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MICROBIOLOGICALLY INFLUENCED CORROSION

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27.1 INTRODUCTION

Low alloy steel pipelines, used to transport crude oil, petroleum products, and natural gas, are located in a variety of microbiologically active environments, including belowground in soils and undersea [1]. The U.S. Department of Transportation (DOT) Office of Pipeline Safety has complied statistics for pipeline releases, including oil and gas, from 2002 to 2011 [2]. Over that period of time approximately 34% of all releases were attributed to corrosion. National Association of Corrosion Engineers (NACE) International [3] estimated the cost of corrosion for onshore gas and liquid transmission pipelines was $7 billion. However, there are no specific statistics related to microbiologically influenced corrosion (MIC) of low alloy steel pipelines. Russian investigators [4] estimated that 30% of the corrosion damage in equipment used for oil exploration and production was directly attributable to MIC.

The term MIC is used to designate corrosion due to the presence and activities of microorganisms, that is, those organisms that cannot be seen individually with the unaided human eye. Causative microorganisms are from all three main branches of evolutionary descent, that is, bacteria, archaea (methanogens), and eukaryota (fungi). The list of microorganisms involved in MIC and the mechanisms by which they influence corrosion is continuously growing. Mechanisms are the result of specific metal/microbe/electrolyte interactions. Corrosion is directly related to oxidation (anode) and reduction (cathode) reactions and microbial processes require one- and two-electron transfers (either oxidation or reduction reactions). Microorganisms can accelerate rates of partial reactions in corrosion processes or shift the mechanism for corrosion. MIC can involve a conversion of a protective metal oxide to a less protective layer (e.g., a sulfide) or removal of the oxide layer, for example, by metal oxide reduction or acid-production. Microorganisms can produce localized attack, including pitting, dealloying, galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement. Microorganisms can also produce non-tenacious corrosion products, for example, sulfides that are easily detached by mechanical sheer, resulting in enhanced erosion corrosion. However, microorganisms do not produce a unique corrosion morphology that distinguishes MIC from abiotically produced corrosion.

Discussion in the following sections will be limited to MIC of low alloy steels, for example, carbon steel. The main alloying element in carbon steel is carbon and its mechanical properties depend on the percentage of carbon. Carbon content has little effect on the general corrosion resistance [5]. Low-carbon steel contains approximately 0.05–0.3 wt% carbon and mild steel, 0.3–0.6% carbon. In referencing the work of others in this chapter, the alloy terminology used in the original work will be maintained.

Both internal and external oil and gas pipeline surfaces can be affected by MIC. DOT statistics [2] suggest that 7 and 16% of releases of crude oil in the United States are due to external and internal corrosion, respectively. Information in this chapter related to internal MIC will be limited to petroleum-based hydrocarbon fuels in low-alloy steel piping. The focus of most testing, monitoring, and research related to MIC in the oil and gas industry for internal and external pipeline surfaces is on sulfate-reducing bacteria (SRB) [6]. Consequently, any discussion of causative microorganisms, in this chapter, will be dominated by references to SRB. The

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significance of other causative microorganisms will be acknowledged and discussed.

27.2 REQUIREMENTS FOR MICROBIAL GROWTH

Microorganisms have developed several strategies for survival in natural environments: (1) spore formation (2) biofilm formation (3) dwarf cells, and (4) a viable, but non-culturable state. Many microorganisms produce spores that are resistant to temperature, acids, alcohols, disinfectants, drying, freezing, and other adverse conditions. Spores may remain viable for hundreds of years and can germinate when conditions become favorable. However, there is a difference between survival and growth. MIC requires growth of the causative organisms and growth requires water, electron acceptors/donors, and nutrients. The potential for MIC is determined by the availability of these essentials and any proposed mechanism must account for their availability.

27.2.1 Water

Liquid water is needed for all forms of life. Microbial interaction, distribution, and growth with oil and gas are limited by water availability. Microbial growth in hydrocarbons is concentrated at oil/water interfaces, that is, emulsified water, and separate water phases. The volume of water required for microbial growth in hydrocarbon fuels is extremely small. Since water is a product of the microbial mineralization of organic substrates, it is possible for *in situ* microbial mineralization of a hydrocarbon to generate a water phase that can be used for further proliferation.

27.2.2 Electron Donors and Acceptors

Microorganisms obtain energy through electron transfer processes. Not all electron donors and acceptors are water soluble. Electrogenic bacteria are capable of moving electrons to and from solid materials. Petroleum hydrocarbons, organic matter, reduced inorganic compounds, molecular hydrogen, and iron can act as electron donors, which release electrons during cellular respiration. Electrons are then channeled to electron acceptors. During this process the electron donor is oxidized and the electron acceptor is reduced. Microorganisms can use a variety of electron acceptors for respiration in dissimilatory reactions, that is, the acceptors are not assimilated. In aerobic respiration, energy is derived when electrons are transferred to oxygen, the terminal electron acceptor. In anaerobic respiration, a variety of organic and inorganic compounds may be used as terminal electron acceptors, including sulfate, carbon dioxide, nitrate, nitrite, Cr^{+6}, Fe^{+3}, and Mn^{+4}. There is specificity among anaerobes for particular electron acceptors; bacteria are routinely grouped based on the terminal electron acceptor in anaerobic respiration, for example, sulfate-, nitrate-, and metal-reducing bacteria.

Facultative anaerobic bacteria can use oxygen or other electron acceptors. Obligate anaerobic microorganisms cannot tolerate oxygen for growth and survival. Obligate anaerobic bacteria and archaea are, however, routinely isolated from oxygenated environments associated with particles, crevices, and most importantly, in association with aerobic and facultative bacteria that effectively remove oxygen from the immediate vicinity of the anaerobe.

SRB are a group of ubiquitous, diverse anaerobes that use sulfate as the terminal electron acceptor, producing hydrogen sulfide (H_2S). Several SRB can also reduce nitrate, sulfite, or thiosulfate. Under specific conditions, some SRB can accept electrons directly from iron and transfer the electrons for sulfate reduction. Enning et al. [7] demonstrated direct uptake of electrons from iron through a semiconductive ferrous sulfide corrosion crust. Many archaea can also produce sulfides. The inclusive term for all sulfide-producing microorganisms is sulfide-producing prokaryotes (SPP).

Several corrosion mechanisms have been attributed to SPP, including cathodic depolarization by the enzyme dehydrogenase, anodic depolarization, production of iron sulfides, release of exopolymers capable of binding metal ions, sulfide-induced stress corrosion cracking and hydrogen-induced cracking or blistering [8]. During corrosion of carbon steel influenced by SPP, a thin (approximately 1 μm), adherent layer of mackinawite [$(Fe,Ni)_9S_8$)] is formed. If the ferrous ion concentration is high, mackinawite and green rust 2, a complex ferrosoferric oxyhydroxide will form. Under some circumstances, green rust 2, unstable in the presence of oxygen, can be an electron acceptor for SRB [9]. Once electrical contact is established between corrosion products and carbon steel, the carbon steel behaves as an anode and electron transfer occurs through the iron sulfide. In the absence of oxygen, the metabolic activity of SPP causes accumulation of H_2S near metal surfaces. At low ferrous ion concentrations, adherent and temporarily protective films of iron sulfides form on low-alloy steel surfaces with a consequent reduction in the corrosion rate. High rates of SPP-induced corrosion of carbon steel are maintained only when the concentrations of ferrous ions are high.

In the absence of oxygen, sulfides, from whatever source, react with carbon steel to from a layer of iron sulfide that prevents further reaction, that is, diminution of corrosion. Aggressive SPP corrosion of low alloy steel has been reported in the presence of dissolved oxygen. Hardy and Bown [10] investigated the weight loss of mild steel exposed to successive aeration-deaeration shifts. In their experiments the highest corrosion rates were observed during periods of aeration. In laboratory seawater/hydrocarbon fuel incubations, Aktas et al. [11] demonstrated that there was minimal sulfate reduction and no corrosion of carbon steel in the total

absence of oxygen. Aggressive corrosion was observed when low levels of dissolved oxygen (<100 parts per billion) were present in the seawater. Hamilton [12] reviewed mechanisms for MIC and concluded that oxygen was the terminal electron acceptor in many MIC reactions. Following this logic, when SPP are involved in corrosion sulfate could serve as the terminal electron acceptor in respiration, but oxygen will be the terminal electron acceptor in the corrosion reaction.

27.2.3 Nutrients

Waters with suitable forms of carbon, nitrogen, phosphorus, and sulfur are required to support microbial growth. Hydrocarbons can be degraded under aerobic and anaerobic conditions to provide a carbon source for microbial assimilation [13–18]. Aerobic biodegradation of hydrocarbons is faster than anaerobic degradation. Rates depend on the specific electron acceptors used in the process ($O_2 > NO^{3-} > Fe^{3+} > SO_4^{2-} > CO_2$). As a practical matter, carbon availability is not typically the main constraint to crude oil degradation. Low concentrations of assimilable forms of nitrogen and phosphorus can limit hydrocarbon biodegradation.

27.3 INTERNAL CORROSION

Pipelines are classified by function. Gathering pipelines collect products from sources, such as wells, tankers or other pipelines. They move products to storage or processing facilities. Transmission pipelines transport liquids or natural gas over longer distances. These pipelines lines deliver crude oil to refineries or refined products to markets. Distribution pipelines move products to customers.

Pitting is the typical type of internal corrosion in pipelines, both isolated pits and overlapping ones [19]. Internal corrosion due to MIC is directly related to the biodegradability of the contents, water, and electron acceptors/donors. Some microorganisms are naturally occurring in hydrocarbon fuels; others are introduced from air or water. Susceptibility of hydrocarbons to microbial degradation can be generally ranked as follows: linear alkanes > branched alkanes > small aromatics > polyaromatics > cyclic alkanes. Some compounds, such as the high molecular weight polycyclic aromatic hydrocarbons, may not be degraded. Walker and Colwell [20] concluded that bacteria showed decreasing abilities to degrade alkanes with increasing chain length.

The sulfur content of crude oils is a particular concern from a MIC perspective because SRB could use oxidized sulfur compounds, including sulfate, as electron acceptors to produce H_2S. However, in past surveys, sulfur content did not correlate to H_2S content [21]. Most of the sulfur in crude oils is organic sulfur in heterocyclic ring structures, for example polycyclic saturated carbonaceous ring structures. Gogoi and Bezbaruah [22] concluded, ". . . most prevalent naturally occurring microorganisms do not effectively breakdown sulfur-bearing heterocycles," suggesting that these compounds are not readily biodegradable.

27.3.1 Production

SPP-related MIC of carbon steel, used in oil production, has been reported around the world. The petroleum production environment is particularly suitable for the activities of SRB because it handles large volumes of water from underground reservoirs, which contain nutrients [23]. Ciaraldi et al. [24] concluded that the factors influencing MIC in production lines in the Gulf of Suez were low flow velocities, deposit accumulations, water flooding and increased levels of bacteria. El-Raghy et al. [25] reported that pipelines used to transport El-Morgan field crude in the Gulf of Suez lost 75% of their original wall thickness due to the activities of bacteria, particularly SRB.

27.3.2 Transmission

Petroleum transmission lines are less susceptible than production lines to MIC because oxygen, water, and sediment are removed to specified limits. For example, in Canada, the National Energy Board (NEB) requires that crude transmission pipelines cannot accept a product that contains more than 0.5% basic sediment and water (BS&W). Lillebo et al. [26] demonstrated that growth of SRB was inhibited in crude oils containing <0.5% water. In the United States, the Federal Energy Regulatory Commission (FERC) allows BS&W levels of 1.0%. At these low levels, the water in crude oil exists as a microemulsion, resulting in carbon steel surfaces being oil-wetted and corrosion is negligible. BS&W values are averaged readings, meaning that it is possible to have slugging events that are not detected. Despite the potential differences in the water content, Friesen et al. [27] demonstrated there was no direct relationship between water content of crudes and corrosivity. Furthermore, internal corrosion has been observed in crude pipelines with <0.5% BS&W at locations where water can accumulate [28]. Unintentional introduction of water or oxygen into crude oils increases the likelihood for MIC.

Papavinasam [29] concluded that "bulk crude oil may indirectly affect the corrosion by influencing the locations where water accumulates, by influencing the type of emulsion, by impacting the wettability of phases on the steel surface and by supplying chemicals that can partition into the water phase." Accumulation of water depends on inclination of the pipe, the flow velocity and the cleanliness of the pipeline. Water solubility increases with hydrocarbon molecular weight [30]. However, industrial experience indicates that heavier crudes, while high in water content, are less corrosive owing to their elevated viscosity and resulting low conductivity ($<10^{-7}$ S/cm) [30]. Asphaltenes and resins in

heavy crudes act as surfactants to stabilize water-in-oil emulsions.

Crudes carry water-wetted particles that can drop out at locations downstream of over-bends. Sludge deposits concentrate water from oil at the pipeline surface shifting the oil-wet surface to a water-wet surface. Sludge deposits are combinations of hydrocarbons, sand, clay, corrosion products, and biomass that can reach 50% water by weight. Mosher et al. [28] demonstrated that high bacterial activity and/or water content in the sludge alone did not produce corrosive conditions over a 3-month period. Analyses of pipeline deposits obtained from pigging operations indicated a range of particle sizes with diameters from 44 to 400 μm. Most of the solids were fine particles of silica sand and iron minerals. Larger sand particles were uniformly coated with very fine clay surrounded by a film of water. Under low flow conditions, these particles precipitate and form a sludge deposit.

27.4 TESTING

27.4.1 A Review of Testing Procedures

One of the first attempts to quantify microorganisms related to MIC in oil and gas systems was published in 1975 by the American Petroleum Institute (API) [31]. "*Recommended Practice (RP) 38 Biological Analysis of Subsurface Injection Waters*" describes liquid media for cultivation of SRB and heterotrophic bacteria. The RP states that the presence of SRB is "a potential problem." It further states, "The extent of the problem will depend upon additional evidence . . ."

In 1990, the Gas Research Institute (GRI) published "*MIC: Methods of Detection in the Field*" [32]. The GRI guide, "designed to help gas industry personnel determine whether or not the corrosion occurring at a particular site is MIC . . ." was the first to emphasize the importance of acid-producing bacteria (APB) to the corrosion of carbon steel gas pipelines. The guide also specified localized corrosion morphologies that were suggestive of MIC, including cup-type, scooped-out hemispherical pits, and striation lines. The guide provided a numerical rating for predicting the probability that MIC had occurred based on two parameters, that is, the number of bacteria and the characteristics of pit morphology. The guide did not suggest using either parameter independently to diagnose MIC. The guide was not meant to be a predictive tool. Unintended consequences of the guide [32] were the proliferation of liquid media test kits, a strong reliance on numbers of particular types of bacteria to diagnose and predict MIC, and an over interpretation of pit morphology to diagnose MIC [33].

In 2004, NACE International Standard Test Method TM0194-2004 "*Field Monitoring of Bacterial Growth in Oil and Gas Systems*" [34] provided sampling procedures for planktonic and sessile bacteria, a lactate-based culture medium, and a serial dilution to extinction methodology for enumerating SRB. Vials that turned black due to formation of iron sulfide within a 28-day period were scored as positive for SRB. Additionally, the time required for blackening was suggested as a measure of the "strength (i.e., activity) of the growing culture." There is an acknowledgment within TM0194-2204 that the lactate-based medium cannot be used to grow SRB requiring other carbon sources, for example, acetate, propionate, or butyrate.

Several attempts have been made to improve liquid culture media used for the detection of SRB. A complex medium was developed containing multiple carbon sources that could be degraded to both acetate and lactate [35]. In comparison tests, the complex medium produced higher counts of SRB from waters and surface deposits among five commercially available media [36]. Jhobalia et al. [37] developed an agar-based culture medium for accelerating the growth of SRB. The authors noted that over the sulfate concentration range from 1.93 to 6.50 g/l, SRB grew best at the lowest concentration. Cowan [38] developed a rapid culture technique for SRB based on rehydration of dried nutrients with water from the system under investigation. The author claimed that using system water reduced the acclimation period for microorganisms, ensuring that the culture medium had the same salinity as the system water used to prepare the inoculum. Cowan [38] reported quantification of SRB within 1–7 days.

The distinct advantage of culturing techniques to detect specific microorganisms is that low numbers of cells grow to easily detectable higher numbers in the proper culture medium. Under all circumstances though, culture techniques underestimate the organisms in a natural population [39,40]. Kaeberlein et al. [41] suggested that 99% of microorganisms from the environment resist cultivation in the laboratory. A major problem in assessing microorganisms from natural environments is that viable microorganisms can enter into a non-culturable state [42]. Another problem is that culture media cannot approximate the complexity of a natural environment. Growth media tend to be strain specific. As previously mentioned, lactate-based media sustain the growth of lactate-oxidizers, but not acetate-oxidizing bacteria. Incubating at one specific temperature is further selective. Zhu et al. [43] demonstrated dramatic changes in the microbial population from a gas pipeline after samples were introduced into liquid culture media. For example, using culture techniques SRB dominated the microflora in most pipeline samples. However, using culture-independent quantitative polymeric chain reaction (qPCR) techniques they found that methanogens were more abundant in most pipeline fluid samples than denitrifying bacteria and that SRB were the least abundant bacteria. Similarly, Romero et al. [44] used molecular monitoring to identify bacterial populations in a seawater injection system. They found that some bacteria

present in small amounts in the original waters were enriched in the culture process.

It is well established that the microbial constituents in the sessile population (attached to the surface) are different from those of planktonic population (passively floating). Wrangham and Summer [45] used metagenomic analyses of planktonic and sessile samples from three different geographical locations to demonstrate that the planktonic population was not representative of the sessile population from the same location. They reported, ". . . planktonic and sessile populations from the same location may be as different from each other as they are to samples obtained from other locations." Similarly, Larsen et al. [46] used molecular microbiological methods (MMM) to demonstrate that the bacteria and archaea in scale and produced water were "somewhat different" from each other.

27.4.2 Current Procedures

More recent test methods, for example, NACE International Standard Test Method TM0212-2012 "*Detection, Testing, and Evaluation of MIC on Internal Surfaces of Pipelines*" [47] acknowledge that many types of microorganisms, including archaea, can contribute to MIC. In Section 7.2.4, the method clearly indicates that the type of medium used in liquid culture techniques determines, to a large extent, the numbers and types of microorganisms that grow. In addition to liquid culture, the document describes other techniques to identify microorganisms, including microscopy, adenosine triphosphate photometry, hydrogenase measurements, adenosine phosphosulfate reductase, 4′,6-diamidino-2-phenylindole (DAPI), and MMM. MMM include qPCR, fluorescence *in situ* hybridization (FISH), denaturing gradient gel electrophoresis (DGGE), and clone library building. The advantages and disadvantages for each test have been described in detail elsewhere [8,48,49]. TM0212-2012 stresses the need to collect microbiological, operational, and chemical data from corroded sites and to compare with similar types of data collected from areas that are not corroded.

Alabbas et al. [50] reported that DGGE was an ineffective method for fingerprinting DNA, specifically DNA from sour crude oil and seawater injection pipelines, because it is difficult to reproduce among different users and the information is visual, that is, there are no databases for comparative purposes. Investigators have used other approaches to describe microbial populations in petroleum reservoirs. Guan et al. [51,52] used phylogenetic analyses of gene fragments of the dissimilatory sulfite reductase (dsr) gene that encodes for the key enzymes in the anaerobic dissimilatory respiration of sulfate. The dsr gene is present in all SPP. Their investigation demonstrated the diversity of SPP that could potentially be involved in reservoir souring and corrosion.

Sequencing can provide the order of nucleotides in DNA or RNA. DNA sequencing can be used to determine the sequence of individual genes, gene clusters, chromosomes, or full genomes. Wang et al. [53] compared the results from pyrosequencing data and clone library searches to estimate bacterial diversity in aqueous and oil phases from a water-flooded petroleum reservoir. Pyrosequencing is a method that involves extracting DNA, suspending it in a fluid, breaking it apart using chemiluminescent enzymatic reactions, and using a high resolution camera to infer its makeup. In molecular biology a library is a collection of DNA fragments. The term can refer to a population of organisms. Using both pyrosequesncing and clone library approaches, Wang et al. [53] determined that at a high phylogenic level, the predominant bacteria detected by the two methods were identical. However, they reported, ". . . pyrosequencing allowed the detection of "more rare bacterial species than the clone library method."

Prediction of MIC in gas and oil carbon steel pipelines has been unreliable because of uncertainties in the time to pit initiation and the rate of propagation. There have been attempts to predict MIC based on corrosivity factors. For example, Pots et al. [54] considered SRB the major contributor to MIC and determined that the following parameters influenced SRB activity: water, pH of the water, salinity, temperature, and nutrients, for example, sulfate, total carbon, nitrogen, and C:N ratios. Each parameter was given a rating factor (F) based on their influence. In addition, the operational history of the pipeline was reviewed, for example, duration of periods of stagnation. Sooknah et al. [55,56] used a similar approach to develop an internal pitting corrosion model that predicts susceptibility to MIC (Figure 27.1). Use of this type of model requires a thorough understanding of the specific system to which it is applied.

Risk-based inspection programs that include MMM have been designed and are being tested [57,58]. Larsen et al. [59] developed a model that estimates corrosion risk and time-before-pit initiation using qPCR enumeration of MIC-causing microorganisms and reverse transcript qPCR as a measure of cellular activity. Larsen et al. [59] used the approach during an inspection of two pipelines in the North Sea to develop a strategy for remediation.

27.4.3 Monitoring

Many techniques claim to monitor MIC, however, none has been accepted as an oil and gas industry standard or as a RP by ASTM or NACE International. NACE Standard TM0194-2004 "*Field Monitoring of Bacterial Growth in Oil and Gas Systems*" [34] describes a standard test method for monitoring growth of microorganisms and evaluating the effectiveness of control chemicals, but does not relate directly to corrosion. The major limitation for MIC monitoring programs has been the inability to relate microorganisms to corrosion in real time. Some techniques can detect a specific modification in the system due to the presence and activities

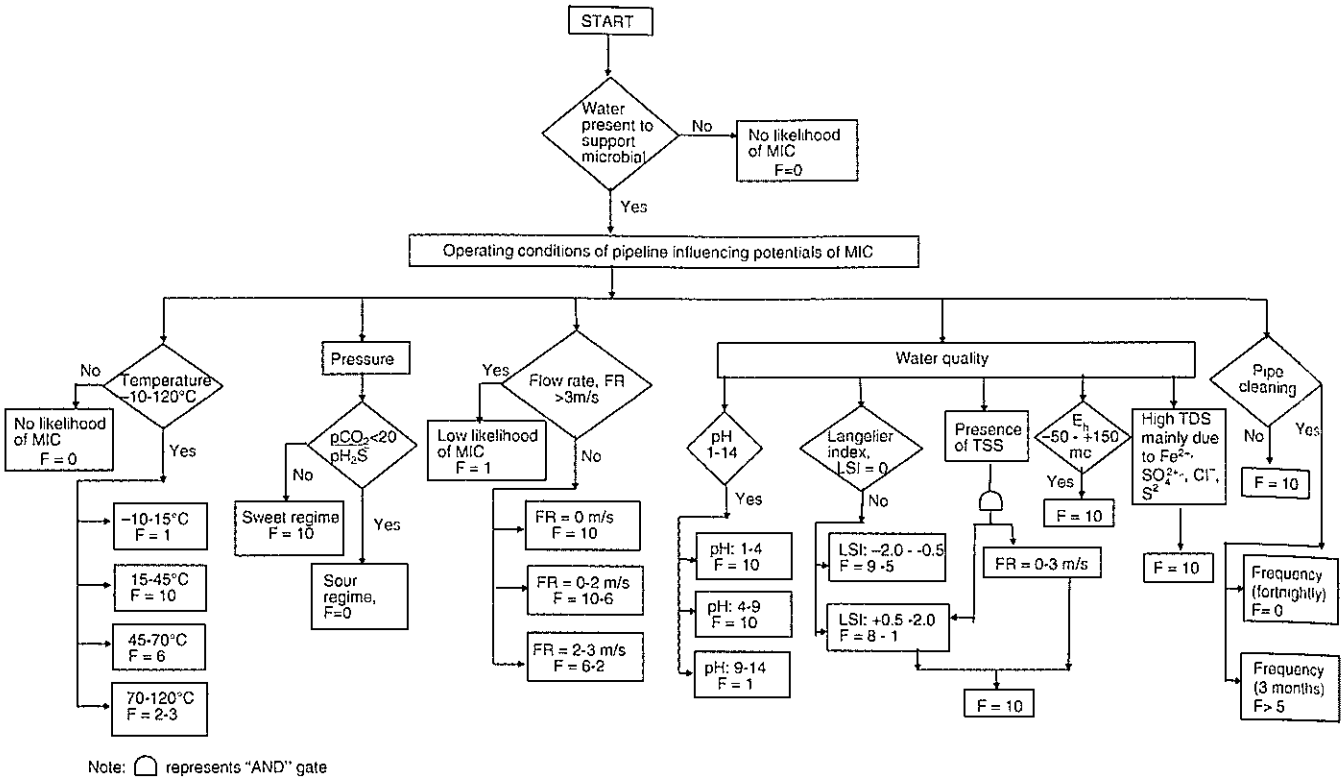

FIGURE 27.1 Internal pipeline MIC—risk assessment flowchart (© NACE International 2007 [56].)

of microorganisms (e.g., heat transfer resistance, fluid friction resistance, galvanic current) and assume something about the corrosion. Others measure some electrochemical parameter (e.g., polarization resistance, electrochemical noise) and assume something about microbial activities. Either experience or knowledge of a particular operating system can be an effective monitoring tool, especially for evaluating a treatment regime (biocides or corrosion inhibitors).

There have been approaches to derive real-time microbiological data. Chattoraj et al. [60] suggested that fluorogenic bioreproters could be used to determine total microbial contamination/activity on line and in real time. Fluorogenic bioreporters are compounds that undergo a change in their fluorescent signal after interaction with microorganisms. Chattoraj et al. [60] demonstrated that fluorescence, monitored with a fluorometer, before and after addition of the bioreporter, provided a ratio related to microbial activity. Several investigators have attempted to simultaneously quantify corrosion and some property related to microorganisms. For example, Haile et al. [61] developed a four-probe sensor for simultaneously monitoring corrosion rate and sulfide oxidase to detect sulfides. The probe has been demonstrated in the laboratory.

The application of MMM techniques for monitoring microbial populations has been suggested [62,63]. Hoffmann et al. [64] concluded, ". . . there are no 'off the shelf' solutions and standardized methods will ultimately be required if comparative data are to be generated across the industry."

27.4.4 Control

Standard mitigation procedures for controlling internal corrosion in oil and gas pipelines include physical removal of deposits (pigging) and chemical treatments that include nonoxidizing biocides (e.g., glutaraldehyde, quaternary amines, and tetrakis (hydroxymethyl) phosphonium sulfate). Biocides kill or slow the growth of microorganisms by a number of mechanisms, including protein cross-linking, disrupting cell membranes, or by inhibiting a vital process (e.g., synthesis or respiration) [65]. Maxwell and Campbell [66] used the approach developed by Pots et al. [54] described earlier to predict the risk of MIC in oil transportation lines. Maxwell and Campbell [66] concluded, ". . . frequency of pigging—which will have no biocidal effect—is predicted to provide the greatest mitigation of MIC compared to the possible bacteriostatic effect of high salinity and the bactericidal effect of biocide additions."

Harris et al. [67] used maximum pitting rate to evaluate the impact of film forming corrosion inhibitors as a means of controlling MIC of carbon steel in produced waters. Film

forming inhibitors (e.g., quaternary amines) are frequently used to control CO_2 corrosion and can be used in combination with biocides (e.g., glutaraldehyde) intended to reduce numbers of microorganisms. In addition, some corrosion inhibitors contain toxic components. Harris et al. [67] indicated the following: (1) MIC pitting rates increased in the presence of some corrosion inhibitors, presumably because of the biodegradability of the inhibitor, (2) some microorganisms developed a resistance to supposedly toxic inhibitors, (3) MIC control was not related to toxicity, that is, a less toxic inhibitor provided better MIC control than a more toxic one, and (4) severe corrosion was not related to numbers of SRB.

Similarly, Campbell et al. [68] suggested that evaluating MIC control or mitigation by monitoring a decrease in bacterial numbers is inaccurate and misleading. In their experiments, they concluded that biocides can injure cells in a biofilm, rather than kill the cells. Recovering SRB had significantly reduced doubling times compared with SRB that had not been exposed to biocides.

Ciaraldi et al. [24] described the following tactics to prevent MIC in oil production lines and equipment:

- "Scale inhibition and paraffin dispersal/dissolution;
- Periodic chemical and mechanical cleaning;
- Use of fiberglass linings, coatings, and sacrificial anodes in vessel and piping bottoms;
- Reroutings of production to increase flow velocities;
- Resizing of needed replacement piping to increase flow velocities;
- Rotation of piping to extend life (damaged areas relocated from 6 o'clock position);
- Refurbishment pigging of pipelines (i.e., multiple pig runs with increased aggressiveness to restore to near bare-metal condition; experience has shown that in many cases 50–100 pig runs are required);
- Routine, periodic, and aggressive maintenance pigging of refurbished pipelines;
- Routine, batch biocide treatments (when possible, immediately following pigging, mechanical, or chemical cleaning); and
- Improved monitoring with coupons, gas analyses, bacterial culturing of liquid, deposit and pigging debris samples, and increased UT surveys/smart pig inspections." UT refers to ultrasonic testing.

27.4.5 Alter Potential Electron Acceptors to Inhibit Specific Groups of Bacteria

Biocides control MIC by decreasing the microbial population, whereas control by manipulation of electron acceptor relies on growth stimulation or retardation of specific microbial populations. Both removal and addition of electron acceptors have been used as a means of controlling microbial populations and MIC in seawater injection systems where seawater is injected into oil reservoirs to maintain pressure. In these applications, oxygen is removed to minimize corrosion. However, in the anaerobic environment, growth of SRB is encouraged. The concentration of sulfate in seawater is typically >2.0 g/l. Rizk et al. [69] used nanofiltration to reduce sulfate in seawater from 2.6 to 0.05 g/l. In laboratory studies they demonstrated that the amount of H_2S in the seawater was a direct function of the amount of sulfate in the water. The authors discussed the implication for corrosion, but did not make corrosion measurements. In contrast, Jhobalia et al. [37] demonstrated that high-sulfate concentration in a laboratory medium (increase from 1.93 to 6.5 g/l) could inhibit growth of *Desulfovibrio desulfuricans* and the corrosion rate of mild steel. Addition of sulfate was presented as a "biochemical approach" for dealing with MIC [37], but has not been tested as a practical control strategy for MIC. The authors hypothesized that the observation was due to increasing toxicity of sulfate toward SRB metabolism or sulfate reduction.

Laboratory and field experiments have demonstrated that nitrate, an alternative electron acceptor, treatment can be an effective replacement for biocide treatment to reduce the sulfide production by SRB [70,71] a process known as biocompetitive exclusion. The addition of nitrate can induce a shift in the dominant population from SRB to nitrate-reducing bacteria (NRB). NRB reduce nitrate to N_2 with several possible intermediate by-products, including nitrite and ammonium. One motivation for nitrate injection is to prevent souring due to SRB. The other is to reduce corrosion risks.

Nitrate treatment was implemented on an oil platform in the North Sea (Veslefrikk) [72]. The change from glutaraldehyde treatment to nitrate resulted in a dramatic change in the bacterial community. The SRB population decreased and the numbers of NRB increased. After 4 months of nitrate addition the activity of SRB in the biofilm was markedly reduced as measured with radiorespirometry and an enrichment of NRB was measured. After 32 months of nitrate treatment, SRB numbers were reduced 20,000 fold and SRB activity was reduced 50-fold. Corrosion measurements decreased from 0.7 to 0.2 mm/year. Similar applications have been made to reduce souring [73,74]. Gullfaks platforms have been treated with nitrate to reduce H_2S production [75]. The authors also observed a 1000-fold reduction in SRB numbers and a 10- to 20-fold reduction in sulfate respiration activity and a 50% reduction in corrosion.

Voordouw et al. [76] and Hubert et al. [77] demonstrated a nitrate-reducing, sulfide-oxidizing bacterium capable of reducing nitrate to nitrite, nitrous oxide, or nitrogen and oxidizing sulfide to sulfate or sulfur. The stoichiometry of the reactions catalyzed by the organism depended on the ratio of sulfide to nitrate. Dunsmore et al. [78] isolated an organism

from a Danish North Sea oilfield water injection system that had been continuously treated with nitrate since the start of the injection. This species, an SRB, could reduce nitrate and produce ammonium in the presence of sulfate, increasing the likelihood of corrosion. Hubert et al. [79] demonstrated that both nitrate and nitrite were effective treatments for decreasing sulfide concentrations. The required dose depended on the concentration of oil organics used as the energy source by the microbial community. Sunde et al. [75] suggested that reservoir characteristics and nutrient availability have a significant impact on the effectiveness of nitrate injection.

There are several potential mechanisms for the observed inhibition of SRB due to addition of nitrate. Microbial nitrate reduction produces more energy than sulfate reduction. It follows that if both nitrate and sulfate are present, nitrate will be the preferred electron acceptor. Toxic reaction products from the reduction of nitrate to N_2, for example, nitrite, may inhibit SRB. A shift in the redox potential in the system may also inhibit SRB. As a consequence of nitrate reduction, the redox potential will likely increase, producing unfavorable conditions for sulfate reduction. Nitrite may also act as a scavenger for H_2S. When competing for the same carbon source, nitrate-utilizing bacteria out-compete SRB. This argument is valid only in carbon-limited waters.

The success of nitrate addition relies on a population of nitrate-utilizing bacteria in the system. Hubert et al. [77] suggested that bioaugmentation, in which *ex situ* grown microorganisms could be injected with the nitrate if indigenous NRB were lacking. Despite the possibility of bioaugmentation, there are several reports of failures. Bouchez et al. [80] attempted to inoculate a nitrifying sequencing batch reactor with an aerobic denitrifying bacterium. The added bacterium disappeared after 2 days. Similarly, Hubert et al. [79] reported that introduction of microorganisms into natural communities was difficult. Microorganisms other than SRB and NRB may be involved in subterranean nitrogen cycling. For example, in an anaerobic environment, ammonium-oxidizing (anammox) bacteria can convert ammonium and nitrite into N_2. Li et al. [81] have identified five genera of anammox bacteria in high-temperature petroleum reservoirs.

In summary, nitrate addition and sulfate removal/reduction both attempt to control MIC caused by SRB. The long-term consequences on the microbial populations and MIC are unknown. There are limited data indicating that nitrate injection is ineffective at slowing H_2S production where souring has already occurred [82].

27.5 EXTERNAL CORROSION

As is the case with internal corrosion, the potential for MIC impacting the outer surfaces of buried or submerged pipelines is controlled by availability of water, electron acceptors/donors and nutrients in the environment. All line pipe is externally coated (e.g., asphalts, polyolefin tapes, and fusion bonded epoxies) and can be further protected with cathodic protection (CP). Coatings isolate the pipe exterior surface from the environment. CP is the application of current to a pipeline, overriding local anodes and making the entire pipeline surface a cathode. Coatings reduce the exposed area of pipeline surfaces, making CP economically feasible.

NACE International Standard Practice (SP) SP0169-2007 (formerly RP0169-2002) "*Control of External Corrosion on Underground or Submerged Metallic Piping Systems*" [83] describes the ". . . procedures and practices for achieving effective control of external corrosion . . . ." The SP lists the following conditions in which CP is ineffective "elevated temperature, disbonded coatings, thermal insulating coatings, shielding, bacterial attack, and unusual contaminants in the electrolyte." Microorganisms can affect CP in several ways. Some microorganisms are attracted to the areas surrounding a cathodically polarized pipe, that is, microbial abundance, activity and diversity in saturated soils, seawater or sediments could increase as a result of CP. If microorganisms compromise the coating, the potential required to prevent corrosion will be more negative than the −850 mV versus saturated copper/copper sulfate reference electrode recommended in SP0169-2007. Barlo and Berry [84] confirmed that the criterion for CP of buried pipelines was valid in concept; however, the actual protection potential varied with environment. Microorganisms can increase the kinetics of corrosion reactions, necessitating a current increase to maintain a specific potential. When sufficient CP levels exist, corrosion is mitigated even in the presence of bacteria. The difficulty is determining the adequate protection potential.

27.5.1 Buried Pipelines

One of the earliest reports of MIC [85] identified SRB as the cause of external corrosion of iron pipe failures in sulfate-rich soils. SRB are still the organisms that are most frequently cited as causing external corrosion on pipe surfaces. Soil corrosivity increases with moisture, salts, and dissolved oxygen concentration. Jack et al. [86] reported that MIC was responsible for 27% of all corrosion deposits on the exterior of line pipe in a survey of Nova Gas Transmission Ltd. (Calgary, Alberta) pipe lines. Peabody [87] indicated that soil moisture and numbers of bacteria were greater in back fill material than in undisturbed soil adjacent to a pipeline. Backfill was less consolidated and allowed greater penetration of moisture and oxygen.

Microorganisms can degrade adhesives and coatings exposing metal. Pope and Morris [88] indicated that almost all cases of MIC on external surfaces were associated with disbonded coatings or other areas shielded from cathodic protection. Abedi et al. [89] reported the failure of an oil transmission line due to external corrosion. In their study a

polyethylene tape coating on the exterior of the pipeline became loose, exposing the pipe surface to wet soil. The failure was attributed to SRB and stress corrosion cracking. With adequate cathodic protection fusion bonded epoxy coatings allow for cathodic protection of the pipe surface should the coating bond fail [90] because they do not shield the cathodic current. NACE International Standard TMO106-2006 "*Detection, Testing, and Evaluation of MIC on External Surfaces of Buried Pipelines*" [91] is meant to identify MIC after it has occurred and does not describe a predictive methodology.

27.5.2 Submerged Pipelines

DOT [19] reports, "although salt water is more corrosive than most soil environments, cases of significant external corrosion on offshore pipelines are extremely rare." The report concludes that control of external corrosion in the offshore environment has been "mastered" because of the homogeneity of the offshore environment.

27.6 CONCLUSIONS

Enumeration of microorganisms by any of the available methods (culture- or molecular based) cannot be used to independently diagnose MIC in the field, predict risk due to MIC or evaluate of biocide efficacy to prevent MIC. In all cases there must be some accompanying measure of corrosion. Current MIC corrosion risk assessment models attempt to assign corrosivity factors to operational and environmental parameters. The weight attributed to each factor is arbitrary and requires a complete understanding of the system. Much of the information included in this chapter relates to processes that have been evaluated at 40 °C or less. The present standards and methodology will not be adequate for evaluation of MIC in deeper, hotter reservoirs. Future testing may require different methodologies (i.e., higher pressure vessels and flow cells) and new standards to measure and monitor corrosion.

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