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Subsea Corrosion Management: Challenges and Limitations

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ABSTRACT

Subsea structures such as manifolds, line pipes and flow lines are important investments. Also because of the sensitivity of environmental issues, corrosion of these structures is of vital importance. Subsea corrosion management is different from on-shore and shallow water off-shore corrosion management in mainly three factors: materials, corrosion management practice and cathodic protection. There are important limitations in many aspects of these three factors that make them different from their "counterparts" in other industries. In this paper, some of these differences especially with regards to corrosion prediction softwares and associated design strategies are addressed and discussed.

1. Introduction

Deep sea oil and gas industry is becoming more and more an attractive option for energy-thirsty industry. In addition to its various economical benefits, it also has its dangerous downsides, mainly ecological. With no doubt corrosion is a significant issue in these structures that can lead into ecological disasters. Any failure in the deep sea structures (manifold, line pipe, flow lines …) could be disastrous. Unlike on-shore structures or even shallow water structures, the access for regular monitoring and repair is not an easy option, in terms of both the cost and the accessibility. Therefore corrosion management for the subsea structures mostly rely on the estimation of corrosion rates. These corrosion rates themselves are calculated based on semi-experimental research results and therefore, are always limited in terms of their assumptions and applications. In this paper we will review some important features of deep sea corrosion issues and the main counter-measures to address such issues.

2-Some of the highlights for the corrosion management of deep sea structures:

There are mainly three aspects of deep sea structures corrosion management (DSCM) that make them different from on-shore and shallow water structures corrosion management (OF/SW CM) techniques:

- Materials
- Corrosion Management Practice
- Cathodic Protection

These three issues are important in the sense that when they are taken together, they can define the job description of a typical subsea corrosion engineer and differentiate it from that of a, say, corrosion engineer who works in mining industry.

Materials

The variety of materials that are used in OF/SW CM applications is not seen with DSCM. This is in fact dictated by the corrosion models and their underlying design philosophy. The materials of frequent use in pipes for subsea applications are [1]: (carbon) steel, stainless, duplex and superduplex stainless steels, clad and titanium pipes. A more general classification of t he materials can be either:

-Carbon steel (clad or lined)
-Corrosion resistant alloys (CRA) such as but not limited to duplex stainless steels (DSS)

Clad steel plate is a composite steel plate made by (metallurgical) bonding the cladding material (such as all types of stainless steels, nickel and nickel-copper alloys and Titanium) to either or both sides of a carbon steel or low alloy steel plate (base metal). While different methods may be used to apply the cladding, both the economy and the available sizes of the final product are important factors, in addition to mechanical properties, that will affect the use of these materials. However, it must be noted that as application of these methods can change the overall microstructure, it can have some unwanted effects as well: a study on stainless-cladded carbon steels by hot-rolling shows that the following changes in the bimetallic microstructure has happened [2]:
-formation of a decarburized region near the carbon steel side,

- a hardened region with high carbon content at the stainless steel side where a partial Cr depletion had occurred.

These micro structural changes along with the formation of residual stresses –which mostly have tensile natures- can be leading into premature failures.

An example of CRA is duplex stainless steel. These steels are mainly charcterised by their “dual” crystal structure, Figure 1:

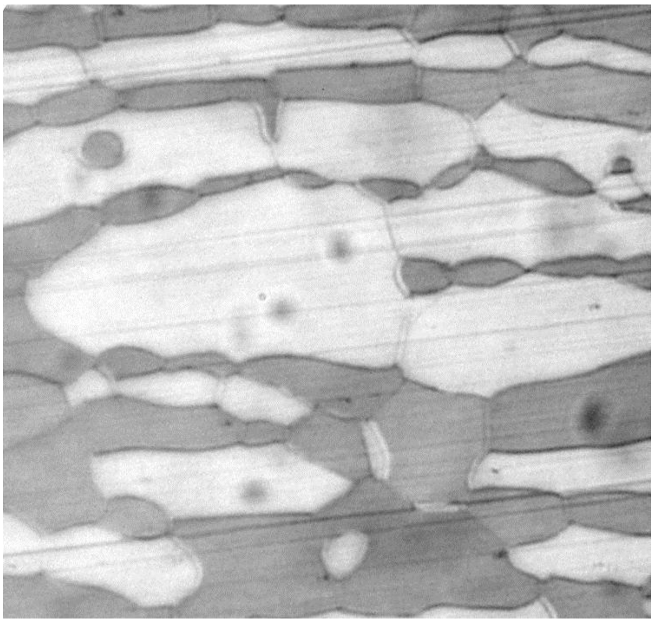

Figure 1. An example of the microstructure of a duplex stainless steel (SAF2205): (bright: austenite, dark: ferrite). The structure shows 52 ± 2 wt% retained austenite.

Duplex stainless steels are taken more corrosion resistant than austenitic stainless steels owing to their relatively higher chromium content. A very important issue with duplex stainless steels is the spacing between austenite islands as short austenite spacing is normally preferred due to both shorter hydrogen diffusion paths, more “hydrogen” tapping and crack stop properties [3].To avoid hydrogen induced stress cracking (HISC), based on deformation mode and induced strains, an austenite spacing from less than or equal to 30μ to 60 μ [4].

Corrosion Management:

Corrosion management includes items such as corrosion allowance, corrosion models and inhibitor availability and the like.

In contrast to many on-shore corrosion management techniques, subsea corrosion management still applies “corrosion allowance”. This is in essence the extra thickness of the pipe wall to compensate for corrosion. While it may appear as a simple issue of just adding “a few” millimeter to the net thickness of the pipe (to get the nominal thickness), this corrosion management technique has huge economical and application impacts, a rather “classical” example in this regard is for a pipe line of 8-in. diameter and 225 miles (~362 km) long and a wall thickness of 0.322 inches, by increasing the thickness by only 0.250 inches, an extra 3700 tons of steel will be needed as well as well as decreasing the internal capacity by 5% [5].

Corrosion modeling and inhibitor availability are the main two features that define the main differences between corrosion prediction models [6]. In these models the type of inhibitor (cathodic, anionic or mixed) is of no importance and the assumption is that whatever the mechanism of action, it is the availability of the inhibitor that matters. Corrosion models can be classified into two groups, “conservative” BP (Cassandra) and NORSOK (and their various in-house alternatives) and rather “liberal” Shell model [6]. Figure 2 schematically shows some of the features of these modeling approaches:

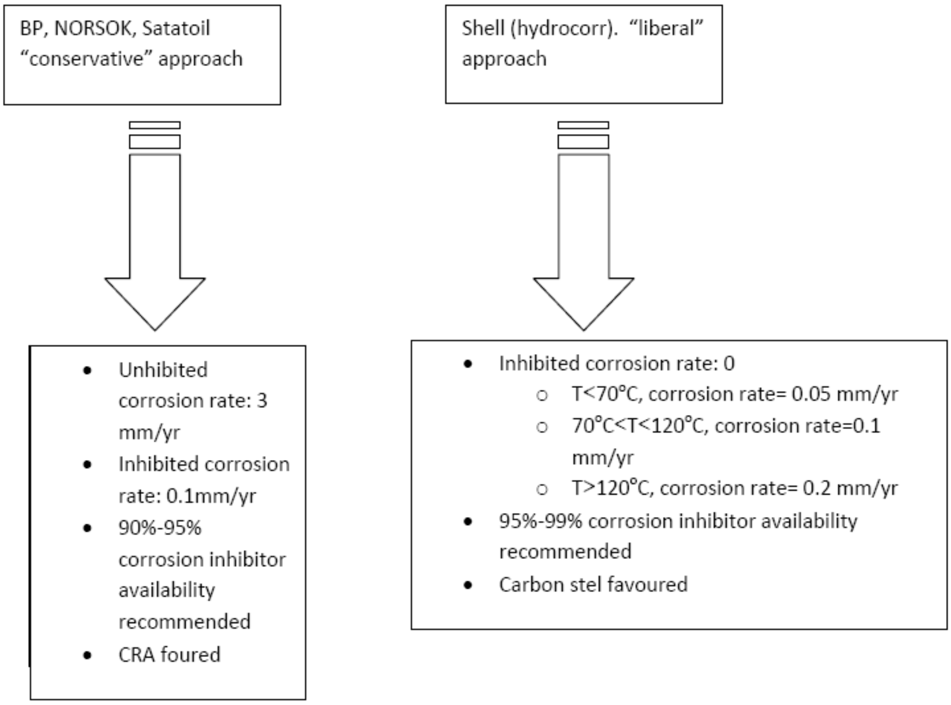

Figure 2. Schematic comparison between two most frequently used corrosion prediction models for subsea structures

Although so-called BP model is based on papers published by de Waard [7]-[8] , and they essentially show similar results, there are slight differences between the model and the work by de Waard, in issues such as use of a correction factor for carbon dioxide fugacity and its lack in the BP model [9]. Figure 3 shows a typical input for a BP 93 (flow insensitive) model:

Assumptions:	- Hold up conservatively assumed to be all water. - DW pH model has been used - We assume a total shear stress of 1 Pa. -The values given for TOL BP93 have been calculated based on the assumption that it is top of line condensing corrosion only and that wetting occurs only 10% of time (F=0.1).
CO_2	Value in mol.%
H_2S	Value in mol.%
pH Model	DW
Glycol	Value %
Internal Diameter	Value in m
Water SG (specific gravity)	(Normally accepted as 1.00)_
Acetates as acid?	False/True
Water Chemistry (mg/l)	Na, K, Ca, Mg, Sr, Ba, Fe, Cl, SO_4, HCO3

Figure 3. Typical Input data for a BP 93 Cassandra corrosion prediction model

The Norwegian NORSOK model, de Waard model and the BP model predict the same corrosion rates at temperatures below or equal to scaling temperature, after the scaling temperature these models will predict corrosion rates that can be different from each other (Figure 4) , and thus will dictate different strategies.

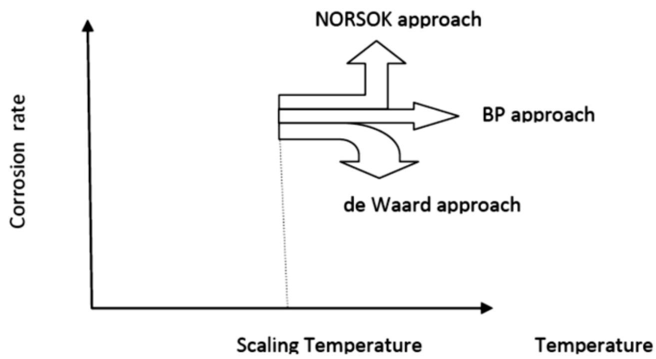

Figure 4. Corrosion rates as predicted by three models for temperatures above scaling temperature (NORSOK, by default, calculates ferrous ions unsaturated rates).

To illustrate how the same data can result in different corrosion management strategies according to these models, Marsh and Teh consider the example of 100,000ppm sodium chloride brine with 500ppm of bicarbonate ions, 100bara, 5% CO2 (gas phase), 100oC, No significant flow effects considered, 20 year design life. In addition, we can take In this example, Cassandra model by assuming 95% availability upper limit, inhibited corrosion rate 0.1mm/yr will recommend the use of CRA (such as 13% Cr supermartensitic stainless steel or SAF 2205) whereas for the same set of data, NORSOK M-506 by assuming 99% availability upper limit, inhibited corrosion rate 0.05/0.1 mm/yr (65oC/100oC) recommends carbon steel with 3mm corrosion allowance. Considering that the average costs of 13% Cr supermartensitic stainless steel and SAF 2205 are, respectively, 4 and 10 times of carbon stel, the readers can easily calculate that the economic impact of differences in corrosion rate calculations and design philosophies. In addition to de Waard, Cassandra and NORSOK, there are other corrosion prediction models such as [10] Cormed (Elf), Lipucorr (Total), Predict (InterCorr), CorPos (CorrOcean/FORCE Technology), as it can be expected while all these models have the same basics, the input and results will differ.

One important shortcoming of corrosion prediction models is that in models such as BP, deWaard and NORSOK, microbial corrosion is not considered. Cassandra [9] for example, is not valid for liquid velocities less than 1.5 $ms^{-1.}$ It is interesting to know that this is also the velocity limit where microbial corrosion can be expected [11]. Even the standards frequently used in subsea corrosion management (such as DNV) [12] do not address microbial corrosion properly. This matter becomes important when we consider that microbial corrosion has been shown as a cause of failure in subsea structures [13].

Table 1. Methods and techniques for corrosion monitoring

METHOD	MEASURES OR DETECTS	NOTES	USE
Linear polarization (polarization resistance)	Corrosion rate is measured by the electrochemical polarization resistance method with two or three electrode probes.	Suitable for most engineering alloys providing process fluid is of suitable conductivity. Portable instruments at modest cost to more expensive automatic units are available.	Frequent
Electrical resistance	Integrated metal loss is measured by the resistance change of a corroding metal element. Corrosion rates can be calculated.	Suitable for measurements in liquid or vapor phase on most engineering metals and alloys. Probes as well as portable and more expensive multichannel units are available.	Frequent
Potential monitoring	Potential change of monitored metal or alloy (preferably plant) with respect to a reference electrode.	Measures directly state of corrosion of plant, e.g., active, passive, pitting, stress corrosion cracking via use of a voltmeter and reference electrode.	Moderate
Corrosion coupon Testing	Average corrosion rate over a known exposure period by weight loss or weight gain.	Most suitable when corrosion is a steady rate. Indicates corrosion type. Moderately cheap method with corrosion coupons and spools readily made.	Frequent
Analytical	Concentration of the corroded metal ions or concentration of inhibitor.	Can identify specific corroding equipment. Wide range of analytical tools available. Specific ion electrodes readily used.	Moderate
Analytical	pH of process stream	Commonly used in effluents. Standard equipment available through robust pH responsive electrodes such as antimony, platinum, tungsten can be preferable to glass electrodes. Solid Ag/AgCl is useful reference electrode.	Frequent
Analytical	Oxygen concentration in process stream.	Useful where oxygen control against corrosion using oxygen scavengers such as bisulfite or dithionite is necessary. Electrochemical measurement.	Moderate
Radiography	Flaws and cracks by penetration of radiation and detection on film.	Very useful for detecting flaws in welds. Requires specialized knowledge and careful handling.	Frequent
Ultrasonics	Thickness of metal and presence of cracks, pits, etc. by changes in response to ultrasonic waves.	Widely used for metal thickness and crack detection. Instrumentation is moderately expensive but simple jobs contracted out at fairly low cost.	Frequent
Eddy current testing	Uses a magnetic probe to scan surface.	Detects surface defects such as pits and cracks with basic instrumentation of only moderate cost.	Frequent
Infrared imaging (thermography)	Spot surface temperatures or surface temperature pattern as indicator of physical state of object.	Used most effectively on refractory and insulation furnace tube inspection. Requires specialized skills and instrumentation is costly.	Infrequent
Acoustic emission	Leaks, collapse of cavitation, bubbles vibration level in equipment. b) Cracks: by detection of the sound emitted during their propagation.	A new technique capable of detecting leaks, cavitation, corrosion fatigue pitting and stress corrosion cracking in vessels and lines.	Infrequent
Zero resistance Ammeter	Galvanic current between dissimilar metal electrodes in suitable electrolyte.	Indicate polarity and direction of bimetallic corrosion. Useful as dewpoint detector of atmospheric corrosion or leak detection behind limings.	Infrequent
Hydrogen sensing	Hydrogen probe used to measure hydrogen gas liberated by corrosion.	Used in mild steel corrosion involving sulfide, cyanide and other poisons likely to cause hydrogen embrittlement.	Frequent in petrochemical industry
Sentinel holes	Indicates when corrosion allowance has been consumed.	Useful in preventing catastrophic failure due to erosion at pipe bends, etc. Leaking hole indicates corrosion allowance has been consumed.	Infrequent

3- The Concept of Corrosion Monitoring for subsea structures

The concept of corrosion monitoring has developed from two distinct areas, plant inspection techniques and laboratory corrosion testing techniques, with the original aim of assessing or predicting corrosion.

Use of Corrosion Monitoring Data:

- **To provide operational or management information**

Corrosion can often be controlled by maintaining a single operational variable (e.g., temperature, pH, humidity) within limits determined by prior monitoring or other investigations. If the significant variable is measured for other reasons, this measurement can be used directly for corrosion control. If the variable is not otherwise measured, or in more complex cases where several variables interact, corrosion monitoring information can be used by plant operators to control plant operation so as to control corrosion. Any process change may have significant effects on corrosion, and corrosion monitoring techniques allow full scale trials to proceed with a minimum of risk to plant.

- **Corrosion Monitoring Techniques**

A wide range of corrosion monitoring techniques is now available allowing determination of total corrosion, corrosion rate, corrosion state, analytical determination of corrosion product or active species, detection of defects or changes in physical parameters. Associated costs can be small where simple instrumentation and a few measurements are appropriate but in some cases may be extremely costly and require expert skills.

Much of the progress which has been made in the past few years has been due to advances in electronics which have allowed multiprobe measurement and recording at a tolerable cost. Instantaneous feedback of corrosion information can be obtained from various parts of the plant, which can be fed to the plant control room and/or plant computer to permit control of the necessary process variable to provide corrosion control. Table 1 indicates corrosion monitoring techniques

- **Selecting a Technique for Corrosion Monitoring**

Many techniques have been used for corrosion monitoring (see Table 1), it is clearly possible to develop others. Consequently when a possible new application is being considered, a problem arises in choosing the most appropriate technique. Each has its strong points and its limitations, and none is the best for all situations.

Any monitoring technique can provide only a limited amount of information, and the techniques should be regarded as complementary rather than competitive. Where more than one technique will give the information required, the information is obtained in different ways; a cross-check can be valuable and differences in detail can add meaning.

A corrosion monitoring technique rarely gives wrong information, unless the equipment used is faulty. "Nonsense" results arise because the information is correct, but irrelevant in the corrosion sense.

The polarization resistance method, for example, measures the combined rate of any electrochemical reactions at the surface of the test sample. If the main reaction is the corrosion ones, the rate measured is the corrosion rate. If however, other reactions are possible at rates that are comparable or greater, the measured rate includes the other reactions. Useful deductions can still be made provided it is recognized that the corrosion rate has not been measured. The choice of a monitoring technique is a complex problem requiring expert knowledge. The first essential is to establish what type of information is needed. This necessarily involves an input from the management of the plant in question.

Cathodic Protection

For obvious reasons, impressed current CP cannot be an option for deep sea water applications. According to DNV- OS-F101 [14], “duplex and martensitic stainless steel linepipe, and C-Mn steel linepipe with SMYS > 450 MPa require special considerations of the susceptibility of environmentally assisted cracking (including SSC and hydrogen induced cracking related to cathodic protection)”.

NORSOK workshop agreement [4] seems more detailed about the joint use of CP and duplex stainless steels. According to this document duplex stainless steels are well protected for potentials more negative than -600 mV (Ag/AgCl) on the condition that a complete electrical insulation from the structural elements, that are protected at -1050 mV, is also applied. Although some modifications in CP system design may be promising in using both CP and supermartinsitic stainless steel together [15]. As it can be seen, two major limitations on applying CP to subsea structures are that only one method of CP can be applied and that we are limited to use of certain alloys whose yield stress is lower than a certain limit.

4- Conclusion

Subsea structures like on-shore and other off-shore (shallow water) structures need to be protected from corrosion. However the practice of corrosion management for these structures is different from on-shore and off-shore in not only the materials used but also in applications such as cathodic protection. Due to factors such as difficulty in having access to the subsea structures and the costs involved, different corrosion prediction models have been developed. These models-with their in-house variants- are frequently used in not only estimation of corrosion but also selecting the strategy that will be the most feasible one to apply. Although these models have similar basics, due to their assumptions and conservative approaches , the very same inputs may result in different corrosion ,management strategies and therefore different budgeting for the projects. When applying these models, their limitations must be considered and their approaches must be taken with required precautions.

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