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Evaluation of Susceptibility to Crevice Corrosion in Drinking Water of Stainless Steel Pipes with Connections

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Abstract

A new electrochemical corrosion testing method has been established for evaluating the crevice corrosion resistance of stainless steel pipes joined with stainless steel connections. The test has been used for approval of such systems for drinking water in Denmark.

The test program is based on the assumption that stainless steel in both hot and cold domestic water can reach maximum susceptibility to crevice corrosion in the oxygen containing media. Intensified conditions due to high corrosion potentials in the cold water are related to the risk of special biofilm formation. In the hot water the possibility of attack is higher due to increased reaction kinetics at high temperature.

The test of a particular connection geometry involved measurements of the critical crevice corrosion potential in water having various concentrations of chloride at 20, 40 or 65°C. A specially designed test-setup with highly alloyed transition pieces was required to limit crevice corrosion to the connection intended for test. The breakthrough potential of the connection was determined using slow stepwise polarisation. The overall evaluation of a connection system was done by correlating the measured breakthrough potentials with the typical levels of corrosion potential of stainless steel in domestic drinking water.

1 Introduction

The test method has been established in order to assess the corrosion resistance of stainless steel piping with connections in domestic water. The connection types in question include threaded fittings, press-fittings and compression fittings, all entirely made of stainless steel. Such connections always contain crevices, why the test method mostly deals with the risk of crevice corrosion.

Hot and cold domestic water may in principle be equally aggressive as to the concerned form of corrosion. Intensified conditions in the cold (20°C) water are related to the risk of biofilm formation, whereas the high temperature in very hot water (65°C) leads to increased reaction kinetics. At the intermediate temperature level of 40°C corrosion may to some extent be affected by all conditions, why it is relevant to test all three temperature levels. Since the concerned systems are closed systems where air cannot escape, the effect of oxygen is considered unchanged for the full temperature range.

It has been chosen to characterise the corrosion resistance of the concerned connection by measuring the breakthrough potential for crevice corrosion in water with various concentrations of chloride. The application window of the connection type is evaluated by correlating the measured potentials with the natural potential level of stainless steel (corrosion potential) in different water types. In case the breakthrough potential is larger than the natural level, the tested connection type is considered as resistant in the actual type of water.

Based on our existing experience, the evaluation considers two types of water:

- Common Danish domestic water, where it is unlikely the corrosion potential is larger than 250 mV SCE.
- Rare conditions, where the water is excessively chlorinated or certain biofilm form, which may result in corrosion potentials of about 400 mV SCE.

At a later stage when more detailed information about the potential level in Danish domestic waters is available, it may be appropriate to establish a finer graduation of different water types, which can be correlated with the measured crevice corrosion potentials.

The determination of critical thresholds for crevice corrosion of stainless steel is technically a difficult and elaborate task in comparison to other types of corrosion. The reason for this is:

- Small random variations in crevice geometry strongly affect the test result.
- The initiation time for crevice corrosion is rather long.
- It is difficult to mount a test specimen without introducing new crevices susceptible to corrosion.

As it appears from the following, the consideration of the above circumstances has led to a quite complex and thorough test procedure.

2 Crevice Corrosion Mechanism

In neutral aqueous solutions stainless steel is normally passive, whereas stainless steel in strong acidic environments can exhibit active corrosion that causes a uniform attack on the activated surface. This possibility of transition from active to passive state makes the material susceptible to crevice corrosion. In a crevice, localized anodic dissolution of metal occurs causing an acidic environment due to hydrolysis of metal ions:

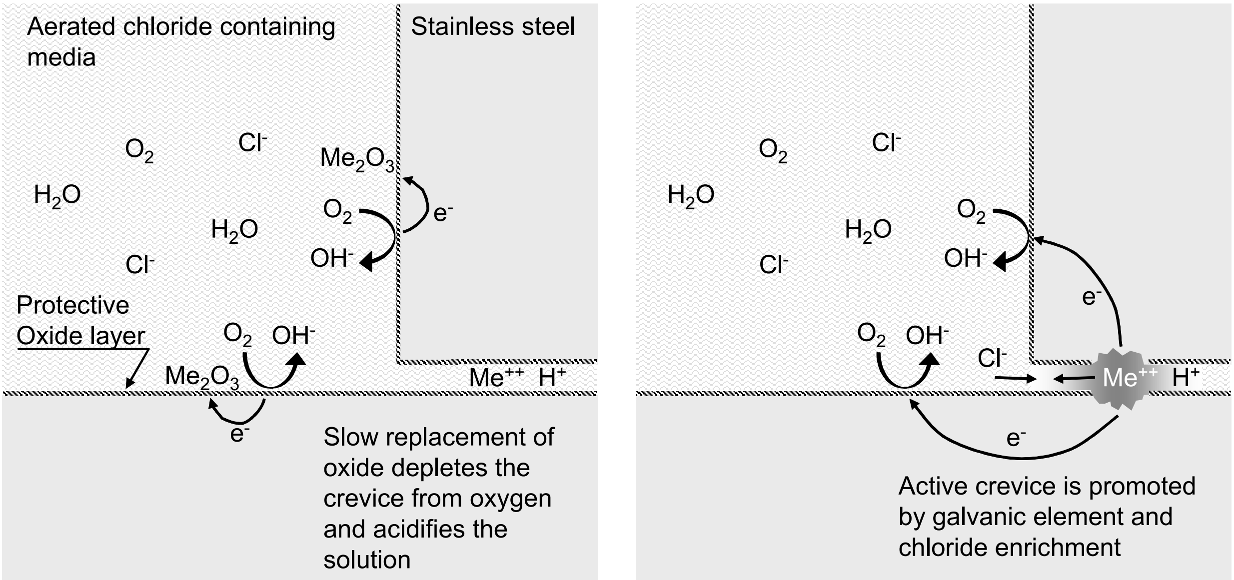
Anodic dissolution: $Me \rightarrow Me^{++} + 2\ e^-$
Hydrolysis: $Me^{++} + H_2O \rightarrow MeOH^+ + H^+$

At the freely exposed surfaces of the metal, the acidification is neutralized by hydroxyl ions formed by oxygen reduction:

Cathode reaction: $\frac{1}{2}\ O_2 + 2\ e^- + H_2O \rightarrow 2\ OH^-$

The reduction of oxygen is hindered in the crevice by the limited oxygen diffusion, thus the acidification in the crevice is controlled by a balance between the anodic reaction, given by the passive current density of the material, and the supply of oxygen, which is determined by the geometry of the crevice.

Figure 1 shows the processes involved in the initiation and propagation of crevice corrosion.



Initiation

Propagation

Figure 1. Schematic of crevice corrosion mechanism.

For a certain alloy type and crevice geometry, such as a connection, the resistance against crevice corrosion basically depends on the combination of four environmental parameters:

- pH
- Chloride concentration (or in fact the overall effect of aggressive and inhibitive ions)
- Temperature
- Electrochemical potential (i.e. the oxidising properties of the media)

In the test method for the connections, the pH, chloride concentration and temperature are fixed while the potential is raised until crevice corrosion occurs.

3 The Test Method

3.1 Objective

The objective of the established experimental technique is to determine the breakthrough potential for crevice corrosion of stainless steel connections in domestic water containing various amounts of chloride. The tests are made in cold (20°C), warm (40°C) and hot (65°C) water.

3.2 Test Matrix

The test matrix is shown in Table 1.

The chosen chloride concentrations represent the existing maximum level (150 mg/l) according to Danish national regulation for stainless steel in drinking water[1] as well as a level (300 mg/l) slightly above the maximum allowable chloride concentration of domestic water (i.e. 250 mg/l) according to DWD 98/83/EC[2].

One combination of pipe diameter and connection type is selected to test a particular system. As a basis, tee-pieces and stainless steel tubing in the dimension of 22 mm is tested.

The critical crevice corrosion potential for each temperature/chloride combination is determined by stepwise (staircase) polarisation, which involves a slow increase of the potential until corrosion is observed.

The variation in geometry of different connections requires testing of a relatively large number of test specimens. It has been chosen to test three tees, each containing three crevices. By this, a total of nine crevices are tested for each temperature/chloride combination.

Table 1. Standard matrix for testing stainless steel connections for Danish drinking water.

Temperature	Chloride content (mg/l)	Repetitions
65°C	150	3
20°C	300	
40°C		
65°C		

It is evaluated at what potential crevice corrosion initiates under the defined chloride/temperature conditions.

3.3 Test Solution

The test solution should as far as possible simulate Danish domestic water, but since the water quality varies between different regions of Denmark, it is practically impossible to define a typical level of water parameters.

On this basis the following test solution has been chosen for the tests:

- The test solution is made up from demineralised water.
- NaCl is added to obtain the desired chloride concentration.
- The solution is unbuffered.
- The tests are carried out under aerated conditions (i.e. air saturated solution at the given temperature).

In contrast to this solution, domestic water normally exhibits buffer capacity and contains various amounts of scale forming agents, such as Ca^{2+}, HCO_3^-, SO_4^{2-}. Both circumstances inhibit the build-up of the critical media that result in initiation of crevice corrosion. This means that the test solution represents slightly intensified conditions when compared to most domestic waters. However, this choice is necessary, since the test must reflect conservative conditions.

3.4 Test Specimen and Experimental Set-up

The major objective of the experimental plan is to test the crevice corrosion resistance of the crevices in a particular connection system. Thus, it is important that the exposed test specimen is free from other crevices that possibly may develop corrosion and thereby compromise the test result. To avoid such crevices, specially made transition pieces, Figure 1, are inserted in the connection.

Each pipe piece consists of a standard pipe from the concerned pipe/connection-system (EN 1.4404), which is welded to a smaller pipe piece of the highly alloyed stainless steel, type 254SMO (EN 1.4547). In this way electrodes etc. can be mounted without forming other sensitive crevices that may disturb the test result.

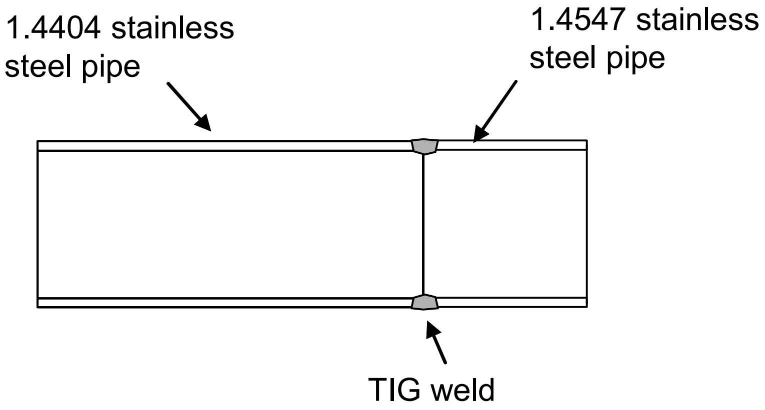


Figure 2. Transition piece consisting of the test pipe welded to highly alloyed SMO-steel.

The complete test set-up is shown in Figure 3. The tested tee contains three pipe pieces similar to one shown in Figure 2. Two pipes are used for inlet and outlet as well as the mounting of the counter electrode by which the connection is polarised by impressed current. The third pipe contains the salt bridge for the reference electrode.

The circulation system includes a heated glass flask containing approx. 12 litres of test solution that is circulated by means of a circulation pump.

Polarisation and current measurement is made by use of a conventional potentiostat and data logger equipment.

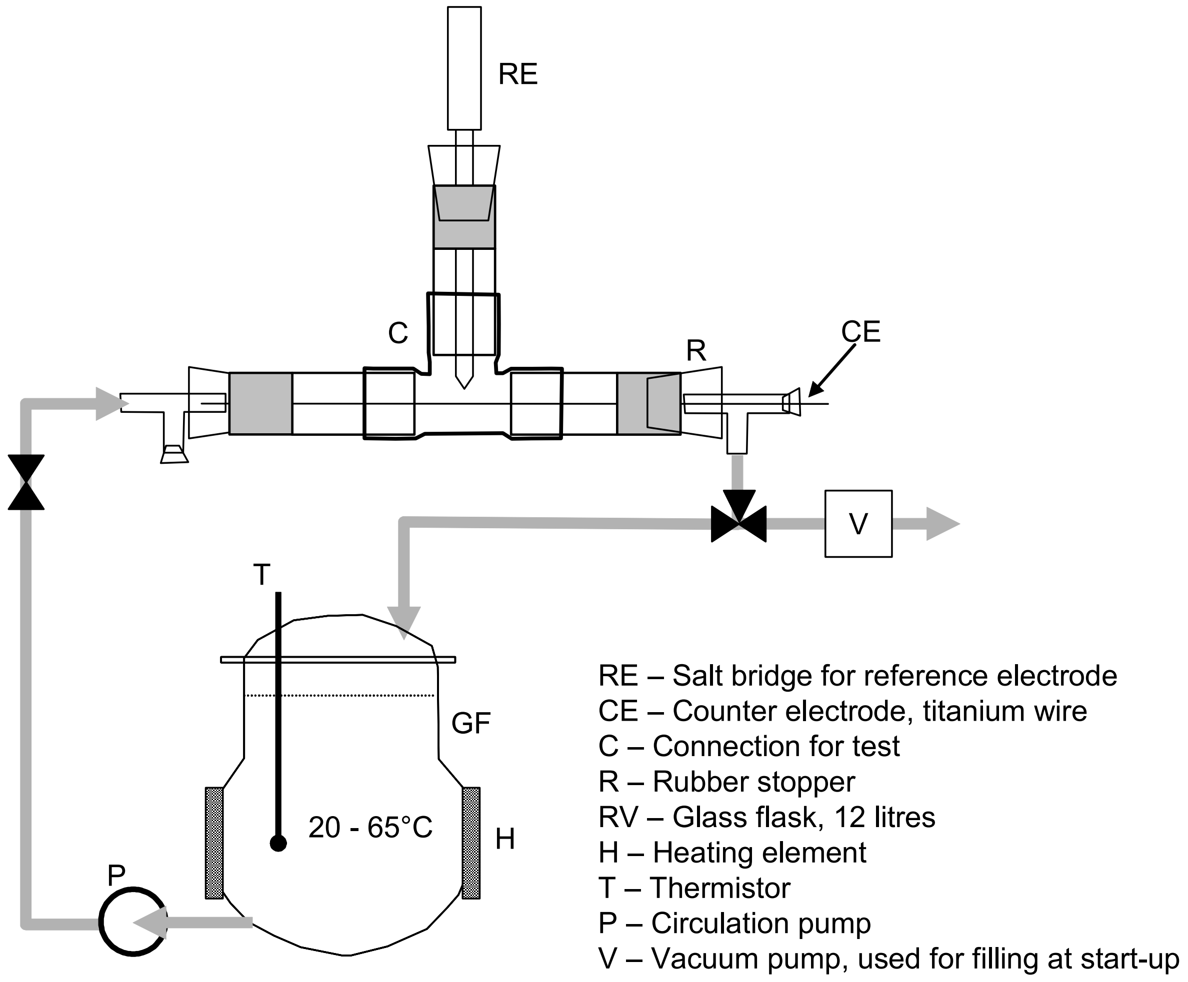


Figure 3. Schematic of set-up for potential measurement and stepwise polarisation on stainless steel connections.

3.5 Test Procedure

The wetting of the crevice is an important parameter that strongly affects the reproducibility of crevice corrosion. Dependent on temperature and geometry conditions (capillary forces), it may take more or less time before the crevice in a practical system becomes water-filled. In some cases it is even possible that the crevice never becomes water-filled.

To obtain the same starting point as concerns wetting, the connections were filled with water before the test. This is achieved by putting the test specimen under vacuum while supplying the test solution. The test specimen is mounted in the test set-up immediately after this operation.

The test is carried out in the following way:

1. The test solution is circulated for approx. 20 hours while recording the corrosion potential.
2. Stepwise polarisation is performed from 0 mV SCE. The potential is stepped 25 mV every 6 hours.
3. The test is stopped within 1 day from the time where the corrosion current exceeds 1 mA.
4. The breakdown potential is noted.
5. The exposed test specimen is sectioned and the form of corrosion is characterised.

It should be mentioned, that the selected polarisation rate always is a compromise between test duration and a suitable slow rate that takes the initiation time of crevice corrosion into account.

The ideal situation is an infinitely slow polarisation rate, which of course is impossible in practice. The chosen polarisation rate (25 mV / 6 hours) corresponds to the level often reported in the literature[3,4]. On this basis the test duration was 5-10 days.

4 Results

4.1 Development during Test

Two examples of the obtained curves are shown in Figures 4 and 5. In total, more than 45 tests have been carried out with this method for testing different types of connections.

Prior to polarisation, the corrosion potential is measured over 20 hours to ensure that the flow system and potential measurement operates well. The first part of the result curves shows the corrosion potential development. Generally, the corrosion potential slowly rises over the first period as changes in the passive oxide film occur.

After stabilisation for about 20 hours, the potential is raised in steps of 25 mV every 6th hour from the starting potential of 0 mV SCE. In some cases this involves cathodic polarisation of the sample, why a small negative current may be measured when polarisation starts.

Activation of corrosion is in all cases noticed by a significant increase in current. The current rises more rapidly at the high temperatures (65 and 40°C), whereas the 20°C-tests in some cases show extremely slow development in current, Figure 5.

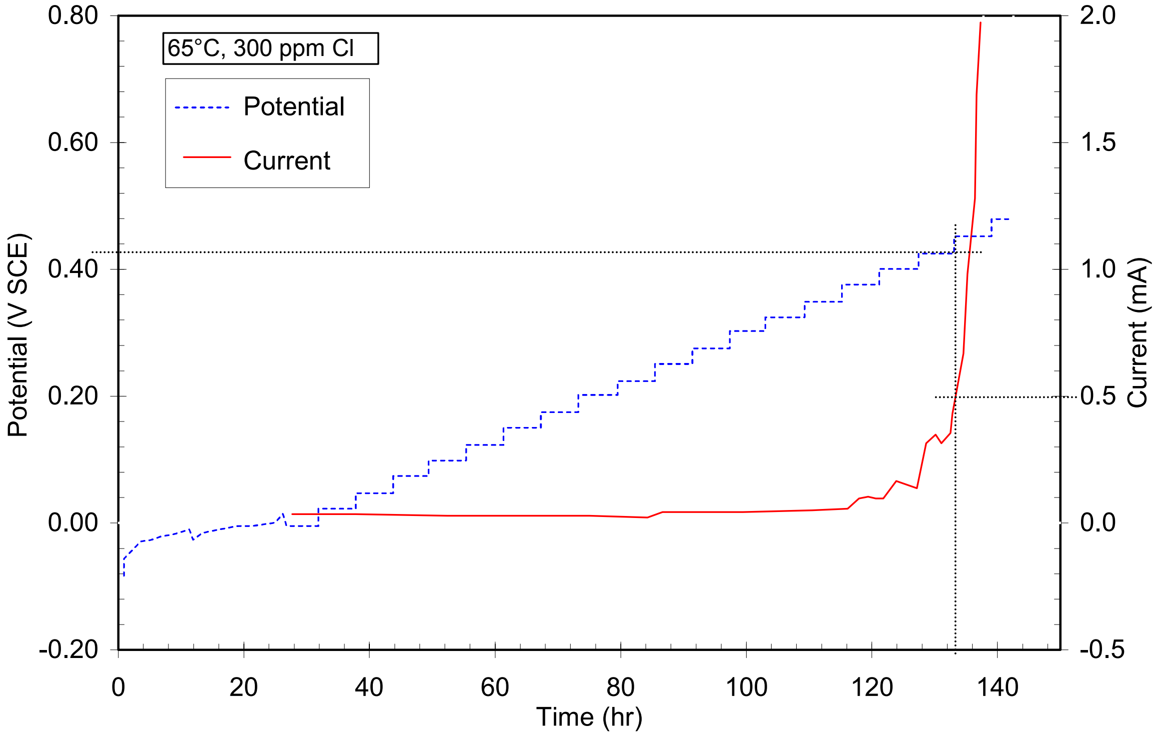


Figure 4. Stainless steel connection tested at 65°C in water containing 300 ppm chloride. The free corrosion potential is recorded during the first 24 hours. Subsequently, stepwise polarisation is performed until the current exceeds 1 mA. Initiation of crevice corrosion is read at 0.5 mA (≈10μA/cm^2) which in this case corresponds to 425 mV SCE.

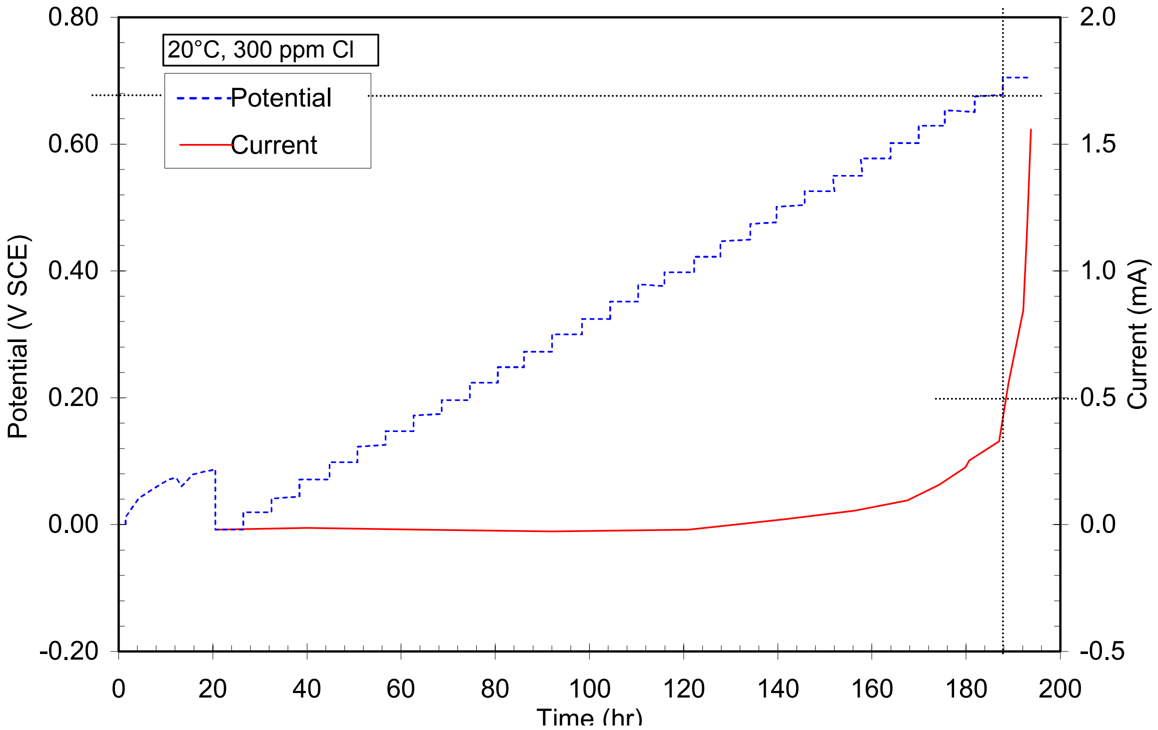


Figure 5. Stainless steel connection tested at 20°C in water containing 300 ppm chloride. The specimen shows extremely slow initiation of crevice corrosion. The break-through potential is read at 0.5 mA (≈10μA/cm^2), which in this case corresponds to 675 mV SCE.

There is a tendency that the current curve breaks to rapid increase from a level of about 0.5 mA. This behaviour indicates transition from passive to persistent corrosion. Consequently, it has been chosen to read the breakthrough potential at the point where the corrosion current permanently exceeds 0.5 mA, which corresponds to a current density of approximately 10 μA/cm^2 in respect to the total crevice area of the metal/metal contact faces, i.e. approx. 50 cm^2. The total area of the freely exposed surfaces of the test specimen is typically 150 cm^2.

After initiation of corrosion, the experiments were typically continued for several hours in order to develop visible attacks on the samples.

4.2 Corrosion Morphology

To characterise corrosion more closely, all exposed parts were cut up and examined visually. The location and number of active spots was counted.

Both crevice corrosion and pitting is observed on the tested connections. Apparently, there is only a small margin between initiation of crevice corrosion and pitting for the tested connections.

Crevice corrosion, when present, always appears in areas representing the closest contact points within the connection. In all cases, this form of attack is limited to superficial etching of both pipe and connection. As concerns distribution and amount of active crevices, there is no clear correlation to the applied test conditions. The corroded areas appear in both vertical and horizontal connections, which correlate well the stochastic nature of crevice corrosion.

Pitting is observed on the free pipe or connection surfaces, especially for those coupons where corrosion was extensively developed after initiation, i.e. the end current was high. The location and distribution of the pits do not follow any particular pattern, unless susceptible areas like pores in welds are present.

Moreover, it appears that the ad-welded 254SMO pipe end is able to prevent crevice corrosion at the rubber stoppers in all cases, thereby restricting crevice corrosion to the connections.

5 Discussion

5.1 Test Conditions and Reproducibility

The described test method has been carried out in pure water added chloride. This circumstance makes the test conditions slightly more severe than those met in plain Danish domestic water, where scale forming elements (e.g. Ca^{++}, HCO_3^-, SO_4^{--}) to some extent suppresses corrosion.

Moreover, domestic water has a certain buffer capacity, which evens out sudden changes in pH. These circumstances have an inhibitive effect on the build-up of the critical (acidic) environment that causes crevice corrosion.

It is difficult to define typical levels of scale forming properties and buffer capacity for Danish domestic water. Consequently, the test solutions were made from pure water, which implies that the tests have been performed under the most conservative conditions. In addition, the polarisation rate represents a safe choice as far as it is possible with accelerated short-term tests. This has been kept in mind when interpreting the results.

On the whole, the applied test technique proved to work as intended. By using 254SMO pipe ends for the tested pipe/connection, crevice corrosion was restricted to connections that were the main target of the tests.

The tests also show fair reproducibility as to measured breakthrough potentials. Typically, the standard deviation is less than 25 mV, which is acceptable for this kind of test. The tests also show the expected trend between test temperature and chloride concentration giving the decreasing breakthrough potentials when increasing temperature and chloride concentration.

5.2 Corrosion Morphology

The provoked corrosion appeared as crevice corrosion at contact faces within the crevice of the connection as well as pitting on free surfaces. The weak distinguishing between crevice corrosion and pitting indicates that the geometry of the crevice in the some connections is less critical than that observed for other types of crevices (e.g. flanges) where corrosion initiates much faster and at lower potential than pitting. Whether this behaviour is related to the low chloride concentration of the test solutions is not fully clarified.

5.3 Test Interpretation

The measured breakthrough potentials of the pipe/connection can be correlated to the natural potential level of stainless steel (corrosion potential) in different water types. In case the breakthrough potential is larger than the natural level, the tested pipe/connection system is considered as resistant in the concerned type of water.

As stated in the introduction, it is unlikely that the corrosion potential is above 250 mV SCE in Danish domestic water, which also agrees well with the free potentials measured during the first 20 hours of the tests. In all cases, the measured breakthrough potentials are at least 100 mV above this potential level at all three test temperatures in water with 300 mg/l chloride. On this basis, the tested pipe/connection systems are considered safe in Danish domestic water in the full temperature range from cold (20°C) to very hot (65°C) conditions.

To our knowledge, there are only very few cases in domestic water, where the corrosion potential of stainless steel exceeds a potential of 250 mV SCE. To obtain such high potentials special conditions are required, such as growth of certain biofilm or excessive chlorination. Both circumstances may result in potentials up to 400 mV SCE.

The breakthrough potentials measured at 65°C may be within this potential level. However, growth of biofilm is not possible at such high temperatures, leaving excessive chlorination as the only unlikely risk that might cause crevice corrosion of the tested pipe/connection system at 65°C. In such cases deposit corrosion on free pipe segments may be equally critical as crevice corrosion for the tested pipe/connection systems.

At 20 and 40°C the measured breakthrough potentials is down to 475 mV SCE, typically higher, for 300 mg/l chloride. This level is above the expected potential level in case of growth of biofilm, which might take place in this temperature range.

6 Conclusion

A new electrochemical corrosion testing method has been established for evaluating the crevice corrosion resistance of stainless steel pipes joined with stainless steel connections.

Corrosion is restricted to the crevices in the tested connecting type by using highly alloyed transition pieces. The testing method implies slow stepwise polarisation until a breakthrough potential is observed. Moreover, the test solution is considered slight accelerating due to absence of scale forming elements.

The applied technique shows fair reproducibility and gives the expected trend as function chloride concentration and test temperature. This is based on the results of more than 45 tests have including different connection types of the 1.4404 grade.

Based on the obtained break-through potentials, the tested pipe/connection systems are considered safe in Danish domestic water in the full temperature range from cold (20°C) to very hot (65°C) conditions.

Literature

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