

**Investigation of Under Deposit
Corrosion (UDC) in Halfdan Production Tubulars**

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ABSTRACT

Based on tubulars retrieved from Halfdan producing wells with low CO₂ and H₂S content an under deposit corrosion mechanism has been suggested involving multiple parameters including scale buildup, microbiologically influenced corrosion (MIC) and the formation of green rust.

Laboratory experiments were conducted with the aim to propose a predictive tool that may be used to establish the risk of corrosion in Halfdan production tubulars. A simplified laboratory test design was developed to evaluate the influence of different chemical parameters including gas composition, general water chemistry and temperature to simulate downhole conditions.

Initially, experiments with the simplified test design have shown that it is possible to simulate conditions where scales formed on weight loss coupons develop a structure with good resemblance to scales found in production tubulars in the Halfdan field.

Results from weight loss coupons and electrical resistance (ER) probes showed that temperature plays an important role in the morphology of scales formed under comparable chemical conditions. Consequently, changes in temperature play a role in the likelihood of initiating localized corrosion.

Laboratory experiments, field data and mechanistic understandings suggest a predictive tool to evaluate the risk of corrosion may be proposed based on known parameters and experimental results.

Key words: Danish Sector of the North Sea, Halfdan oil field, Microbiologically Influenced Corrosion (MIC), green rust (GR), under deposit corrosion (UDC), predictive corrosion risk tool.

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INTRODUCTION

The Halfdan field is located in the Danish sector of the North Sea. Many of the wells have produced primarily oil in the recent years, but have seen increasing water cuts over time, with water cuts reaching more than 90 % in many cases. Most producing wells at the Halfdan field are completed with API/ISO L80-1 tubings and exhibit low corrosion rates and formation of thin, sulphide rich scales. However, in some wells localized corrosion under a 5-10 mm thick scale has been observed. Examinations of retrieved tubing parts have revealed that these scales are typically layered with a thick iron sulphide scale on top of chloride rich corrosion products (green rust) close to the metal surface at sites of corrosion, figure 1.

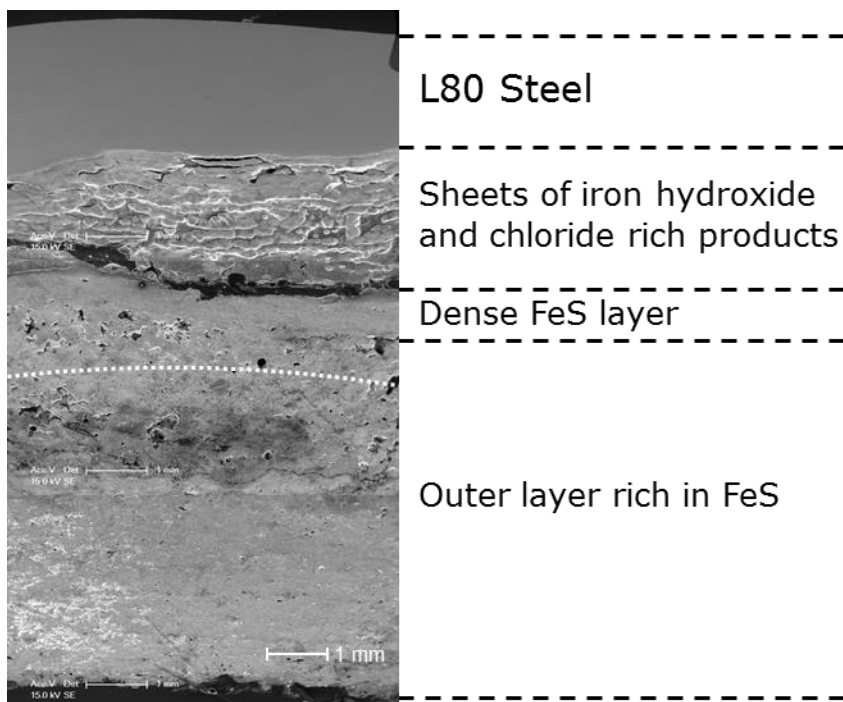
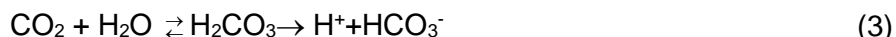
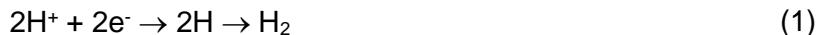


Figure 1. SEM photos merged to show the entire cross-section of scales observed in retrieved tubing parts from the Halfdan well HDA-01XD. The dotted red line indicates the position of the original inner diameter of the tubing.

Based on the chemistry of the Halfdan produced water and the assumed well conditions, pH in the production fluids may be in the range of 6.3-7.0, and in case of seawater ingress may be slightly lowered. The redox potential E_h is presumably -0.5 V vs SHE. In the anoxic media, the dominating cathode reaction is reduction of hydrogen ions, reaction (1), delivered by the weak acids present, reactions (2)-(5).



Thermodynamical calculations for seawater with low CO₂ contents representative of the Halfdan field have shown, that iron carbonates are not likely to form, and in the pH range considered Fe²⁺, FeOOH and Fe₃O₄ may form¹. However, if H₂S is present even in low amounts, iron sulfides (FeS, FeS₂) may thermodynamically be the stable product formed. Based on potential-pH diagrams it was shown that uniform corrosion may dominate as long as the media lacks H₂S, but the corrosion rates are limited by the fairly low H⁺ activity¹. Formation of oxides and hydroxides may occur. As the H₂S concentration increases, formation of iron sulfide film may reduce corrosion rates, if it is protective, or facilitate localized corrosion, if it is patchy or porous. At neutral pH and low H₂S concentration the latter is the most likely.

CO₂ and H₂S concentrations are very low in the Halfdan field. Recent papers by Crolet and Bonis describe that for downhole conditions, oil wells with high H₂S or high CO₂ concentrations are not corrosive, since protective corrosion product layers are formed, however, for low concentrations there is a large risk of corrosion^{2,3}. In their logigram on downhole weak acid corrosion, Halfdan wells would probably be predicted to be corrosive by the category “FeS + other salts”. This category is defined by a certain very low H₂S mole fraction and the formation of deposits of iron sulfide (mackinawite FeS), iron carbonate (siderite FeCO₃) and iron chloride (FeCl₂). These layers are non-protective, yet insoluble, layers of corrosion products in which an internal high solubility of iron is withheld due to a local shortage in either H₂S or in both H₂S and CO₂, which would otherwise deliver the anionic ions needed to form iron sulfides or iron carbonate. Due to shortage of both gasses, the liquid media inside the porous deposits may locally become totally unbuffered by HCO₃⁻ and reach very low pH values (6,7).



A mechanism has been suggested that may explain the observed deposits and the development of localised corrosion observed in samples from tubings retrieved from the Halfdan field¹.

The suggested mechanism is based on examinations of samples from retrieved tubing parts with slightly oxidized corrosion products (due to onshore storage) supplemented with calliper data from wells and information on the prevailing water chemistry during operation.

The mechanism is an under deposit corrosion type facilitated by non-protective iron sulphide and an acidic, chloride rich media keeping the anode pits active. Central in the suggested mechanism is a green rust GR(Cl⁻) layer characterized as an ionic water containing mineral.

The history of the completion may be linked to the mechanism through three main phases: pretreatment, initiation, and propagation.

Pretreatment during the completion involves that tubulars covered with mill scale may be exposed to fluids based on seawater like completion fluids, hydrochloric acid for stimulation, residues of drilling mud, as well as formation water. This may lead to formation of a moderate layer of partially protective corrosion products and microbial cells from the seawater-based fluids may settle on the surfaces.

Initiation occurs after production has started. Depending on operating conditions, water cut and presence of scale forming compounds, other organic and inorganic deposits may form. Chlorides may migrate to the metal surface increasing anodic dissolution, or may be incorporated in the corrosion products present on the surface. Localization may be triggered under the deposit if the film properties facilitate the development of a different media at the metal surface. The initiation of a pit may be random or linked to a specific condition, e.g. the spatial distribution of MIC related organisms supporting pH and redox variations, or a more sensitive metallurgical site. Corrosion may also be triggered by external factors affecting the scale protectiveness, e.g. increased water cut, seawater breakthrough, increased H₂S concentration, production variations, redox potential and pH variations as e.g. under acid jobs and workovers.

Propagation initially results in growth of pits. When a corrosive media has formed under a non-protective layer, corrosion may proceed as a selective leaching of the ferrite phase in the steel, which requires inwards diffusion of chloride, and outwards diffusion of ferrous ions. The ferrous ions are deposited in the scale, e.g. as iron hydroxides or iron sulphides, when the ferrous ions reach a sulphide rich zone. Green rust and iron chlorides keep the anode area active and ensure presence of a liquid phase. The cathode area may either be located at the mouth of the pit, on the adjacent surfaces of steel, or on conductive products formed, e.g. iron sulphides or magnetite. Potentially the mechanism is self-sustaining and independent of the bulk environment. The suggested mechanism is illustrated in figure 2.

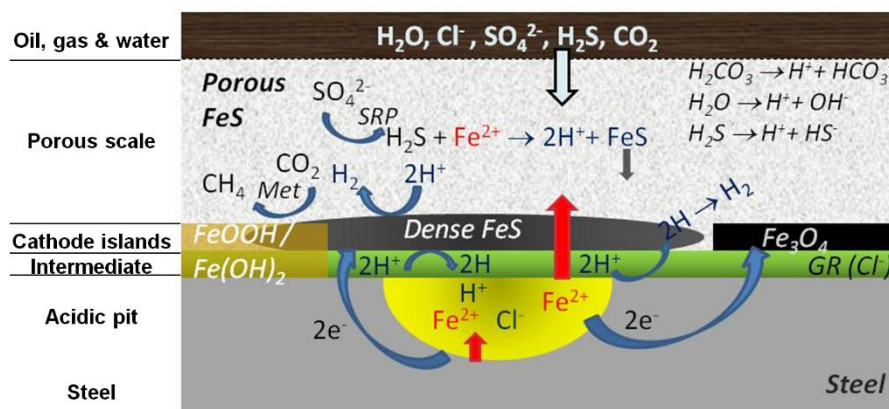


Figure 2. Schematic illustration of the proposed Halfdan under deposit corrosion mechanism, showing a fully developed attack.

The hypothesis needs further documentation and clarification. Especially the factors involved in initiation of localized corrosion sites including the interconnection between chemical and microbiological reactions in the deposit. The presence of microbial activity is of importance to the corrosion attack in some – but not in all – cases.

The chemistry of the sulphide compounds inside the deposit is of major importance, as the effect of hydrogen sulphide may vary from forming an efficiently protective passive film to being oxidised to corrosive sulphur compounds. Also, on Halfdan nitrate is added continuously to the injection seawater in order to mitigate reservoir souring. Nitrate is microbiologically reduced to nitrite, nitrogen or ammonium. In terms of corrosion the presence of nitrite could be critical as a potent oxidising agent which in the anoxic system could act as a cathodic reaction in a corrosion cell.

Examples from Halfdan wells

The current understanding of the corrosion mechanism of production tubulars is partly based on examination of tubings retrieved during workovers. A large variation in condition and extent of corrosion is observed. Selected chemical and physical parameters for two producing Halfdan wells are shown in Table 1 and 2.

**Table 1
Selected chemical data for produced water (approximate levels)**

Well	Na	Cl	SO ₄ ⁻	Mg	Ca	K	Sr
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
HDA-06	25,000	42,000	750	270	1,100	250	180
HDA-01XD	12,000	20,000	2,200	1,200	550	400	20

Table 2
Selected chemical and physical parameters

Well	BHT	THT	Watercut	H ₂ S	CO ₂
	°C	°C	%	ppm	mole-%
HDA-06	82	68	45-82	20-60	0.05-0.2
HDA-01XD	75-60	52-48	0-70	8-140	0.05-0.1

THT: Tubing head temperature. **BHT:** Bottom hole temperature.
Gas concentrations measured at test separator.

HDA-06

Examination of tubulars from the producer HDA-06 after 12 years of production showed that the tubing parts were generally in good to moderate condition with varying amounts of pits having a depth of 0.5 to maximum 1.5 mm. The surfaces were covered with a very thin scale of less than 1 mm thickness, and scale analyses showed that the thin deposits consisted primarily of sodium chloride and sodium bromide as well as magnetite.

The HDA-06 well had been in production for 12 years and was not affected by seawater ingress, so the produced water resembled formation water (Table 1). From the beginning, the watercut had been quite high, but H₂S and CO₂ concentrations were low. The dominating corrosion mechanism was pitting, presumably due to local breakdown of the thin magnetite layer caused by the high salinity of the well media. No MIC investigation was carried out, as only very thin scale layers were present.

HDA-01XD

Examination of tubulars from the spine well HDA-01XD after 12 years of production revealed severe corrosion with corrosion attacks of 3-4 mm depth and penetration in pin ends, and multiple full wall penetrations in tubulars with a wall thickness of 7 mm were identified by multifinger caliper tests. The examination of the tubing parts showed that corrosion in HDA-01XD occurred under a 5-10 mm thick layer of iron sulphide minerals covering chloride-rich corrosion products (green rust) and magnetite close to the metal surface (i.e. under-deposit corrosion facilitated by iron sulphide). The risk of MIC was evaluated using the Maersk Oil[†] in-house MIC model⁴ and q-PCR analyses of solid samples retrieved from the wells. The risk of MIC was regarded as low since no MIC related microorganisms were detected in the analysed solids.

Overall, fast permeating injection water (seawater) ingress has dominated the water phase throughout most of the well's production life (Table 1). Corrosion of the tubing parts has supposedly started as pitting corrosion on a steel surface originally covered with magnetite, which locally has been attacked by media rich in chloride. Galvanic corrosion has then occurred due to the relative nobility of the magnetite. A thick layer of iron sulphide minerals has afterwards been formed on top of the corroding surface, thus changing the mechanism to under deposit corrosion over time.

Based on experience from the Halfdan wells it has been a goal to develop a tool for prediction of corrosion risk in Halfdan downhole tubular materials and to simulate under deposit corrosion. The initial objective was to attempt to reproduce scales with similar characteristics as scales found in Halfdan producing wells, where under deposit corrosion has been observed (figure 1). Thus, initial coupon experiments were performed with the primary concern to reproduce the visual appearance of scales.

[†] Trade name

EXPERIMENTAL

Weight loss coupon tests

Weight loss coupons of API/ISO L-80-1 steel, table 3, were exposed in deaerated artificial seawater, table 4, at ambient pressure and preconditioned with a gas mixture of 0.25% H₂S, 5% CO₂, rem. N₂.

The first set of exposure tests were carried out at three temperatures; 40 °C, 60 °C and 80 °C. Test temperatures represent temperatures reported in production data from Halfdan producing wells. Temperatures of 80 °C and 60 °C represent bottom hole temperature, BHT, and tubing head temperature, THT, at initial production and temperatures of 60 °C and 40 °C represent BHT and THT in wells with direct fracture to injection wells.

During exposure of coupons the artificial seawater was purged with a gas mixture of 0.25% H₂S, 5% CO₂, rem. N₂ interrupted for short periods of purging with atmospheric air. Details for test conditions and purging times are shown in table 5.

Injection water used at the Halfdan field is deaerated seawater with biocides, thus purging for short periods with atmospheric air was chosen to accelerate scale growth rather than to simulate the actual environment. However, in case of interventions where oxygen-containing seawater for some reason enters the tubings, oxygen may potentially be introduced temporarily, and effects may be severe⁵.

Test coupons were removed from the test solution after 1 week of exposure and after 2 weeks of exposure respectively.

Table 3
Specification and chemical composition of API/ISO L80-1 steel coupons

	C%	Si%	Mn%	P%	S%	Cu%	Cr%	Ni%	Mo%	Al%
Spec. (min)	-	-	-	-	-	-	-	-	-	-
Spec. (max)	0.43	0.45	1.90	0.030	0.030	0.35	-	0.25	-	-
Measured	0.26	0.29	0.78	0.012	0.003	0.02	0.99	0.03	0.29	0.044

Table 4
Chemical composition of artificial seawater

Compound	NaCl	MgCl ₂	Na ₂ SO ₄	CaCl ₂	KCl	NaHCO ₃	KBr	H ₃ BO ₃
Concentration g/L	24.53	5.20	4.09	1.16	0.695	0.201	0.101	0.027

The chloride content of the artificial seawater is 19.38 g/L and the pH value (after adjustment with 0.1 mol/L NaOH solution) is 8.2.

Table 5**Test conditions. First set of exposure of API/ISO L80-1 steel coupons at fixed temperatures.**

Period		time [h]	Purging gas	Test temperatures		
A-B	Preconditioning	24	0.25% H ₂ S, 5% CO ₂ , rem. N ₂	40 °C	60 °C	80 °C
B-C		24	atmospheric air			
C-D	Test week 1	144	0.25% H ₂ S, 5% CO ₂ , rem. N ₂			
D-E		20.25	atmospheric air			
E-F	Test week 2	144	0.25% H ₂ S, 5% CO ₂ , rem. N ₂			
F-G		20.25	atmospheric air			

The second set of exposure tests were carried out at three temperatures; 40 °C, 60 °C and 80 °C. During exposure of coupons the artificial seawater was purged with a gas mixture of 0.25% H₂S, 5% CO₂, rem. N₂. The test solution was kept free from oxygen during the entire test period. Details for test conditions and purging times are shown in table 6.

Table 6**Test conditions. Second set of exposure of L-80 steel coupons at fixed temperatures.**

Period		time [h]	Purging gas	Test temperatures		
A-B	Preconditioning	1	0.25% H ₂ S, 5% CO ₂ , rem. N ₂	40 °C	60 °C	80 °C
C-D	Test period 1	265-266	0.25% H ₂ S, 5% CO ₂ , rem. N ₂			
E-F	Test period 2	431-433	0.25% H ₂ S, 5% CO ₂ , rem. N ₂			

After removal from the test solutions, coupons were dried in ambient environment and examined visually. Coupons for weight loss were weighed, cleaned in inhibited hydrochloric acid, rinsed with demineralised water and weighed again. The weight of scales and weight loss of the base material was determined on 5 coupons from each exposure, and 2 coupons from each exposure were prepared for examination of cross sections in light optical microscope, LOM, and scanning electron microscope, SEM.

Electrical resistance probe tests

As an initial approach to further investigate the temperature dependency of corrosion rates and the formation of scale, a revised test setup with fixed chemical environment and alternating temperatures was designed.

Tests were carried out in test cells with artificial seawater continually purged with a gas mixture of 0.25% H₂S, 5% CO₂, rem. N₂ at ambient pressure. The test cells were equipped with electrical heating elements that allowed the possibility to stepwise change the test temperature during test. Corrosion was measured using electrical resistance probes (ER). Corrosion rate measurements were carried out by use of a specialized, non-intrusive, high sensitive ER-technique based on a differential measurement on a test coupon and a reference coupon⁶. The ER-probes used were laboratory coupons with an element thickness (d_0) of 100 μm and an area of 1 cm^2 . This technique was selected, as previous investigations have shown it to provide reliable measurements in sulphide media, where electrochemical measurements may disturb the corrosion processes and/or give unreliable results⁷.

Two test cells with different initial temperatures were set up with one test cell starting at 40 °C and one test cell starting at 80 °C. During test, the temperature was increased/decreased in steps of 5 °C per day.

RESULTS AND DISCUSSION

Weight loss coupons

Scales formed on coupons during the first set of exposures with short periods of purging atmospheric air had different visual appearances depending of the temperature during exposure. Coupons exposed at 80 °C appeared very black with thin dense scales uniformly distributed over the entire surface of the coupons. Coupons exposed at 40 °C appeared dark greyish with loose porous scales that had an almost dust like appearance. Scales were uniformly distributed over the entire surface. Scale formed on coupons exposed at 60 °C did not have the same appearance over the entire surface. Some areas had an appearance resembling the scales seen on coupons exposed at 80 °C and on other areas the scale showed better resemblance to the scales seen on coupons exposed at 40 °C.

The weight of scales after drying and the weight loss of the base material was determined. Results calculated as average scale-growth rates and average corrosion rates are shown in figure 3.

At 80 °C the calculated average corrosion rate on coupons after 14 days of exposure was significantly lower (2/3) than the average corrosion rates calculated after 7 days of exposure. This indicates that the scales formed during the first week have a protective nature. Coupons exposed at 40 °C and 60 °C did not show any measurable decrease in average corrosion rate on coupons exposed for 14 days. The highest corrosion rates were measured on coupons exposed at 60 °C.

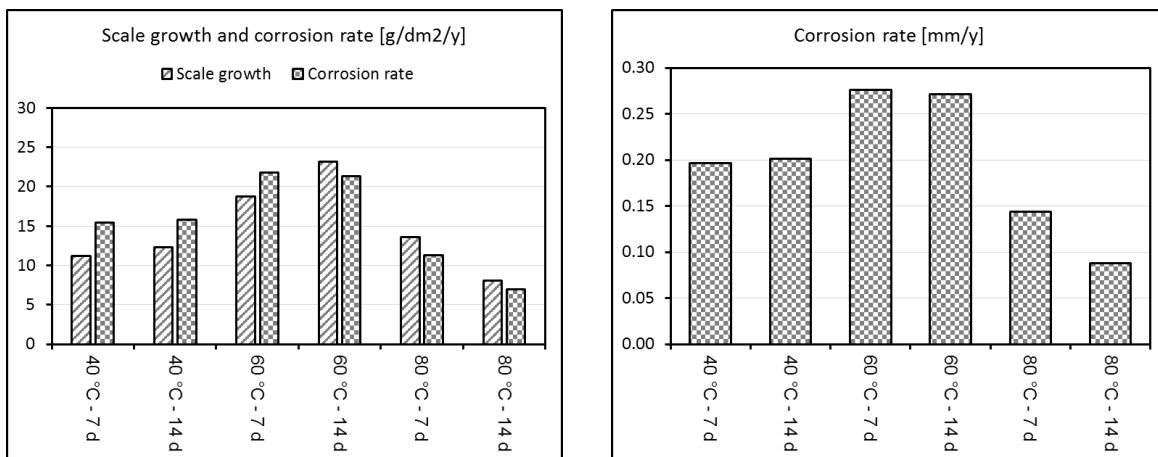


Figure 3. Average scale-growth rates and average corrosion rates calculated from weight of scales after drying and weight loss of the base material. Coupons exposed to alternating environment with periods of purging with atmospheric air

SEM/EDX examinations of coupon cross sections showed that the scales formed during the test showed good resemblance to the scales formed in Halfdan production tubulars. A relatively dense iron sulphide layer was observed close to the API 5CT L80 steel surface. On top of the relatively dense layer more porous iron sulphide rich layers were observed. The thickness of the scales varied considerably, but scales formed on coupons exposed at 60 °C were generally thicker than scales formed at 40 °C or 80 °C. An example of a scale formed after 14 days exposure at 60 °C is shown in figure 4, including selected results from element mapping by SEM/EDX.

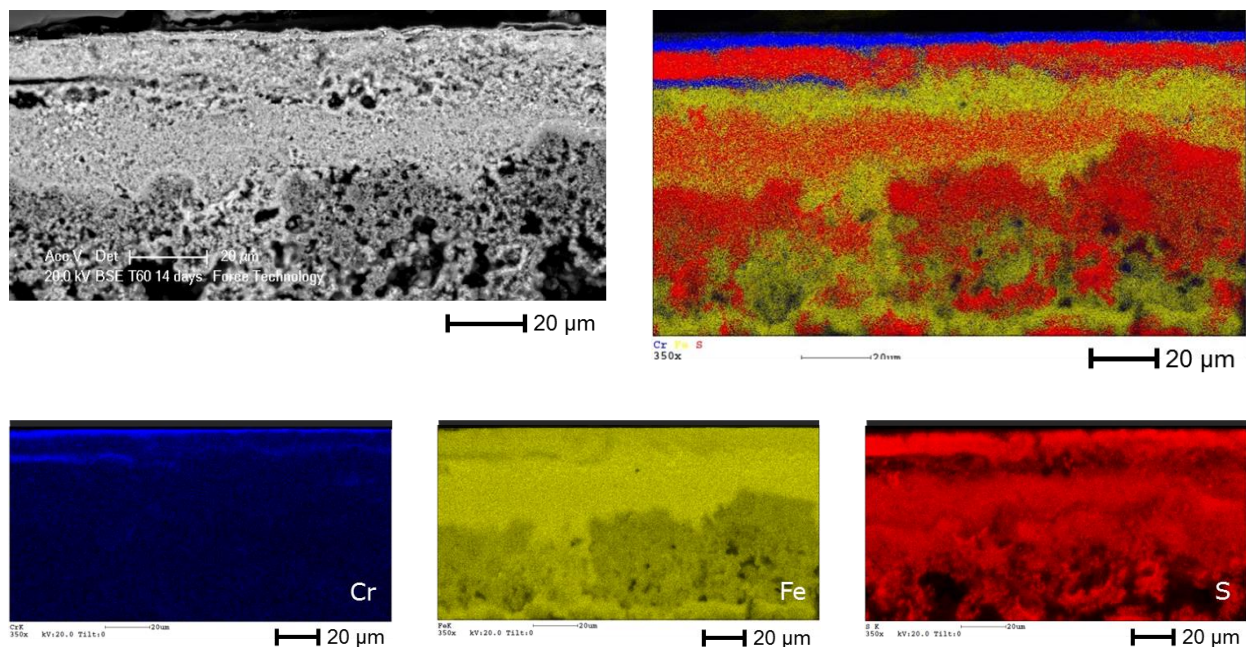


Figure 4. SEM photo of cross section of scale formed during 14 days exposure at 60 °C including selected results from element mapping. A relatively dense iron sulphide layer is observed close to the API 5CT L80 steel surface (top).

Scales formed on coupons during the second set of exposures with no purging of atmospheric air also varied in visual appearance depending of the temperature during exposure. However, the visual difference between coupons exposed at 40 °C and 60 °C was less pronounced. The scales formed at coupons exposed at 60 °C appeared more uniform than scales observed on coupons exposed in artificial seawater with short periods of purging with atmospheric air. Scales formed on coupons exposed at 80 °C were very similar in both sets of exposure, with black, thin and relatively dense scales uniformly distributed over the entire surface of the coupons. Scales formed at 80 °C during the second set of exposures with no purging of atmospheric air appeared visually thinner than scales formed during the first set of exposure.

Cross sections of scales formed on coupons revealed common characteristics in morphology but with variations depending on temperature of exposure, figure 5. At all temperatures, the scales observed in the cross sections were layered. Closest to the coupon surface one or two dense layers have formed on top of which a very loose porous layer was observed. The difference in thickness of scales formed after app. 265 h and app. 430 h was little, suggesting that the first period of exposure is very important to the formation of more or less protective sulphide scales.

At 80 °C a very thin scale had formed (<20 µm). Dense scales formed closest to the coupon surface varied from 5-10 µm and the thickness of the outer porous scales was similar. Scales formed at 40 °C and 60 °C was 4-5 times thicker (40-50 µm) than scales observed on coupons exposed to 80 °C. At 60 °C the thickness of the inner dense scales was comparable to the thickness of scales found on coupons exposed at 80 °C. The outer porous scales were very thick (30-50 µm). At 40 °C the dense scales formed closest to the coupon surface was incoherent. In some areas dense scales were thick (15-30 µm) and in other areas of the cross sections the dense layers were absent. Areas with thick dense scales showed signs of initial phases of localized corrosion. The total thickness of scales formed on coupons at 40 °C was app. 50 µm.

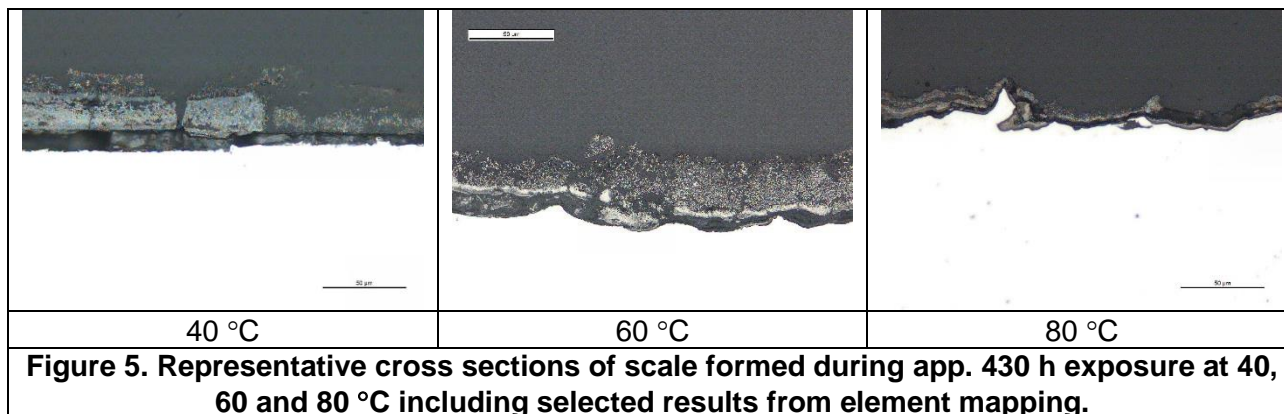


Figure 5. Representative cross sections of scale formed during app. 430 h exposure at 40, 60 and 80 °C including selected results from element mapping.

The weight of scales after drying and the weight loss of the base material was determined. Results calculated as average scale-growth rates and average corrosion rates are shown in figure 6.

At 80 °C the calculated average corrosion rate on coupons was significantly lower than the average corrosion rates observed from weight loss on coupons exposed at 40 °C and 60 °C. The difference in calculated corrosion rate after 265 h and 431 h was low indicating that the initial formation of a stable iron sulphide scale with protective nature occurs within a very short period after starting exposure. Coupons exposed at 40 °C for 266 h showed high corrosion rates compared to corrosion rates at other exposures. It is suspected that this may have been caused by unintentional oxygen ingress.

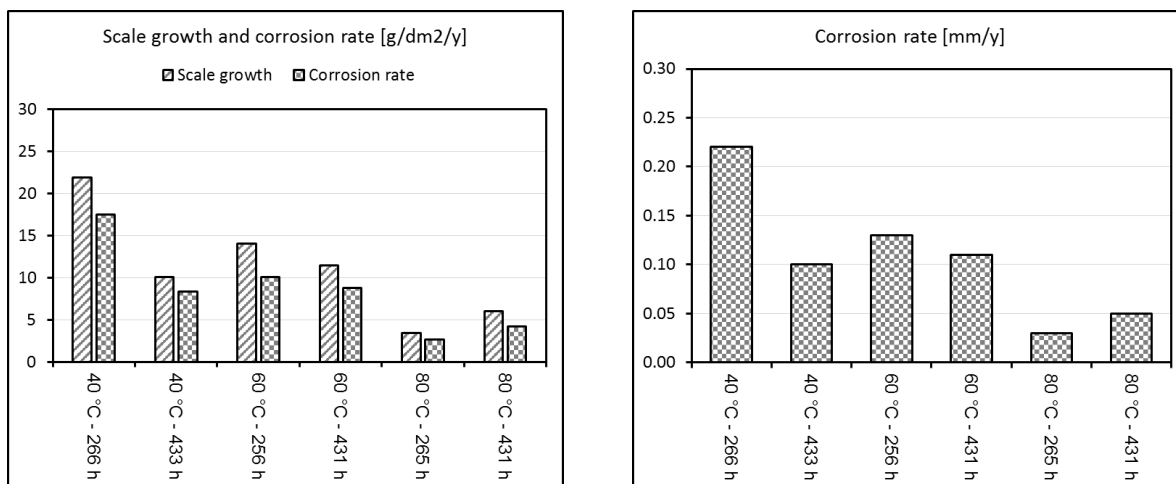


Figure 6. Average scale-growth rates and average corrosion rates calculated from weight of scales after drying and weight loss of the base material. Coupons exposed artificial seawater constantly purged with a gas mixture of 0.25% H₂S, 5% CO₂, rem. N₂.

ER-probe tests

The results of the ER-probe tests at varying temperatures are shown in figure 7 below.

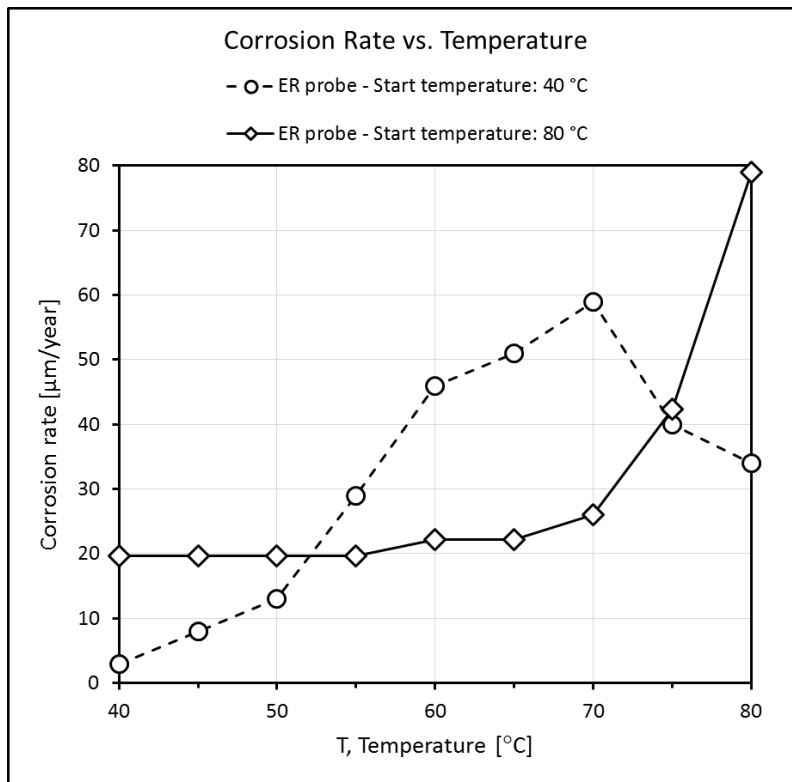


Figure 7. Corrosion rate vs. temperature measured with ER probes. One test cell starting at 40 °C and one test cell starting at 80 °C. During testing, the temperature was increased/decreased in steps of 5 °C per day.

The ER probe starting exposure at 40 °C measured an increasing corrosion rate with increasing temperature until 70 °C. From 70 °C to 80 °C the measured corrosion rate decreased. The ER probe starting exposure at 80 °C measured a decreasing corrosion rate with decreasing temperature until approximately 65 °C. At temperatures below 65 °C the corrosion rate was relatively constant at approximately 20 μm/y.

The results show that the initial test temperature greatly affected the resulting corrosion rates when the test temperature was changed. The correlation between corrosion rate and temperature was different when starting exposure at high temperature as opposed to starting exposure at low temperature.

Results were consistent with findings in earlier experiments indicating that the scale formed during the first week at 80 °C have a more stable protective nature than scale formed at 40 °C. In addition, the results suggest that the protective nature of the scale formed at 80 °C was a controlling factor to the resulting corrosion rate as the temperature was lowered.

The rate of temperature change used in the test has been 24 h. However, 24 h at a constant temperature might not be sufficient to achieve a stable corrosion rate at a specific temperature thus affecting the absolute values measured.

CONCLUSIONS AND OUTLOOK

Comparison of examined coupons from exposure tests and the examined samples from production tubulars indicate resemblance in composition and structure, though the short duration of the exposure test was insufficient to achieve a fully developed UDC.

Both coupon exposure tests and ER-probes indicate that temperature is of major importance for the type and rate of corrosion. At high temperatures (app. 80 °C) the surfaces are passivated relatively fast, and corrosion rates decrease, whereas somewhat lower temperatures result in poor passivation and higher corrosion rates. Coupon exposure tests suggest that the scale formed at lower temperatures (40 °C and 60 °C) are poorly protective and increase the risk of localized corrosion. This result is supported by observations from producing wells, where fast permeating injection water and lower resulting temperatures have been associated with fast developing corrosion in production tubulars. On the other hand wells with high initial water cut, relatively high H₂S-partial pressures and high production temperatures will normally have fast passivation of steel tubular surfaces resulting in long tubular life.

The results presented are part of an ongoing project, and parameter studies have been initiated to further establish the effect of variations in temperature, water composition, gas composition etc.

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