hypochlorite, chlorine dioxide does not typically react with water and its performance is not sensitive to pH. The solubility of chlorine dioxide gas in water varies with temperature and pressure. It can normally be used safely when handled in dilute aqueous solution, but the volatile gas is often easily stripped from water systems with slight aeration or pressure drop.

Chlorine dioxide is a powerful oxidizing agent and is very reactive with both organic and inorganic materials found as contaminants in oil and gas field waters. The product is often effectively used in the treatment of alkaline as well as acidic brines because the biocidal effectiveness of chlorine dioxide is not dependent on pH. Under appropriate conditions, chlorine dioxide also oxidizes H_2S to soluble sulfate ions and insoluble sulfur.[68] Thus, the presence of high concentrations of H_2S, iron sulfide, or other oxidizable species in the system can increase the demand for the oxidizer. Residuals of chlorine dioxide are typically measured by the chlorophenol red method.[69] Extensive laboratory testing[70,71] and field applications[72,73,74] have proved chlorine dioxide to be an extremely powerful agent in the control of a great variety of microorganisms.

Because chlorine dioxide is hazardous to transport, aqueous solutions of chlorine dioxide are usually generated in a small reactor on site and immediately injected into the water that is being treated. The product can be generated by oxidation of sodium chlorite ($NaClO_2$)[75,76,77] or by reduction of sodium chlorate ($NaClO_3$).[78,79,80,81,82,83] Reactors usually operate under pressure to keep chlorine dioxide dissolved in water, and adequate mixing and dilution ensure that complete solution takes place. The chlorine dioxide solutions exiting the generators are of very low pH and extremely corrosive. At the injection point at which oxidizer residuals are the highest concentration, corrosion-resistant alloys (CRAs) or corrosion inhibitors are typically used.[84]

<u>Nonoxidizing Biocides</u>

Filming and Quaternary Amines

The oldest and most widely used type of biocide in oil and gas field systems is the filming amines. This class of biocides includes fatty diamine salts. Quaternary amines (quats) contain nitrogen that is bonded to four chemical groups instead of the normal three, for example, as in ammonia. Thus, quats are cationically charged. One or two of the chemical groups are usually coco- (C14) or soya- (branched C18) groups. The other groups are typically methyl- and/or benzyl- groups. However, quats come in many types and descriptions, from the older, more commonly used alkyldimethylbenzylammonium chloride (ADBAC), to the slightly newer dialkyl quats, such as didecyldimethylammonium chloride (DDAC). More recently, branched dialkyl quats have also been introduced.[85] This class includes the difunctional cocodiamine diacetate and oxydiethylenebis (alkyldimethylammonium) chloride molecules. Properties of these products can vary substantially in foaming tendency, salt tolerance, and biocidal efficiency.

The formation of foam in gas-liquid separation facilities often causes liquid carry-over into downstream vessels, dramatically lowering the efficiency of the separation process. For this reason, surface-active chemicals that cause the formation of persistent foams are not typically used in many facilities. The foaming tendency for quats varies dramatically with molecular structure.[86] The dialkyl quats generally produce the largest volumes of the most stable foam. ADBAC quats also cause extensive foaming, although at slightly lower levels and with less foam stability. The newest generation of branched dialkyl quats has extremely low foaming tendency, and any foam generated is of low stability.[86] As the hardness of the water used is increased, the foaming tendency generally increases dramatically.

Salinity can adversely affect the biocidal properties of quat formulations. High salinity generally decreases the biocidal performance of quats, but the performance of ADBAC quats is often decreased significantly more than the performance of the dialkyl quats such as DDAC. Quats may also precipitate when added to high-calcium brines. The compatibility of quats with other treatment chemicals and with the system fluids is typically verified before quats are applied.

For handling concentrated quaternary ammonium compounds, type 316L SS (UNS[(1)] S31603), polyvinyl chloride (PVC), polyolefin, polytetrafluoroethylene (PTFE), polyvinylfluoroethylene, perfluoroelastomer, and vinyl ester have been routinely used materials of construction.[46] Carbon steel (CS), natural rubber, neoprene, and acrylonitrile-butadiene rubber (NBR) are incompatible materials (see Table 3). Methods to monitor residuals of quaternary ammonium compounds are often available. To

[(1)] Metals and Alloys in the Unified Numbering System (latest revision), a joint publication of ASTM International (ASTM) and the Society of Automotive Engineers Inc. (SAE), 400 Commonwealth Drive, Warrendale, PA 15096.

evaluate whether constituents in the brine interfere with the analysis, operators typically measure a known concentration of the quat in the field brine. Available case histories provide further information on the use of quat biocides. [87,88,89]

Aldehydes

Aldehydes are another class of chemicals that are often used as biocides in oil and gas field applications. Aldehydes react with proteins in the bacterial cell membranes, toughening the membrane and decreasing its permeability to nutrients and waste products. The same loss of permeability occurs when leather is tanned. One disadvantage of this toughening action is that the use of aldehydes can cause the formation of an extremely tenacious slime on pipes and vessels.

Formaldehyde. Chemically the simplest aldehyde, formaldehyde (CH_2O), has been used for many years in the oil and gas field, particularly in drilling mud preservation applications. The primary advantage of formaldehyde is low product cost. However, oil and gas field systems often have a high demand for formaldehyde. The chemical not only reacts with proteins in the cell membrane, but also with macromolecules such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and cytoplasmic proteins inside bacterial cells. Formaldehyde typically causes alkylation in amines, carboxylic acids, sulfhydryl groups, and hydroxyl groups on these macromolecules.[90] As a result of its reactivity with DNA, formaldehyde is a suspected carcinogen. Formaldehyde also reacts with H_2S. Even though the product cost is low, comparatively large quantities of the biocide are often needed to meet system demands. The primary disadvantage of formaldehyde is that bacterial cells often become resistant to the biocide. The concentration of formaldehyde residuals in field brines is normally measured with an aldehyde test kit. Farquhar[91] and Kriel, et al.[92] provide case histories on the use of formaldehyde.

Glutaraldehyde. Glutaraldehyde (1,5-pentanedial) is a dialdehyde that has gained wide acceptance as a broad-spectrum biocide in the oil and gas industry.[93] The broad activity of the biocide is attributed to the ability of the dialdehyde to crosslink primary cellular amines such as lysine residues in the bacterial cell wall. Field-strength products typically contain 25 wt% or 50 wt% glutaraldehyde in water, but other registered formulations are available commercially. Glutaraldehyde reacts with and can become deactivated by ammonia, primary amines, and H_2S. The reaction of H_2S with glutaraldehyde, however, is significantly slower than the reaction of H_2S with other aldehydes. Because oxygen scavengers that contain ammonium bisulfite can also react with and increase the system demand for glutaraldehyde, the product is typically injected downstream from the oxygen scavenger, or the oxygen scavenger feed is turned off during biocide treatment.[46] Glutaraldehyde is effective at both acidic and basic pH, but the rate of kill is often approximately 20 times faster at pH 8.5 than at pH 5. At all pH levels, the rate of kill is faster at higher temperatures and higher concentrations. In addition, surfactants reportedly can enhance the activity of glutaraldehyde by wetting the bacterial cell surface, permitting faster penetration. Field-strength products (e.g., 25 wt% active in water) are corrosive to mild steel, galvanized iron, aluminum (Al), tin (Sn), and zinc (Zn), but are normally stored and handled in stainless steel (SS), polyethylene, or certain reinforced plastics (see Table 3). Solutions of 25 wt% glutaraldehyde freeze at about -10°C (14°F) while 50 wt% glutaraldehyde solutions freeze at -21°C (-6°F). Winterized formulations that remain flowable at temperatures below -28°C (-18°F) are also registered and commercially available. Concentrated solutions of glutaraldehyde sometimes cause skin sensitization. The concentration of glutaraldehyde residuals in oil and gas field brines is typically measured with a glutaraldehyde test kit. Many case studies on the use of glutaraldehyde[67,93,94,95,96] are available.

Table 3: Compatibility of Common Biocides with Various Metals and Elastomers[46]

Biocide	Compatible[(A)]	Incompatible
Quaternary Amines	UNS S31603 (Type 316L SS) Polyvinylchloride Polyolefin PTFE Polyvinylfluoroethylene Perfluoroelastomer Vinyl ester	Carbon steel (CS) Natural rubber Neoprene Acrylonitrile-butadiene rubber (NBR)
Glutaraldehyde	Stainless steel (SS) Polyethylene Reinforced plastics	CS Galvanized iron Aluminum (Al) Tin (Sn) Zinc (Zn)
Acrolein	SS Butyl rubber Perfluoroelastomer PTFE Polyethylene Polypropylene	Neoprene Fluoroelastomer Acrylonitrile-butadiene rubber (NBR) Polyvinylchloride Polyurethane Galvanized metals
Isothiazolone	UNS S31603 Fiberglass-reinforced epoxy Polyester Vinyl ester Polyethylene Polypropylene PTFE Hydrocarbon rubber Fluoroelastomer Polyphenylene sulfide (PPS)	
THPS	SS Al Polyvinylchloride Nylon PTFE Polyethylene Polypropylene Polyurethane Silicone Fluoroelastomer Nitrile rubber Natural rubber	Copper Brass Mild steel Cast iron Zn
DBNPA	Fluoroelastomer PTFE Polyethylene Polypropylene Polyvinylfluoroethylene Fiberglass-reinforced plastic.	Mild steel UNS S30400 (Type 304 SS) Al Nickel (Ni)

[(A)] Compatibile with field strength product at ambient temperature. Compatibilities are typically verified under use concentration and conditions.

Acrolein. Acrolein (2-propenal) is another broad-spectrum aldehyde biocide that is effective against many types of oil and gas field bacteria. The high order of biocidal activity is attributed to the chemical's ability to inhibit several enzyme systems and its reactivity with sulfhydryl groups in bacterial cell membranes. A liquid at temperatures below 52°C (125°F), acrolein is typically supplied in pressure cylinders and tanks to increase the product's shelf life and minimize chances of exposure to vapors. Acrolein is an inhalation poison. The registered biocide contains a minimum of 92 wt% acrolein with the principal impurity being water. The product reacts rapidly with H_2S,[97,98,99,100] iron sulfide, and bisulfite oxygen scavengers; the presence of these chemical species often increases the system demand for acrolein. The compatibility of acrolein with brine that contains other treatment chemicals is typically checked before the biocide is applied.[46] Acrolein is not compatible with neoprene, fluoroelastomer, acrylonitrile-butadiene rubber (NBR), polyvinylchloride, and galvanized metals.[46] Acrolein is compatible with PTFE, butyl rubber, polyethylene, polypropylene and SS (see Table 3). Classified as a restricted-use pesticide in the United States, acrolein is normally only sold to and used by certified applicators or persons under their direct supervision. The concentration of acrolein residuals in oil and gas field brines is often measured by polarography using a dropping mercury electrode.[46] An aldehyde test kit often produces misleading results because the product degrades to other aldehydes. Case histories regarding the use of acrolein are available.[43,98,99,100,101]

Sulfur-Based Biocides

The metabolism of the bacterial cell is controlled by enzymes that catalyze most of the chemical reactions that produce energy for the cell. Sulfur-based biocides inhibit these enzymes or their associated biochemical reactions. Several of the biocides that act by interfering with cell metabolism are specific for certain types of bacteria because they only inhibit enzymes that are unique to a particular group of bacteria.

MBT. Methylene-bisthiocyanate (MBT) is an effective, low-cost biocide typically used in drilling muds and produced-water systems. In more alkaline systems, the product rapidly hydrolyzes. Therefore, the product is often limited to use in systems in which the pH is below approximately 8. The product is packaged in liquid and solid forms. A 10 wt% active solution has a freeze point of -8°C (18°F). There is no field-convenient test method for measuring the concentration of MBT residuals in field brines. However, samples are often sent to the laboratory for residual analysis.

Isothiazolone. Isothiazolone, a mixture of 5-chloro-2-methyl-3(2H)-isothiazolone and 2-methyl-3(2H)-isothiazolone, has been an excellent preservative and is typically used in fracturing fluids and drilling muds. It has also been used in other oil and gas field applications, such as waterfloods. The product typically functions by reacting with and disrupting proteins involved in respiration and adenosine triphosphate (ATP) synthesis. Growth inhibition rapidly becomes irreversible and often results in cell death. The product is effective at low-use concentrations over a wide range of pH. In use concentration, isothiazolone is compatible with chlorine, and most anionic, cationic, and nonionic treatment chemicals. However, the product does react with sodium bisulfite oxygen scavengers. The field-strength product is often compatible with type 316L SS (UNS S31603), fiberglass-reinforced epoxy, polyester, vinyl ester, furan, polyethylene, polypropylene, PTFE, hydrocarbon rubber, fluoroelastomer, and polyphenylene sulfide (see Table 3). The primary limitation of isothiazolone is a comparatively slow rate of kill. Isothiazolone has been known to sensitize skin. The concentration of isothiazolone residuals are typically preserved in the field and measured in the laboratory by isocratic reverse-phase high-performance liquid chromatography, with an ultraviolet absorbance detector at 275 nm. Ruseska, et al.[34] report the results of laboratory comparison of isothiazolone with DBNPA, glutaraldehyde, ADBAC quat, and a filming amine in controlling sessile populations.

Thiocarbamates. Alkyl thiocarbamate salts have been used successfully in guar-based fracturing fluids and in drilling fluid preservation. Registered products include potassium dimethyldithiocarbamate and a blend of sodium dimethyl dithiocarbamate with disodium ethylenebisthiocarbamate. The products are insoluble in oil, reportedly do not adsorb on metal surfaces, and do not react with H_2S. As a result, they are often propagated through long lines and high-surface-area systems. The primary disadvantage of this class of compounds is their formation of insoluble iron salts in produced brines containing greater than 2 mg/L (ppm) of dissolved ferrous iron.[46]

Other Nonoxidizing Biocides

THPS. Tetrakishydroxymethyl phosphonium sulfate (THPS) is a nonfoaming, broad-spectrum biocide that is less toxic to aquatic and marine species than other biocides currently registered for oil and gas field use. Bacteria are killed by disruption of proteins in the bacterial cell membrane and inhibition of lactate dehydrogenase activity. Field-strength products typically contain 20 wt% to 35 wt% THPS, but formulations with 75 wt% THPS are also registered and commercially available. The 35 wt% solutions typically freeze at about -5°C (23°F), while the concentrated products remain flowable at temperatures below -40°C (-40°F). Compatibility of the product with various metals and elastomers is reported in Table 3. Under certain conditions, THPS can dissolve iron sulfide in produced waters,[102,103] but the biocidal properties of THPS are unaffected by the presence of H_2S. The field-strength product is a strong skin sensitizer. The THPS molecule is often monitored on site with an iodometric titration procedure. Case histories on the use of THPS in various oil and gas field applications are available.[103,104,105,106,107]

DBNPA. 2,2-Dibromo-3-nitrilopropionamide (DBNPA) effectively treats produced water, injection water, water disposal systems, and hydrostatic test fluids. Bacteria are rapidly killed by a mechanism that appears to involve reaction of DBNPA with cell membrane proteins and inactivation of enzyme systems. The primary advantage of the product is a fast kill rate at very low concentrations. The primary disadvantage of DBNPA is its incompatibility with reducing agents such as H_2S and bisulfite oxygen scavengers. The presence of these species typically increases the system demand for the biocide. In addition to being rapidly biodegradable, DBNPA is often easily degraded with bisulfite oxygen scavengers to allow discharge of the treated fluids into environmentally sensitive areas.[46] Depending on system conditions, the degradation of DBNPA sometimes occurs with a half-life of less than 30 minutes.[46] The product is temperature-sensitive and decomposes exothermically at elevated temperatures. Compatibility information is presented in Table 3. The concentration of DBNPA residuals in oilfield brines is typically measured by reverse-phase liquid chromatography and spectroiodometric methods. DBNPA has been tested to control bacteria upon start-up of plant vessels and process piping.[67]

Bronopol. The active compound 2-bromo-2-nitropropane-1,3,-diol (bronopol) is registered for typical use in a broad range of oil and gas field applications, including drilling mud and workover fluids. The biocide functions by oxidizing thiol groups in the cellular proteins.[108] Bronopol, like other electrophilic biocides, has a slow biocidal effect and may take as long as 24 hours to effect kill. However, the long persistence of the molecule, especially at acidic pH, makes the slow biocidal activity less of a concern. Consequently, bronopol is often most effective in the 5 to 9 pH range. At acidic pH, anionic, cationic, and nonionic treatment chemicals do not affect bronopol. However, at a pH above 7, bronopol can break down and release formaldehyde, bromide, and nitrates; the produced nitrates may further react with amines to form nitrosamines and nitrosamides. The biocide is easily soluble in water and alcohol.

Biocide Blends

Many biocide products have been formulated as blends of more than one biocide type, or as a blend of a biocide with another chemical, such as a surfactant. The blend is typically registered as a biocide. Glutaraldehyde/quaternary amine (glut/quat) and THPS/surfactant blends are examples of commercially available blends. There are several reasons for using a blended biocide: to develop a broad-spectrum product that will kill bacteria by more than one mechanism, to make it more difficult for another population of a different bacterial strain to thrive, and to produce a product that demonstrates synergy between components in the blend. The glut/quat and THPS/surfactant blends generally allow the biofilm-dispersing properties of one chemical (either the quat or the surfactant) to be combined with a broad-spectrum biocide (either the glutaraldehyde or THPS) in a single product. In these cases, care is often taken to ensure that the products do not comprise an unregistered formulation at the point of application.

Alternatives to using biocide blends typically include alternation of biocides or injection of a surfactant at an alternate injection point in the system. Alternating biocides is described more fully in Section 4. Case histories on the use of alternating biocides are available.[109,110]

Alternatives to Chemical Biocides

Although bacteria are ubiquitous in oil and gas field systems, not all systems are treated with chemical biocides. Ulman and Kretsinger[47] report a methodology that is often used to estimate the economic incentives for controlling oil and gas field bacteria and establish the cost-effectiveness of various treatment options. The alternative methods described below have been used alone or in combination with chemical biocides to control bacterial contamination.

One typical alternative to implementing a chemical biocide treatment program is to monitor the system and replace system components prior to failure. Replacement of system components is generally viewed as the least desirable method for dealing with MIC.[111] There are often high risks associated with failures. Because the cause of the corrosion failure (i.e., bacteria) is still present, the new components are also susceptible to MIC. Nevertheless, cost analysis has shown that along with increased attention to cleanliness, replacement using either the same metallurgy, more MIC-resistant metallurgy, or coated and lined components is sometimes the most appropriate economic decision.[112]

Eliminating or changing the environment that is conducive for bacterial growth is another typical approach. It is often difficult for bacteria to form thick biofilms on surfaces exposed to high-velocity (greater than 1 m/s [3 ft/s]) water.[111,112,113] Quiescent regions within the production system are ideal locations for bacteria to thrive. Physical removal of sludge and deposits from tank bottoms and rat holes often eliminates some environments that favor bacteria growth. Keeping lines free of suspended solids, scale, and other deposits normally helps control bacteria.

Mechanically cleaning lines with pigs, brushes, and scrapers can remove deposits that shelter sessile bacteria from high-velocity fluids and direct chemical contact. Pigs are typically most suitable for use in long straight runs of pipe that do not change direction or section size. Although pigs are only partially effective in removing deposits from crevices and pits, they expose much of the bacteria in the biofilm to direct contact with a subsequent biocide. Thus, the effectiveness of a biocide program can be greatly enhanced by preceding the biocide treatment with mechanical cleaning.[114] Mechanical cleaning without the use of biocides, however, may not be completely effective in controlling bacteria and MIC.

Changing the oxygen content of the environment is another technique that has been used to control SRB and other anaerobic populations. This technique has been effectively used to reduce the level of H_2S gas generated by SRB flourishing within the anaerobic environment of concrete ballast legs of a North Sea oil production platform.[37] Air was sparged through the ballast legs to aerate the fluids and reduce planktonic populations. Although H_2S production was minimized, SRB were still active within the biofilms, and corrosion may have proceeded at an accelerated rate.

Irradiation of water with ultraviolet light has been used to control bacteria in seawater for injection into a North Sea oil field.[115] By using this technique, the concentration of viable SRB was reduced by more than three orders of magnitude in a unit that treated 36 m^3/hr (160 gal/min) of water. To achieve this level of effectiveness, the water was irradiated at an intensity of 110 mW/m^2 with 254 nm light for one second. For ultraviolet light to be effective, the water is typically of low turbidity and free of slime, silt, suspended hydrocarbons, and dissolved hydrocarbons.[116] Clark, et al.[115] indicated that the ultraviolet treatment program was 62% more cost-effective than a prior biocide treatment. Ultraviolet irradiation, however, only treats planktonic bacteria that pass through the light beam. There are no residual effects that are carried with the treated water.

Planktonic bacteria that escape death, as well as sessile colonies, can thrive immediately downstream from the ultraviolet irradiation point. Therefore, ultraviolet treatments are often augmented with biocide treatments.[116]

Bacteria are often able to produce energy for cellular activities by any of several alternate respiration processes. A biostat is a chemical compound that halts one of the respiration pathways without harming the microorganism. The use of biostatic compounds often stops the formation of certain detrimental metabolic products, such as acids and H_2S. Anthraquinone is one biostat that has recently been used in oilfield operations.[117,118] This product interrupts the electron transfer process that the SRB use to reduce sulfate to sulfide, reducing biogenic H_2S.[119,120] The overall treatment with a biostat may result in a lower environmental toxicity. There are only a limited number of biostats available for application in the oil and gas fields.

Selective chemical inhibitors based on nitrate and nitrite have been used in a number of oilfield applications to prevent the activity of harmful SRB.[121,122,123,124,125,126] The objective of nitrate and nitrite treatment is the control of sulfides in reservoir fluids by the selective manipulation of indigenous bacteria through nutrient addition. There are several possible mechanisms by which nitrate can prevent the accumulation of sulfide in oilfield produced fluids:

(1) Nitrate-using bacteria may outcompete SRB for common carbon and energy sources such as acetate and longer-chained fatty acids. This shifts the flow of electrons in energy-generating metabolism of bacteria away from sulfate reduction toward nitrate reduction;

(2) Nitrate-using bacteria may produce compounds such as nitrite that are toxic to SRB;

(3) Nitrate-using bacteria may produce compounds that raise the redox potential of the environment to a level that inhibits the growth of SRB;

(4) Some strains of SRB preferentially use nitrate instead of sulfate as the electron acceptor in their energy-generating metabolism; and

(5) Nitrate-using bacteria may use the sulfide produced by SRB as the electron donor for nitrate reduction. In this case, the production of sulfide would not be inhibited, but the use of sulfide by nitrate-using bacteria would prevent its accumulation.

Depending on the microbial populations present, any of the above mechanisms or combinations of mechanisms may be operative.

Section 3: Monitoring and Surveying Oil and Gas Field Systems

Typical Objectives for Monitoring and Surveying

Bacteria are present in virtually every oil and gas field system, but not every system is treated with biocides. The presence of even large bacterial populations does not necessarily cause operating problems. Instead, the decision of whether to implement a biocide treatment program is typically based on a careful accounting of the total operating costs and a thorough evaluation of the health, safety, and environmental risks associated with not treating the bacterial contamination. A previous section (Problems Caused by Oil and Gas Field Bacteria) details some of the costs and risks that normally affect the treatment decision. Operators or service companies often continue to routinely monitor the systems in which biocides are not used for bacterial contamination, ensuring that costs and risks cannot be lowered by initiating an effective biocide program.

Operators and service companies often conduct microbiological surveys to determine whether bacterial contamination is the cause of operational problems such as MIC, high failure rates, and high or increasing concentrations of iron sulfide, H_2S, and suspended solids. Surveys are typically designed to profile the bacterial populations throughout the production, treatment, storage, transportation, injection, and disposal systems. Profiling the bacterial population is typically accomplished by enumerating the bacterial populations and by measuring the chemical and physical parameters (such as sulfide levels, iron counts, and suspended solids) that are indicative of infestation. Analysis of the bacterial, chemical, and physical profiles helps to identify the source, distribution, severity, and type of microbiological activity, and guides the development of effective monitoring and treatment strategies.

No single biocide is the most cost-effective treatment in all systems at all times. Biocides have different physical, chemical, and compatibility properties that may preclude their use in some locations. Biocides that are particularly effective in penetrating biofilms may work well in systems with established biofilms, but this attribute is not as essential in systems that are not heavily fouled. A biocide may be particularly effective toward one type of bacterium, but ineffective toward other bacteria in the consortia. In addition, bacterial populations can change and adapt due to changes in system conditions, nutrient availability, and biocide application. Biocide performance in a given system is typically monitored to ensure that appropriate adjustments in the biocide program are made to maintain the most cost-effective treatment program.

The tools and techniques discussed in this section are routinely used to monitor microbial populations in systems that do not use biocide treatment to determine whether biocide programs need to be initiated, and to optimize the efficiency of existing biocide programs.

Background Information Useful Prior to Field Work

The first step in conducting an efficient survey typically involves identifying the operational problems that are being caused by bacteria in the system. These operational problems, previously listed in Table 1, often include high corrosion failure rates, filter plugging, loss of injectivity, production of H_2S and iron sulfide, and stuck pumps. Interviewing field personnel and reviewing field records often identify these problems. Identifying the operational problems caused by bacteria helps to define the objectives and cost requirements for the subsequent bacterial treatment program.

Prior to starting field work, background information on the conditions and fluids throughout the production, treatment, injection, and disposal system is typically gathered. Useful background information is summarized in Table 4. Schematic diagrams of the system, showing oil, gas, and water production rates, along with the location and size of all vessels and tanks, help the analyst thoroughly understand the system and identify potential sources of bacterial contamination. Special attention is often directed toward stagnant areas in wells (e.g., rat holes and annular spaces), lines (dead legs), vessels, and locations where brine compositions change (for example, through the mixing of nutrient-rich produced water with bacteria-laden source water). These locations are typical areas for increased bacterial activity.

Table 4: Background Information Useful Prior to Conducting Surveys

Potential problems caused by bacteria
Details of existing bacteria-treatment program (if any)
Schematic flow diagrams showing location of all vessels, tanks, and lines
Water cut and flow rate throughout system
Location of potential biocide injection points
Injection location and treatment rate for other production chemicals
Metals and elastomers that may come in contact with biocide
Water analyses
Temperature profiles
Health, safety, and environmental restrictions

The location and identity of metals and elastomers in the system, as well as the types and injection points for all treatment chemicals, are also useful background information. This information is used to prescreen potential biocides for their compatibility with the system components and other treatment chemicals. Table 3 lists compatibilities of various biocides with metals and elastomers.

Water analyses and temperature profiles throughout the system are useful in the selection of the proper culture media and incubation temperature to use in microbiological evaluation and biocide selection tests. Bacteria are normally cultured at salinity, pH, and temperature conditions matching those in the system to ensure that the growth conditions in the laboratory are representative of those within the system.[127]

Sampling

The field portion of the survey typically begins with sampling the water phase and deposits at various locations, enumerating the planktonic and sessile bacteria, and measuring the concentrations of by-products (primarily sulfides and total suspended solids) from bacterial action. Potential sampling points are listed in Table 5. It is often possible to determine whether bacteria are especially active in a particular vessel by sampling the inlet and outlet of the vessel. Samples of make-up water and drilling fluids, packer fluids, well-completion fluids, and any other source of water that enters into the system are typically obtained to ensure that these fluids are not potential sources of bacterial contamination. If the system is currently being treated with a biocide, it is often useful to suspend the biocide treatments in several representative sections of the system so that background bacterial populations are determined.[127]

Table 5: Partial List of Potential Sampling Locations

Rods and tubing
Production wellheads
Two- and three-phase separators
Free water knock-outs
Heater-treaters
Production pipelines
Pig solids
Oil storage tanks
Flotation equipment
Produced water storage tanks
Surge tanks
Water pits
Water plant vessels
Filter strainers and backwash
Pumps
Water injection flowlines
Injection/disposal wellheads

Planktonic bacteria are typically easy to sample and are enumerated quickly and accurately by various commercially available techniques.[127] In comparison, sessile bacteria are generally not as easy to sample because of their location in biofilms on inside surfaces of the production equipment. Consequently, monitoring for sessile populations is often neglected. However, there is no clear correlation between the numbers and species of planktonic and sessile populations in a given environment, and monitoring planktonic bacteria alone may not provide essential information when biofouling and MIC are a concern. Therefore, increased attention is often given to monitoring sessile populations.

Deposits containing sessile bacteria are often obtained at a number of different locations throughout the system. Corrosion coupons,[128] bioprobes, and removable pipe sections (i.e., spools) are typically useful for monitoring sessile populations. Samples from tubing and rods are sometimes obtained as soon as they are removed from service and analyzed for sessile bacterial populations.[127] In addition, samples from production and injection wells have been obtained by shutting in the well, removing a bull plug or breaking open the line and swabbing a given area inside the line. Deposits from field lines, pigging fluids, pits, filters, and injection well strainers have also been collected and analyzed for sessile bacterial contamination.

After sessile and planktonic samples have been obtained, determining the number (i.e., enumeration) of bacteria in the samples obtained from each location in the system is often the next step. The following sections summarize typical enumeration techniques and chemical analyses commonly used during surveys. Some of the procedures for determining water quality are not unique to microbiological surveys, but they are included because of their usefulness in assessing bacterial activity. Each section outlines how the procedures have been used in developing a treatment program. Typical procedures for sampling and enumerating both planktonic and sessile bacteria, as well as for evaluating biocides, are covered in NACE Standard TM0194.[127] Little and Wagner [129,130] have provided excellent reviews for indicators of SRB in MIC and include discussions of typical SRB culture techniques, biochemical assays, and field test kits.

Enumeration Methods

Serial Dilution

The most common test for detecting bacterial presence in the oilfield is the “bug bottle”—a series of sealed vials that each contain 9 mL of sterilized nutrient media for growing and detecting bacteria. In the serial dilution method, the first media vial in a series is inoculated with 1 mL of the field sample. After thorough mixing, 1 mL of the sample from the first vial is added to the second media vial in the series. After thorough mixing, 1 mL is withdrawn from the second vial and then added to the third vial in the series. This sequential dilution process is repeated with the remaining vials in the series. A total of six to eight media vials are usually sufficient to enumerate bacteria in all but the most heavily fouled systems. The complete series of media vials is typically incubated at a temperature within 5°C (9°F) of the system temperature for seven days (aerobic and facultative anaerobic bacteria) or 14 to 28 days (SRB), depending on the type of media. Because each media vial contains an indicator for the presence of bacteria, the number of serial dilution vials that show a positive test for bacteria is approximately logarithmically related to the number of bacteria contained in each mL of the original sample. The relationship is shown in Table 6.

Table 6: Correlation of the Number of Positive Serial Dilution Vials with the Concentration of Bacteria in the Sample

Number of Positive Vials	Actual Dilution of Original Sample	Growth Indicates (Bacteria per mL)	Reported Number of Bacteria per mL
1	1:10	1 to 9	10
2	1:100	10 to 99	100
3	1:1,000	100 to 999	1,000
4	1:10,000	1,000 to 9,999	10,000
5	1:100,000	10,000 to 99,999	100,000
6	1:1,000,000	100,000 to 999,999	1,000,000
7	1: 10,000,000	1,000,000 to 9,999,999	10,000,000
8	1: 100,000,000	10,000,000 to 99,999,999	100,000,000

Sessile bacteria as well as planktonic bacteria can be enumerated by the serial dilution method.[127] Samples of sessile populations are normally scraped from metal surfaces or coupons using a sterile scalpel or swab. The deposit is thoroughly dispersed into either sterile phosphate buffer solution, sterilized produced water from the field, or sterile media from one of the vials used in the subsequent serial dilution. The slurry is serially diluted, incubated, and analyzed as described above. NACE Standard TM0194[127] sets forth the standard procedure for enumerating both sessile and planktonic bacteria by the serial dilution method.

Several types of media are available, each one being specially formulated to provide nutrients essential for growth of a specific type of bacteria. Only bacteria that are able to use the nutrients provided in the media grow in that particular formulation. In addition to containing specific nutrients, each medium is normally adjusted with additional salts so that the salinity of the medium closely matches the salinity of the system brine.

The most commonly used media for SRB enumeration are the modified Postgate media[17] and API[(2)] RP 38 SRB Medium.[131] These media contain an organic acid, usually lactic acid, and soluble ferrous iron. If viable SRB are present in the sample, they normally generate sulfide ions that react with the soluble iron to form black, insoluble iron sulfide. Thus, the presence of a black precipitate in the media suggests that SRB are present in the vial. However, many produced brines contain sulfide ions that when added to SRB vials often quickly react with the iron, forming iron sulfide and giving false positive readings. If this occurs, the color change often happens fairly rapidly (within two hours) in the first couple of vials.

Aerobic and facultative anaerobic bacteria are typically grown in standard bacteriological nutrient broth, tryptic soy broth, or phenol red dextrose medium.[127] If aerobic or facultative anaerobic bacteria are present, all three media become turbid within seven days of incubation at the system temperature. With the phenol red dextrose medium, a change in the color of the medium from red to yellow accompanying the turbidity is a positive test for APB.

The most common medium for detection of anaerobic and facultative anaerobic bacteria is thioglycolate medium. A positive reaction for this medium is indicated by turbidity. Several factors affect the results obtained from serial dilutions. Only a small percentage of the total bacterial population in a sample is typically enumerated by culturing techniques. Some bacteria in a population are not able to grow on culture media at all. Changes in temperature, pH, pressure, salinity, and oxygen concentration occur when a sample for bacterial analysis is obtained, and any one of these changes can have an adverse affect on bacterial growth. Consequently, culture media methods significantly underestimate the number of bacteria in a sample.[127] If lactate-based media invariably and unexpectedly yield low SRB populations in situations in which high SRB populations are expected, NACE Standard TM0194 discusses screening other media (e.g., those containing alternate organic acids or those made from source water). Nonstandard media are often prepared relatively simply and economically by local laboratories.

Media Techniques—Plate Counts

The plate-count technique is occasionally used to enumerate aerobic bacteria in some oilfield fluids such as drilling muds and fracturing fluids. The method is conducted by spreading a dilute water sample containing bacteria on the surface of a nutrient agar gel. After allowing an appropriate incubation period, the number of colonies on the gel is counted. Because each colony theoretically grew from a single bacterium called a colony-forming unit, the number of colonies is approximately equal to the number of bacteria in the original sample. Plate counts are not commonly used in the oil and gas field, because it is difficult to detect anaerobic bacteria using this method, unless the plates are inoculated and incubated in an anaerobic chamber. The method is normally used only for enumeration of aerobic bacteria.

ATP Photometry

Adenosine triphosphate (ATP) is present in all living cells, and bacterial cells contain roughly the same amount of ATP. When cells die, however, ATP rapidly degrades.

[(2)] American Petroleum Institute (API), 1220 L St. NW, Washington, DC 20005-4070.

Consequently, the quantity of ATP in an oil and gas field sample is approximately proportional to the number of living bacteria in that sample. ATP photometers measure the amount of ATP in a sample by measuring the amount of light emitted during an enzymatic reaction. Although the technique has been used to monitor the effectiveness of a biocide program,[132] the technique suffers from several significant interferences that often limit its use in the oil and gas industry.[133]

APS-Reductase

SRB use an enzyme—APS-reductase—to reduce sulfate to sulfide anaerobically. Measurement of the amount of APS-reductase in a bacterial sample provides an estimation of the total number of SRB that are present in the sample. Disposable test kits have been developed to rapidly immunoassay the quantity of APS-reductase in field samples.[134] The test is rapid, it is not essential for bacteria to be grown in a culture media, and it is independent of sample temperature, salinity, and redox conditions.[130,135,136] However, the method is several orders of magnitude less sensitive than culture techniques, and the test kits have a short shelf life, especially in warm climates.

Fluorescence Microscopy

Fluorescence microscopy[131] is a direct enumeration technique that typically involves visual counting of the number of bacteria in a sample. Bacteria cells are stained with a fluorescent dye, such as acridine orange, fluorescein isothiocyanate (FITC), and 4,6-diamidino-2-phenylindole dihydrochloride (DAPI), that fluoresces when irradiated with ultraviolet light. Using a fluorescence microscope, an analyst counts the total number of bacterial cells in a known volume of the sample. As with ATP photometry, this technique does not normally distinguish between SRB, general aerobic bacteria, and anaerobic bacteria. While most of the fluorescent dyes do not clearly distinguish living cells from dead ones, recent advances in fluorescent stains often enable direct enumeration of living and dead cells.[137,138]

Other Methods

The techniques discussed above are not meant to be an all-inclusive list of microbiological enumeration techniques, but rather a list of techniques that have been most widely used for enumerating oil and gas field bacterial populations. Several other techniques are available for enumeration of bacteria. The reader is directed to excellent references on hydrogenase measurement,[130,139] radiorespirometry,[130,140] and fluorescent antibody microscopy.[130,141]

Typical Chemical and Physical System Parameters

As previously discussed, a microbiological survey normally provides an opportunity to measure and observe a number of the physical and chemical factors that are often indicative of increased bacterial activity. These parameters are typically observed and measured, while samples are being collected for bacterial enumeration.

Visual Inspection

It is virtually impossible to obtain conclusive proof of MIC activity by visual inspection alone. However, visual inspection of the wetted surfaces of oilfield equipment often suggests areas of increased microbiological activity and locations for sampling and subsequent bacterial enumeration. Biofilms can often be seen inside vessels as a layer of sludge or a thick mat of slime. Bacteria often thrive in the sludge and biofilm layers, causing MIC and pitting of the metal surfaces underneath. NACE Standard TM0194[127] observes that rods and tubing pulled during workovers of production wells are typically examined for pits. If pitting is observed, a sessile sample is typically obtained from the pit to determine whether high numbers of bacteria are present. Dead legs and low spots in lines and vessels are prime locations for build-up of bacterial slime and sludge.

Sulfide Levels

Increases in the total sulfide content (H_2S in gas, hydrocarbon, and water phases, sulfide ions dissolved in the water phase, and metal sulfides) throughout a system are often used to identify areas of high SRB activity. In some locations, the hydrogen sulfide concentration in the gas phase and/or the sulfide concentration in the water phase are used to identify locations of high bacterial activity and to assess biocidal effectiveness. However, these parameters alone are sometimes misleading because nonbacterial factors such as pressure changes and deposition of iron sulfide can also change the distribution of sulfides between phases.

Suspended Solids

Because SRB produce H_2S that can precipitate as metal sulfides, an increase in the suspended solids content of brine sometimes identifies locations of increased SRB activity. Produced brines containing high levels of suspended solids generally show slower filtration rates than brines containing lower levels of suspended solids. Consequently, filtration rates are sometimes used to monitor water quality and assess the effectiveness of biocide treatment programs. Monitoring suspended solids sometimes gives an indication of the relative suitability of the water for injection. A standard procedure for conducting membrane filtration tests has been published.[142]

Iron Counts

Iron counts are generally used to identify areas of corrosion often associated with MIC, ingress of oxygen, reactions with carbon dioxide, or the presence of iron in produced minerals and clays. Although the data derived from this technique are not typically conclusive for the presence of bacteria, they can be very helpful when used in conjunction with other survey information. Standard methods for iron counts have been published.[143]

Dissolved Oxygen

Oxygen can enter oilfield systems through make-up water, open ponds, tanks, pits, and pump seals, allowing proliferation of the aerobic and facultative anaerobic slime-forming bacteria in the system. These bacteria often grow rapidly, depleting the oxygen concentration in the system, producing nutrients needed by anaerobic bacteria, and creating ideal conditions for the proliferation of the facultative anaerobic bacteria, including acid-producing bacteria (APB) and true anaerobes, including SRB. Thus, the ingress of dissolved oxygen results in an overall increase in bacterial activity, starting with the aerobes, but ultimately resulting in increased SRB activity. Several methods for measuring dissolved oxygen in oilfield brine have been published.[143]

Redox Potential

A redox potential is a measure of the relative oxidation/reduction potential of an environment. Growth of aerobic bacterial is typically favored at highly positive redox potentials (oxidizing environments). Anaerobic bacteria, including SRB, grow much better in reducing environments, where the redox potential of the system is less than -100 mV relative to a standard hydrogen electrode potential. In general, the lower the redox potential, the more conditions favor proliferation of anaerobic bacteria, including SRB. Some operators continuously monitor the redox potential of the brine in their system to minimize growth of bacteria.

Temperature

Water temperatures may fluctuate dramatically in different portions of a system. Because bacterial cultures need to be incubated within 5°C (9°F) of the system temperature, the temperature of the system is normally measured at the sampling point.[127] Bacteria in a given sample can often adapt to temperature changes, but the various types of bacteria in the sample often do not grow at the same rate when incubated at a different temperature. Therefore, a different bacterial population is enumerated if the culture is incubated at a temperature different from that where the bacterial sample is obtained.

Salinity

Salinities of oilfield brines vary significantly from one field to another and sometimes within the same field at different locations and from season to season. Bacteria are normally cultured in media having a salinity that matches the salinity where the bacterial sample was obtained.[127] If the salinity of the culture media is significantly different from the salinity in the system, the population that is cultured may not be truly representative of that where the bacterial sample was obtained.

Alkalinity and pH

Some bacteria can grow in water with a pH as low as 1, while other bacteria can grow in water having a pH as high as 11. The pH of most oil and gas field brine is typically in the 5 to 7.5 range. Specific culture media, formulated to the appropriate pH range of the system, are often used to grow a bacterial population representative of the one that is thriving in the system. Therefore, the pH of the system at each sample location is generally measured.[143] A brine that becomes more acidic as it flows through the system to regions of lower pressure may indicate the presence of APB.

None of the methods listed in this section for monitoring and surveying an oilfield system is fail-proof. All of the enumeration methods have limitations and interferences. As a result, oilfield microbiologists often use two or more of the techniques discussed above to identify the source, distribution, severity, and type of bacterial contamination throughout the system.

Section 4: Implementing and Optimizing Biocide Treatment Programs

The procedures and methods described in the previous section often help to identify the source, distribution, severity, and type of bacterial contamination in oil and gas systems. If the survey shows that bacterial contamination is indeed the cause of operational problems, an effective biocide treatment program is typically used. This section discusses the procedures and issues typically considered when biocide programs are designed, implemented, and optimized.

<u>Designing Biocide Programs</u>

Every oil and gas facility is different, and each one has its own set of requirements that often limits the type of biocide used, the biocide injection point, and the application method. The microbiological survey that was discussed in the previous section often helps in identifying the system characteristics. If careful consideration is given to the system requirements, the number of biocides that need to be evaluated in laboratory tests is often reduced.

Health, Safety, and Environmental Considerations

By design, biocides are intended to be toxic to living cells. Careful consideration is typically given to ensuring that the selected biocide is applied in a safe and efficient manner, with minimal risk to the health and safety of everyone who may come in contact with the product, and with a minimal risk to the environment. Essential information about safe handling of products is found on material safety data sheets, labels, and product data bulletins.

In most cases, the health, safety, and environmental (HSE) risk associated with biocide use is minimized through proper engineering controls, process safety management programs, and training. However, after careful review, the hazards associated with the use of certain biocides sometimes preclude their use at certain locations.

Regulatory Considerations

In some countries, biocides are registered with the appropriate governmental agencies where sale, distribution, and use occurs. Not all biocides used in the oil and gas field are permitted for use by all countries or in all applications within the same country. The label on the product often gives details about the registered applications and approved dosage rates. Further details regarding typical product registrations in various countries are discussed in Section 5.

Governmental agencies also typically regulate the packaging and transportation of biocides. In the United States, for example, those products that are classified as Dual Hazard Packing Group II[144] cannot currently be transported in certain types of containers, and this restriction may preclude the use of certain products in certain locations. Manufacturers that provide biocides generally are responsible for packaging and transporting biocides in containers that comply with all governmental regulations.

Special Considerations for Offshore Use

The unique operating conditions that occur on offshore platforms often limit the types of biocides that are used and the locations where various products are injected. In addition to the HSE considerations discussed above, products for offshore use often are subject to regulations, which sometimes state that products need to:

- be approved for maritime transport;
- comply with water discharge permits; and
- have the capability to degrade into low-toxicity by-products prior to being discharged.

Similar to their use in onshore systems, biocides are typically used in offshore systems to control bacterial contamination in the produced water-handling and seawater-injection systems. In many offshore locations, however, the treated brine is often discharged into the environment if the discharge complies with governmental regulations and permits. In the United States, for example, the toxicity of the treated brine is typically below the limits specified by the Environmental Protection Agency (EPA)[(3)] in the National Pollutant Discharge Elimination System (NPDES) permit[144] for the platform (see Section 5). Nevertheless, even though the discharge of treated brine is sometimes permitted, some major oil and gas producing companies typically have initiatives to reinject all produced brine and completely eliminate discharges.

If treated brine is discharged into the environment, the produced water handling system is typically treated with biocides that are more environmentally friendly, rapidly degrade into low-toxicity by-products, or can be neutralized prior to discharge. Even when the most environmentally friendly biocides are used, many operators carefully monitor the application to ensure that the toxicity of the discharge complies with governmental regulations.

As with all chemicals, a number of physical, chemical, and biological processes typically degrade biocides within the system before the treated brine is discharged. System conditions such as temperature, pH, produced solids, and residence time control the rate at which the biocide residual concentration decreases. While some biocides such as oxidizers and DBNPA are fast acting and degrade rapidly, other biocides, such as quats and diamines, are more persistent and therefore not always suitable for use in some offshore systems.

To meet governmental discharge regulations, residual concentrations of the biocide in the treated brine are often chemically degraded or “neutralized” before discharge. Such a neutralization process generally includes contacting the treated brine with a neutralizing solution in special equipment such as a static mixer or holding tank, ensuring that adequate degradation has occurred. Some biocides such as glutaraldehyde and acrolein are easier to neutralize than other biocides.

Biocides are typically used in several locations in seawater injection systems. As soon as the seawater is pumped onto the platform, it is often continuously treated with a biocide to kill fouling organisms that are present in seawater. For this application, one of the chlorination processes (chlorine, hypochlorite, or chlorine dioxide; see Section 2) is typically used due to its cost-effectiveness in the relatively clean seawater. The treated seawater usually passes through sand filters and deaeration towers where sessile populations of bacteria can accumulate. As a result, sand filters and deaeration towers are periodically batch treated with biocide to control this sessile contamination.[145] Downstream from the deaeration towers, some facilities also treat with a second more persistent biocide, such as glutaraldehyde, that may control bacteria throughout the injection lines.

Special Considerations for Hydrostatic Testing

Biocides are sometimes used in hydrostatic testing fluids to inhibit growth of bacteria,[146] particularly when seawater is the testing fluid. Not all biocides are approved for this application, and special consideration is typically given to ensure that the product is approved for use in hydrostatic testing fluids. Information about the approved applications and suggested dosage rates are found on the product label. When the hydrostatic testing operation is completed, the hydrotest fluids are often discharged into the environment.

(3) U.S. Environmental Protection Agency (EPA), Ariel Rios Building, 1200 Pennsylvania Ave. NW, Washington, DC 20460.

In the United States, NPDES permits specify the requirements of the discharge. More information about meeting these requirements by neutralizing the biocide is discussed in the section on Special Considerations for Offshore Use.

Biocides used in hydrostatic testing are sometimes active for long periods of time and function more as a preservative than as a quick-killing bactericide. Therefore, isothiazolone as well as THPS and glutaraldehyde are widely used for this application.[147]

Special Considerations for Arctic Use

Chemicals that are used in cold environments have additional considerations.[148] For biocides, one concern is often the viscosity of the product at low temperatures. Many biocides are too viscous to be pumped or contain inactive ingredients that form precipitates at the cold temperatures typical of those found in the arctic and many other cold-weather environments. In order for a product to be used in these cold environments, stable biocide formulations normally have pour points below -40°C (-40°F).[149]

Biocide Compatibility Considerations

As with all other production chemicals, biocides are normally tested for compatibility with the fluids and components in the system.[127] A partial list of the potential compatibility issues is summarized in Table 7.

Table 7: Partial List of Potential Compatibility Issues

Metals wetted by product
Elastomers and seals wetted by product
Linings and coatings wetted by product
Production system:
Water cut
Impact of foaming
Desolvation of product
Product viscosity
Product pour point
Produced brine:
Product solubility
Solubility of degradation and reaction products
Other production chemicals in use:
Chemical compatibility
Formation of precipitates

One of the first concerns is the compatibility of the biocide with the metals, elastomers, seals, linings, and coatings that sometimes come in contact with the biocide. Some biocides, such as the oxidizers, are notoriously corrosive. Other biocides are corrosive at elevated temperatures that may be experienced in downhole capillaries. Some biocides are incompatible with elastomers present in the system. Likewise, some biocides may be incompatible with the linings and coatings used in various tanks, vessels, and lines. Therefore, as mentioned in NACE Standard TM0194,[127] the compatibility of the biocide with all system components in use is normally verified at the concentration and conditions that are likely to occur in the application.

Many operators consider the physical characteristics of a biocide in relation to the location where the biocide is used. The water cut in the system is one such consideration. A biocide that partitions more strongly into an oil phase is often effective in penetrating oil-wet solids in a biofilm. However, that same biocide is sometimes ineffective when used in low water cut systems, because substantial amounts of the biocide may be lost to the oil and therefore be unavailable for contacting bacteria in the water phase. The surface activity of a biocide is another typical consideration. Some biocides, such as quats, may have a strong surfactant nature. This feature may allow these biocides to effectively penetrate and remove biofilms, but it also may lead to foaming and formation of reverse emulsions. Consequently, surface-active biocides are often unsuitable for application at some injection points, such as upstream from deaeration towers. In gas applications, the solvent in some biocide formulations may volatilize out of the product. The ability of the desolvated product to remain flowable is often considered in applications such as these. In some applications, biocides are pumped great distances in cold environments. In these applications, the viscosity and pour point of the product are frequently considered.

Most biocides are soluble in most brine compositions. However, a biocide is occasionally applied at a concentration that could exceed the solubility limits of the product or its degradation products. In squeeze applications, for example, the concentrated biocide pill may not be soluble in all proportions with formation fluids.

Likewise, some biocides may degrade (i.e., hydrolyze) in water or react with dissolved metals in water to form new chemical species having limited water solubility. Oxidizing biocides, for example, may form large amounts of solids when injected into certain produced brines. Therefore, the solubility of each potential biocide in the field brine at the maximum expected use concentration is typically verified.

Finally, the compatibility of each potential biocide with the other production chemicals in use at the location is frequently part of the evaluation process. Some biocides react with or are degraded by other production chemicals in the system. In particular, certain biocides may not be compatible at their use concentration with oxygen scavengers, corrosion inhibitors, scale inhibitors, and other types of production chemicals. Biocides are sometimes incompatible with various polymers and drilling fluids when rheological properties of the additive are considered. In these cases, the effective concentration of the biocide in the brine may be lower than intended. As noted in NACE Standard TM0194,[127] biocidal efficacy is determined in the presence of all production chemicals that might be present.

Biocide Selection

The next step in designing a biocide program is typically to test the biocides still under consideration and to evaluate the relative effectiveness of each toward the bacteria in the field samples. NACE Standard TM0194[127] specifies the procedures for obtaining field samples and conducting biocide time-kill tests for both planktonic and sessile populations. In general, the time-kill test is conducted by treating field bacterial samples with the desired concentration of biocide for a desired contact time. After the appropriate contact time, bacteria in the treated samples are enumerated by the serial dilution or the alternate methods described in the previous section. TM0194[127] specifies that the test conditions are generally as similar as possible to those prevailing in the system. Test conditions that affect bacterial growth include nutrient composition, dissolved oxygen, redox potential, temperature, salinity, and pH. Sessile populations may be significantly different from planktonic populations, and time-kill tests are often conducted with both types of populations to identify the most cost-effective biocide for the system.

Results from time-kill tests normally show the biocide dosage rate that achieves a certain level of bacterial control in the laboratory tests, along with the duration of the slug application. Biocide treatments that show a reduction to 10^1 or 10^2 bacteria/mL in the treated samples are normally considered to be effective. From the time and dosage rate and knowing the price of the biocide, preliminary treatment costs are typically estimated for each biocide tested. The biocides that show the most cost-effective performance in the laboratory tests are usually selected for field test application.

Various biocides have different levels of toxicity toward individual species of bacteria. Moreover, the biofilm and bacterial consortium that surround the individual species modify the sensitivity of the bacteria to a biocide. Therefore, for the time-kill test to be valid, it is normal to evaluate the efficacy of each biocide toward the bacteria in the field sample.[127] A common misconception is that stock cultures of individual bacterial types or cultures of bacterial populations from other systems are substituted to perform the test in the laboratory. The complex nature of a bacterial consortium—as it exists in a sessile biofilm—renders it unique in its specific resistance to biocidal challenge. Therefore, if the field survey shows that different bacterial populations are thriving at different locations in the system, individual biocidal kill tests are normally conducted with samples taken from each of the different locations.

Implementing Biocide Applications

Selection of Injection Points

As discussed in Section 3, one of the typical goals of the system survey is to identify the location of the bacterial contamination in the system so that the biocide is applied upstream from the contamination and effectively contacts the bacteria. In general, biocides are applied as far upstream in the system as possible to ensure that the biocide contacts all contaminated areas in the system. However, system parameters sometimes interfere with the treatment and increase the system demand for the biocide (Table 8).

Table 8: System Parameters That Typically Affect Biocide Demand

Deaeration towers
Filtration units
Produced solids
High salinity
H_2S
Oxygen
pH
Temperature
Mixing different source waters downstream from injection point
Use of incompatible production chemicals

If the system parameters such as those listed in Table 8 are present, various strategies are generally followed to minimize their interference with the biocide treatment. In some cases, the application point is made downstream from the interfering component. The use of two or three injection points typically ensures that biocidal residuals reach all contaminated areas. For example, surface-active biocides such as quats may strongly adsorb on the media used in filters. Therefore, if a surface-active biocide is used upstream from a filter, a second injection point downstream from the filter is often used. In cases in which multiple upstream batteries are treated, biocide injections are sometimes timed so that downstream, the biocide is not diluted below its effective concentration. If another treatment chemical is interfering with the biocide application, injection of an incompatible chemical is often temporarily suspended. For example, the oxygen scavenger ammonium bisulfite reacts with aldehyde biocides such as formaldehyde, glutaraldehyde, and acrolein to reduce the residual concentration of biocide. Injection of the oxygen scavenger is sometimes temporarily suspended for the few hours required for the biocide application. For these reasons, residual biocide levels are frequently measured throughout the system to verify that a sufficient biocidal concentration is present in regions of high bacterial contamination.

Application Methods

To be effective, biocides typically must be able to contact the bacteria. In general, mechanically cleaning the system prior to the biocide application facilitates contact of the biocide with the biofilm. Depending on the system, cleaning typically involves removing solids from tank bottoms, hydroblasting the walls of vessels, pigging of pipelines, and the like.

There are three general treatment methods normally used for biocides—batch, semi-continuous (or slug), and continuous. The batch application method is the most common. In batch applications, a specific quantity of biocide is typically injected quickly into a system on a periodic basis. An example of a batch application is the addition of 20 L (5.3 gal) of biocide to a 318-m^3 (2,000-bbl) water holding tank or producing well every week. Another example of a batch treatment is the application of a biocide between pigs. Batch applications have the advantages of speed and specificity; high concentrations of biocide are typically injected within a few minutes exactly where they are needed most—at the site of highest bacterial contamination. The contact time during batch treatments is normally dictated by the size of the vessel or fluid volume. Most batch applications are designed to provide sufficient contact time (typically more than two hours) to allow thorough penetration of the biocide throughout the biofilm. Poor mixing of the biocide due to channeling, chemical degradation of the biocide, or inadequate contact time often results in an ineffective treatment. For these reasons, batch treatments from single injection points are not normally used for treating water injection lines and wells. To treat production wells without packers, biocide is usually batched into the annulus and the well is then shut in and circulated for at least six to eight hours. To treat a specific vessel, biocide is usually batched into the tank and incubated for the contact time determined by the kill test; if possible, the tank is often removed from service and circulated or "rolled" to facilitate mixing of the biocide throughout the vessel.[67] To batch treat injection wells, it is common to inject biocide upstream from the injection manifold or the booster pump.

In contrast to batch treatments, the semi-continuous (slug) method is designed to deliver specific concentrations of biocide at locations downstream from the injection point. The semi-continuous method is typically suited for injection well and surface treatments from a single injection point. For example, 50 kg (110 lb) of acrolein is often added to the suction side of a triplex pump over a four-hour time interval on a daily basis. In this case, the slug of acrolein is four hours long and is injected at a precise concentration that allows contact with slime masses and sessile bacteria in a single application. A key concern is whether a biocidal concentration of active biocide effectively contacts all locations of high bacterial infestation downstream from the application point.

Continuous applications are treatments in which the biocide is injected continuously into the system at a specific dosage. Continuous treatments, for example, have been used extensively to control planktonic bacteria in seawater systems.[65,66] However, to control sessile populations, continuous applications are frequently augmented with semi-continuous treatments at higher dosages. Semi-continuous treatments tend to be more cost-effective than continuous treatments in controlling sessile populations: the higher biocide concentrations that are achieved in semi-continuous injections provide higher concentration gradients, which facilitates penetration of the biocide throughout the biomass.[15,93]

After the biocide application has been initiated, the system is typically monitored to determine whether the biocide needs to be applied at a different injection point, whether the dosage or duration of the injection needs to be increased, or whether an alternate biocide needs to be applied. Careful monitoring and improvements in a program often ensure that bacterial control is achieved and the biocide treatment is optimized.

Program Costs

Typically, batch, semi-continuous, and continuous treatment methods are each used in specific situations. The choice of application method is dependent on a number of factors including:

- The objectives of the treatment;
- The type of bacteria (planktonic and/or sessile) causing the operational problem(s);
- The location and size of the injection point;
- Whether the contamination is localized;
- Whether the contaminated system component(s) can be isolated or removed from service;
- Whether H_2S is present in the system; and
- The presence, type, and concentration of other treatment chemicals.

The most cost-effective treatment method focuses on controlling only those bacteria causing the operational problems. If the operational problems are caused by planktonic bacteria, then injection of the biocide generally targets only the planktonic bacteria in the system. To control planktonic bacteria, biocide is usually injected continuously in an effort to treat the entire volume of water that is continuously entering the system. On the other hand, if the operational problems are caused by sessile populations, then injection of the biocide generally targets only the sessile bacteria in the system. The most cost-effective method to treat sessile bacteria usually is to inject the biocide in a slug application, because higher concentrations of biocide are often more effective in penetrating biofilms. Continuous biocide injection is generally not a cost-effective method for treatment of sessile bacteria, unless fluid volumes are low. In some heavily contaminated systems in which 10^6 bacteria/mL or more are present in the injection water, a combination slug-continuous treatment program is sometimes used to treat for both the planktonic and the sessile bacteria. In this case, the continuous portion of the treatment is typically designed only to reduce the number of planktonic bacteria to acceptably low levels, as defined by water-quality specifications for the injection water.

Optimizing Biocide Treatments

An acceptable level of bacterial control is typically established when the operational problems caused by bacteria in the system are reduced to a manageable level. To maintain bacteria at manageable levels, the number and type of bacteria in the system are usually monitored on a weekly basis following the initial biocide treatments. The optimum batch and slug treatment frequency is typically determined by monitoring regrowth of bacterial populations and other system parameters (see Section 3). The point at which the population has increased again to undesirable levels is normally the maximum amount of time between batch applications. If the time interval between batch applications is extended beyond this maximum, other operational problems often become evident.

One of the keys to an effective monitoring program is obtaining samples for bacterial enumeration at the correct locations in the system.[145,150-152] This is often difficult, especially for samples of sessile populations. Consequently, a number of devices and methods have been used to obtain samples of sessile populations for subsequent enumeration.[151-153] These devices include bioprobes, coupons, removable spools, and sidestream units. More than four weeks often pass before sessile bacteria establish a stable biofilm on these devices and a reliable sessile monitoring program is initiated. After a stable biofilm has developed, the procedures specified in NACE Standard TM0194[127] are sometimes used to determine the extent of sessile bacterial contamination.

Bacteria have a rapid growth rate (minutes to hours) that allows the population to respond to the biocide being used for treatment. Under this selective pressure, biocide-resistant strains of bacteria can develop and ultimately repopulate a system. Such a response can occur as rapidly as within a few months. The most notable symptom is that the biocide treatment program begins to lose efficacy. Replacing the biocide with another cost-effective biocide has often precluded this problem. If the second biocide becomes ineffective after an additional period of time, then the original biocide has been applied again, often resulting in an alternating treatment pattern. Khattab and El-Hattab cite case histories on the use of alternating biocides.[109,110]

Section 5: Regulatory Aspects of Biocide Use

Biocides are chemical products that are intended to kill or render harmless biological organisms. When used properly, biocides often have profound beneficial effects on human lives, the environment, and the oil and gas industry. Furthermore, if used properly, the products are often applied in oil and gas field systems without significant risk to people and the environment.[154] Thus, the goal of all regulations that apply to biocides has typically been to delineate the conditions under which the various products can be manufactured, stored, transported, and used in a safe and environmentally responsible manner.

Because governmental regulations change frequently, this section simply provides a high-level overview of many of the applicable regulations and directs the reader to the appropriate governmental agencies for specific, current, and accurate information. Contact information for the respective competent authorities is listed in Table 9 and useful Web sites are listed in Table 10.

Table 9: Contacts for Competent Authorities

United States of America	
Toxic Substances Control Act (TSCA)	Office of Pollution Prevention and Toxics U.S. EPA 1200 Pennsylvania Ave. NW Mail Code 7401-M Washington, DC 20460 Email: tsca-hotline@epa.gov http://www.epa.gov/oppt/newchems/
Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	Office of Pesticide Programs Information Resources and Services Division U.S. EPA 401 M St. SW Washington, DC 20460 ATTN: Antimicrobial Pesticides http://www.epa.gov/oppad001/
NPDES	Water Permits Division Office of Wastewater Management U.S. EPA 1200 Pennsylvania Ave. NW Washington, DC 20460 http://www.epa.gov/owm/
Canada	
	Pest Management Regulatory Agency (PMRA) 2720 Riverside Dr. Ottawa, ON K1A 0K9 http://www.pmra-arla.gc.ca/english/main/notices-e.html
Europe and Scandinavia	
Biocidal Products Directive (BPD)	**AUSTRIA** Federal Ministry of Environment, Youth and Family Affairs Division I/7 Stubenbastei 5 A–1010 Vienna, Austria
	BELGIUM Ministerie van Volkesgezondheid RAC Vesalius V2-309 Pachecolaan 19 1010 Brussels, Belgium
	DENMARK Danish Environmental Protection Agency 29 Strandgade DK-1401 Kobenhavnk, Denmark
	FINLAND Finnish Environment Institute Kesakatu 6 Helsinki 00260, Finland OR National Product Control Agency for Welfare and Health PO Box 210 Helsinki 00531, Finland
	FRANCE Ministere de l’Environnement Bueau des Substances et Preparations Chemiques 20 Avenue de Segur Paris 07 SP, France

	OR Institut National de l'Environnement Industriel et des Risques B.P. 2 Verneuil-en Halatte 60550, France
	GERMANY Bundesumweltministerium Berntkasteler Strabe 8 Bonn–53175, Germany OR Umweltbundesamt FG IV 1.4 Seeckstr. 6-10 Berlin 13581, Germany
	GREECE National Drug Organisation 284 Messogion Street Athens 15562, Greece OR Ministry of Agriculture 3-5 Ippocratous str. Athens 10679, Greece
	ICELAND Environmental & Food Agency Armuli 1a Reykjavik 108 Iceland
	IRELAND Pesticide Control Service Abbotstown, Castleknock Dublin 15, Ireland OR Environment Policy Section Department of the Environment and Local Government Customs House Dublin 1, Ireland
	ITALY Ministry of Environment Via Cristoforo Colombo 44 Roma 00147, Italy OR Ministero della Sanita 7 Villa della Civilita Romana Roma, Italy
	LUXEMBOURG Ministre de l'Environnement 18 Montee de la Petrusse 2918 Luxembourg
	NETHERLANDS Ministry of Health, Welfare & Sport P.O. Box 20350 The Hague 2500 EJ, The Netherlands OR Board for the Authorization of Pesticides

	P.O. Box 217 Wageningen 6700 AE, The Netherlands
	NORWAY Norwegian Pollution Control Authority Stroemsveien 96 Oslo 0032, Norway
	PORTUGAL Direccao Geral de saude Ambiontal Divisao Saude Ambiental 45 Mesa de P. Enriches Lisboa 1049-005, Portugal
	SPAIN Ministerio de Sanidad y Consumo D.Gral de Salud Publica Paseo del Prado 18-20 Madrid 28972, Spain OR Ministerio de Agricultura, Pesca y Alimentacion C/Corazon de Maria, 8, 4a planta Madrid 28020, Spain
	SWEDEN Plant Protection, Biocidal and Biotechnical Products National Chemicals Inspectorate Sundbybergsvagen 9, Box 1384 Solna 17127, Sweden OR National Chemicals Inspectorate Sundbybergsvagen 9, Box 1384 Solna 17127, Sweden
	UNITED KINGDOM Biocides and Pesticides Assessment Unit Health and Safety Executive Magdalen House Trinity Road Bootle, Merseyside L20 3QZ United Kingdom Email: biocides@hse.gsi.gov.uk
Harmonized Offshore Chemical Notification Format (HOCNF)	**Oslo and Paris Commissions** New Court 48 Carey Street London SC2A 2JQ, England
	NORWAY Statens forurensningstilsyn (SFT) Stromsveien 96 Postboks 8100 Dep. 0032 Oslo, Norway
Offshore Chemical Regulations 2002 (OCR 2002)	**UNITED KINGDOM** Department of Trade and Industry Oil and Gas Directorate 4th Floor, Atholl House

	86-88 Guild Street Aberdeen AB11 6AR, Scotland OR Centre for Environment, Fisheries & Aquaculture Science Fisheries Laboratory Remembrance Avenue Burnham-on-Crouch Essex CMO 8HA, England

Table 10: Useful Web Sites

Information on the following regulations:	Can be obtained from the following Web sites:
Toxic Substances Control Act (TSCA)	http://www4.law.cornell.edu/uscode/unframed/15/ch53.html and http://www.epa.gov/region5/defs/html/tsca.htm
Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)	http://www.epa.gov/pesticides/fifra.html and http://www.epa.gov/compliance/civil/federal/fifra.html
National Pollutant Discharge Elimination System (NPDES) Permits	http://www.gpo.gov/nara/cfr/ and http://www.epa.gov/Arkansas/6en/w/offshore/home.html
European Inventory of Existing Chemical Substances (EINECS)	http://www.eurunion.org/legislat/chemical.htm and http://europa.eu.int/comm/environment/index_en.htm
European List of Notified Chemical Substances (ELINCS)	http://www.eurunion.org/legislat/chemical.htm and http://europa.eu.int/comm/environment/index_en.htm
Biocidal Products Directive (BPD)	http://ecb.jrc.it/biocides/
Offshore Chemical Notification Scheme (OCNS)	http://www.cefas.co.uk/ocns
Oslo and Paris Commission (OSPAR)[(A)]	http://www.ospar.org

[(A)] Oslo and Paris Commission (OSPAR), New Court, 48 Carey Street, London WC2A 2JQ, United Kingdom.

The information in this section is not intended to suffice as legal verification and is subject to varying interpretation. It is provided as a useful tool for those who wish to do further research.

As chemicals, biocides may be subject to the following types of governmental regulations: chemical substance registrations, biocide/pesticide regulations, transportation regulations, offshore chemical regulations, and discharge permits. These types of regulations are briefly discussed for several of the major oil and gas producing jurisdictions in the world.

United States of America

In 1976, the United States Congress enacted the Toxic Substances Control Act (TSCA) to give the EPA the ability to track industrial chemicals produced or imported into the United States. The EPA repeatedly screens these chemicals and can require reporting or testing of those chemicals that pose an environmental or human health hazard. Under TSCA, the EPA can ban the manufacture and import of those chemicals that pose an unreasonable risk.[155] Biocides, however, are specifically exempted from TSCA regulations.[156] Instead, oil and gas field biocides (also termed antimicrobial pesticides) are regulated by the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA).

Before a biocide can be marketed and used in the United States, it is normally registered with the U.S. EPA as specified under FIFRA.[157] The process of registering a biocide is a scientific, legal, and administrative process in which the EPA examines the ingredients of the product, details concerning the ways in which the product is used, the amount, frequency, and timing of the product's use, and storage and disposal practices. During the registration process, the EPA approves the language that appears on each biocide label. In evaluating a registration application, the EPA assesses a wide variety of potential human health, occupational, and environmental risks associated with use of the product. Potential human risks range from short-term toxicity to long-term effects such as cancer and reproductive system disorders.

There are many varied types of registrations under FIFRA. Primary registrations, formulator's exemptions, and supplemental registrations are the three more common types. Primary registrations are usually held by a single company that conducts the toxicity and physical testing of the biocide, files the product registration, develops the product label and confidential statement of formula, and fulfills all document and data requirements by the federal and state governments. A formulator's exemption indicates that a registrant has purchased the biocidal active ingredient from another registered source and then formulated the active ingredient into the end-use field product. The supplier of the active ingredient is responsible for satisfying all testing and data requirements for the EPA under FIFRA. Supplemental registrations give suppliers the ability to distribute a product even when the primary registration is owned by another company. Several other types of registrations that are available to registrants under varying conditions and circumstances include special local need registrations, experimental use permits, and emergency exemptions.

The EPA assigns a registration number to every product that is registered. There are different types of registration numbers depending on the type of product registration (primary, formulator, supplemental) and EPA establishment numbers, which denote the origin of product manufacture or repackaging. This number is used in correspondence and for reporting purposes with the EPA. Under FIFRA, registrants are typically responsible for keeping records and reporting annual production amounts, including manufacturing, relabeling, repackaging, and blending. Any unreasonable adverse effects are also reported in a timely manner.

Use classifications of biocides vary with the end use, toxicity, and local restrictions. Three common types of use classifications include restricted use, general use or unclassified, and state-limited use or state-restricted use. The restricted-use classification means that typically only certified applicators or persons under their direct supervision can apply the product. Acrolein is an example of an oil and gas industry biocide that has a restricted-use classification. Restricted-use regulations and certifications vary by state law, and applicator certifications are often obtained from the state where the product is used. The general-use classification indicates that the biocide products can be used by any adult using discretion on directions for use, application, and disposal. State-limited use indicates that states have the right to restrict certain biocides based on their evaluation of use within that particular state.

In addition to federal registrations, FIFRA specifies that biocides be registered in the states where they are sold or used.[157] In general, states may regulate the sale or use of any federally registered biocide only if the state regulation does not permit any sale or use that is prohibited under FIFRA. States have primary responsibility for enforcing compliance with FIFRA.

After being registered both federally and in the states where it is sold and used, a biocide is normally applied in oil and gas field operations only if the transport, storage, application, and disposal are conducted in accordance with label directions. The overall intent of the label is to provide clear directions for effective product performance while minimizing risks to human health and the environment. The U.S. courts consider a label to be a legal document. It is a violation of federal law to manufacture, formulate, transport, store, use, or dispose of a biocide in a manner that is inconsistent with the FIFRA registration and product labeling.

After biocides are applied in oil and gas field systems, specific regulations may apply if the treated fluids are discharged into the environment. In general, such discharges need to be permitted under the National Pollutant Discharge Elimination System (NPDES) permit program. Authorized by the Clean Water Act, the NPDES program controls water pollution by regulating point sources that discharge pollutants into waters of the United States. Point sources are typically defined as discrete conveyances such as pipes or man-made ditches. For the purposes of NPDES permitting, waters of the United States include navigable waters, tributaries of navigable waters, interstate waters, and intrastate lakes, rivers, and streams. The NPDES permit program is typically administered by authorized states.

Effluent guidelines and standards are established by the EPA for different industrial categories. Guidelines for the oil and gas extraction category are reported in the Code of Federal Regulations Title 40, Part 435.[158] Permits under this category may establish effluent limitations, prohibitions, reporting requirements, and other conditions on discharges from oil and gas facilities engaged in production, field exploration, developmental drilling, well completion, well treatment operations, and well workover and abandonment operations. Regulated discharges include drilling fluids, produced water, excess seawater used in fire control systems, excess seawater from pressure maintenance and secondary recovery projects, excess seawater used to pressure test piping and pipelines, ballast water, and once-through noncontact cooling water.

In general, effluent discharges from offshore oil and gas operations are normally monitored to ensure they comply with several limitations.[159,160] Depending on the limitations specified in the permit, drilling fluid discharges are typically monitored for cadmium and mercury concentrations in the barite, toxicity to Mysid shrimp, and the presence of a static sheen. Produced-water discharges are monitored for oil and grease concentrations, toxicity to Mysid shrimp and Inland Silverside minnow, and the presence of a visible sheen. Other chemically treated miscellaneous discharges (listed in the previous paragraph) are often monitored for the residual concentration of the treatment chemical, visible sheen, and toxicity to Mysid shrimp and Inland Silverside minnow.

This overview in no way covers all aspects of the laws and regulations that affect use of biocides in oil and gas field operations in the United States of America and is intended only as a general overview of certain requirements. The above information is not intended to suffice as legal verification. Specific references to both state and federal laws are available to be further researched for specific, current, and accurate information.

Europe and Scandinavia

In 1967, the European Union (EU)[(4)] introduced legislation on chemicals manufactured in or imported into the EU member countries. With this legislation, the EU sought to eliminate the disparity among national laws that could pose barriers to the free movement of goods. For purposes of the chemical inventories, EU countries include Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, The Netherlands, Norway, Portugal, Spain, Sweden, and the United Kingdom. National laws of member countries generally follow EU directives. Switzerland also has chemical control laws that generally follow EU directives.

Procedures for the classification, packaging, and labeling of dangerous substances are outlined in EU Directive 67/548/EEC.[161] The directive is complex, but it can be distilled into two distinct categories:

- Manufacturers and importers of chemicals typically classify all substances according to the law's description of dangerous—ranging from explosive to toxic to carcinogenic to flammable. Currently, there are 15 classes of danger in Directive 67/548/EEC. Once classified, chemicals are then packaged and labeled accordingly; and
- The competent authorities (listed in Table 9) of the member states are notified of new products. Products considered to be new are those that were not included in the European Inventory of Existing Chemical Substances (EINECS) when the inventory was closed on September 18, 1981. A substance is subject to notification if it is not covered by one of the exemptions granted by Directive 92/32/EEC.[162] To register a new product, manufacturers or importers of the new substance typically provide results of specific testing in a technical dossier. When accepted, the new substance is added to the European List of Notified Chemical Substances (ELINCS). The ELINCS registry is then updated and issued annually in cumulative form.

In 1998, the EU adopted the Biocidal Products Directive (BPD), 98/8/EU,[163] to harmonize the European market for biocidal products and their active substances, and to provide a high level of protection for humans, animals, and the environment.[154] Under the BPD, a biocidal product is an active substance, or a preparation containing at least one active substance, intended to destroy, deter, render harmless, prevent the action of, or exert some controlling effect on harmful/unwanted organisms by chemical or biological means. The scope of the directive is very wide, covering 23 different product types. These include disinfectants used in different areas, chemicals used for preservation of products and materials, nonagricultural pesticides, and anti-fouling products used on hulls of vessels.

The basic principles of the directive are:

- Active substances are typically assessed and decisions on their inclusion into Annex I of the directive are typically taken at the community level.
- Comparative assessment is often made at the community level when an active substance, although in principle acceptable, still causes concern. Inclusion into Annex I is denied if there are less harmful, suitable substitutes available for the same purpose.
- Member states authorize the biocidal products in accordance with the rules and procedures set in Annex VI of the directive. Only active substances included in Annex I are authorized.
- The producers and formulators responsible for placing biocidal products and their active ingredients on the market apply for authorization and submit all necessary studies and other information needed for the assessments and decision making.
- A biocidal product authorized in one member state is also authorized upon application in other member states unless there are specific grounds to derogate from this principle of mutual recognition.

Each EU member state established a competent authority to implement the BPD according to each member's legislative system. A list of competent authorities for BPD is listed in Table 9.

Before new active substances can be introduced on the market, they are typically approved under the provisions of the BPD. Active substances that were on the market prior to May 14, 2000, are subject to a 10-year transition period and review program. During the transitional phase, member states continue to apply their national rules on biocidal products containing existing active substances until the decision on the inclusion of the particular substances has been made.

Under BPD, biocidal products undergo two levels of review:

- A dossier of data on the active substances is evaluated to determine whether (a) the active substance can be used in biocidal products without posing unacceptable risks to humans, animals, and the environment, and (b) the active substance can be shown to be sufficiently effective. When member states reach agreement, the active substance is normally listed on Annex I, IA, or IB of the BPD and subsequently can be considered for use in a biocidal product.
- In the second level of review, biocidal products that contain specific active substance(s) listed on Annex I, IA,

[(4)]European Union (EU), Rue de la Loi, 175 B-1048, Brussels, Belgium.

or IB of the BPD are then evaluated to determine whether the products themselves can be used effectively without posing unacceptable risks. If so, the products are often authorized for supply, storage, and use in that member state, subject to any specified conditions. A system of mutual recognition allows for this authorization to be extended to other member states, following an application to them, unless there are exceptional circumstances.

After the transition period, it is an offense to market any active substance that is not listed on Annex I, IA, or IB of the BPD for use in biocidal products.

Biocides and all other production chemicals used in oil and gas facilities located in European waters also comply with Decision 2000/2—the Harmonised Mandatory Control System for Use and Reduction of the Discharge of Offshore Chemicals.[164] This regulation was introduced in June 2000 by OSPAR as an update to the HOCNF. In the United Kingdom, Decision 2000/2 came into force on May 15, 2002. It replaces the older OCNS for most chemicals and is administered by the Department of Trade and Industry under the Offshore Chemical Regulations 2002 (OCR 2002).

Decision 2000/2 and its supporting recommendations typically conclude that offshore chemicals are to be prescreened, ranked according to their calculated hazard quotients (HQ), and considered for replacement if less hazardous alternatives are available. The prescreen evaluates the biodegradability, toxicity, and bioaccumulation of each chemical constituent in a product.[165] If a product passes the prescreen, competent authorities calculate the HQ, defined as the ratio of predicted environmental concentration (PEC) to predicted no-effect concentration (PNEC), using the chemical-hazard assessment and risk-management (CHARM) module. Organic chemicals of similar function are often ranked (color-coded) according to their HQ and placed on the list of notified chemicals. A product having a poor environmental ranking may be recommended for replacement by a less hazardous alternative. Products typically need to be recertified once every three years.

Operators of offshore facilities in Europe typically apply for permits to use and discharge chemicals. In the application dossier, the operator lists the products, the amounts intended to be used, and the amounts intended to be discharged. In addition, the operator presents a site-specific risk assessment (RQ) of the consequences of the use and discharge of these chemicals on the receiving environment. After reviewing the dossier and consulting with territorially appropriate agencies (for example, the Center for Environment, Fisheries & Aquaculture Science [CEFAS] for English and Welsh waters and the Marine Laboratory of the Fisheries Research Service [FRS] for Scottish waters), the competent authority typically issues a permit to the operator. The permit sometimes specifies the conditions under which the chemical product may be used and discharged.

As stated above, this overview in no way covers all aspects of the laws and regulations that affect use of biocides in oil and gas field operations in the European Union and is intended only as a general overview of certain requirements. The above information is not intended to suffice as legal verification. Specific references to laws and directives are available to be further researched for specific, current, and accurate information.

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[(5)]American Society for Microbiology (ASM), 1752 N Street NW, Washington, DC 20036-2904.

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[6]Society for Industrial Microbiology (SIM), 3929 Old Lee Highway, Suite 92A. Fairfax, VA 22030-2421.
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Appendix A: Glossary

Aerobic Bacteria: Bacteria that grow and reproduce in the presence of oxygen (pp. 4, 7, 9, 21, 22, 23).

Aerobic Environment: An environment that contains oxygen.

Algae: Unicellular to multi-cellular plants that occur in fresh water, marine water, and damp terrestrial environments. All algae possess chlorophyll for photosynthesis.

Anaerobic Bacteria: Bacteria that grow and reproduce in the absence of oxygen (pp. 4, 7, 9, 22, 23).

Anaerobic Environment: An environment that is oxygen-free (pp. 5, 7, 17).

Anode: The electrode of an electrochemical cell at which oxidation occurs. Electrons flow away from the anode in the external circuit. Corrosion usually occurs and metal ions enter the solution at the anode (p. 9).

APB: Acid-producing bacteria (pp. 4, 5, 9, 21, 23).

Bacillus: Bacteria that are rod-shaped (pp. 4, 6).

Bacteria: Microscopic organisms that multiply primarily by binary fission and lack chlorophyll (pp. 4, 5, 6, 7, 9, 10, 11, 12, 13, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28).

Bacteriostat: Agents that inhibit bacterial growth. The affect of the agent is reversible; when agent is removed from the system, growth and reproduction resume.

Barophilic: Organisms that grow under conditions of high pressure.

Biocide: A chemical product that is intended to kill or render harmless biological organisms. Also termed antimicrobial pesticide (pp. 4, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 22, 23, 24, 25, 26, 27, 28, 32, 33).

Biofilm: A matrix of bacteria, exopolymer, debris, and particulate matter that adheres to a surface (pp. 6, 7, 9, 10, 11, 17, 18, 20, 22, 25, 26, 27, 28).

Cathode: The electrode of an electrochemical cell at which reduction is the principal reaction. Electrons flow toward the cathode in the external circuit (p. 9).

Chlorine Demand: The amount of Cl_2, hypochlorous acid,

(16) Synthetic Organic Chemical Manufacturers Association (SOCMA), 1850 M Street NW, Suite 700, Washington, DC 20036-5810.
(17) American Chemical Society (ACS), 1155 16th St. NW, Washington, DC 20036.

and hypochlorite that is used up through reactions with various chemical species in the brine. These reactions use up the biocide thereby making it unavailable for control of bacteria (p. 12, 13).

Coccus: Round or spherical-shaped bacterium (p. 4).

Consortium: A grouping of various types of bacteria that may live in symbiotic relationships. In the consortium, one type of bacteria may create a microenvironment that is conducive to the growth and reproduction of another type of bacteria (pp. 9, 26).

Demand: The amount of biocide that is used up through reactions with various chemical species in the brine, making it unavailable for control of bacteria (pp. 11, 12, 13, 14, 15, 16, 26).

Enumerate: Count (pp. 20, 21).

Enzyme: An organic catalyst produced by a living cell and capable of influencing a chemical reaction (i.e., enzymes mediate metabolic processes) (pp. 15, 16, 22).

Exoenzyme: An enzyme secreted by bacteria to convert nutrients into chemical species that are more readily adsorbed by the bacteria (p. 9).

Exopolymer: Organic polymer of microbial origin that is excreted from the cells; exopolysaccharide (EPS) is an example of a highly hydrated anionic polysaccharide polymer that the microbial cells produce to mediate their adhesion to surfaces. See also *glycocalyx* (pp. 6, 9, 10).

Exopolysaccharide: See *Glycocalyx* (p. 6).

Extracellular: Outside the cell (p. 6).

Facultative Anaerobic Bacteria: Bacteria that are able to carry out both aerobic and anaerobic metabolism and therefore are able to grow and reproduce in both anaerobic and aerobic environments (pp. 20, 21, 23).

Glycocalyx: Also called *exopolysaccharide* (EPS), glycocalyx is secreted by microorganisms to control their immediate environment, help filter nutrients, protect the cell membrane from harsh environments and chemical treatments, and to cement the bacteria to each other and to surfaces producing a biofilm (p. 6).

Growth Media: See *Medium, Media.* (p. 4).

Halophilic: Literally means “salt-loving” organism; facultative halophiles grow in a medium with NaCl but do not require it, while obligate halophiles require NaCl for growth.

IRB: Iron-Related Bacteria (p. 5).

Medium, Media: Formulated substrate(s) where certain types of bacteria may grow (pp. 6, 9, 19, 20, 21, 23, 27).

Mesophiles: *Mesophilic* bacteria have optimum growth at moderate temperatures between 25 and 37°C (77 and 98°F) (p. 4).

Metabolism: The electron transfer pathways where living organisms derive energy (pp. 4, 5, 16, 18).

Microaerobic Bacteria: *Microaerophiles* are bacteria that use oxygen in their metabolic pathways but prefer to grow and reproduce in environments containing low levels of oxygen (p. 5).

Microbiologists: Scientists who study bacteria, fungi, algae, and other microorganisms (pp. 4, 9, 23).

Microbiologically Influenced Corrosion (MIC): Many corrosion mechanisms can be influenced by the presence of microbiological organisms, such as bacteria, fungi, and algae. Bacteria are usually associated with an acceleration of corrosion mechanisms, but recent studies also suggest that the presence of some species of bacteria may mitigate corrosion (p. 5, 9, 10, 17, 18, 20, 22).

Morphology: The study of form and structure of living organisms, principally, the size and shape of a single organism as well as the arrangement of a collection of organisms. Principal bacteria morphologies include bacillus (rod-shaped), vibrio (curved rods), spirillum (corkscrew-shaped) and coccus (spherical) (p. 4).

National Pollutant Discharge Elimination System (NPDES): U.S. EPA permit system controlling the discharge of pollutants into the environment (p. 24, 29, 32, 33).

Obligate Aerobic Bacteria: Bacteria that require oxygen to grow and reproduce. Obligate aerobic bacteria do not survive in the absence of oxygen (p. 4).

Obligate Anaerobic Bacteria: Bacteria that require an oxygen-free environment to grow and reproduce. Obligate anaerobic bacteria do not survive in the presence of oxygen (p. 4).

Oxidation-Reduction Potential (ORP): The potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given electrolyte. For the purposes of this report, the term *Redox potential* is used (pp. 18, 23, 26).

Pesticide: An agent that is intended to kill or render harmless certain living organisms that are classified as pests (pp. 16, 29, 30, 31, 32, 34).

Planktonic Bacteria: Bacteria that are freely floating in brine. Planktonic bacteria can become sessile bacteria by adhering to a surface (pp. 9, 10, 17, 18, 20, 21, 27, 28).

Polysaccharide: A complex sugar that is secreted by bacteria. See also *glycocalyx* (p. 6).

Population: A group of organisms of the same species (pp. 4, 9, 10, 16, 17, 18, 19, 20, 21, 22, 23, 24, 27, 28).

Psychrophilic Bacteria: Bacteria that grow and reproduce best at temperatures near freezing (4 to 10°C [40 to 50°F).

Redox Potential: See *Oxidation-Reduction Potential*.

Sessile Bacteria: Bacteria that are attached to surfaces. Bacteria that live in biofilms are sessile bacteria (pp. 9, 17, 19, 20, 21, 27, 28).

Slime: Also called *glycocalyx* or EPS and relates to biofilms in which the immobilized microorganisms are embedded in the organic polymer matrix (pp. 6, 14, 17, 22, 27).

SOB: Sulfur-oxidizing bacteria (pp. 4, 6).

Spirillum: Bacteria that are shaped like a corkscrew (p. 4).

SRB: Sulfate-reducing bacteria (pp. 4, 5, 6, 9, 10, 17, 18, 20, 21, 22, 23).

Substrate: The substance on which an enzyme acts to form the product.

Symbiotic Relationship: Two or more types of bacteria living in close association that may be of benefit to each (pp. 4, 7).

Taxonomy: The science of the arrangement, classification, and naming of bacteria (p. 4).

Thermophilic Bacteria: Bacteria that grow and reproduce best at temperatures near or above 50°C (122°F) (p. 4).

Tubercle: A nodule or deposit on a metal surface. The tubercle may contain inorganic compounds and bacteria such as SRB as well as iron- and manganese-oxidizing bacteria (p. 5).

Vibrio: Bacteria that are shaped like curved rods (p. 4).