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Corrosion of carbon steel by bacteria from North Sea offshore seawater injection systems: Laboratory investigation

Marko Stipanicev [a,b,*], Florin Turcu [a], Loïc Esnault [a], Omar Rosas [b], Régine Basseguy [b,**], Magdalena Sztyler [c], Iwona B. Beech [c,d]

[a] Det Norske Veritas, Johan Berentsens vei 109-111, 5163 Laksevåg, Bergen, Norway
[b] Laboratoire de Génie Chimique CNRS-INPT, Université de Toulouse, 4 Allée Emile Monso, 31030 Toulouse, France
[c] School of Pharmacy and Biomedical Sciences, University of Portsmouth, Michael's Building, White Swan Road, Portsmouth PO1 2DT, UK
[d] Department of Microbiology and Plant Biology, University of Oklahoma, 770 Van Vleet Oval, Norman, OK, USA

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ABSTRACT

Influence of sulfidogenic bacteria, from a North Sea seawater injection system, on the corrosion of S235JR carbon steel was studied in a flow bioreactor; operating anaerobically for 100 days with either inoculated or filtrated seawater. Deposits formed on steel placed in reactors contained magnesium and calcium minerals plus iron sulfide. The dominant biofilm-forming organism was an anaerobic bacterium, genus *Caminicella*, known to produce hydrogen sulfide and carbon dioxide. Open Circuit Potentials (OCP) of steel in the reactors was, for nearly the entire test duration, in the range $-800 < E(\mathrm{OCP})/\mathrm{mV}\,(\mathrm{vs.\,SCE}) < -700$. Generally, the overall corrosion rate, expressed as $1/(R_p/\Omega)$, was lower in the inoculated seawater though they varied significantly on both reactors. Initial and final corrosion rates were virtually identical, namely initial $1/(R_p/\Omega) = 2 \times 10^{-6} \pm 5 \times 10^{-7}$ and final $1/(R_p/\Omega) = 1.1 \times 10^{-5} \pm 2.5 \times 10^{-6}$. Measured data, including electrochemical noise transients and statistical parameters ($0.05 < \text{Localized Index} < 1$; $-5 < \text{Skewness} < -5$; $\text{Kurtosis} > 45$), suggested pitting on steel samples within the inoculated environment. However, the actual degree of corrosion could neither be directly correlated with the electrochemical data and nor with the steel corrosion in the filtrated seawater environment. Further laboratory tests are thought to clarify the noticed apparent discrepancies.

1. Introduction

The economic consequences of corrosion of iron and its alloys in various industrial sectors, including oil and gas operations, are well documented [1–3]. Undisputedly, corrosion causes considerable damage to marine steel infrastructure, such as offshore oil installations and pipeline systems, leading to revenue losses. It has been estimated that nearly 20% of the total corrosion cost is due to Microbially Influenced Corrosion (MIC) [3,4]. MIC is often seen as pitting attack that is generally associated with the presence of surface-associated microbial communities embedded in a bioinorganic matrix, referred to as biofilm [5]. In both natural habitats and man-made systems, biofilms implicated in corrosion failures, comprise diverse microbial genera and species that often exhibit synergistic and synthropic behavior [6,7]. Key microorganisms are phylogenetically diverse Sulfide-Producing Prokaryotes (SPP) of which some, but not all, represent Sulfate-Reducing Bacteria (SRB) and Archaea (SRA), i.e. Sulfate-Reducing Prokaryotes (SRP) [8,9]. In addition to SPP, Sulfur-Oxidizing Bacteria (SOB), Iron-Reducing and -Oxidizing Bacteria (IRB and IOB respectively), Manganese-Oxidizing Bacteria (MOB), carbon dioxide reducing bacteria [3] and methanogenic archaea have been associated with marine corrosion failures [10–12].

It is now acknowledged that microbial metabolic activity, which depends on the availability of nutrients and of suitable electron donors and acceptors, can influence electrochemical processes on steel surfaces, therefore, plays an important role in the processes governing MIC [13,14]. Indeed, it has been reported that differences in metabolic activities within biofilms established under identical conditions can result in dissimilar corrosion rates [4]. It is also recognized that biofilm formation and associated MIC damage are dependent on the physical and chemical conditions of a given environment [15]. For example, temperature, pH, pressure, light radiation, oxygen content, salinity and redox potential will influence the nature and metabolic activity of a bacterial community [16], thus governing the potential risk of MIC. It is noteworthy that conditions at surfaces may differ significantly from those in bulk liquid; for example, anaerobic niches may exist within biofilm in a fully oxygenated system or oxygen may be formed in an anoxic environment due to bacterially-mediated disproportionation reactions [17–19].

Further, fluid flow directly impacts mass transfer and biofilm formation [20,21]. High shear stress is likely to decrease microbial

* Correspondence to: M. Stipanicev, Det Norske Veritas, Johan Berentsens vei 109-111, 5163 Laksevåg, Bergen, Norway.
** Corresponding author.

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cell attachment and may even cause detachment of an established biofilm [21–23].

Importantly, the chemical composition and microstructure of the construction materials determine their susceptibility to both abiotic corrosion and MIC [24,25]. Carbon steel is a major alloy used in offshore oil extraction and transport systems, including Sea-Water Injection Systems (SWISs). During their operational lifetime, SWISs are exposed to a range of damage-provoking conditions. The presence of microorganisms can lead to complex, and not yet fully understood, deterioration of pipeline material. Carbon steel is particularly vulnerable to sulfide attack; hence biotic sulfide production resulting from SPP activity is of great concern.

In offshore Oil and Gas (O&G) industry, the main target in MIC control and remediation is taxonomically and metabolically diverse SRP. Able to grow within a wide temperature range, SRP are routinely detected in parts of the offshore oil extraction systems where sulfate-rich seawater-containing fluids are being produced or processed and anoxic conditions may prevail [26,27].

It has to be emphasized that not just SRP, but also other classes of anaerobic dihydrogen sulfide producing organisms, pose equal, if not greater, MIC threat [32]. These include spore forming bacteria belonging to the phylum *Firmicutes* and the class *Clostridia*, which are readily detected in oilfield systems using advanced molecular ecology techniques [28–31].

The interdisciplinary investigation reported herein aimed to determine whether the selection of S235JR low carbon steel as pipe material for a North Sea offshore seawater injection system would result in an unacceptable MIC risk. The laboratory set-up was constructed as an anaerobic continuous-flow bioreactor, circulating North Sea seawater. Its operating parameters were selected to mimic field conditions. The system was designed as a closed test loop comprising an inoculation vessel and two flow-through cells fitted with steel test specimens. Bioreactor inoculum was obtained from sessile (biofilm) field populations enriched in an anoxic sulfate medium and subsequently re-enriched in sulfate and other anaerobic microbial cultivation media. Special emphasis was placed on the on-line use of electrochemical techniques, in particular Linear Polarization Resistance (LPR) and Electrochemical Noise (EN), to monitor and characterize corrosion events on surfaces of steel specimens. The bioreactor inoculum and the planktonic and biofilm communities in the experimental and control flow cells were characterized employing tools of molecular microbial ecology, namely Polymerase Chain Reaction (PCR), Denaturing Gradient Gel Electrophoresis (DGGE), cloning and sequencing. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis of surfaces of test specimens were performed to image biofilms, visualize topography and to provide elemental composition of corrosion products.

2. Material and methods

2.1. The bioreactor loop

A high and stable flow rate of seawater, constant temperature, and anoxic conditions were prerequisites of the study. A closed flow-loop bioreactor design was selected as the most suitable system complying with those requirements. The final bioreactor set-up benefitted from the past 20 year experience in MIC research for the selection of construction materials, flow cell design, real-time monitoring techniques, etc. [33–36]. The main components of the bioreactor were manufactured in-house and comprise a vessel and two cylindrical flow-through cells. While the inoculated seawater freely enters the experimental flow cell, it passes through a 0.2 μm filter (Sartopore 2 MaxiCaps®, Sartorius AG, France) before reaching the control flow cell. The bioreactor set-up is depicted in Scheme 1.

The bioreactor vessel consists of a polypropylene body and an acryl lid, fitted with an optical oxygen dipping probe, a temperature sensor interfaced with Fibox 3 fiber optic oxygen transmitter (Presens, Germany), one nitrogen gas inlet (99.999% purity, Yarapraxiar, Norway), one gas outlet and a pH electrode (pH-meter HI-9125N, Hanna Norden AB, Sweden). The lid also incorporates an in-house fitted sampling point and a fluid injection system. The vessel is also equipped with a heating unit (ISOPAD IP-DASI®, Tyco, USA) and a thermostat (Raychem® AT-TS-14, Tyco Thermal Controls, USA).

A peristaltic pump (W-M 520SN/REL, Watson-Marlow, UK), draws media from the bioreactor vessel, and the output flow is split between the two flow cells. Perfluoroalkoxy (PFA) tubing (PFA-T8-062-50, Swagelok, UK) was used. Two regulation needle valves (PFA-4RPS8, Swagelok, UK) were installed before and after each flow cell. Each flow cell was also equipped with a flow meter (FTB332 infra-red light beam micro-flow meter, Omega Engineering, UK) located after the exit regulation valve. The flow rate through each of the flow cells was controlled at 180 mL/min with the regulation valves. After passing through the flow cells, the liquid stream rejoins and returns to the bioreactor vessel. Liquids were re-circulated in the bioreactor loop for100 days.

The entire bioreactor flow system was constructed from polymers to minimize contamination with exogenous metal ions. Furthermore, materials, including perfluoroalkoxy (2 mm thickness), polyolefin (1 mm thickness), polypropylene (2 cm thickness) and acrylic (1 and 2 cm thickness) polymers with minimal oxygen permeability and minimal deterioration under test conditions were chosen. Prior to operation the bioreactor loop was flushed with technical grade alcohol (art. no.601441, Kemetyl Norge AS, Norway) and flow cells were exposed for 6 h under UV light (XX-15 sterilization UV lamp, UVP, USA).

Flow cells were made from acrylic tubes (6 cm inner diameter, 1 cm wall thickness and 48 cm length). Six pairs of feedthroughs (M20 size fittings, produced by OBO Bettermann, Germany) were installed on each flow cell. A schematic drawing of a flow cell showing its cross section and distribution of feedthroughs is presented in Scheme 2.

Electrodes for the measurements of corrosion rates and open-circuit potentials were installed in the two flow cells, in identical arrangements. The electrode configuration was designed to reproduce that used in offshore electrochemical probes. Six carbon steel Working Electrodes (WE) with a circular, exposed area of 0.785 cm^2 (cylindrical specimens, 1 cm long, 1 cm diameter, dressed in polyolefin sleeve and leaving only the flat bottom of cylinder exposed, Scheme 3) were installed in the 10 o'clock (F2, F4, and F6) and 2 o'clock positions (F8, F10, and F12), see Scheme 2. Each cell was also fitted with four additional electrodes. Their design was the same as that of the working electrodes (Scheme 3), except that Inconel® C276 (E(Inconel®C276 in anoxic seawater)/mV (vs. SCE) ≈ 350) was used instead of carbon steel as electrode material and the exposed area was 3.95 cm^2 as the cylinder side was not dressed in polyolefin sleeve. Two of these electrodes, installed in the F5 and F9 positions, were used as Counter Electrode (CE). The other two, installed in the F3 and F11 positions, served as Pseudo-Reference Electrodes (PRE). Two laboratory-made Salt-Bridges (SB) filled with 2 M KCl solution (VWR, US) were placed between the F1 position in each flow cell and a reference cell, which was also filled with the 2 M potassium chloride solution and fitted with two Saturated Calomel Electrodes (SCE). An in-house manufactured liquid Sampling Port (SP) with a septum was installed at F7 position in each cell. To monitor biofilm formation, five carbon steel specimens (half-pipe sections with a 5 cm length, a 5.5 cm outer diameter and a 0.5 cm wall thickness) were installed at 6 o'clock position in each flow cell (Scheme 2).

The test specimens (half-pipe and circular disks) were manufactured from S235JR carbon steel (Descoure and Cabaud, France). The S235JR carbon steel is composed of the following elements and corresponding mass percentage: 0.17% carbon (C), 1.4% manganese (Mn), 0.045% copper (Cu), 0.03% sulfur (S) and 0.03% phosphorus (P). All exposed surfaces were ground manually using silicon carbide (SiC) paper of increasingly fine grain, ending with 600-grit. Grinding debris were rinsed off the electrode surface with sterile deionized water.