SOURING AND MICROBIAL INFLUENCED CORROSION IN PRODUCED WATER RE-INJECTION SYSTEMS - CHALLENGES AND CONTROL STRATEGIES

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INTRODUCTION

Produced water re-injection (PWRI) into petroleum reservoirs presents a potent water management solution and may become obligatory for the exploration and production of oil and gas in environmental sensitive areas, such as in the Arctic, the Barents Sea and the Caspian Region. A key challenge to PWRI implementation is reservoir souring (RS) caused by the production of sulphide in the reservoir by sulphate reducing prokaryotes (SRP). Souring can be mitigated by the addition of nitrate prior to PWRI, but this has only rarely been implemented in full scale. In seawater injection water systems, nitrate has been applied with great success to control RS. During a PWRI pilot on the Draugen platform in 2006, nitrate effectively mitigated souring, but as a side effect, accelerated corrosion (1). Corrosion rates dropped after biociding the system and it was concluded that stimulation of corrosive microorganisms by nitrate most likely accelerated the corrosion. A Joint Industry Project (JIP) was initiated (2007-2010) to study the mechanisms and find mitigation methods to control corrosion in presence of nitrate. In this JIP the impact of nitrate on souring and corrosion was tested in an anaerobic flow-through systems in which biofilms from the Draugen produced water system were grown on mild steel coupons at 60°C (2). The effect of the addition of a biocide (BIO) and a corrosion inhibitor (CI) to control microbial influenced corrosion (MIC) was assessed on clean systems and on systems with existing sulphidic biofilms.

MATERIAL AND METHODS

Corrosion experiments. The corrosion experiments were performed in flow-through systems comprised of a glass corrosion flow cell containing mild steel coupons operating at 60ºC (Figure 1). Biofilms were grown from Draugen produced water inoculum and de-aerated artificial produced water which was continuously pumped at 10 ml/h through the systems. Sodium nitrate (SN40 Petrocare, Yara International ASA, Norway) was continuously added at an organic carbon (from total VFA plus lactate) to nitrate ratio of 1 to 3, equally to 5.4mM nitrate. As shown in Figure 2, nitrate was added from the start of the experiment in Tests 1-4 and from week 14 in Tests 5 and 6, accordingly:

- The effect of CI on the mitigation of MIC was examined in Tests 1-3 and in Test 5. The CI (RX-2059, Roemex Lt., UK) was continuously added to the systems. The initial CI concentration was 25ppm (product concentration) and was increased stepwise when LPR corrosion rates increased. The maximum CI concentration applied in Tests 1, 2 and 5 were 100, 200 and 400ppm, respectively.
- The effect of a BIO (Biotreat 4622; Clariant, Norway) on the mitigation of biofouling and MIC was assessed in Tests 1-3. BIO was added to the corrosion flow cells at 1000 ppm of product with a contact time of three hours once in a week over 4 weeks.
- Tests 4 and 6 served as controls with and without added nitrate.
- The effect of pigging on MIC mitigation was examined in Test 3, where the biofilm was physically removed with a brush before BIO addition (weeks 14 and 17).

Microprofiling, LPR corrosion rates and weight loss. The redox potential in biofilms was measured with microelectrodes (Unisense, DK) at the end of experiment. LPR corrosion rates were detected with a 3-electrode system positioned downstream of the flow-through cells (Figure 1). General corrosion was measured by metal weight loss.

Coupon surface profilometry and microscopy. Acid cleaned coupons were scanned by white light axial chromatism using a non-contact 3-D optical profilometer. Coupons were cut, embedded into Epoxy, ground, polished, washed with isopropanol and dried. Cross-sections were inspected under a metal optical microscope and pitting depth was quantified.

Corrosion product analyses. The corrosion products were qualitatively analysed with X-ray diffraction. Sessile sulphide was quantified using the methylene blue method.

RESULTS AND DISCUSSION

Biofouling and corrosion

Two scenarios were assessed:

1) A clean system without biofilm. CI was added together with nitrate to a clean system from week 1 of the experiments (Tests 1-3). This simulated a system to which nitrate and CI are added to mitigate souring and corrosion from day one of production.
2) A system with an established sulphidic biofilm. During the second scenario (Test 5), CI and nitrate were added together to an established sulphidic

biofilm. This simulated a sour field to which nitrate and CI are added to mitigate reservoir souring and corrosion in the topsides.

Biofouling

Clean systems. The biofilms gradually grew to form thick (200-1500µm), and were fluffy, and yellow-brown in colour (Figure 3). At the end of the experiment, the redox potential in biofilms treated with BIO (Tests 1) and BIO/CI (Test 2) was consistently positive at +375mV in the water and throughout the entire biofilm (Figure 3). In contrast, the redox potential in the nitrate control (Test 4) dropped to -460mV on the metal surface.

Systems with sulphidic biofilm. Before nitrate addition to Tests 5 and 6, a thin (40-70µm), compact and crusty black (sulphidic) film developed on the metal coupons within one week after starting the experiment (Figures 3 and 5). The redox potential below -600mV on the metal surface of the same coupons indicated the presence of highly reduced corrosion compounds, such as iron(II), H_2, sulphide and iron sulphides (2, 5), originating from corrosion and sulphate reduction (Figure 3). After nitrate addition, the redox potential increased to -250mV at the metal surface within the sulphidic crust and more than -100mV in the biofilm. This implies presence of a persistent sulphate reduction occurring at the metal surface even in presence of high nitrate concentration in the surrounding water. Nitrate addition supported microbial growth leading to biomass accumulation in all tests. Independent of when nitrate was added, all biofilms became more stratified and structurally heterogeneous with time, showing alternate structures of clusters, voids, and channels in the upper part of the biofilm and a black sulphidic crust on the base (Figures 3 and 5).

Nitrate functionality. Nitrate provides a potent electron acceptor for nitrate reducing microorganisms and is energetically more favourable than sulphate providing growth. Substantial biofilm growth is problematic during produced water re-injection where it can lead to biofouling and subsequent reduced flow and injectivity loss. The conditions in the biofilm largely vary from those in the bulk water, providing niches for microbial growth under otherwise rough conditions. Once nitrate becomes depleted with increasing depth in the biofilm, sulphate is reduced by SRP and converted to sulphide that itself corrodes or form corrosion products with the metal iron. The structural heterogeneity on the metal surface may provoke corrosion by forming differential corrosion cells.

General corrosion

General corrosion rates were determined by weight loss of the corrosion coupons over the length of the experiment (Figure 4). In clean systems the highest rate was measured in presence of CI only (Test 1) while the lowest rates occurred in the presence of CI and BIO (Test 2). When nitrate was added to sulphidic systems, higher rates occurred in presence of CI in Test 5 relative to the control (Test 6). LPR corrosion rates were highest in the biofilm systems to which nitrate was added from week 14 (Tests 5 and 6) and in the nitrate control (Test 4) before CI and BIO addition (Figure 4). The addition of CI (Test 1), CI/BIO (Test 2), and the application of CI/BIO/pigging (Test 3) was shown to reduce the corrosion rate. The largest relative decrease in corrosion rate occurred in (in decreasing order) Tests 3, 2, 4, and Test 1. In contrast, the corrosion rates in Tests 5 and 6 increased.

Pitting

Pitting rates basically showed the same pattern as general corrosion rates as determined by weight loss (Figure 4). The deepest pits occurred on coupons which were exposed to CI only independent when nitrate was added (Tests 1 and 5); the least attack occurred in Test 2 (Figure 4). No certain pattern of pitting across the metal surface was observed on coupons among the tests, but it was positively related to the amount of present biomass in all tests (Figure 5). Pitting particularly occurred under thick accumulating biomass as revealed by 3-D profiling of the corrosion coupon surface (Figure 5). This implies the involvement of bacteria in the apparent corrosion, either by direct attack of the metal surface or indirectly by the excretion of corrosive metabolic products. In the absence of nitrate (as initially occured in Tests 5 and 6), sulphide produced by SRP can be corrosive. Nitrate can be reduced by heterotrophic and autotrophic NRB to corrosive nitrite and nitric oxide (3, 4, 5). In addition, the nitrate-driven oxidation of sulphide can lead to the production of highly corrosive polysulphides and elemental sulphur. The latter has in fact been detected in biofilms of Tests 2 and 5, while polysulphides have not been determined in this study.

The corrosion products were composed of the iron sulphides and iron oxides. Greigite (Fe_3S_4) was found in biofilms from Tests 4, 5, and 6, while Pyrite (Fe_2S) was present in biofilms from Tests 4 and 5. Indications for the presence of elemental sulphur (S_8) were found in Tests 2 and 5. The iron-oxides Goethite (FeOOH) and Magnetite (Fe_3O_4) were found in biofilms from Tests 1, 4, and Test 5.

The strongest attack predominantly occurred across the long edges of the metal coupons where they touched the coupon holders during the experiment. These areas experience reduced nutrient availability and reduced shear forces due to the low flow. This protected biofilm from detaching and could have provided niches in which corrosive bacteria persist and proliferate. Deep pits were also present on the edges of two neighbouring coupons, probably as a result of galvanic corrosion between the metal coupons and the present accumulating corrosion products. Results obtained here can be extrapolated to the field where weak points in the pipelines occur, such as welding joints and connections, as well as failures and impurities in the steel matrix (e.g., manganese sulphide inclusions). Such areas are most prone to biofouling and corrosion and particularly MIC.

Control of microbial activity

Souring control. The continuous addition of nitrate to Tests 1-4 kept the sulphide level in the bulk water low and sulphide was removed from the water within three weeks after nitrate addition to Tests 5 and 6. Consistent to the trend in sulphide was the stimulation of NRB and NR-SOB and the coinciding decrease in SRB numbers upon nitrate addition. Even though the concentration of sessile sulphide decreased towards the end of the experiment upon nitrate addition in all tests, trace amounts were detected in biofilms of Tests 4-6. This implies that with the addition of nitrate at a carbon to nitrate ratio of 1:3, souring control can be quickly achieved in the bulk water phase and more gradually achieved in the biofilm with a persistent sulphidic layer. Souring mitigation most likely was a result of nitrate-coupled sulphide oxidation.

Corrosion control. Comparison of the LPR rates from Tests 1-3 with Test 4 implies that the addition of CI together with nitrate, mitigated general corrosion (Figure 4). The CI was most effective in the tests with clean systems receiving nitrate. Dosages between 100ppm (Test 1) and 200ppm (Tests 2 and 3) of the product were used. The surface active compounds of the CI have presumably formed a film on the metal surface that effectively protected from general corrosion attack before the corroding biofilm developed. This is contrary to Test 5 where the CI was less effective. The sulphidic biofilm present in this system before CI addition commenced may have hindered the CI to diffuse to the metal and from forming a protective film. In fact, general corrosion rates in the same test were not affected by CI despite dosage increase over time from 25 to 400ppm. The concentration of 400ppm was eight times higher than that originally recommended by the manufacturer (50ppm). The unexpected high rates of both general and pitting corrosion in Tests 1 and 5 indicate that the CI did not mitigate pitting but induced or accelerated pitting under the test conditions. Many CI actually promote severe MIC pitting (6), particularly in high dosages, which demands for careful selection and further assessment of CI before and during field application when biofilm formation is involved.

The addition of BIO and combined pigging and BIO improved the mitigation from general corrosion in systems with nitrate present from day one. Since BIO addition reduced the corrosion damage this indicates that corrosion was influenced or caused by corrosive bacteria which were killed by the BIO. The proportion of MIC to the general corrosion rate is unknown from the current experiments. The removal of biofilm before shock dosing with BIO at 1000 ppm in presence of the CI and nitrate resulted in decreased general and pitting corrosion in Test 3 compared to all other tests. Whereas thin uniform iron sulphide layers on steel surfaces may protect from corrosion, thick and layered heterogeneous biofilms particularly when combined with scale, oil, waxes, and production chemicals often - but not always - cause destruction to the metal infrastructures in petroleum systems (1, 6). For this reason, any sort of biofilm and schmoo are regularly removed from the pipelines and tanks by pigging and jetting. The removal of biofilm can however be problematic if the released planktonic cells quickly re-grow to a biofilm. The elimination of planktonic cells by shock dosing with BIO may reduce biofouling and keep corrosion to a minimum. Based on LPR measurements, the treatment mitigated corrosion in the following order:

Combined BIO/CI/Pigging (Test 3) > BIO/CI (Test 2) > CI alone (Test 1)

The results show a direct interrelation of biomass and corrosion attack. They imply that the formation of differential corrosion cells on the metal surfaces through a mixture of biogenic matter and accumulating inorganic corrosion products (iron sulphides and oxides) are causative for the pitting attack. These findings highlight the need for further investigation of the complex microbial consortia involved in MIC, the potential role of nitrate in stimulating growth of the corrosive bacteria, and the microbe-metal interaction.

The redox potential at the metal surface in Tests 1 and 2 was elevated relatively to the control, indicating the presence of a lower amount of highly reduced species deriving from corrosion and microbial metabolic activity. One possible explanation for this is iron sulphide mineral oxidation with nitrate as the electron acceptor by

chemolithoautrotrophic bacteria, such as *Thiobacilli* (8) using inorganic sulphur compounds for growth. The role of the CI and BIO in the difference in redox potential inside the biofilm is unknown.

Sulphide produced by SRP reacts with iron from the anodic reaction during corrosion to form the iron sulphide products (5) Mackinawite, Greigite, and Pyrite as well as elemental sulphur. Except of Mackinawite, which has not been detected but nonetheless may have been transiently produced, Greigite and Pyrite have been detected in Tests 4-6. The presence of these minerals implies the presence of SRP activity. The formation of Greigite from Mackinawite requires the presence of an oxidant, which in the present tests are potentially iron oxides (Goethite, Magnetite), O_2 and S^0. The reactions occur according:

$$3\ FeS + S^0 \rightarrow Fe_3S_4 \text{ (Greigite)} \quad (1)$$

$$Fe_3S_4 + 2\ S^0 \rightarrow 3FeS_2 \text{ (Pyrite)} \quad (2)$$

The formation of Pyrite from Greigite requires strongly reducing (Eh below -250mV) conditions and high temperature (9). These conditions occurred on the metal surface as revealed by the microprofiles of redox potential (Figure 3) and pH (2). Nitrate could have served as terminal electron acceptor during the reactions either directly and abiotically or indirectly through microbial nitrate reduction, driving the formation of Greigite and Pyrite. The presence of a mixture of biogenic matter, iron sulphides, iron oxides, polysulphides, and elemental sulphur might have enhanced the formation of local differential corrosion cells that either caused or accelerated pitting. This also implies the presence of interacting microorganisms of the N- and S-cycle.

CONCLUSIONS

- The implementation of nitrate addition during PWRI requires to compromise between achieving souring control by using a rather high nitrate to carbon ratio and by minimizing corrosion with using a rather low nitrate dosage.
- The observed corrosion is proposed to be largely influenced by or due to microbiological activity. The results suggest that biofouling and corrosion can be managed in PWRI systems when control of microbial activity is achieved.
- Biofouling and MIC can be easier controlled in clean PWRI systems to which CI and BIO are added together with nitrate from the start, and is more difficult to control in systems with existing sulphidic activity.
- The recommended sequence of chemical application to obtain the best mitigation and protection of corrosion during nitrate injection to PWRI system is:
  1. Regular removal of existing biofilms;
  2. BIO addition to aid biological control during and after pigging;
  3. Continues CI addition to protect the cleaned surfaces, after pigging and preferentially at a low dosage.
- The dosages of added chemicals need to be adjusted according to the characteristics of and the dynamics in the given system. Chemicals and clean-in-place systems need to complement each other.

- The chemical addition need to be monitored to avoid unexpected changes with the age of the reservoir.

Understanding the corrosion mechanism and the identification of the bacteria responsible for corrosion requires more detailed studies. This sets a demand for the application of combined methods that resolve the interaction of the microorganisms and their ecosystem, i.e., the biofilm, the underlying surface, and the bulk water (2).

Onsite monitoring in dynamic flow through systems in the field is the best solution. Aquateam has recommended to operators that an integrated microbial monitoring system is built into the water system offshore, integrating the understanding of the operation of the injection water and the PWRI systems; if this is not possible or cost-efficient, laboratory studies simulating field conditions can be carried out (10).

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FIGURES

Figure 1. Flow-through systems. Biofilm coupons were placed horizontally in corrosion flow-through cells inoculated with produced, and receiving de-aerated artificial produced water.

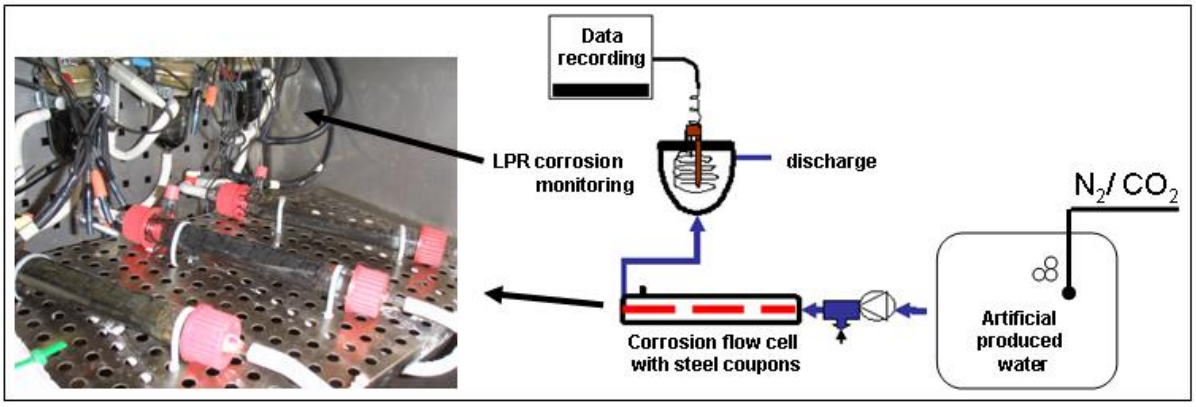
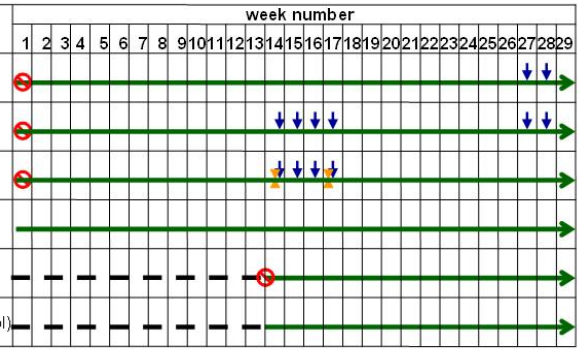


Figure 2. Tests performed. CI= Corrosion Inhibitor addition; BIO= Biocide addition

Test number	Aim of test
1	Effect of CI on nitrate-receiving biofilm
2	Effect of combined CI & BIO on nitrate-receiving biofilm
3	Effect of combined CI & BIO & pigging on nitrate-receiving biofilm
4	Nitrate-receiving biofilm without any other addtion (nitrate control)
5	Effect of combined CI & nitrate addition to biofilm without nitrate
6	Nitrate addtion to biofilm without any other addtition (no nitrate control)



Legend: Nitrate addition Biocide addition CI addition Pigging

Figure 3. Redox potential profiles in biofilms from test systems to which nitrate was added from week 1 (Tests 1, 2, 4) and from week 14 (Tests 5, 6). The position of the metal surface and the approximate biofilm-water interface is indicated by zero depth and by black horizontal lines, respectively.

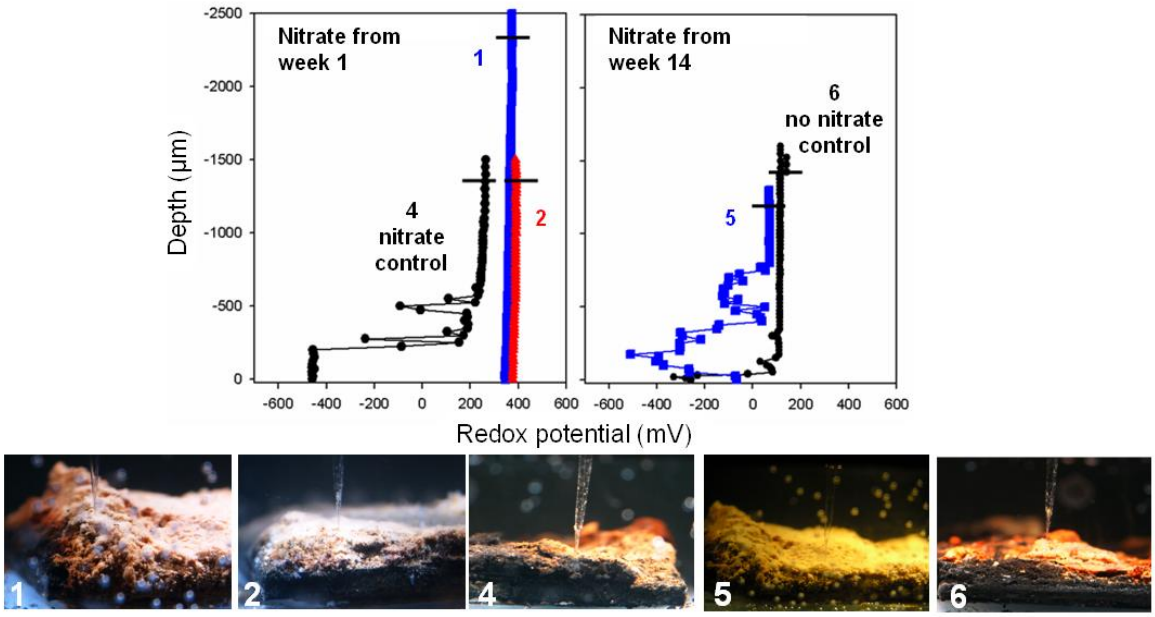


Figure 4. (**A**) Pitting rates (bars) and general corrosion rates from weight loss (black rectangles) of coupons from systems receiving nitrate from week 1 or from week 14.
(**B**) Average general corrosion rates as detected by Linear Polarisation Resistance over the course of the experiment.

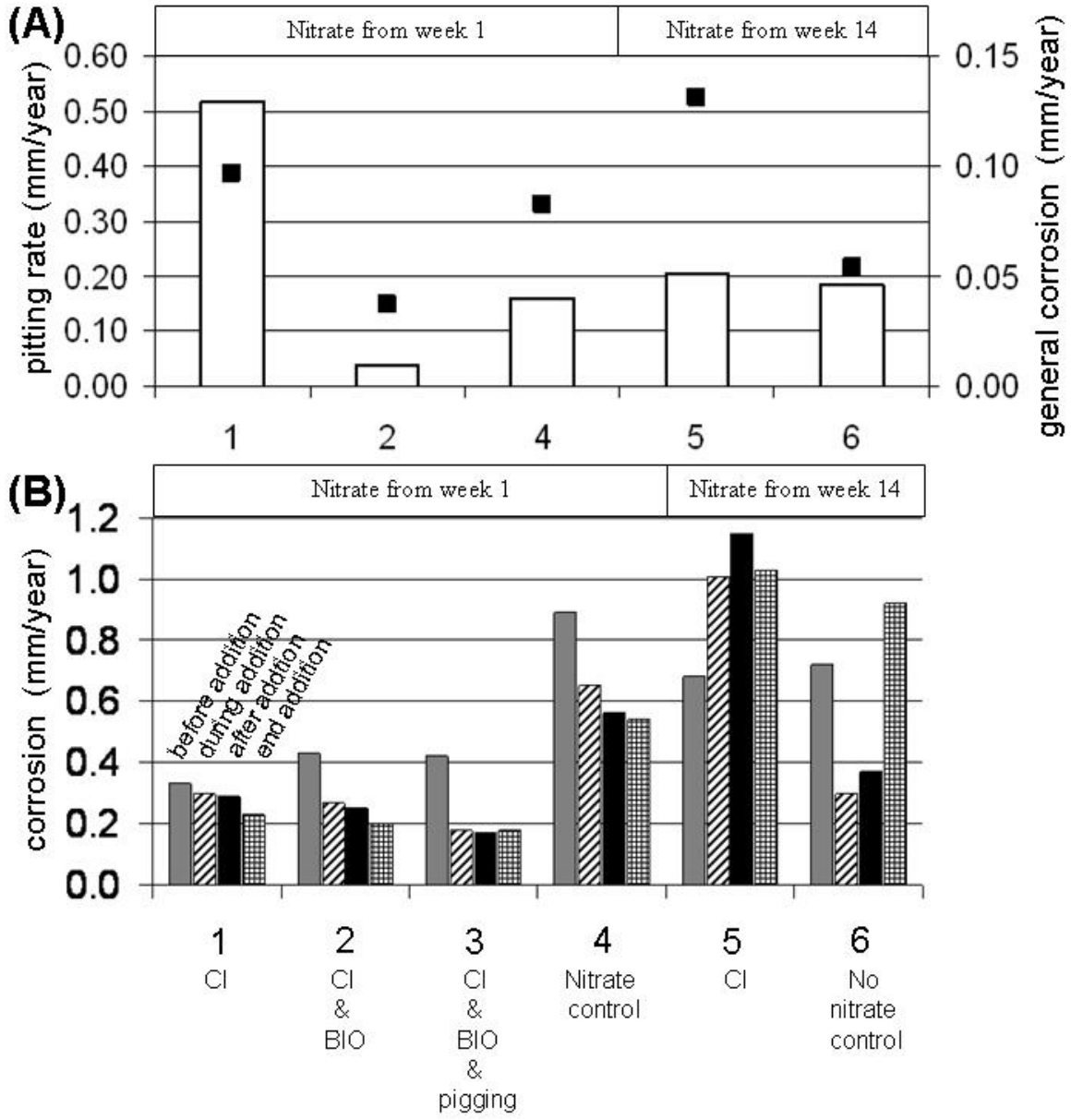
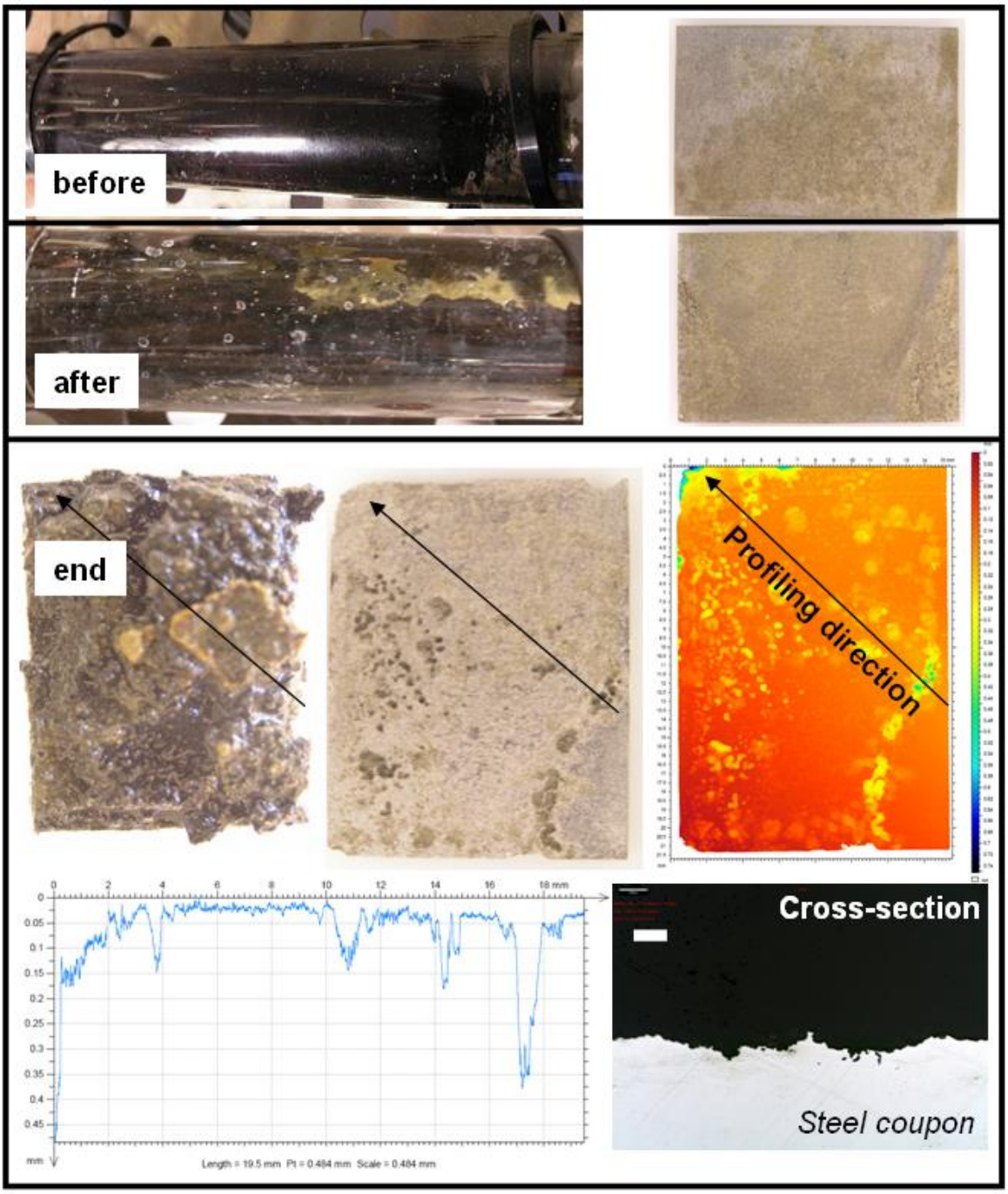


Figure 5. Biofilms and coupons before (top) and after (middle) combined addition of corrosion inhibitor and nitrate (Test 5). 3-D profilometry results at the end of the experiment (bottom); black arrows indicate the direction of the surface scan. Scale bar = 100 µm



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