



Corrosion of low carbon steel by microorganisms from the ‘pigging’ operation debris in water injection pipelines



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ABSTRACT

Present in all environments, microorganisms develop biofilms adjacent to the metallic structures creating corrosion conditions which may cause production failures that are of great economic impact to the industry. The most common practice in the oil and gas industry to annihilate these biofilms is the mechanical cleaning known as “pigging”. In the present work, microorganisms from the “pigging” operation debris are tested biologically and electrochemically to analyse their effect on the corrosion of carbon steel. Results in the presence of bacteria display the formation of black corrosion products allegedly FeS and a sudden increase (more than 400 mV) of the corrosion potential of electrode immersed in artificial seawater or in field water (produced water mixed with aquifer seawater). Impedance tests provided information about the mechanisms of the interface carbon steel/bacteria depending on the medium used: mass transfer limitation in artificial seawater was observed whereas that in field water was only charge transfer phenomenon. Denaturing Gradient Gel Electrophoresis (DGGE) results proved that bacterial diversity decreased when cultivating the debris in the media used and suggested that the bacteria involved in the whole set of results are mainly sulphate reducing bacteria (SRB) and some other bacteria that make part of the taxonomic order *Clostridiales*.

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1. Introduction

Microbial development occurs in almost all environments throughout biofilm formation and may be responsible for microbial influenced corrosion (MIC), also known as microbially influenced corrosion or biocorrosion which can be defined as the enhancement or acceleration of corrosion by the presence of bacteria [1]. MIC is not a new corrosion mechanism but it integrates the role of microorganisms in corrosion processes. Thus, an inherently abiotic process can be influenced by biological effects [2].

Corrosion represents a considerable economic stake projected between 1 and 4% of the gross national product (GNP) of developed countries [3]. Fleming et al. [4] estimate that 20% of corrosion problems are linked to the presence of microorganisms and more over Jack et al. [5] estimated that 34% of the corrosion damage experienced by oil companies was related to MIC.

Oil and gas industries battle MIC problems and its potential damages in pipelines by different methods such as the use of biocides, coatings, corrosion inhibitors and different chemicals that could reduce or control bacterial growth and/or reduce corrosion rates but probably the best

way to avoid microbial influenced corrosion is an appropriate design and operation to keep the systems clean combined with regular mechanical cleaning [6].

Mechanical cleaning involves any method capable of the physical removal of deposits formed on the surface. It includes brushing, pigging and the use of cleaning spheres or water jet, and it is applied to remove sludge, scale, and encrustations as well as the biomass associated with these deposits [7]. Mechanical cleaning is mainly performed in water injection and production pipeline systems of oil and gas industries by the use of mechanical pigs.

Pipeline operators now describe any device made to pass through a pipeline for cleaning and other purposes with the word pig. The process of driving the pig through a pipeline by fluid is called a pigging operation [8]. Operators need to run cleaning pigs to dewax and descale the inside surface of the pipe and remove debris (corrosion products and biofilm), which help improve pipeline performance [9]. This debris collected in the receivers of the pipelines may be used to analyse not only corrosion products, organic matter, oil and water residues but also biofilm and bacterial presence.

Depending on the operating system, oil and gas companies combine different methods for the prevention and/or protection of corrosion of their pipelines. For instance, pigging operations are combined with biocide treatments and/or corrosion inhibitor treatments in order to reduce bacterial development. However, it is known that bacteria can adapt to drastic conditions posed by these treatments and resist rough

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environmental conditions still causing a threat for the materials. For example sulphate reducing bacteria (SRB) show considerable adaptability to extreme conditions making it possible to isolate active cultures from sites where bacteria are exposed to O₂ regardless of the anaerobic nature of this group [10–12].

One of bacteria's defensive mechanisms against corrosion treatments is precisely the secretion of slime or extracellular polymer substances (EPS) that leads to the formation of biofilms forming a gel matrix on the metal surface that not only may enhance corrosion rates but also protects bacteria from biocides [12]. It also may aid to the entrapment of corrosion inhibitors such as aliphatic amines and nitrites to be later degraded by microorganisms. Biofilms also reduce the effectiveness of corrosion inhibitors by creating a diffusion barrier between the metal surface and the inhibitor in the bulk solution [12–16].

Due to biofilm formation in diverse environments such as pipelines, microorganisms can coexist in naturally occurring biofilms with a wide bacterial community including fermentative bacteria, often forming synergistic communities (consortia) that are capable of affecting electrochemical processes through co-operative metabolisms [1,17]. Nevertheless, most of the research on anaerobic microbially influenced corrosion has focused on SRB primarily for the hydrogen sulphide generation and the fact that there is injection of sulphate-containing seawater into the reservoirs during the secondary recovery of oil which favours the proliferation of these bacteria [18,19]. However, recent studies suggest that SRBs need not be present in abundance in the microbial communities responsible for MIC [20] and that other types of bacteria could be involved, such as metal reducing-bacteria and methanogens [1,19,21]. Thus, studies with other bacterial groups or consortia must be enhanced.

This study has as objective to explore the influence of a consortium of microorganisms present in a sample of pigging debris on the corrosion of low carbon steel and determine its corrosive activity. For this, samples of pigging debris extracted from a water injection system of an oil and gas company located in Norway were used. Electrochemical experiments were performed, simulating some of the field conditions, comparing two different electrolytes as medium: artificial seawater (ASW) and a mixture of water from the field used in the water injection pipelines (MIXED). Furthermore, microbial diversity present in the debris and in the water used for the electrochemical experiments was characterised by Denaturing Gradient Gel Electrophoresis (DGGE) analysis of the Polymerase Chain Reaction (PCR) products for bacterial 16S rRNA genes (550 bp) aiming to comprehend the influence of bacterial consortia involved in corrosion.

2. Experimental procedure

2.1. Sample collection

Pigging debris samples were collected from a water injection pipeline "A" located in the installation "A" of an Oil and gas company located in Norway between November 2010 and June 2011. The pipeline consists of 10–15 km long pipe made of low carbon steel with an average operating temperature of 35 °C. Pig 1 was used for the electrochemical experiments and Pigs 1 and 5 were used for the weight loss experiments. Pig 1 corresponds to the first debris collected after the first pigging operation and Pig 5 corresponds to the fifth debris collected after the fifth pigging operation. Samples were transported to the lab in Schott bottles, flash with an inert gas and sealed.

Water passing through the water injection system is a mixture of 50% aquifer water plus 50% produced water recycled from the production pipelines. This water is re-injected into the oil-bearing formations to maintain pressure and facilitate oil recovery. The mixture of these waters is used for the electrochemical and weight loss experiments and will be called MIXED throughout this paper. Corrosion inhibitor KI-3804, imidazoline type, is added regularly in the production lines.

Thus, 4 ppm of corrosion inhibitor is expected to be in the water injection pipelines according to the information provided by this company.

2.2. Inoculum and medium

Two different mediums were tested for the electrochemical experiments: ASW and mixed water from the field (MIXED) previously mentioned. ASW consists of: NaCl 408 mM, Na₂SO₄ 28 mM, KCl 9.3 mM, NaHCO₃ 24 mM, KBr 839 μM, H₃BO₃ 36 μM, MgCl₂·6H₂O 53 mM, CaCl₂·2H₂O 10 mM and it was supplemented with 10 mM of sodium acetate and 25 mM of sodium fumarate. MIXED water was supplemented with 24 mM of NaHCO₃ and generally after 300 h of running with 10 mM of sodium acetate and 25 mM of sodium fumarate when indicated.

The supplementation with acetate and fumarate is done to enhance a faster growth of heterotrophic species contained in the consortia. CO₂ added as part of the injected gas and inorganic substances such as iron (metal coupon) and sulphate were also present for the growth of autotrophic and lithotrophic species that may be present in the consortia.

Approximately 10 g of pigging debris was used to inoculate the electrochemical reactors and 3 g for the anaerobic vials used for the weight loss experiments. Inoculation was performed after de-aerating the medium with N₂/CO₂. An approximate number of planktonic cells were evaluated by bacteria counting in a Thoma counting chamber after performing serial dilutions.

2.3. Electrochemical measurements

Anaerobic reactors of 0.5 L were used adjusting the liquid level to 400 mL of total volume. The anaerobic conditions were obtained by bubbling N₂/CO₂ 80:20 into the reactors for no less than 45 min before inserting the metal coupons. The flow of N₂/CO₂ was maintained during the whole experiment. Reactors were kept at 35 °C during experiments. pH was measured for all the experiments at the initial time (h = 0) and the final time (h ≥ 700 h).

The working electrodes (WE) were 2 cm diameter cylinders of carbon steel S235 JR. The nominal chemical composition for the steel S235 JR is shown in Table 1. The WE was covered by a polymeric coating (thermo-contractible polyolefin, ATUM®) leaving uncovered a flat disc surface with a total exposed area of 3.14 cm². Connections were made through titanium wire protected with the same polymeric coating. The electrodes were ground with SiC paper using P120–P600 until achieving a 600 grit surface followed by a cleaning with ethanol (70%) and throughout rinsing with sterile deionised water.

For all the experiments, electrochemical measurements were performed using a multipotentiostat (VMP-Bio-Logic) with a platinum grid (Pt, Ir 10%) used as counter electrode (CE) and a silver wire coated with silver chloride (Ag/AgCl 0.5 M) was used as reference electrode (RE).

The open circuit potential (OCP) was measured in function of time for all the experiments. Electrochemical impedance spectroscopy (EIS) was used to obtain information on the interface, using a frequency from 100 kHz to 10 mHz and an amplitude of 10 mV.

2.4. Surface analysis

Scanning Electron Microscopy (SEM) pictures were taken using a TM3000 Hitachi Analytical Table Top Microscope at 7000× magnification working at 15 kV acceleration voltages, immediately after removing the coupons from the solution. The coupons were washed with

Table 1
Chemical composition of AISI S235 JR (wt.%). Main compound: iron.

Alloy	C	Mn	Cu	S	P	N
S235	0.17	1.40	0.55	0.03	0.03	0.01

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