Corrosion Science 170 (2020) 108641

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Review

Microbially influenced corrosion—Any progress?

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ARTICLE INFO

Keywords:
Microbially influenced corrosion
Paint coatings
Cathodic protection

ABSTRACT

Microbially influenced corrosion (MIC), is acknowledged to be the direct cause of catastrophic corrosion failures, with associated damage costs ranging to many billions of US$ annually. In spite of extensive research and numerous publications, fundamental questions relating to MIC remain unanswered. The following review provides an overview of current MIC research and stresses the lack of information related to MIC recognition, prediction and mitigation. The review establishes a link between management decisions and root causes. A holistic, proactive approach to MIC is suggested in which an entire system is considered, monitored and improved.

"MIC is mainly a result of poor material selection and bad management decisions" (Quote from a MIC workshop with the authors, held June 2018 in Singapore)

1. Introduction

Microorganisms, including bacteria, fungi, archaea, and microalgae, can influence corrosion directly or indirectly, depending on microorganism/material/electrolyte specific reactions. The underlying mechanisms are collectively subsumed in the term "microbially influenced corrosion" (MIC). More than 2000 papers on MIC have been published in the last 25 years. The papers are dedicated to anecdotal failures, and laboratory or field testing under varying conditions.

MIC is the result of the confluence of the "three M´s" (Fig. 1): microorganisms (microbiology), media (chemical composition and physical parameters, *e.g.*, temperature and flow), and metals (metallurgy). Further, these different disciplines are typically addressed by specialists in a single area, compounding the difficulty in studying MIC. The three disciplines have different vocabularies which must be mutually understood, as well as different views on MIC investigations. Defining the specific contribution of MIC to corrosion is further complicated because MIC and abiotic corrosion often occur simultaneously. Furthermore, all non-sterile corrosion experiments conducted in aqueous environments at temperatures below 100 °C are carried out in presence of microorganisms. Thus, biofilm formation and the influence on corrosion processes can be assumed but are typically ignored.

MIC is a problem in numerous industries where biofilms form on metal surfaces. Systems with high microbial populations and ineffective control, and those experiencing periods of stagnation or low flow conditions and temperatures permitting microbial life are susceptible to MIC, *e.g.*, power plants, refineries, petrochemical facilities, steel mills, pulp and paper mills, and maritime infrastructure.

Despite the large numbers of publications dealing with MIC, a remarkable gap remains between the body of information and effective approaches to recognizing and solving the practical problems caused by MIC. In 1993, Stott [1] published a review paper in *Corrosion Science*, entitled "*What progress in the understanding of microbially influenced corrosion has been made in the last 25 years?*" He concluded, "*The most commonly asked question about MIC is: what will be the expected corrosion rate of material X in an environment where aggressive microorganisms proliferate? … For many materials we can no more answer this question now than we could 25 years ago.*" Now, after an additional 25+ years, that question is still an open one. The authors of this paper ask the following

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https://doi.org/10.1016/j.corsci.2020.108641
Received 4 November 2019; Received in revised form 19 March 2020; Accepted 25 March 2020
Available online 06 April 2020

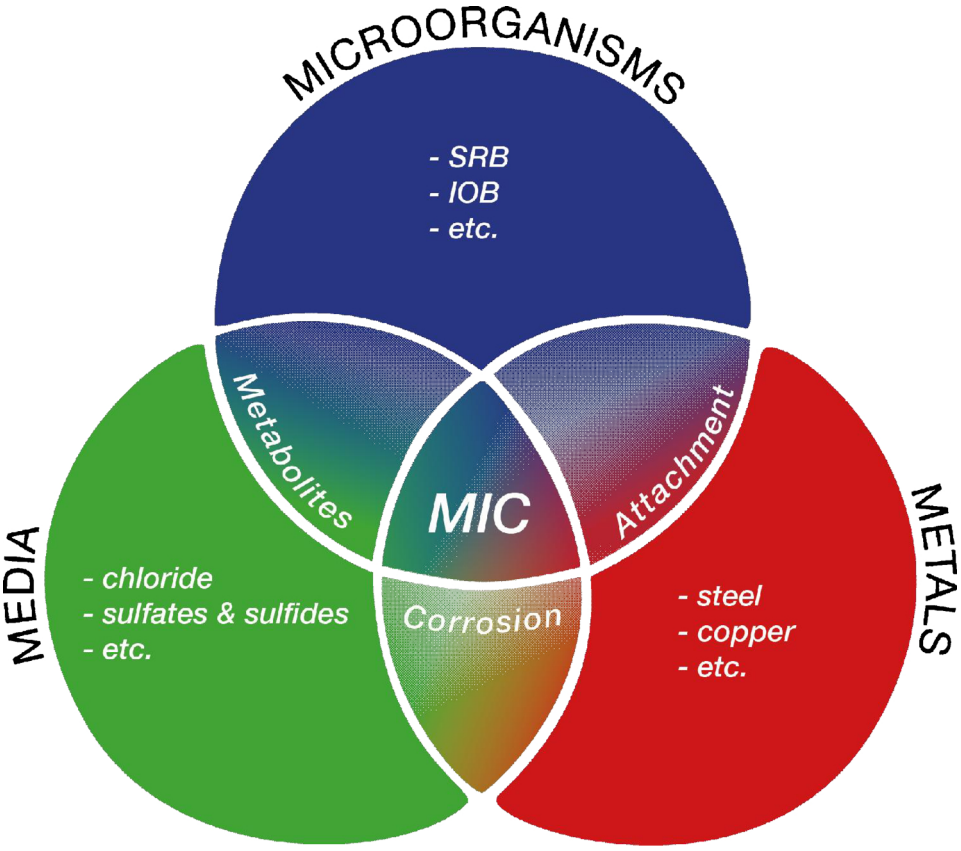

Fig. 1. MIC occurs where the effects of microorganisms, media and metals overlap (SRB – sulfate-reducing bacteria, IOB - iron-oxidizing bacteria).

additional question, "Does MIC research address the questions relevant for practical solutions to MIC?"

1.1. Definition of MIC

The acronym MIC is widely used and recognized as corrosion caused by the presence and activities of microorganisms. "Biocorrosion," a term that is increasingly used as a synonym for MIC in Europe and Latin America, is confusing because of the current trend in the United States is to use "biocorrosion" to describe corrosion of implants within a living body due to both biotic and abiotic processes [2,3].

Corrosion is mainly an interfacial process, strongly depending on the concentration of dissolved oxygen (DO), the presence and chemical composition of salts, conductivity, redox potential and pH-value of the associated electrolyte. Each of these can be influenced, in a very localized fashion, by microbial biofilms, which colonize the interfaces [4].

1.2. Cost of MIC

Most MIC publications state in their introduction that MIC is a costly problem and costs are used as a motivation to justify funding for research. However, very few publications offer a detailed basis for cost estimates. It is next to impossible to find globalized data on MIC-related costs in the literature.

Viable microorganisms can be found in virtually any environment with sufficient water activity, traces of nutrients and life-permitting temperatures. Thus, microorganisms are likely present and metabolically active in all corrosion sites that offer such conditions. Moreover, MIC and abiotic corrosion processes work in concert, hence it is difficult to differentiate the costs allocated to MIC independently of abiotic corrosion.

The challenge of calculating the cost of MIC is further exacerbated when secondary costs, resulting from environmental damage, regulatory fines and human costs (*e.g.*, injuries, diseases or deaths) are added to the direct dollar amount. In the following examples all costs are provided in US$.

For example, an oil pipeline in Prudhoe Bay, Alaska, developed an almond-sized hole that led to a 750,000 L oil spill, covering about 8000 m^2 [5]. The associated leak was ultimately attributed to internal pipeline corrosion by sulfate-reducing bacteria (SRB). As a result of the leak, 27 km of pipeline was replaced, interrupting oil transport, and adding to the economic losses. Overall, the increase in Prudhoe Bay integrity-related spending amounted to ~$200 million in 2007 and $250 million in 2008. Fines of $25 million were also levied and the total fine paid to the state of Alaska was upwards of $250 million [5].

A more recent example of the costs associated with a catastrophic MIC failure involved release of over 100,000 tons of methane that leaked from a well casing in a storage field in Aliso Canyon, CA USA, causing a huge single source climate impact [6]. The leak was attributed to methanogens in ground water causing external corrosion (www.cpuc.ca.gov/aliso/) and after several unsuccessful attempts, the leak was eventually closed with concrete [7]. The operator reached a $120 million settlement with state and local agencies [8]. The overall cost for the utility was more than $1 billion [9]. However, civil lawsuits from residents are on-going, related to significant health claims due to toxic gas emissions [10,11]. Closing the gas leak and subsequent overhaul of wells led to a substantial limitation of gas supply for power stations.

The overall cost of corrosion has been estimated to be approximately 3.4 % of the global Gross National Product [12] which equates to ~$2.9 trillion in 2018. A conservative estimate is that approximately up to 20 % of all corrosion in aqueous systems is MIC [13,14]. This estimate reflects the considerable uncertainty in the exact contribution of MIC, which is largely a result of the problems to diagnose MIC (see Section 2.1).

1.3. Bad material selection and management decisions

Material selection is often based on idealized operating conditions, *e.g.*, continuous flow in a pipe of over 2.5 m s^{-1}, the velocity required to keep water suspended in oil, or containment of a water-free medium, conditions which are impossible to maintain. Actual operating conditions may include long periods of stagnation, introduction of water, and changes in the properties of the stored or transported fluid. From the 1970's to the present, the consequences of this optimistic approach to material selection have been demonstrated by pitting failures in 300 series austenitic stainless steels and martensitic alloy EN1.4313 in power plants (nuclear and conventional), fire protection systems, fuel farms, hydroelectric plants and numerous other applications. Under ideal conditions, these alloys are designed for service in low-chloride containing waters; up to 100 ppm for 304 and 304L (18-8 stainless steel alloys) and 2000 ppm for the molybdenum-containing alloys 316 and 316L [14]. However, pitting corrosion has been reported for many of these materials after exposure to stagnant hydrotest waters [15], or waters containing low levels of chloride with iron- and manganese-oxidizing bacteria (FeOB and MnOB, respectively) [16].

In the case of the Prudhoe Bay spill, regulators determined that failure to anticipate MIC of the materials occurred because the materials were used under non-ideal conditions., "*…low crude oil flow velocities, the corrosivity of the materials transported, the presence of water and sediments, an ineffective corrosion inhibitor program, and a lack of maintenance pigging*" [17].

Management practices also contribute to the poor performance of materials. These include prioritization of delivery schedules and concerns for immediate costs rather than overall life cycle costs. In addition, senior management incentives are typically based on production and profitability. Furthermore, because there are few methods for rapid, real-time monitoring for MIC, most research and management tends to be *reactive* when ideally both should be *proactive*, based on data collected under realistic conditions to enable strategies for intervention and prevention. For example, following the large oil spill, management of the Prudhoe Bay facility was required to improve standard practices, including a proactive plan to perform internal inspections using a smart pipeline inspection gauge (pig) at regular intervals (not to exceed 5 years) and to schedule repair of anomalies identified in those inspections. Further, management was instructed to develop a management plan to reduce internal corrosion, including use of maintenance pigs, corrosion inhibitors, emulsion breakers and mechanisms to reduce water and solids. Importantly, Amendment 3 of the US Department of Transportation March 15, 2006, Corrective Action Order (CAO) [18] specified that monthly reports should include the name, title, and contact information of person(s) responsible for collecting, analyzing and reporting to Pipeline and Hazardous Materials Safety Administration as well as to the person in the plant responsible for taking appropriate action when data indicated that an action was required.

A 2000 US National Transportation Safety Board (NTSB) investigation [19] into the explosion of a gas transmission pipeline near Carlsbad, New Mexico, determined that management-related decisions had contributed to the corrosion failure. NTBS concluded that: "*The corrosion that was found …at the rupture site, was likely caused by a combination within the pipeline of microbes and such contaminants as moisture, chlorides, oxygen, carbon dioxide, and hydrogen sulfide… This severe corrosion had occurred because the corrosion control program failed to prevent, detect, or control internal corrosion within the company's pipeline. Contributing to the accident were ineffective Federal pre-accident inspections of a dated drawing for the exploded line. The ruptured section could not accommodate cleaning pigs. There were no written requirements that corrosion technicians follow up on of out-of-specification gas being received. Corrosion monitoring devices were not used in the ruptured section of line because operators believed that the gas was noncorrosive. Consequently, corrosion inhibitors were not added into the line. At the time of the explosion the operating and maintenance standards did not address the relationship between flow velocity and liquid accumulation in a pipeline*" [19].

The Office of Pipeline Safety (OPS) issued a CAO that required the development of a risk-based plan to inspect all pipelines for indications of internal corrosion and to further assess and correct areas in the pipeline that could not be inspected with an internal inspection tool, areas with no-flow conditions and areas where liquids might accumulate [19].

A root cause failure analysis (RCA) of the Aliso Canyon incident concluded, "*The approach to well integrity at Aliso Canyon had been reactive rather than proactive*." [20]. The list of specific deficiencies is too long for this paper. However, the RCA differentiated direct and root causes for the incident. The report defined direct causes as those that, if identified and mitigated, would have prevented the incident. Root causes are those that, if identified and mitigated, would have averted the Aliso Canyon type of incidents "and all other types of well integrity incidents through the use of procedures, best practices, design, management system, standards, and regulations". The report cites the following direct cause: an axial rupture due to external MIC. The root causes were identified as follows: lack of detailed follow-up investigations of past failures, lack of any form of risk assessment for wellbore integrity management, lack of a dual mechanical barrier system in the wellbore, lack of internal policy or regulations requiring production casing wall thickness inspections, lack of understanding of groundwater depths relative to the failed casing, lack of systematic practices of external corrosion protection for surface casings strings. Revised well integrity practices by the operator and regulations from the California Division of Oil, Gas, and Geothermal Resources address most of the root causes identified during this investigation.

Summary of section 1

MIC is the influence of microorganisms on the kinetics of corrosion processes of materials, particularly metals, by microorganisms adhering to the interfaces (biofilms). The damage amounts to many billion US$ annually. There must be ample room to develop ways to reduce such damage rather than to just accept it. Published details regarding recent MIC failures indicate that the failures had several features in common. In all cases the managerial approach to corrosion at the time of the incidents was reactive, not proactive. After the incidents, management was required by regulatory mandate to implement a proactive approach with risk-based assessments.

2. MIC in the field

The following sections will review current methods used in the field to diagnose, monitor, control/prevent and model MIC. Remarkably, MIC has been documented for the following metals and alloys in industrial settings: carbon steel, austenitic and martensitic low alloy stainless steels (< 6 % molybdenum), copper and its alloys, nickel/copper alloys, and aluminum alloys. The authors are not aware of any reports of field failures due to MIC of titanium or high nickel alloys [21].

2.1. MIC diagnosis and its limitations

2.1.1. Bacterial identification and quantification

Typical for most failure analyses, MIC is only considered when abiotic, physio-chemical explanations are not sufficient to understand the nature of deposits, damage and progress of corrosion. Lee and Little [21] recently reviewed the procedures for diagnosing MIC. The authors concluded that many traditional (culture techniques) and more modern molecular technologies have produced misleading results. Metallographic features and pit morphologies cannot be used to diagnose MIC. Tubercles and hemispherical pits in 300 series stainless steel localized at welds and tunneling in carbon steel, are consistent with some mechanisms for MIC, but cannot be interpreted unequivocally as MIC [22]. Commonly, the presence of microorganisms in general and SRB, in particular, is used as a crude indicator for MIC. However, identification

of microorganisms from a single corrosion site cannot be used to determine a cause and effect relationship [23].

Several reviews provide detailed information regarding sample collection, storage and examination techniques for MIC, their advantages and disadvantages and, most importantly, their limitations [24–27].

Characterization and quantification of microorganisms in the bulk medium/electrolyte (*i.e.*, planktonic microorganisms) cannot be used to estimate numbers and types of microorganisms causing corrosion [28]. Planktonic microorganisms do not indicate the quantity or location of microorganisms within the biofilm [29]. All cultivation techniques for quantification have a "cultivation bias", meaning that culture media are selective and essentially do not account for the majority of non-culturable organisms in a natural microbial population. To solve this issue, more recent efforts have focused on direct counting of cells stained with DNA specific dyes and molecular microbial community analyses. However, these methods also have their limitations and biases which should be taken into account [30].

Unfortunately, and not yet understood, the numbers of cells and MIC kinetics cannot be correlated, regardless of the quantification method [25]. Therefore, microbial quantification can only indicate the extent of microbial presence but, counterintuitively, does not allow one to predict or diagnose MIC. Low numbers of microorganisms can be responsible for MIC, while large numbers of the same organisms do not necessarily indicate strong involvement in the corrosion process.

The following NACE International test methods designed to guide diagnosis of MIC in the field do not embrace all the above measures:

- *TM0106-2016, Detection, Testing, and Evaluation of Microbiologically Influenced Corrosion (MIC) on External Surfaces of Buried Pipelines;*
- *TM0194-2014, Field Monitoring of Bacterial Growth in Oil and Gas Systems; and,*
- *TM0212-2018 Detection, Testing, and Evaluation of Microbiologically Influenced Corrosion on Internal Surfaces of Pipelines.*

2.1.2. Mineralogical methods

As an alternative to culture or molecular-based methods focused on identifying organisms, investigators have used mineralogy of corrosion products to diagnose MIC and to provide insight into the causative microorganisms and the conditions under which the corrosion took place. Microorganisms proliferating within biofilms generate a microenvironment at the biofilm-substratum interface, which can be different from that of the bulk electrolyte in terms of temperature, pH-value, pressure, dissolved oxygen (DO), as well as concentration and type of organic and inorganic species [31]. Consequently, the corrosion products resulting from biomineralization can be different from those produced in abiotic environments. For example, corrosion of steel under abiotic conditions produces iron oxides and oxyhydroxides, such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), lepidocrocite (FeOOH), goethite (FeOOH), and hematite (Fe_2O_3) [32,33]. In contrast, the dominant mineral phase in bacteriogenic iron oxides (BIOS) from both fresh and marine waters is 2-line ferrihydrite [34]. Ferrihydrite is found on the sheaths and stalks produced by iron-oxidizing bacteria (IOB), *e.g.*, *Leptothrix* and *Gallionella*. Ferrihydrite is a poorly ordered mineral that transforms into goethite and/or hematite over time. The instability of ferrihydrite means that aged or improperly handled corrosion products associated with IOB cannot be distinguished from abiotic corrosion products. However, Chan et al. [35] reported that Fe-encrusted, twisted, polymeric stalks provide a "robust biosignature" for lithotrophic, iron-oxidizing based metabolism.

McNeil et al. [36] evaluated corrosion product mineralogy using X-ray diffraction data, thermodynamic stability diagrams, *i.e.*, two-dimensional presentations of phase equilibria controlled by two independent variables (*i.e.*, pH-value and potential; [37]) and the simplexity principle for precipitation reactions. They concluded that some metal sulfides in near-surface natural environments could only be produced by microbiological activity. For example, tetragonal mackinawite (FeS_{1-x}) is produced by SRB from iron oxides and its presence is indicative of SRB influenced corrosion. This conclusion was supported by Jack [38] for buried carbon steel gas transmission pipelines. Djurleite, covellite, and the high-temperature polymorph of chalcocite are mineralogical fingerprints for SRB-influenced corrosion of copper-nickel alloys [39]. There are specific mineralogical signatures for SRB MIC of silver (*i.e.*, Ag_2S (argentite; [39])). Under aerobic conditions, the presence of manganese oxide and manganese and/or iron oxidizing bacteria can be used as possible indicators for MIC [40–42].

Dissimilatory microbial sulfate reduction results in sulfides that are deficient in the heavy sulfur isotopes (^{33}S, ^{34}S and ^{36}S) relative to the most abundant isotope ^{32}S [43,44]. Little et al. [45] showed that ^{32}S accumulated in sulfide-rich copper corrosion products and ^{34}S was concentrated in the residual sulfate in the culture medium. Similarly, in sewer systems microbial sulfate reduction produces sulfides that are oxidized by sulfur-oxidizing bacteria to sulfuric acid (H_2SO_4) that reacts with the concrete to produce gypsum ($CaSO_4{\cdot}2H_2O$). Grengg et al. [46] reported sulfur isotope fractionation of up to 13 % between sulfate in wastewater and newly formed gypsum in a concrete sewer system. El Menjra et al. [47] reported sulfur isotopic fractionation between abiotically (electrochemically generated in a solution of Na_2S) *versus* biologically (by SRB) generated sulfides on iron surfaces.

2.1.3. Chemical methods

In suspected MIC cases in the field, it is helpful to determine if microorganisms are present at the corroded site. A very simple qualitative field test is to scratch some of the material from the surface, *e.g.*, with a knife, heat it with a lighter and check for the smell of burnt hair or meat. This indicates the presence of proteins, *i.e.*, biological material. More sophisticated and commercially easily available protein tests are recommended.

Elements in corrosion deposits can provide information as to the cause of corrosion. Because all living organisms contain adenosine triphosphate (ATP), simple test kits for ATP or phosphorus determination help in the field. In the laboratory, a phosphorus peak in an energy dispersive X-ray spectrum can be related to cells associated with the corrosion products. Other sources of phosphorus, *e.g.*, phosphate water treatments, however, must be taken into account. The activities of SRB and MnOB produce surface-bound sulfur and manganese, respectively. Chloride is typically found in crevices and pits and cannot be directly related to MIC.

Summary of section 2.1.

Three test methods for diagnosing MIC have been designed specifically for oil and gas pipelines. There are no test methods in other industries. The current MIC test methods rely on quantification of specific groups of indicator microorganisms, especially bacteria or associated proxies, *e.g.*, DNA or ATP. Attempts to correlate numbers and types of microorganisms to corrosion have produced misleading results. Mineralogical fingerprints can provide unequivocal evidence for microbial involvement in the production of the corrosion products. Biomineralization can result in amorphous, unstable minerals that require special handling and equipment for identification. Similarly, isotope fraction is specific for microbial processes, but also requires specialized equipment.

2.2. Monitoring

As noted in the CAOs mentioned above, one of the actions required by regulators after MIC-related failures was improved monitoring for MIC. Monitoring can be implemented by analyzing corrosion coupons on a regular schedule or using an electrochemical probe [48] to detect MIC at an early stage. Furthermore, monitoring can assess the success of biocide treatment. Historically, techniques for monitoring sessile bacteria growth include corrosion coupons [49,50], NiCr mesh coupons, beads and BioBox panels [51]. For example, the exposure of test

coupons in cases where MIC could potentially occur is feasible. Corrosion monitoring using coupons in a bypass rack is one of the most common methods for early detection. Coupons can be easily removed and visually inspected for signs of MIC, such as presence and smell of slime and pitting. If a problem is suspected, coupons can be removed and further examined by cultivation-based, microscopic and molecular biological methods.

Commercially available probes (*e.g.*, BIoGEORGE, BIOX and ALVIM) designed to detect biofilms have been used in MIC studies [52–58]. The probes are typically installed into a piping system, heat exchanger water box, cooling tower, or side stream *via* a threaded connection. The probes help to reduce the use of biocides because of their early warning capacity and allowing for timely countermeasures. The probes have different designs, but all measure an electrochemical response to biofilm formation on a passive metal, *e.g.*, titanium or stainless steel. Industries which have demonstrated a direct relationship between biofilm formation, electrochemical response and MIC for materials in their systems can use biofilm monitors to schedule preventive measures, *e.g.*, pigging or biocide additions. Iannucci et al. [59] proposed a system to monitor for electroactive bacteria based on currents flowing through a microbial fuel cell, with the anode fabricated from the same metal/alloy as the structure to be monitored.

Summary of section 2.2.

There is a range of corrosion monitoring techniques, both electrochemical (*e.g.*, half-cell potentials) and physical (*e.g.*, electrical resistance probes), but these cannot distinguish MIC from forms of abiotic corrosion, so may not alert the operator to take the correct remediation steps. A similar comment can be made for the range of nondestructive testing techniques that are available to corrosion inspectors. A major drawback to all monitoring techniques is that one only monitors in the location of the probes, or the accessible areas for inspection, which may not be the areas that are colonized by the destructive microorganisms.

2.3. Control/prevention/inhibition of MIC

2.3.1. Sanitation

Sanitation addresses the efforts to overcome the influence of microorganisms on a system and restore the original properties and performance. If MIC is supposed to be eliminated as far as possible, sanitation is required. However, effective solutions for MIC sanitation are not featured in any of the recent, comprehensive reviews on MIC [25,60,61] and if so, only in terms of biocide application [61]. The official book of the European Federation of Corrosion with the title "Understanding Biocorrosion" [62] is the only reference to give suggestions for sanitizing against MIC. Replacement of the affected parts is costly and not necessarily effective because new materials will be put into identical locations and environments where MIC has occurred. It can be assumed that the local conditions which led to MIC, *e.g.*, low flow, stagnation, metal vulnerability have not changed. Fig. 2 presents a very general flow diagram on treatment steps for MIC-vulnerable systems which will be supported in detail in section 3.

By far the most frequent approach to controlling MIC is the application of biocides with or without subsequent cleaning. However, killing is not cleaning, and biomass, even inactivated, can influence corrosion abiotically, by creating heterogeneities on the surface. Furthermore, surviving cells can multiply and "cannibalise" the biomass, rapidly regrowing [29].

Loto [63] rightly generalized the sanitation measures: "…*the control measures are a combination of physical clean-up, mechanical changes and the use of biocide to obtain good results. The biocide formulation may contain dispersion agents for more effective results.*" The ecotoxicity of biocides can be an issue since they create a disposal problem. In general, sanitation costs are high.

In a comprehensive book chapter, Javaherdashti [64] summarized the sobering level of effort required to sanitize operating systems. Another major conclusion on sanitation was that in the absence of replacement of failed parts by MIC-resistant materials and a thorough evaluation of the environmental and operational conditions there can only be mitigation [56], no real sanitation in terms of eliminating the cause and avoiding further damage.

2.3.2. Physical treatment

2.3.2.1. Pigging. Physical cleaning methods are commonly used as countermeasures against general corrosion, regardless of any microbial contribution. In many cases, the tool of choice is the so-called "pig". Such devices, similar to plugs or sponge balls [56], are moved inside pipes to dislodge corrosion tubercles and deposits mechanically [64–67]. Pigs can be quite sophisticated but can only be applied to "piggable" lines with constant diameter and without obstacles impeding the pig. If pigging is successful and corrosion products/tubercles are removed, the remaining cleaned surfaces present highly active anodes. If not passivated, *e.g.*, by phosphate, pigging can potentially accelerate corrosion [65]. Furthermore, as a result of the change of environmental conditions, microorganisms will respond. In case of pigging this might be the development of a particularly firmly attached, thin biofilm, which may be no less corrosive than the initial community [68].

2.3.2.2. Ultraviolet (UV) irradiation. UV light can inhibit/kill microorganisms and has been advocated as an "alternative to biocides "[69] for MIC control. However, practical implementation is not realistic. UV-light only affects the microorganisms directly exposed to the light. If the microorganisms are encased in corrosion products, theyare well-protected from UV irradiation; furthermore, internal piping surfaces are not suited to UV-treatment. While irradiation may inactivate living cells, the cells are still not removed and hence still remain in the biofilm matrix, where they serve as nutrients for subsequent organisms, including those that promote MIC.

2.3.2.3. Ultrasonic treatment. In principle, ultrasound produces cavitation bubbles in water which, when they collapse, have detrimental effects to microorganisms. Such treatment was suggested for mitigation of MIC [70]. However the effectiveness of ultrasonic energy to kill microorganisms within corrosion products has never been demonstrated, and it must be expected that corrosion products, in which MIC-causing organisms live, mitigate ultrasonic energy drastically. Thus, at this stage ultrasonic treatment for MIC is an idea with little prospect of success.

2.3.3. Chemical treatment

There has been little development of biocides over the last three decades. Regardless of even the most sophisticated microbial community analyses, the response is always the same, which is, application of "broadband biocides", intended to kill as many organisms and as many species as possible. An additional problem is that biocides have to act on microorganisms in biofilms where cells are much more tolerant than planktonic cells [71]. Although it appears intuitively plausible, biofilms, containing up to 98 % water, do *not* represent a diffusion barrier for small uncharged molecules such as biocides [72], therefore, biocide enhancers have been suggested [73]. Only in the case of interaction with the matrix, *i.e.*, "reaction-diffusion-inhibition" [72], do reactive biocides experience a decline of concentration. In this case, the matrix acts as a sacrificial material. Another explanation for biocide tolerance is the transition of biofilm organisms into a viable-but-nonculturable (VBNC) or persister state, a stress reaction to biocide/antibiotic exposure [74]. Tolerance can be lost upon dispersion of the biofilm cells [75].

Glutaraldehyde is a commonly applied biocide in oil industries [64]. Apart from its poor performance for long-term sanitation, glutaraldehyde can be problematic due to non-target toxicity, *e.g.*, to mammalian cells. Further, glutaraldehyde is directly corrosive to carbon steel [76]. In some cases, silver nanoparticles or ionic silver have been

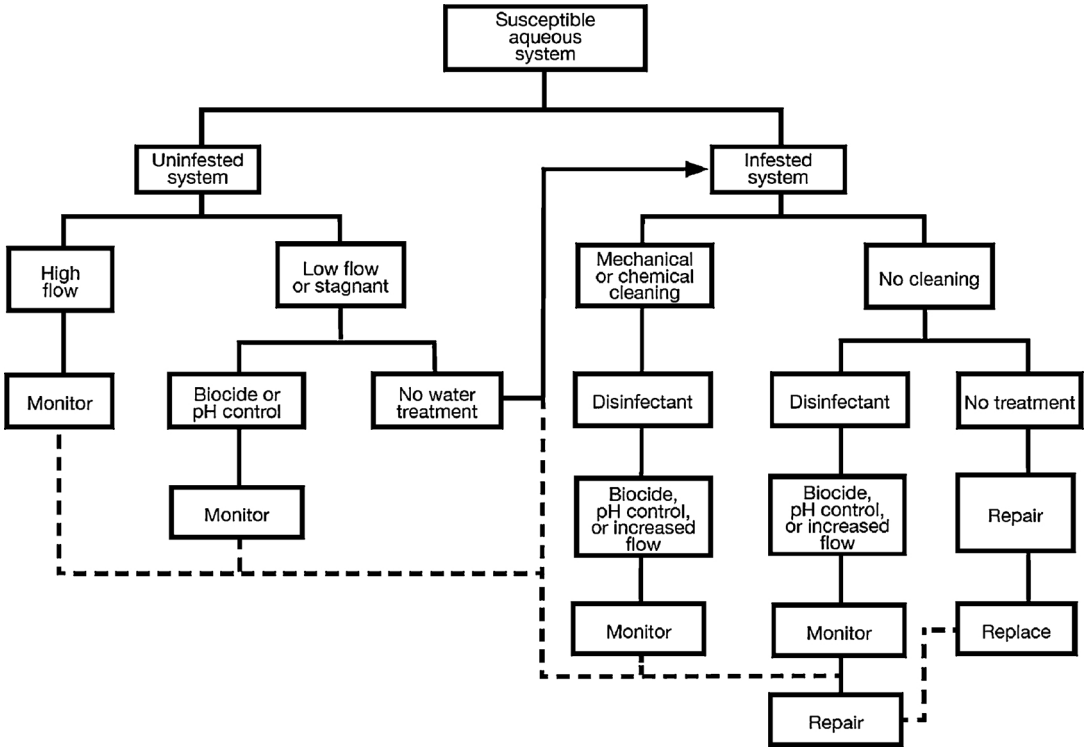

Fig. 2. Flow diagram of treatment of MIC-prone systems.

suggested for microbial inactivation [77]. However, research showed that considerable tolerance to silver ions and nanoparticles developed in biofilms [75]. In terms of field application, silver dosing is non-specific, poorly effective and expensive. Tetrakis-hydroximethyl phosphonium (THPS) has some specificity against SRB [78], but there are few reports of practical applications.

2.3.4. Biological methods

One basic idea of biological methods is to inhibit the activities of MIC-supporting bacteria using non-MIC associated microorganisms. This notion is based on the observation that not all bacteria promote corrosion. The term "microbially *influenced* corrosion" acknowledges that some microorganisms in some media can inhibit [74] or even transform reactive corrosion products such as goethite or lepidocrocite into biogenic stable minerals such as vivianite and siderite [79]. None of the methods for corrosion inhibition by microorganisms has reached practical application and success [80,81].

Approaches such as using extracellular polymeric substances (EPS) against MIC [82], or norspermidine and other quorum sensing inhibition-compounds or strategies to achieve population conversion to non-corrosive species may work in the laboratory under specific conditions, but are not likely to work in the field. The application of quorum sensing blocker in industrial environments will require large quantities, and it must be expected that it will lead to a response of the microbiome of the corroding site in direction of tolerance. Above all, the costs of such treatment would be very high.

Injection of nitrate is common practice meant to suppress reservoir souring and SRB-caused MIC by stimulating nitrate reducing bacteria (NRB). NRB are supposed to outcompete SRB since energy yield of nitrate reduction is greater than that of sulfate reduction. NRB activity limits the H_2S production, and increases the redox potential, which is considered as an alternative to biocide application [80,83]. Quite a few reports of success for both goals are reported [*e.g.*, 84,85], even over long periods of time [83]. SRB are not eliminated but sulfate reduction is suppressed in favor of nitrate reduction. Changes in the nitrate regime should be considered with care [83]. This biological manipulation requires sufficient levels of nitrate, which can be considerable, depending on the volumes of water and the environmental conditions [86,87]. As toluene is a main carbon source for NRB, the composition of oil after nitrate treatment will be altered [86]. In addition, NRB comprise a range of microorganisms some of which enhance corrosion [88]. Furthermore, some SRB can use nitrate and cause MIC [89]. Increases in corrosion rates after nitratemediated souring control have been reported [68,90].

2.3.5. Coatings

Any coating that isolates a corrosion-prone substratum from an electrolyte provides some corrosion protection. Coatings used to protect metal substrata from MIC are typically ones that have been used to provide conventional corrosion protection, *e.g.*, polyurethanes, fluorinated compounds, epoxy resins, polyimides, silicones, coal-tar epoxies, polyvinyl chlorides and amorphous metals [91]. Coatings can be mechanically damaged as well as biodegraded [92] and the resulting defects can develop rapidly into active anodic sites of localized corrosion that may attract microorganisms. Coatings can be modified to improve surface coverage, bonding and reduce biodegradability and surface defects. Coatings can be further modified to control microbial fouling by biocide leaching, adhesion resistance or contact killing [91]. The strategies, used individually or in combination, are reviewed in the following sections.

2.3.5.1. Biocide leaching coatings. Biocidal agents including toxic metal ions (*e.g.*, oxides of tin, copper, zinc and silver) or biogenic compounds (*e.g.*, fatty acids, lipopeptides, amides, alkaloids, terpenoids, lactones, pyrroles, enzymes and steroids) can be incorporated into polymers as anti-foulants. The effectiveness of biocide leaching depends on a predictable leach rate. Biocides can leach freely from the polymer matrix or the release can be controlled by degradation of the polymer. A problem with biocide-leaching approaches is the environmental damage caused by the leached biocides. Furthermore, biocides have a limited lifespan dictated by the release rate and total amount of active compound that can be loaded into the coating. In many parts of the

world, biocide- leaching coatings containing tin and copper ions have been banned as a consequence of their overt ecotoxicity and biomagnification through the food chain [93].

Finally, smart coatings have recently been developed for corrosion protection, including some that release inhibitors in response to the onset of corrosion [94–96]. As yet, these have not been developed to release biocides and no practical experience has been reported.

2.3.5.2. Fouling-release and adhesion-resistant coatings. The adhesion-resistance strategy for MIC control is based on engineered surface properties that prevent or delay the adhesion of bacteria without killing. Adhesion-resistant coatings include biomimetic, hydrophilic, hydrophobic, amphiphilic, and superhydrophobic coatings.

Biomimetic coatings are designed to mimic naturally occurring antifouling surfaces. For example, coatings have been designed to mimic the antifouling properties of shark skin, consisting of overlapping nanoscale plates with parallel ridges. Hydrated hydrophilic polymers such as polyethylene glycol, polyethylene oxide, zwitterions, and polysaccharides form an interfacial layer that prevents direct contact between bacteria and the surface [91]. Hydrophobic coatings (*i.e.*, fouling-release coatings), based on fluoropolymers and silicone-based polymers, form a surface with low surface energy ("easy-to-clean" surfaces) from which bacteria are easily removed. Superhydrophobic coatings with water-contact angles of more than 150° have been engineered with high surface roughness to increase antifouling surfaces [97]. Amphiphilic coatings combine a hydrophobic component to inhibit bacterial attachment on the surface with a hydrophilic component (fouling release) to improve the antibacterial behavior of the coating.

Adhesion resistant coatings are not only exposed to microorganisms but also to abiotic foulants. Humic substances, biopolymers and inorganic particles adhere to the coatings, masking their original properties and compromising their anti-microbial function.

2.3.5.3. Contact-killing and conductive coatings. Contact-killing involves the immobilization of positively charged compounds within a polymer matrix [98]. The compounds consist of long molecules with positively charged groups grafted to the surface. Theoretically, the positively charged groups interact with negatively charged bacterial cell walls, causing cell wall disruption and death [77,98]. Positively charged groups that can be added to polymers include quaternary ammonium salts (QUATS), guanidine polymers, phosphonium salts, chitosan, peptides and conductive polymers.

Conductive polymers, *e.g.*, polypyrrole, polyaniline and polythiophene have been used as anticorrosion coatings for aluminum, mild steel, stainless steels, copper, and its alloys [77,92]. Conducting polymers protect steel against corrosion by producing a mixed oxide layer [99]. Conductive polymers can also have antifouling properties. Positively charged nitrogen groups in their chain can interact with negatively charged bacterial cells leading to cell disruption and death. Counterions in the medium can block the biocidal efficacy of conductive polymers.

Surfaces coated with conducting polymers can be made the anode and uncoated metals which contact the seawater can be set as the cathode [100]. When a weak current is applied between the two electrodes, seawater is electrolyzed to form sodium hypochlorite, a biocide. Wang et al. [101] reported that conducting polyaniline had "special antifouling" properties in the absence of an applied current. Conducting polypyrrole can change the hydrophobicity of a coated surface in response to an electric signal. Conducting polyaniline also produces a synergetic antifouling effect when other antifouling agents are added to the coating, *e.g.*, cuprous oxide or 4, 4′-dichlorodiphenyltrichloroethane. The conductivity of the polyaniline is extremely important for the synergy.

Abdolahi et al. [91] described coatings incorporating multiple antifouling strategies. For example, QUATS were immobilized on a steel surface with embedded silver nanoparticles to provide a biocide leaching-contact killing combination. The coated surface showed superior biocide properties compared to either coating alone. Similarly, a combination of adhesion resistance-contact killing has been used for antibacterial coating, using a combination of a polysiloxane coating with QUATS.

A problem with the contact-killing strategy is the narrow range of candidate compounds and the tendency of the active compounds to aggregate in response to the ionic species and strength of the medium [98]. Thus, the effectiveness of contact-killing coatings is limited to very specific conditions and environmental factors can easily interfere with their efficacy. And even if they might work, the coatings will have a limited capacity because the inactivated cells will remain and mask the original coating. Longtime experiments (months or more) are generally not reported.

2.3.5.4. Graphene. Krishnamurthy et al. [102] suggested that graphene was superior to traditional polymer coatings for the prevention of MIC. Graphene is a one atom thick layer of carbon atoms, bound in a hexagonal honeycomb lattice. The following superlatives have been used to describe graphene: thinnest compound, lightest material, strongest compound, best conductor of heat at room temperature and the best conductor of electricity of any previously identified compound. Furthermore, the authors state that as-grown graphene films are devoid of major defects. They described experiments with 3–4 layered coatings with minimal defect density on a nickel (Ni)-foam working electrode to demonstrate minimum Ni corrosion over an 800-h exposure. However, this is a very delicate coating, easily damaged under field conditions. Once the graphene coating is damaged the issue of rapid galvanic corrosion can create major problems. For example, Schriver et al. [103] demonstrated that the oxidation resistance of graphene-coated copper was less than that of bare copper during long-term exposure in air at 185 − 250 °C. The authors attributed the poor performance of the coating to irregularities in the graphene films. Anodic sites developed at discontinuities in the highly cathodic graphene coatings. For this reason, Tiwari and Singh [104] suggested that multilayered graphene is a better coating option (3–4 monolayers). Extended exposure periods have not been reported. The problem of masking the graphene layer by abiotic substances, as described above, further limits the promise of these coatings for practical, long term application.

Amorphous metallic coatings applied by thermal spray techniques have been used to provide corrosion and erosion protection to coated substrata. The failure mechanism most often attributed to thermal spray coatings is delamination initiated at heterogeneous pores and intersplat locations [105]. Zhang et al. [106] designed an Fe-based amorphous coating ($Fe_{54.5}Cr_{18.3}Mn_{2.0}Mo_{13.9}W_{5.8}B_{3.3}C_{0.9}Si_{1.3}$ wt.%) with reduced porosity for mild steel. The composition was meant to include corrosion resistance and antibacterial properties (Mo, W, Ni, La and Ce). Those properties were evaluated after a 21-day exposure to a nutrientrich medium containing a pure culture of *Desulfovibrio caledoniensis*. The authors reported that the tailored coating reduced both sessile and planktonic SRB numbers and that there was no localized corrosion on coated mild steel surfaces and instead general corrosion was observed.

2.3.5.5. Vivianite. It has been demonstrated that in phosphate-rich media (> 2 mM) some microorganisms, particularly iron-reducing bacteria, induced a surface reaction on mild steel resulting in a phosphate layer [107–109]. Volkland et al. [107] and Lee et al. [108] identified the layer as vivianite ($Fe_2(PO_4)_2{\cdot}8H_2O$). It was concluded that in addition to a specific phosphate concentration, vivianite formation required actively growing bacteria in contact with the steel surface [107]. Three microbially influenced reactions were involved: dissolution of the thin iron oxide layer, release of iron from the steel and precipitation of vivianite. Deposition stopped after carbon depletion or complete surface coverage. The authors noted that "considerable corrosion inhibition" lasted 4–6 weeks in highly

corrosive Cl^- -containing water (pH 7–10). However, they concluded that the continued presence of a biofilm on vivianite resulted in pitting. The authors also suggested that pores were "likely" in the mineral deposition that required "painting" "to optimize corrosion protection." It was reported that the chemical stability of vivianite is between pH 6–9 [110]. Cote et al. [109] concluded that the phosphate-rich layer was *somewhat* more protective than the iron oxide formed in the abiotic control.

2.3.6. Cathodic protection

The relationship between MIC and cathodic protection (CP), particularly MIC caused by SRB, is the topic of extensive published research and continued debate [111]. CP is a corrosion control technique that can be used independently or in combination with coatings to protect buried and submerged metallic structures from corrosion. CP limits the corrosion of a metal structure by making it the cathode of an electrochemical cell, using either a more active sacrificial anode or by impressing a current with an external direct current source. The protection potential is the potential required to prevent or reduce to an acceptable level generalized corrosion of a structure exposed to a corrosive environment. The protection potential typically suggested to protect buried and submerged iron is −0.850 V *vs.* a copper/copper sulfate ($Cu/CuSO_4$ [CSE]) reference electrode (−0.536 V *vs.* standard hydrogen electrode (SHE)) [112].

When cathodic polarization is applied, current is transferred across the metal/electrolyte boundary by one or more of the following reduction reactions:

Dissolved oxygen (O_2) reduction in aerobic environments

$$2H_2O + O_2 + 4e- \rightarrow 4OH- \quad (1)$$

Proton (H^+) reduction in anaerobic or acidic environments

$$2H^+ + 2e- \rightarrow H_2 \quad (2)$$

In neutral or basic media Reaction (2) is often expressed as:

$$2H_2O + 2e- \rightarrow H_2 + 2OH- \quad (3)$$

Reactions (1)–(3) result in an increase in the concentration of OH^- at the metal/electrolyte interface, an increase in pH-value and precipitation of insoluble salts, *e.g.*, $CaCO_3$, $Mg(OH)_2$ [113]. Calcareous deposits are poor electron conductors and cannot support the oxygen reduction, thereby contributing to the effectiveness of cathodic protection, but can lead to blockages in small diameter pipes and tubes. Both micro- and macro-fouling organisms grow on sacrificial anodes, but do not prevent the anodes from effectively protecting steel structures [114].

Biofilms can both influence and be influenced by the resulting interfacial alkaline pH [115,116]. Contrary to broad, generalized opinions that the alkalinity generated by cathodic polarization can "slow down bacterial proliferation" [117], several investigators have demonstrated the opposite. For example, Zavala-Olivares et al. [118] confirmed that under cathodic polarization, SRB populations on coupons at protection potentials were twice as large as populations on coupons with no protection. Similarly, it was confirmed that the alkalinity generated at −0.950 V *vs.* CSE on XL 52 steel did not stop SRB growth in a modified Bold Medium specific for the growth of SRB [119]. Guan et al. [120] suggested that some SRB use cathodes as electron donors for metabolism [116]. Jansen et al. [121] concluded that cathodic polarization could "feed" MIC-causing microorganisms at the steel surface by providing them with energy *via* electrons and/or hydrogen, particularly under anaerobic conditions. Likewise, the alkalinity generated by the application of cathodic protection in aerobic conditions can encourage biofouling by marine organisms on the cathodes, some of which have been reported to catalyze the oxygen reduction reaction, although the mechanism for this is yet to be established [122]. Attempts have been made to harness the oxygen reduction activity of certain marine organisms to power cathodic protections systems in a manner akin to a microbial fuel cell [123].

The presence of SRB has additional implications for the application of cathodic currents. SRB generate hydrogen sulfide (H_2S) that dissociates, based on pH, to H^+, to bisulfide (HS^-) and sulfide (S^{2-}). Insoluble ferrous sulfides can form and move the protective potential to more negative values, typically around 100 mV lower than in absence of sulfides. Consequently, when iron sulfides are present, most standards recommend protection potentials that are at least 100 mV more negative than the normal reference conditions, *i.e.*, −0.950 V *vs.* CSE (DNV-RP-B401:2005). The environment plays an important role in this process. For example, Barlo and Berry concluded that polarized potentials needed to be more negative than −0.950 V *vs* CSE, (−0.636 V *vs* SHE), *i.e.*, 200–300 mV more negative, to prevent corrosion when SRB were present [117].

A potential side-effect of cathodic polarization is the production of atomic hydrogen (H^o). H^o atoms are small enough to pass through the crystalline steel structure and, in some cases, cause hydrogen blistering or hydrogen embrittlement. The additional negative potential applied to protect against MIC increases the amount of hydrogen generated and the risk of hydrogen attack. Lunarska et al. [124] evaluated H^o uptake by structural steels at cathodic protection potentials in seawater inoculated with SRB. They reported that SRB increased the permeation rate of H^o through ferrite-pearlite and sorbite steels. SRB caused hydrogen deterioration of steel at potentials predicted to provide cathodic protection. Robinson and Kilgallon [125] evaluated hydrogen embrittlement of two high-strength, low-alloy steels in seawater containing SRB at a range of cathodic potentials. The concentration of H^o absorbed by the steel was higher at more cathodic potentials and significantly increased when SRB were present. They concluded that increased sulfide produced by SRB at the metal surface promoted increased H^o sorption.

It has also been reported that strong electrical fields and high pH generated by cathodic polarisation can disbond coatings [126]. Disbonding is a process in which protective coatings delaminate from protected structures (cathodes) due to the formation of hydroxyl ions (OH^-) over the surface of the protected material (cathode) [127]. Under simulated disbonding conditions, Fatehi et al. [128] reported that SRB generated sulfide and caused more severe corrosion than that observed in abiotic controls. Large numbers of microorganisms or macroorganisms growing on cathodically protected surfaces indicate that when cathodic protection is intermittent, discontinuous or discontinued, corrosion can be aggressive [129]. SRB may contribute to corrosion associated with cathodic disbondment of coatings and to H^o uptake in some materials.

Summary of section 2.3.6.

Sanitation, pigging and chemical treatments can be used to mitigate, but not prevent, MIC. Prevention of MIC by biological methods is not practical and would require a much better understanding of MIC and the environmental controls. The most effective way to limit microbial growth is to limit nutrients in feed waters, treatment chemicals and system components in a facility.

The value of coatings designed specifically for long-term protection against MIC in industrial applications appears to be limited. The laboratory testing on which more optimistic conclusions are based are brief, typically days to weeks, conducted in nutrient-rich media with pure cultures in closed containers. The limitations of coatings for MIC protection include the following: cost of product and application(s), susceptibility to mechanical and biological degradation and loss of properties due to biofilm formation.

CP is not suitable to prevent biofilm formation. Once biofilms are established, MIC cannot be prevented by cathodic protection unless the applied potential is much more negative than the standard industry practice, which results in increased operating costs. The precise influence of cathodic polarization on the numbers and types of microorganisms cannot be generalized. Confusion and apparent contradictions related to specific influences may be related to differences in

electrolytes, microorganisms and experimental conditions.

2.3.7. What can we learn from failures in bioelectrochemical systems for inhibition of MIC?

Bacteria and archaea can function as electrode catalysts to drive microbial metabolic reactions transporting electrons from anodes or cathodes [130,131]. Extracellular electron transport to an anode such as that described in microbial fuel cells (MFC) and other microbial electrochemical technologies (MET) propose to actively support microbially assisted reduction of metallic ions, metaphorically speaking, exploiting “inverse MIC.” This is similar to the situation where anodic protection is applied. Therefore, studies of MET failures due to loss of anodic current generation may be used to understand how microorganisms and metal surfaces interact. Failures of MET may reveal strategies for MIC inhibition.

As one example, a phenomenon that is frequently observed in MFC is "voltage reversal", in which the voltage from some of the MFC diverge and reverse the direction of electron flow from an anodic current to a cathodic current. Voltage reversal in MFC stacks critically damages or depresses the activity of microorganisms that rely on the bioanode as a terminal electron source for energy conservation [132]. Microbes relying on such electron transport strategies stop respiring and will die as the electrode potential becomes more negative and therefore, not a thermodynamically favorable electron acceptor. Therefore, if a similar phenomenon could be induced at surfaces of interest, it might be possible to suppress cathodic current from the corroding surface to the microbe, and the rate of MIC would also be suppressed. While it is difficult to reverse both the anodic and cathodic current at the same time, one side reversal would be possible even in MIC. Furthermore, potential poising within the potential window of a material would result in low electricity consumption for Reactions (1)–(3) and little loss of Fe(0).

Material selection for reference and counter electrodes is critical for any electron reversal strategy in practical conditions, because as the electrodes corrode, the accuracy of potential poising drifts. However, the positive poise will make the iron surface an attractive electron acceptor for other exoelectrogenic bacteria, which could again lead to MIC by other bacterial processes, *i.e.*, increased pH and generation of peroxide. It is also possible that iron-oxidizing bacteria acclimate to the unfavorable electrode potential and start using iron as an electron acceptor as observed in iron-reducing bacteria [133]. For example, electrode potentials more negative than -0.4 V *vs* SHE provide a cathodic current by which SRB putatively harvest energy from a metallic source of electronse to provide metabolic reducing power [134,135]. Therefore, potential poising probably should oscillate between positive and negative potentials to avoid the creation of thermodynamic niches and to prevent colonization by MIC causing organisms.

Summary of section 2.3.7.

Polarization of iron surfaces could prevent a mechanism by which bacteria influence corrosion. Polarization or voltage reversal could minimise electron transfer between the iron substratum and microorganisms whose metabolism reies on extracellular electron transportcould be inhibited. Potential poisingndard to reverse microbial electron transport with the iron substratum may also be a promising technique to mitigate MIC.

2.4. MIC modelling

MIC modelling in the oil and gas industry was recently reviewed by Wolodko et al. [136] and Marciales et al. [137]. Both publications are recommended to the reader for a more in-depth presentation of the current state-of-the art. Traditional MIC models are based on extending many of the assumptions and principles developed for abiotic corrosion to MIC, resulting in a failure to predict either the initiation or the propagation of MIC under field conditions, in all but a few cases.

The root of the problem is the existence of a biofilm on a metal structure that impacts the mass transport rates of ions to and from the metal surface, thereby influencing the corrosion rate in a way that is poorly understood. To complicate matters further there is no consensus as to how the charge-transfer step is accelerated (or inhibited) by microorganisms. There are two current schools of thought. The first suggests that the microbes do not directly participate in the charge-transfer process, but instead alter the local chemistry making it more corrosive and the mechanisms are thus similar to abiotic corrosion. The second is that the microbes participate directly in the charge-transfer process, which can occur *via* redox mediators located at the cell walls, but evidence for claims of additional pathways is lacking. To complicate these models, it is likely that multiple microbial metabolites play important roles in these processes.

An additional limitation has been introduced by general modelling the biofilm as a single monoculture of SRB instead of considering the behavior of complex biofilms under changing environments and the effects of co-metabolism and the chemical interactions, either stimulatory or inhibitory, between different members of the microbial community. There are few models incorporating sulfate reducers with other microbes and these require validation [138–141]. To be accurate, future models will have to include other types of microorganisms capable of anaerobic respiration, *e.g.*, nitrate-reducing bacteria and methanogens, which could potentially cause MIC and avoid prior assumptions about the biofilm, in terms of its thickness and diffusion rates of reactants. It is sometimes unclear if the values taken for these parameters were chosen to allow the model to fit the corrosion-rate data instead of being empirically measured. Even most recent revisions of the traditional MIC models only consider the synergistic effects of acidproducing bacteria (APB) on the activity of SRB, but not the role of other microbial taxa that, while not being directly involved in the MIC process, might have a mutualistic, commensal or competitive role with APB or SRB [136,137]. Similar issues exist for aerobic MIC. For example Basseguy et al. [142] demonstrated that the activity for oxygen reduction was much lower in pure strains extracted from marine biofilms than the naturally occurring mixed biofilm.

Furthermore, in terms of predicting field corrosion penetration rates, all localized corrosion models, including those developed for MIC, have the problem of not knowing the anode to cathode area ratio. Typically, localized corrosion occurs at a small anode (*i.e.*, the pit) with the driving cathodic current being generated by a large cathode (*i.e.*, the remaining surface outside the pit). Without knowledge of the anode to cathode area ratio the models can only predict trends in penetration rates, not the actual depths. However, most forms of localized corrosion, including MIC, have two distinct stages, initiation and propagation. It therefore may be more useful to model the development of conditions that lead to the onset of MIC and ensure these are avoided, rather than attempt to model the propagation stage. In other words, models will have to assume that once MIC initiates, propagation will be rapid and damage will occur shortly after.

A different approach has been taken by empirically combining various MIC features (*e.g.*, sulfate presence, biofilm thickness, age of the pipeline) [143]. These models are not designed to quantitatively estimate corrosion rates but rather to determine the probability of MIC development based on easily measurable environmental parameters. Limitations, in this case, include the lack of mass transfer and hydrodynamic phenomena.

The progressive reduction in costs associated with DNA, RNA and protein sequencing technology and the increasing availability of software and hardware for single-cell measurements, microscopic image processing and bioinformatics has also opened new possibilities for integrating the physiology, ecology and structural properties of MIC biofilms. One approach could be to develop reaction-diffusion systems of equations such as those developed for lake ecosystems [144] that could accurately quantify the electron fluxes between microbial cells and metal surfaces and estimate the parametric growth kinetics of individual commensal taxa in biofilms. Such models could build on the

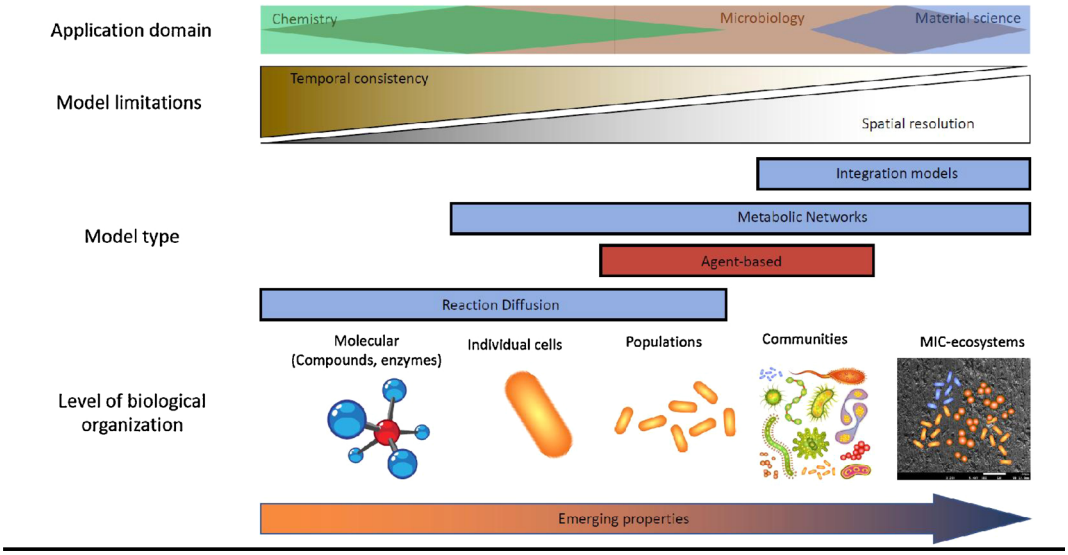

Fig. 3. Different types of models and their applicability to understanding MIC at different spatial and temporal scales. Deterministic models are highlighted in blue and non-deterministic models in red.

integration of next-generation sequencing data and other -omics methods with real-time measurements of cell density, cell physiology, corrosion potential and rates for the estimation of the risk and severity of corrosion processes.

Given that MIC acts over a wide spectrum of spatial and temporal scales and for this reason, different models need to be designed and implemented to understand processes occurring at the different levels of biological organization and complexity and to inform corrosion scientists operating in different disciplines from chemistry to microbiology to material science. Fig. 3 summarizes the deterministic and non-deterministic approaches that will be useful for understanding MIC.

In nature, biofilms are not just the source of metabolites and electron scavengers and should be modelled by considering the entire network of biochemical reactions for a cell population or even microbial communities. To make things more complicated, the composition of such communities can significantly change [145]. The construction of these types of models, collectively known as metabolic networks, has been formalized in software tools such as Merlin [146], which could be used to derive systems of differential equations describing metabolic fluxes to quantify corrosion rates and to generate measurable expected outcomes. Further extensions of metabolic networks using constraints on competition and fitness, deriving from mineralogy and metal surface microstructure, spatial organization and interaction dynamics can also be envisioned. Such integrative models have already been successfully developed for simple communities in groundwater [147–149]. The power of these approaches is that the production and consumption of specific metabolites (including sulfide and organic acids) can be precisely estimated following changes in nutrients or the relative abundance of key taxa. This will allow, for example, simulation of the impact of nitrate dosing in terms of overall effectiveness of this approach and to determine minimum effective concentrations for dosing. Nevertheless, microscale variations in biofilm structure (and hence function) will make metabolic networks less applicable to the prediction of MIC over large spatial scales. Overcoming this limitation will require numerical integration of multiple local models which is a challenging task in determining the dimension of the local models.

Computational requirements will increase with increasing levels of biological complexity as a result of inherent emerging properties in the system and, while counterintuitive, more complex models will be less temporally consistent and reproducible because of the, sometimes, stochastic nature of MIC processes. Another limitation of deterministic models is the requirement for accurate measurements at appropriate scales of observation for development and validation. These measurements are only rarely available in corrosion studies. As a starting point, enrichments of representative communities can be established and can be generally reproducible, at least in terms of the dominant organisms. Detailed investigation of such communities, in combination with a comprehensive understanding of the nutritional, physical and chemical parameters also offers the opportunity to validate and refine computer-based models.

A number of companies have started developing risk-based models to screen and rank potential MIC threats seeking to combine the result with risk-based inspection programmes [136]. Such an approach may not improve our academic understanding of MIC; however, this concept may represent the best hope for industry to control MIC.

Summary of section 2.4.

To be useful, future MIC modeling must link organisms responsible for MIC to interventions to control corrosion processes, meaning that better experimental models are needed which include multispecies biofilms. Furthermore, models for drinking water communities are not likely to be accurate models for marine biofilms. There are currently no such models for MIC, but given the recent advances in genomics, metabolomics and computational biology, perhaps their attainment is at least feasible.

2.5. The case for implementation of an integrated approach

Bowles [150], described a general corrosion damage cycle that includes the following stages: neglect, panic, learning curve and unlearning curve. The cycle predicts that once the initial crisis is over, corrosion control will be neglected and the corrosion will start again. The cycle was confirmed in detail by Staehle [151]. He examined abiotic corrosion failures in the nuclear power industry and pointed out that management-caused failures continue because managements do not act on existing information and the advice from corrosion experts. He pointed out that since the earliest reactors not a single failure type had been predicted despite the application of an abundance of data and literature for specific potential problems, *e.g.*, the premature failures of tubing in steam generators. Research conducted after the failures was *reactive*. Staehle advocated a *proactive* approach meant to provide data for intervention to prevent future failures.

Successful solutions for such problems have been implemented already in other industrial fields, *e.g.*, in food, beverage, cosmetic, pharmaceutical industries and in drinking and process water systems

and can be adopted. The most promising approach to deal with MIC, together with other water-related problems, is an integrated one and is already at hand. It can be derived from the Hazard Analysis and Critical Control Point (HACCP) system [152,153]. In the water industry, this has led to implementation of the Water Safety Plan (WSP) [154]. The big advantage is that the *entire* system is considered, including raw materials. The procedure appears to be bureaucratic and laborious, but in the industries where it was implemented, it has proven to be very successful and is now common and demonstrated to save huge values [155], if only applied.

Summary section 2.5.

There are no simple solutions for MIC. Rather, a holistic, clean system philosophy combined with risk assessment and minimization should be implemented. All elements required for this approach are already developed and only have to be adjusted and implemented.

3. MIC in laboratory studies

3.1. Influence of the medium

MIC reactions are based on oxidations and reductions involving one- and two-electron transfers. These reactions are microorganism/electrolyte (medium)/metal specific. Several recent publications have used electrochemistry to demonstrate metal-specific reactions in the presence of identical electrolyte/microorganism exposures [156,157].

Reports also confirm that the electrochemical impact of a pure culture of a single microorganism on a single substratum is influenced by the electrolyte. For example, the effect of *Geobacter sulfurreducens* on 304L stainless steel depended on electron donor and acceptor concentrations. Mehanna et al. [156] demonstrated that *G. sulfurreducens* biofilms enhanced pit depth in 304L when the growth medium was deficient in electron donor. In contrast, it was reported that at a low concentration of sodium fumarate (electron acceptor) the presence of *G. sulfurreducens* protected 304 L stainless steel against pitting [156]. The authors concluded, "… *the long-term effect of biofilm on pitting drastically depended on the composition of the medium*…". Cote et al. [109] demonstrated that when grown in an anaerobic medium containing 1 mM acetate, 10 mM fumarate and 5 mM phosphate *G. sulfurreducens* produced an Fe(II) phosphate layer on AISI carbon steel (starting potential 750–800 mV *vs* Ag/AgCl) that protected the metal against the effects of oxygen ingress. The formation of the phosphate layer depended on the concentration of phosphate in the electrolyte in addition to the reactivity of the metal. In these examples, the outcome of laboratory experiments with *G. sulfurreducens* depended on the composition of the electrolyte.

Few MIC investigators consider the relationship between abiotic electrolyte composition and corrosivity. Critical pitting potential is used to assess the corrosivity of abiotic electrolytes by evaluating the aggressive-anion to inhibiting-anion ratios [158]. Pitting and crevice corrosion are not stable for an electrolyte/metal combination at potentials below the critical pitting potential. Pitting potentials shift to more active (negative) values when the ratio is greater than 1, *i.e.*, the concentration of aggressive anions (*e.g.*, Cl^-) is greater than that of the inhibiting anions. Conversely, the pitting potential is shifted to more noble (positive) values by increased levels of inhibiting anions (*e.g.*, sulfates, nitrates, phosphates, and nitrites). The oxyanions that serve as nutrients and electron acceptors for microbial growth can be corrosion inhibitors. As microorganisms grow, they alter the relationships between concentrations of inhibitive and aggressive anions, *i.e.*, the electrolyte can become more corrosive. In closed systems, or at the microscale in the environment, microorganisms are constantly altering these ratios during growth (*i.e.*, assimilatory and dissimilatory reactions). Small changes in these ratios can dramatically impact the corrosivity of an electrolyte to a specific metal [21].

Laboratory experiments are designed to demonstrate a particular microbiological oxidation or reduction reaction by selecting very specific combinations of microorganisms/electrolytes (media)/metals and growth conditions. To ensure rapid microbial growth, vitamins, minerals and other growth enhancers, *e.g.*, yeast extract (YE), are typically added to electrolytes. Concentrations of YE as high as 5 g/L [159,160] are used in some MIC experiments. YE, however, sorbs to surfaces, chelates metals and also contains electron mediators, *e.g.*, riboflavin. Lee and Little [23] demonstrated that 1 g/L YE added to abiotic natural seawater decreased the pH and fixed the E_{corr} of 316 L stainless steel to the same value under both aerobic and deoxygenated conditions.

As an alternative to YE, an undefined medium component, some MIC researchers use a defined combination of vitamins [161–163] to stimulate microbial growth. The vitamin mixtures that are routinely added to electrolytes, often at a 1% concentration, also contain riboflavin and other redox mediators, similar to those in YE. Vitamin and mineral supplements can be purchased directly from the American Type Culture Collection (ATCC) [67]. The ATCC vitamin solution (ATCC MD-VS) contains 50 µg of riboflavin per L of test electrolyte (when added at 1 %) which is quite similar to ~75 µg of riboflavin per L of test electrolyte for YE (when YE added at 1 g/L). Further complicating electrochemical measurements, ATCC MD-VS contains 900 mg/L monosodium phosphate (9 mg L of test solution when added at 1% concentration). Phosphate can be a corrosion inhibiting anion and a nutrient.

The current trend among those studying MIC, to either add exogenous redox mediators into experimental systems or unintentionally include them as components of undefined media (*e.g.*, YE) has created a gap in our understanding of MIC mechanisms [164,165]. Many of the redox mediators routinely added to electrolytes, *e.g.*, riboflavin, have been used in microbial fuel cells to expedite the transport of electrons from microorganisms to an anode at a potential that is energetically favourable for the microbe to conserve energy (around 200 mV *vs.* SHE). In microbial fuel cell research, redox mediators improve current production and would be expected to enhance Fe reduction (Fe (III) to Fe (II)) and not oxidation. Adding redox mediators to MIC experiments will influence corrosion through stoichiometric effects that shift the equilibrium of the prevailing chemistry and skew the bioenergetics of the system towards reduction or oxidation based on the redox potential of the mediators.

Zhang et al. [105] demonstrated that 10 ppm of either riboflavin or flavin adenine dinucleotide (FAD) enhanced electron transfer and accelerated pitting corrosion and weight loss of 304 stainless steel coupons covered with a *Desulfovibrio vulgaris* (ATCC 7757) biofilm in ATCC 1249 medium. The authors concluded that the electron mediators did not influence either planktonic or sessile cell numbers. Abiotic controls, consisting of uninoculated media with and without 10 ppm mediators, did not appear to influence corrosion. However, the authors did not evaluate the corrosivity of media alone, including metabolic products, at the conclusion of the experiment after removal of the microorganisms. Obviously, electron mediators can be used to speed up lab tests. The experiments lasted 7 days [105]. The presence of exogenous redox mediators in ppm concentrations is not representative of natural or industrial waters. Furthermore, the 10 ppm addition is not the only source of redox mediators in this experiment. *D. vulgaris* was grown in ATCC 1249 medium with 1 g/L YE. Inoculation (1 mL/100 mL) would have contributed redox mediators and the experiment was conducted in ATCC 1249 medium.

YE added to biofuel cells acts as a catalyst, as well as a mediator. Sayed et al. [166] suggested that the total effects of YE are not completely understood. Matsuda et al. [167] strongly discouraged addition of YE in microbial fuel cell media and suggested that previous results obtained in the presence of YE should be re-analyzed. The minimum concentration of a redox mediator required to influence electrochemical measurements has not been reported. Marsili et al. [168] observed a stimulatory effect on current when 250 nM riboflavin was added to *Shewanella* biofilms. In most laboratory experiments the redox

mediators added as vitamin or YE additions are overlooked as contributors to corrosion reactions. However, if 1 g/L YE (90 mg/kg riboflavin) is added to a medium, that amounts to 0.09 mg/L riboflavin, roughly the same concentration as that reported by Marsili et al. [168] as "stimulatory".

There are some questions as to whether or not redox mediators play any role in MIC in natural ecosystems. It has been estimated that the biosynthetic cost for production of 1 mol of riboflavin could require as much as 25 mol ATP. To accumulate to 250 nM within a 72-h period would be equivalent to an ATP cost as high as 6.7×10^{-3} μmol ATP·mg protein^{-1} h^{-1} 168]. Further, theoretical calculations show that the maximum production of riboflavin is achieved at low biomass and high cytochrome c production rate [169]. These results indicate that riboflavin-mediated electron transfer might be too costly in natural ecosystems and at low nutrient concentrations.

Electroactive genera such as *Shewanella* spp and *Geobacter* spp secrete flavins in laboratory media devoid of vitamins and growth stimulants. The result can be soluble redox mediators in electrolytes. Marsili et al. [168] demonstrated that cell-free supernatants contained riboflavin after 72 h growth of *Shewanella*. Early studies show that steel coupons exposed to spent medium after growth of bacteria extracted from a steel pipe tubercle developed an open circuit potential similar to that observed in fresh medium [170]. Later studies on *E. coli, Pseudomonas* sp., *Desulfovibrio* sp., *and Bacillus* sp. under defined laboratory conditions confirmed that microbial metabolites in spent medium did not affect significantly the corrosion rate [171]. Given the complexity of bacterial metabolism and the composition of nutrient mixtures in natural environments, the authors of this review believe that a systematic study on spent media from mixed biofilm consortia could reveal a non-negligible effect of the medium composition on MIC process. To the best of the knowledge of the authors, such a systematic study has not been carried out yet.

Abiotic control experiments must accompany biotic experiments to differentiate between biotic and abiotic influences on electrochemical parameters. Dexter [172] recommended three approaches for maintaining an abiotic control: use an artificially prepared electrolyte instead of a natural one, treat the electrolyte to control microbial growth (*e.g.*, addition of a biocide) or manipulate the surface of the working electrode by periodically removing the biofilm. All of these recommendations have electrochemical consequences. For example, 50 ppm glutaraldehyde, a common biocide, in an abiotic experiment was 3.6 times more corrosive than an identical experiment inoculated with SRB [76].

Many laboratory-based electrochemical MIC experiments start with a defined medium (often designed specifically for the growth of the microbes) and a carefully calibrated inoculum of specific microorganisms. The experimental conditions, however, tend to be drastically different from realistic field/environmental conditions [173] and can significantly affect the outcomes of the test [174]. At the conclusion of the experiment, the electrochemical observations are attributed to the microorganisms introduced at the beginning of the experiment. Importantly, the identity of the microorganisms on the surface is rarely, if ever, actually checked to ensure that the experiment was not contaminated, confounding test results.

In addition to the chemical composition of the electrolyte, other details can influence the outcome of laboratory experiments [157,173]. Lee et al. [174] demonstrated that the method for deaeration influenced pH which further encouraged or discouraged SRB growth. It was demonstrated that the volume of the head space in SRB cultures influenced corrosion of carbon steel exposed to a medium inoculated with *D. vulgaris* [175]. Using the same broth volumes and varying the headspace volumes in anaerobic vials, researchers showed that a larger headspace allowed more H_2S to escape the growth medium. Less H_2S in the medium permitted a higher sessile *D. vulgaris* cell count which equated to more severe carbon steel corrosion.

3.2. Standards for laboratory experiments necessary

Laboratory experiments are routinely conducted in poorly described culture media that could never be replicated without additional information, particularly regarding the concentration of growth factors. One of the papers studied for this review [156] described use of a "standard medium" for growth of a pure culture of microorganisms and electrochemical measurements. The authors provided a reference for the medium [176]. That reference provided yet another reference for a "*common growth medium already described elsewhere*" and so it went for a total of five additional citations before the complete composition of the medium could be established [163] – a medium developed for the isolation of methanogens. Because there are no standards and no recommended practices for conducting laboratory experiments, each laboratory tends to use an in-house recipe for the electrolyte in MIC experiments. Under these circumstances there can be no inter-laboratory comparisons. Similarly, because there are no standards for reporting details of experimental procedures there is little possibility of independent verification of results. This problem is not unique to MIC studies and is being addressed in related disciplines (*e.g.*, biofilm experiments) through the development of guidelines for the "*minimum information that needs to be reported to guarantee the interpretability and independent verification of experimental results* …" [177].

Much of what we think we know about MIC, particularly mechanisms, is based on electrochemical measurements. Although Committee G1 of the American Society for Testing Materials publishes standard practices for electrochemical techniques for abiotic corrosion measurements, there are no standards or recommended practices for the application of electrochemical techniques to MIC [45]. Techniques and resulting data have been reviewed by multiple authors [44,46–50].

Electrochemical techniques, in general, produce an average signal over a surface area, whereas MIC is a localized phenomenon. Electrochemical techniques requiring no, or small, external signals have been used to demonstrate that MIC can occur in a wide variety of media and microorganisms but have not provided mechanistic information. Mechanistic information can be obtained from large signal polarization techniques which require potential scans ranging from several hundred millivolts to several volts. However, large signal polarizations cause irreversible changes to surface properties and can disrupt biofilms. Electrochemical techniques to evaluate MIC have typically been conducted in nutrient-rich media that do not approximate natural or industrially-relevant electrolytes and for which it is difficult/impossible to maintain sterile controls. Communication between microbiologists and electrochemists has been complicated by the use of the same terms, but with different intended meanings, *e.g.*, direct electron transfer [178].

Summary of section 3.

Despite the recognition that the composition of the electrolyte controls the outcomes of MIC experiments, authors continue to provide lists of causative microorganisms and their "traits", *e.g.*, sulfate-reducing, nitrate-reducing, iron- or manganese-oxidizing or acid-producing, in reference to corrosion mechanisms. The authors of this review suggest that most microorganisms influencing corrosion have multiple traits and that these lists are not helpful in the absence of specific information about the electrolyte, *e.g.*, anion ratios, electron donor/acceptor relationships and exogenous redox mediators. Standards for conducting and reporting experiments, in addition to a standardized glossary of terms, must be established if research is to contribute to practical solutions.

4. Addressing the gaps in MIC research

There are numerous gaps in MIC research – such as the gap between laboratory and field exposure conditions, the communication gap between microbiologists and electrochemists, and the gap between published reports of MIC from laboratory experiments and reproducible

results.

The authors acknowledge that laboratory experiments have contributed many interesting observations related to microorganism-metal interactions. The list of microorganisms associated with MIC is definitely growing but the gaps in our understanding of MIC are not narrowing. Serial publications, changing metal substrata and microorganisms with different permutations of media composition do not increase our fundamental understanding of MIC. Instead one poorly designed and described experiment is reported in the literature, referenced in the next paper and so on until someone stops to ask the difficult questions. For example, the cathodic depolarization theory (CDT), first published as a mechanism for MIC in 1934 has been cited repeatedly during the intervening years. In 2018, Blackwood [178] examined the theory carefully and concluded that the CDT for the role of SRB in the corrosion of carbon steel was incorrect. Blackwood further noted, "*…despite the long history of investigating MIC, we are still a long way from really understanding its fundamental mechanisms, especially in relation to non-sulfate reducing bacterial (SRB) anaerobes*."

The electrochemical influence of growth factors routinely added to electrolytes in MIC experiments has not been fully acknowledged or thoroughly evaluated. Information reviewed in this paper has focused on riboflavin. However, YE and all vitamin formulations contain other redox mediators which must be considered for their contributing influence on electron transfer. Not all microorganisms require exogenous sources of redox mediators, *e.g.*, *Bacillus subtilis, Geobacter* sp.*, and Shewanella* sp. We need to ask why growth factors are routinely added to electrolytes for MIC experiments. We must also relate test media/electrolytes to natural and industrial waters (*e.g.*, oil and gas pipelines, seawater, *etc.*) in which rapid MIC is observed. Omitting mediators from MIC experiments will potentially allow reactions to proceed spontaneously and in a manner more in keeping with natural environments.

The role of interfacial electron transfer between the corroding metal surface and that of the bacterial envelope in MIC is controversial and complicated by uncertainties related to electrolyte composition and the quantity of redox mediators they contain. Systems that do not discount redox mediators and which propose to study MIC are introducing a bias into their systems. Microbial alteration of electrolytes, related to either or both a change in the critical pitting potential or production of redox mediators, in laboratory experiments must be considered as the cause for the observations related to corrosion.

As previously discussed, abiotic controls are essential for the interpretation of electrochemical data attributed to the activities of microorganisms and it is very difficult to maintain sterile controls in the presence of growth factors. Despite the molecular tools for identifying and quantifying microorganisms, few researchers confirm that abiotic controls were properly maintained at the conclusion of an experiment. Does likelihood of contaminated controls drive the decisions to terminate experiments after a few days?

Despite over 50 years of recognition that microorganisms in pure culture behave differently than microorganisms in consortia, experiments continue to be performed with pure cultures in nutrient-rich media. Experiments are designed to demonstrate a particular microbiological oxidation or reduction reaction by altering or limiting electron donor/acceptor relationships without any reference to a natural or industrial water where such a reaction could be observed. Further work is required to understand how consortia of microbes, such as those observed in the environment, can affect corrosion processes.

There are numerous other ways in which laboratory experiments misrepresent actual operating conditions and the significance of results. The role of oxygen as the terminal electron acceptor in a series of electron transfers involved in MIC is widely recognized and oxygen probes are available with ppb accuracy. Yet, very few researchers quantify oxygen. Instead, deoxygenation is described as the period of time over which a replacement gas is bubbled through an electrolyte. Similarly, experiments are described for zero valent metals without any description of the ways in which these reactive metals were handled to prevent oxide formation (for the proper handling of zero valent iron in an experiment to demonstrate metallic iron as an electron donor see Philips et al. [179]). After a successful demonstration, the authors concluded, "*Future studies should also use more realistic iron-based materials (for example steel coupons), instead of Fe(0) powder…to correctly assess the possibly large contribution of Shewanella to biocorrosion.*"

5. Conclusions

The authors of this review conclude that little progress has been made in answering the fundamental question posed by Stott [1] regarding the prediction of the corrosion rate for material X in an environment where aggressive microorganisms proliferate. Equally important, current MIC research does not provide data related to detection and verification in the field, diagnosing, modelling or prediction. Laboratory experiments seldom attempt to recreate relevant natural or industrial electrolytes. A sober, solution-oriented contemplation of the state-of-art and acknowledgement of the substantial deficiencies in our understanding may help shift MIC research into a direction which could actually produce useful answers.

Contributions of the authors

Brenda J. Little: contributed to almost every section, handled submission and serves as the corresponding author and edited the manuscript together with HCF.

Dan Blackwood: lead contributor to the electrochemical sections.

Jamie Hinks: contributed to the electrochemical, microbial fuel cell, and the MIC in laboratory studies sections, and to the critical discussion of the manuscript.

Federico Lauro: contributed the modelling section.

Enrico Marsili: contributed to the cost section and to the electrochemical section and to critical discussion of the manuscript.

Akihiro Okamoto: contributed the microbial fuel cell section.

Scott Rice: organized the workshop on which this collaboration has been assembled, contributed to critical discussion of the manuscript.

Scott Wade: contributed to the cost, electrochemistry and the MIC in laboratory studies sections.

Hans-Curt Flemming: drafted the structure of the paper, contributed most to the introduction, the cost, sanitation and monitoring sections, and the conclusions, orchestrated the collaborative writing process, integrated the contributions and edited the manuscript together with BJL.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge financial support from the National Research Foundation, Prime Minister's Office, Singapore, under its Marine Science Research and Development Programme (award MSRDP-P12) and and the Singapore Centre for Environmental Life Sciences Engineering (SCELSE), whose research is supported by the National Research Foundation Singapore, Ministry of Education, Nanyang Technological University and National University of Singapore, under its Research Centre of Excellence Programme. The workshop was co-supported by the National Research Foundation, Prime Minister's Office, Singapore under its Marine Science Research and Development Program and SCELSE.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.corsci.2020.108641.

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