

# Monitoring Crevice Corrosion via the Coupling Current

## Part I: Detecting Crevice Activation, Inversion, and Inhibition

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### ABSTRACT

A simple crevice corrosion monitor was developed to monitor crevice corrosion in 1018 mild steel, Type 304 SS, and Type 410 SS in NaCl solutions with and without the addition of a chemical corrosion inhibitor. The monitor, which measures the electron coupling current, accurately followed the evolution of crevice activity in a manner that can be understood in terms of the cathodic process that occurs on the external surface and the partial anodic process that develops within the crevice, due to the accumulation of  $H^+$  and  $Cl^-$ . The crevice initiation time is typically very short, but appears to depend upon the chloride concentration and possibly on the inhibitor concentration. The coupling current increases with time after initiation, passes through a maximum and then decreases, eventually changing sign to mark crevice inversion. The inversion is attributed to the gradual build-up of  $H^+$  in the crevice to the extent that proton reduction within the crevice becomes the principal cathodic reaction in the system, while the anodic reaction moves to the external surfaces. In addition, amines are effective corrosion inhibitors of crevice corrosion of mild steel and stainless steels in NaCl solutions, provided that they are present in sufficiently high concentrations.

### INTRODUCTION

Localized corrosion processes, including crevice corrosion, pitting corrosion, stress corrosion cracking, and corrosion fatigue are major forms of corrosive degradation in industrial systems and typically occur where metallic components are in tight juxtaposition, such as in flanges, pipe sleeves, valves, and bearings, or where a pre-existing crack or fissure establishes a tight crevice [1–43]. The mechanism of localized corrosion is well understood, in terms of the differential aeration hypothesis (DAH), with the establishment of the local anode within the crevice and the local cathode on the external surface, locations that have the least and greatest access to the cathodic depolarizer,  $O_2$ , respectively. To compensate for the accumulation of positive charge in the crevice, in the form of metal cations and  $H^+$ , which form from metal cation hydrolysis ( $M^{n+} + nH_2O \rightarrow M(OH)_n + nH^+$ ), anions (most commonly  $Cl^-$ ) are transported from the bulk electrolyte into the crevice. These processes result in a positive current flowing through the solution from the crevice mouth to the external surface and an equal electron current flowing through the metal in the same direction. The positive ionic current and the negative electron current annihilate each other at the external surface via a "charge transfer reaction," such as the reduction of oxygen ( $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ) and/or the evolution of hydrogen ( $2H^+ + 2e^- \rightarrow H_2$ ), as illustrated in Figure 1. This type of model is termed a Coupled Environment (Crevice) Model [35–40], as it emphasizes the strong electrochemical coupling that

exists between the crevice and the external surfaces that results in the flow of the "coupling current" between the crevice and the external surfaces. Extensive experimental and theoretical work by this group [36–39] has demonstrated that the coupling current is an effective indicator of crevice activity and provides a wealth of information on the processes that occur within the crevice.

Two other important conclusions have been drawn concerning the role of the coupling current in localized corrosion, as follows:

- (1) Localized (e.g., crevice) corrosion can be stopped or prevented by ensuring that the coupling current becomes zero; and
- (2) The kinetics of the reactions on the external surface are instrumental in controlling the coupling current and hence determining the rate of damage accumulation within the crevice.

As an illustration of the first conclusion, we note that if the external surfaces are coated with a thin film of electrochemically deposited and baked  $ZrO_2$ , the exchange current density for oxygen reduction is reduced to such a low value that the coupling current is effectively zero and (in this case) intergranular stress corrosion cracking in sensitized Type 304 stainless steel (SS) in high temperature (288 °C) water ceases [37]. The in situ formation of

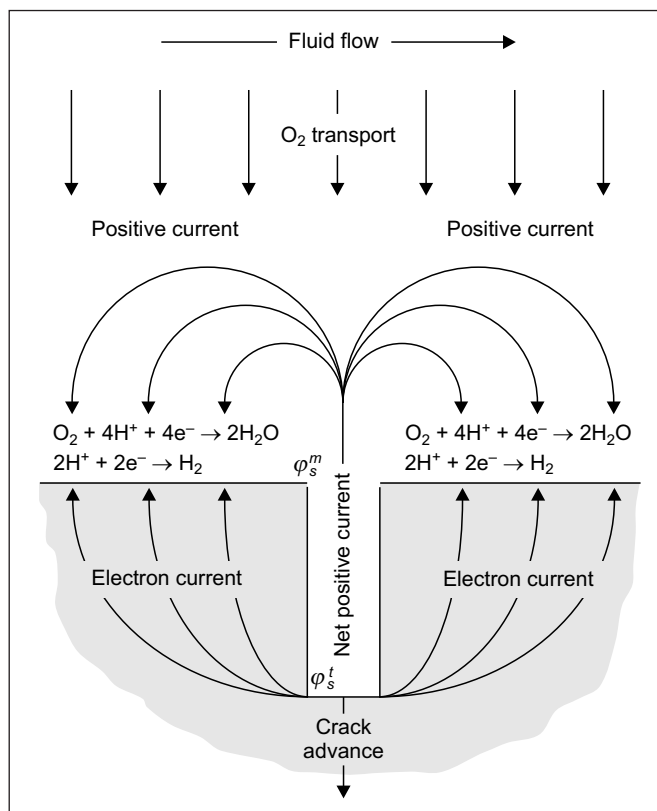


Figure 1:

Coupling of crack internal and external environments. Note that in the steady state, the crack can grow only as fast as the positive current flowing from the crack can be consumed on the external surfaces by oxygen reduction. The quantities  $\varphi_s^m$  and  $\varphi_s^t$  are the electrostatic potentials in the solution with respect to a reference electrode or the metal, respectively.

insulating coatings, such as those by adsorbed inhibitors, is also a major mechanism of the chemical inhibition of localized corrosion and is applicable to all forms of localized corrosion that are sustained by differential aeration. In the case of the second conclusion, we note that the origin of the coupling current is the anodic processes that occur within the crevice. While some researchers have argued that significant cathodic activity occurs within the crevice and that this detracts from the magnitude of the coupling current [41–43], numerous studies have shown that tight crevices, at least, are quickly depleted of cathodic depolarizers, such as  $O_2$ , and that the fraction of the coupling current that is consumed on the crack walls compared to that which flows to the external surface is small and inconsequential. However, the present work demonstrates that the build-up of  $H^+$  within the crevice via the hydrolysis of metal cations may occur to the extent that the reduction of protons within the crevice becomes the principal cathodic reaction in the system, resulting in crevice inversion.

In this paper, we have demonstrated a simple crevice corrosion monitor that employs the electron coupling current

that flows between the crevice and the external surface, where it is annihilated with the positive ion current flowing through the solution in the same direction by a charge transfer reaction, such as oxygen reduction or hydrogen evolution, as an indicator of crevice activity. This monitor has been used to follow the development of crevice corrosion in 1018 mild steel, Type 304 SS, and in Type 410 SS in deionized (DI) water, and in sodium chloride solutions of varying NaCl concentrations with and without an amine chemical corrosion inhibitor (Anodamine). Anodamine, which is a branched, aliphatic polyamine, was specifically developed to meet the metal protection demands of high-pressure steam/water cycles, offering full standards compliance, thermal stability, and protection of all ferrous and mixed metallurgy alloys. The monitor effectively detects crevice inversion and provides a convenient tool for determining inhibitor efficacy in reducing crevice corrosion activity in mild and stainless steels.

## EXPERIMENTAL

Crevice corrosion tests were conducted by measuring coupling current that flows from the local cathode that normally exists on the external surface to the local anode that normally exists within the crevice. Two rectangular coupons were fabricated from sheets of the alloys of interest and stainless steel wires were attached to the edges by silver soldering. Typical dimensions of the two crevice formers (see Figure 2) were 25.4 mm and 63.5 mm (1 in and 2.5 in) in length by 12.7 mm (0.5 in) in width by 2.997 mm (0.118 in) in thickness. Prior to assembling the crevice monitor, the coupons were physically polished with a SiC paper (320 grit), and 3M electroplating tape and Micro-stop lacquer were utilized to isolate both coupons electrically from each other and to prevent any electrochemical reaction on the outer surfaces of the crevice formers and hence to restrict the cathodic reactions to the exposed area of the longest crevice former (colored white in Figure 2). Once coated, the crevice formers were dried in air for 24 h. A polytetrafluoroethylene (PTFE) film, with a thickness of 50  $\mu\text{m}$ , and binder clip were used in order to generate a crevice gap of known dimension (50  $\mu\text{m}$ ), as shown in Figure 2. A GAMRY potentiostat was used as a zero resistance ammeter (ZRA) to measure the coupling current. The crevice monitor was placed in an electrochemical cell containing the solution of interest. Optical microscopy has been used to characterize the morphology of the surface of crevice.

In order to compare the results of coupling current measurement, traditional crevice corrosion tests were conducted for 30 days in 3.5 % NaCl solution<sup>1</sup> at ambient

<sup>1</sup> All data stated in % are mass fractions.

temperature. A test specimen (2.54 mm by 50.8 mm (1 in by 2 in)) was prepared in accordance with ASTM G48 [44] from sheets of the alloys of interest and followed by physical polishing with a SiC paper (320 grit). Two polytetrafluoroethylene (TFE-fluorocarbon) blocks were fastened to the test specimen with O-rings as shown in Figure 3. The

small O-ring (inside diameter of 20.32 mm (0.8 in)) was used for the 2.54 mm (1 in) dimension and the large O-ring (inside diameter of 27.94 mm (1.1 in)) for the 50.8 mm (2 in) dimension. After the test was completed, the test specimens were removed from the bath, then scrubbed with a nylon bristle brush under running water to remove corrosion products, and then cleaned with methanol and distilled water, and dried in air. The mass of the specimens before and after crevice corrosion tests was obtained with a balance having the resolution of 0.1 mg. The mass loss reported in this work is the average of four tests.

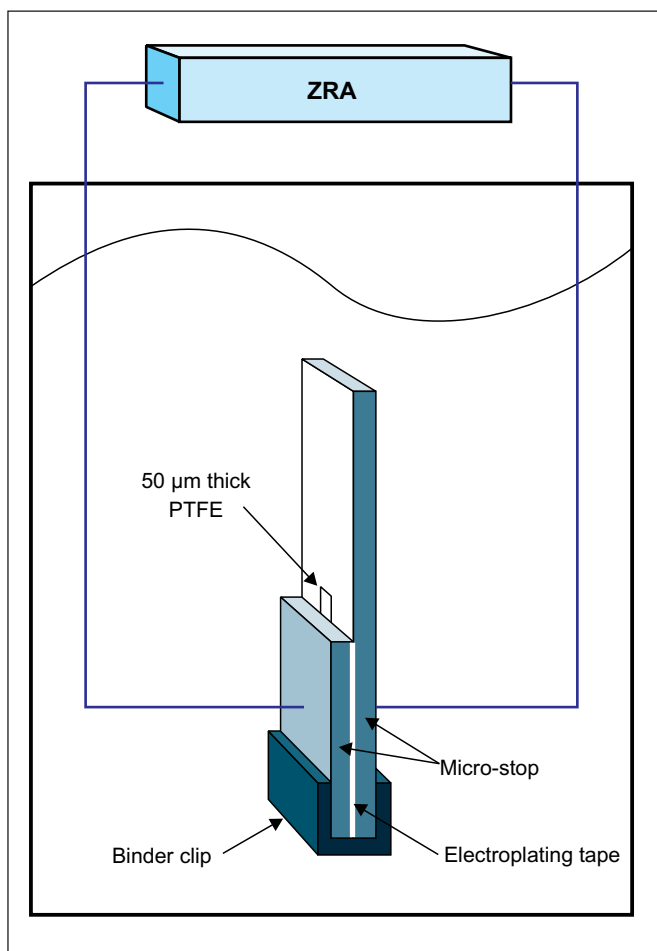


Figure 2: The schematic experimental setup for the crevice corrosion test. Note that the width of the crevice gap is set by the thickness of the PTFE film at 50 µm. Also note that the surface of the longer crevice former is covered with 3M electroplating tape within the crevice.

## RESULTS AND DISCUSSION

### Uninhibited Systems

The coupling current measurements were performed on 1018 mild steel in DI water at 50 °C and in 3.5 % NaCl solution at ambient temperature without an amine chemical corrosion inhibitor (Anodamine). In these experiments, the crevice is electrically coupled to the bare external surface of the longer crevice former via the ZRA, as shown in Figure 2. As the crevice becomes active, due to the establishment of a differential aeration cell, with the local anode occurring within the crevice and the local cathode occurring on the external surface, in the "normal state," a positive current flows through the solution from the crevice mouth to the external surface, which is detected and measured as an electron current flowing through the metal (and through the ZRA) in the same direction (crevice to external surface). As noted above, the coupling current is a direct measure of the net crevice activity and is an ideally suited tool for exploring the chemical inhibition of crevice corrosion.

Figure 4 shows the measured coupling current on 1018 mild steel in both solutions. In the case of the coupling current in 3.5 % NaCl solution, the current started to increase dramatically after about 10 min and reached the maximum current, 51 µA, after about 40 min, indicating that the crevice had become active. However, very small current was measured and no crevice action occurred after more than 20 h in DI water at 50 °C, due to the lack of

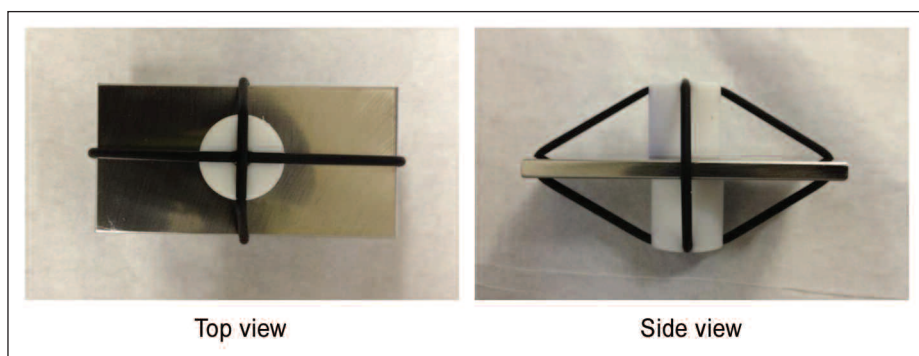


Figure 3: The photographs of the specimens for the chloride crevice corrosion test.

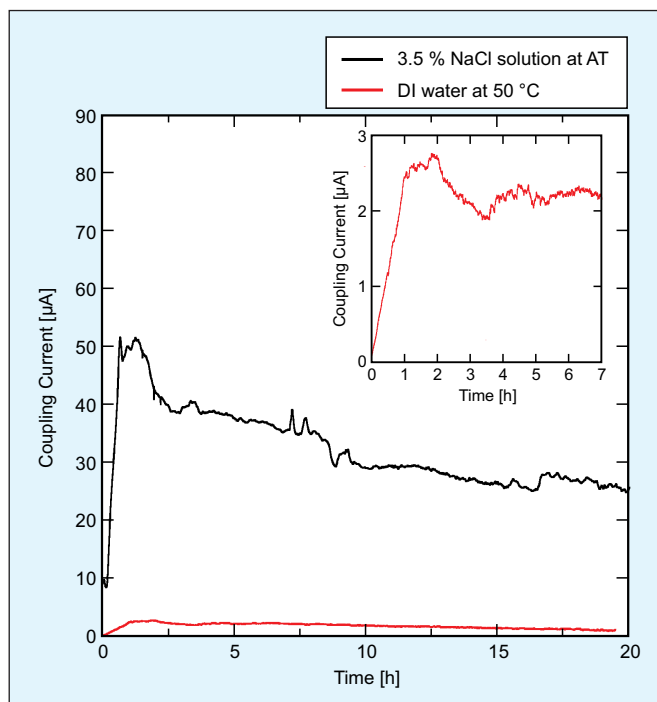


Figure 4: Plots of the coupling current measured with 1018 mild steel in 3.5 % NaCl solution at ambient temperature (AT) and in DI water at 50 °C.

charge-compensating anion (e.g.  $\text{Cl}^-$ ) in DI water. The small current that was observed (insert in Figure 4) is probably the result of the presence of carbonate and bicarbonate anions from the dissolution of atmospheric carbon dioxide. Optical microscope images of the crevice and the external surfaces after the test with 3.5 % NaCl solution are shown in Figure 5. Crevice corrosion damage was

observed in the test with 3.5 % NaCl solution, but not for that in DI water, primarily because of the lack of a charge-compensating anion in DI water and hence the lack of crevice activity. However, general corrosion of the external surface was detected in DI water at 50 °C.

We also carried out crevice corrosion tests with various concentrations of NaCl in the solutions in order to investigate the effect of  $\text{Cl}^-$  concentration. The coupling current started to increase dramatically after exposing the specimens to the chloride-containing solutions and passed through maxima within a day of exposure, as shown in Figure 6. The coupling current then decreased with additional exposure and eventually changed sign, indicating crevice inversion, which has been studied theoretically [40], but which is not well defined experimentally. Inversion occurred after 2 days, 15 h, and 24 min in  $0.1 \text{ mg} \cdot \text{L}^{-1}$  NaCl solution and after 4 days, 8 h, and 20 min in the  $1 \text{ mg} \cdot \text{L}^{-1}$  NaCl solution. The coupling current for the highest chloride concentration ( $10 \text{ mg} \cdot \text{L}^{-1}$  NaCl) sharply decreased after about 30 h and changed sign after 2 days, 21 h, and 26 min. Figure 7 shows photographs of the 1018 mild steel surface in the crevice corrosion monitor after exposure to  $1 \text{ mg} \cdot \text{L}^{-1}$  NaCl solution as a function of immersion time. It was observed that as the experimental time increased, corrosion on the external surface increased. Inversion of the crevice results from the partial anodic process moving to the external surface and the partial cathodic process moving into the crevice, presumably because of the continual build-up of  $\text{H}^+$  in the crevice, which then acts as an effective cathodic depolarizer with the principal cathodic reaction then occurring within the crevice. Theory also predicts that when the  $\text{H}^+$  within the crevice has been consumed, the crevice will

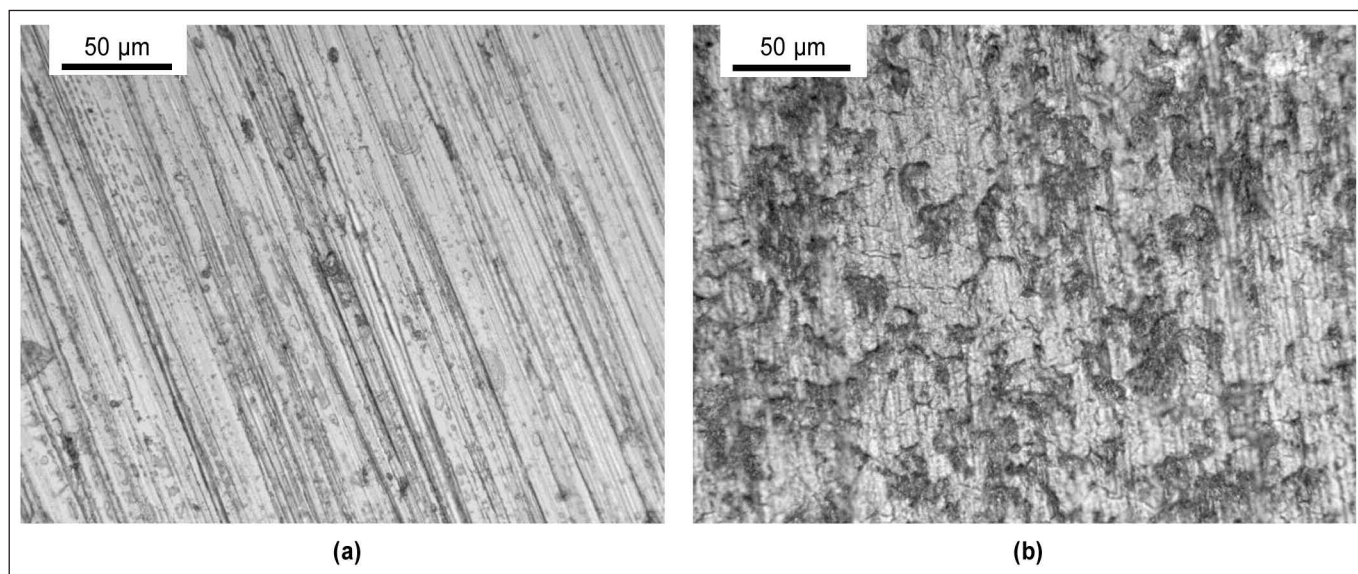


Figure 5: Optical microscope images of (a) the external surface and (b) the crevice wall of 1018 mild steel crevice specimens after the test in 3.5 % NaCl solution at ambient temperature.

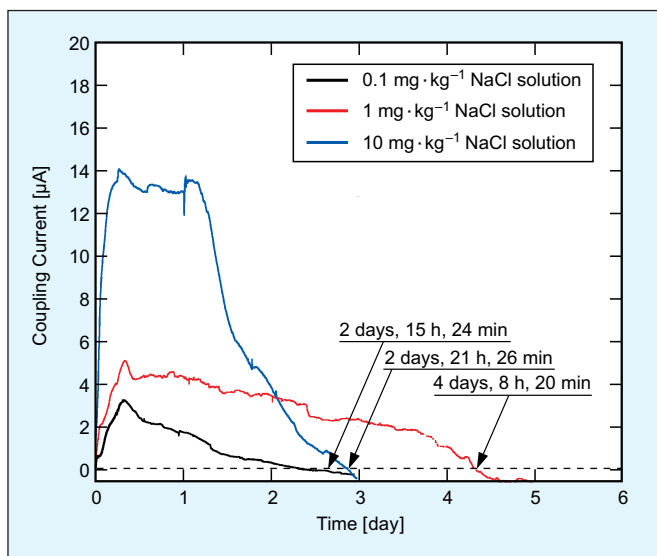


Figure 6:

Plots of the coupling current measured with 1018 mild steel in different NaCl concentrations at ambient temperature.

invert again back to its original, "normal" state, and hence inversion should be a cyclical process. Of course, inversion cannot be expected to repair the damage (metal lost by dissolution) incurred during its normal state, but it does suggest that damage within the crevice should accumulate primarily during the normal, non-inverted state and not when inversion has occurred. The experimental demonstration of these important conclusions has yet to be reported.

Crevice inversion is not an unknown phenomenon, but it has only rarely been discussed [41–43]. Abella et al. [41] reported the inversion of simulated tube/tube support plate crevices in nuclear steam generators under heat transfer conditions, with heat flow occurring from the inside of the tube (the "primary side") through the annular gap (crevice), and into the carbon steel support plate (the "secondary side"). In this case, a positive current was observed to flow through the solution from the external surfaces into the crevice mouth, particularly from the external tube surfaces into the crevice. A large current was

also observed to flow within the crevice from the carbon steel support plate to the Alloy 600 tube surfaces, accounting for the oxidation of iron to magnetite and hence for the phenomenon of denting corrosion. In the absence of heat transport, the crevice was not inverted with the positive current flowing in the "normal" direction from the crevice mouth to the external surfaces. Accordingly, in this case, it may be argued that crevice inversion is the direct result of heat flow. Kennell and Evitts [42] interpreted crevice corrosion in terms of scaling laws, with emphasis on identifying those crevices that will become active as opposed to those that will remain passive, an issue that has also been addressed by Engelhardt and Macdonald [40]. However, these authors did not discuss crevice inversion per se and hence did not throw any light on the cause. On the other hand, Lu and Li [43] reported that crevice inversion is a common phenomenon in the case of copper and copper alloys, where the crevices are commonly observed not to be corroded, but where corrosion is observed on the external surfaces close to the crevice mouth. The authors relate the inversion to the formation of different oxides within the crevice and on the external surface, but the present authors find the explanation to be less than compelling, in that the different oxides are undoubtedly the result of crevice inversion, not the fundamental cause.

Figure 8 shows the coupling currents measured on different materials in 3.5 % NaCl solution. The coupling current of 1018 mild steel started to increase dramatically after immersion of the specimens into the solution with little or no induction time (see inset); the coupling current for Type 410 SS in contrast started to increase more slowly than that of 1018 mild steel in the beginning and eventually attained a quasi-steady state, indicating that the crevice remains active and not inverted. Type 304 SS displayed little crevice activity in these tests, as shown by the coupling current. It is postulated that the magnitude of the coupling current represents the rate of accumulation of crevice corrosion damage; 1018 mild steel showed the highest susceptibility to crevice corrosion and Type 304 SS displayed the least over the selected time period in this work.

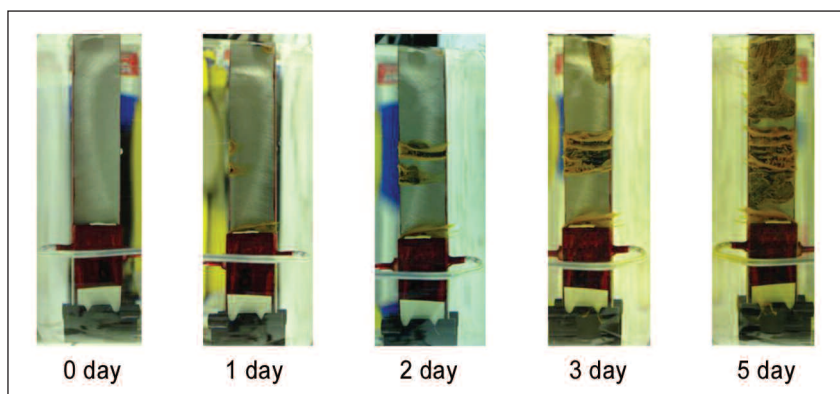


Figure 7:

Photographs of the 1018 mild steel crevice specimens along the immersion time in  $1 \text{ mg} \cdot \text{L}^{-1}$  NaCl solution at ambient temperature.

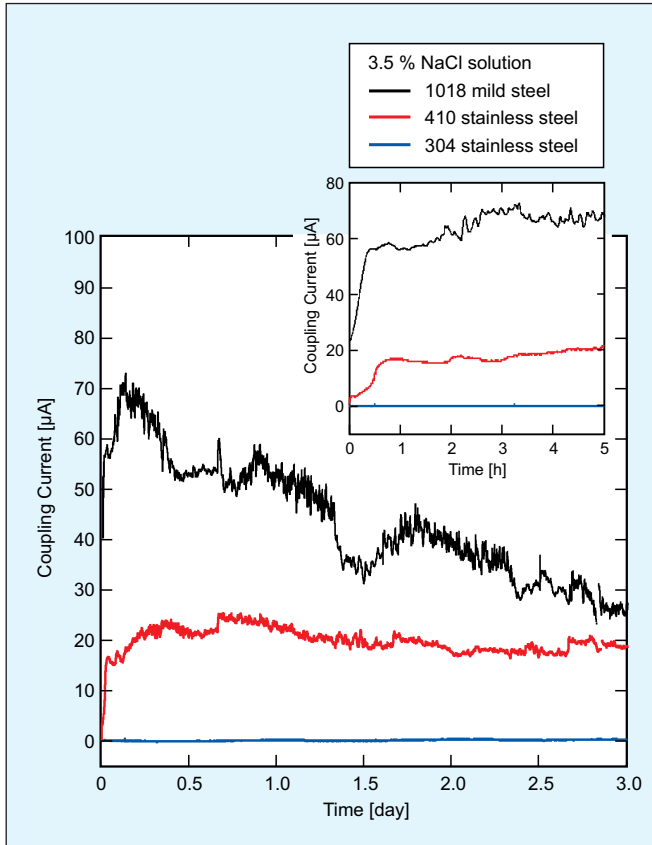


Figure 8:  
Coupling currents measured on 1018 mild steel, Type 304 SS, and Type 410 SS in 3.5 % NaCl solution.

Specimen	Mass loss [mg]	Calculated current [ $\mu\text{A}$ ]
1018 mild steel	$148.85 \pm 9.41$	$198.44 \pm 12.55$
Type 410 SS	$28.9 \pm 6.58$	$38.53 \pm 8.77$
Type 304 SS	$0.025 \pm 0.13$	$0.033 \pm 0.17$

Table 1:

The chloride crevice test results in accordance with ASTM G48.

A conventional crevice corrosion test, measuring a mass loss after immersion of the specimens, as shown in Figure 3, for a certain period of time in a corrosive environment was performed. This immersion test was conducted with each of the specimen materials for 30 days in 3.5 % NaCl solution at ambient temperature in order to make a qualitative comparison with the results of the coupling current measurements. The mass loss obtained from the immersion tests and average current calculated from Faraday's laws are listed in Table 1. As indicated in the coupling current measurement, the immersion tests also showed the same tendency: 1018 mild steel showed the highest mass loss and Type 304 SS displayed the lowest. However, in the case of 1018 mild steel, the majority of the mass loss resulted from damage on the external surfaces. Photographs of the test specimens, taken after the immersion tests in 3.5 % NaCl solution for 30 days, are shown in Figure 9. In Figure 9 (a) it can be seen that inside the

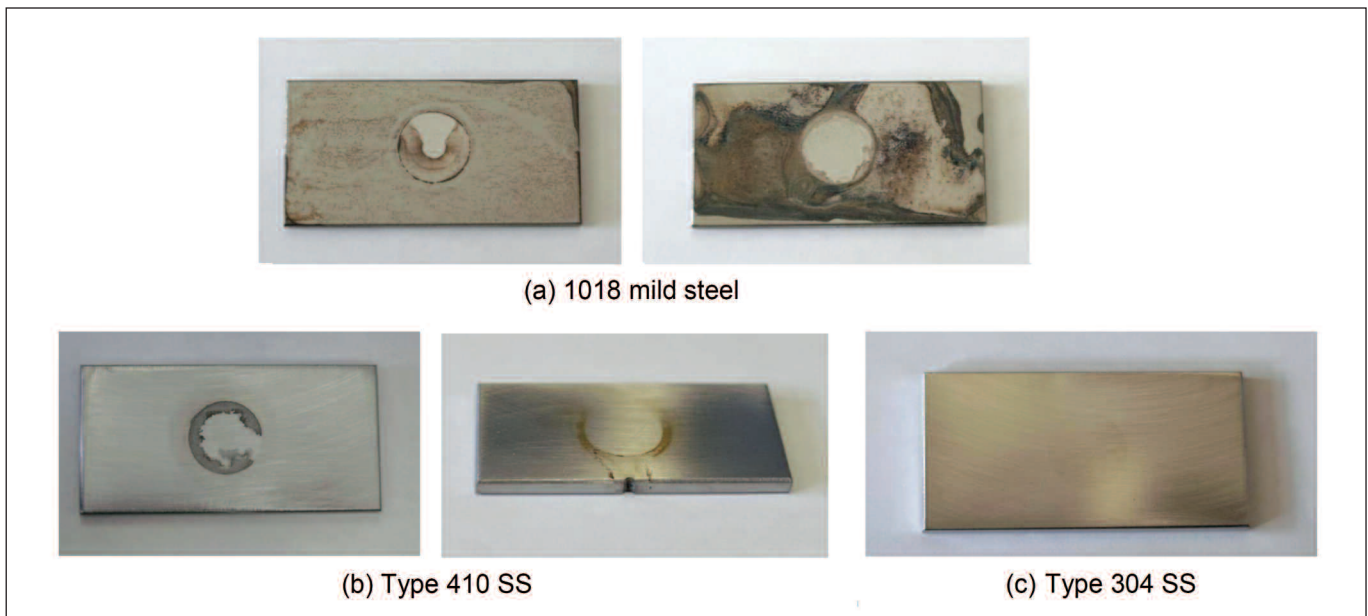


Figure 9:  
The photographs of the test specimens after the chloride crevice corrosion test.

- (a) 1018 mild steel
- (b) Type 410 SS
- (c) Type 304 SS

crevice formers (TFE-fluorocarbon blocks or the O-ring) there was light corrosion damage, but on the external surface significant corrosion damage was observed, which parallels the crevice inversion that is observed in 1018 mild steel in the coupling current measurement. In the case of Type 410 SS, significant crevice corrosion damage under the crevice formers was observed, as shown in Figure 9 (b), but there was no corrosion damage in Type 304 SS, as also indicated in the coupling current measurements. Although it is difficult to compare quantitatively the results obtained from the immersion tests and the coupling current measurements, it is clear that the coupling current provides "real time" monitoring of crevice activity and is particularly effective in detecting crevice inversion.

Figure 10 presents optical microscopic images of the crevice wall of Type 410 SS after the crevice test with coupling current measurements. The bright part of Figure 10 (a) is the crevice tip, which was slightly corroded, while the black part was severely corroded due to crevice corrosion. It is worth mentioning that crevice corrosion is not initiated from the very tip of the crevice. A closer look into the severely corroded area reveals stable pits, as shown in Figure 10 (b) and (c). The occurrence of pitting on the crevice wall has also been reported by Shu et al. [45]. Stockert and Böhni [46] suggested that crevice corrosion is initiated by metastable pitting within the crevice, which may either repassivate or reach a stable state. This suggestion has also been supported by other researchers [47–50]. Therefore, it is thought that the initiation and stabilization of crevice corrosion on 410 SS may also be related to the pitting corrosion on the crevice wall. More detailed work in this connection will be published in the near future.

### Corrosion Inhibition

Coupling current measurements were performed on 1018 mild steel and Type 410 SS at ambient temperature in

3.5 % NaCl solution containing  $20 \text{ mg} \cdot \text{L}^{-1}$  of organic corrosion inhibitor. It should be stressed that the concentration of corrosion inhibitor in the present work is that of as-received Anodamine. In these experiments, like those reported elsewhere in this paper, the crevice is electrically coupled to the bare external surface via the ZRA, as shown in Figure 2. As the crevice becomes active, due to the establishment of a differential aeration cell, with the local anode occurring in the crevice and the local cathode occurring on the external surface, a positive current flows through the solution from the crevice mouth to the external surface, which is detected and measured as an electron current flowing through the metal (and through the ZRA) in the same direction (anode to cathode).

Figure 11 shows the effect of the polyamine corrosion inhibitor on the crevice corrosion behavior of 1018 mild steel and Type 410 SS in 3.5 % NaCl solution. The addition of  $20 \text{ mg} \cdot \text{L}^{-1}$  of polyamine corrosion inhibitor significantly affected the crevice corrosion behavior of 1018 mild steel, as shown in Figure 11 (a). The coupling current increased up to  $89 \mu\text{A}$  in the beginning of the experiment and reached a quasi-steady state for about 10 min. However, after that short period, the coupling current decreased continuously and finally changed sign after about 11 h, indicating crevice inversion, unlike that for 1018 mild steel in the solution that did not contain the organic corrosion inhibitor. After this crevice corrosion test, the 1018 mild steel specimen showed considerable corrosive attack on the external surface, presumably occurring after crevice inversion, when the local anode was forced out onto the external surface in response to the local cathode existing within the crevice, because of the high concentration of  $\text{H}^+$ . Unlike 1018 mild steel, it was difficult to ascertain whether the addition of  $20 \text{ mg} \cdot \text{L}^{-1}$  of polyamine affected the crevice corrosion behavior of Type 410 SS (Figure 11 (b)). Therefore, we increased the polyamine concentration in the 3.5 % NaCl solution and repeated the experiments.

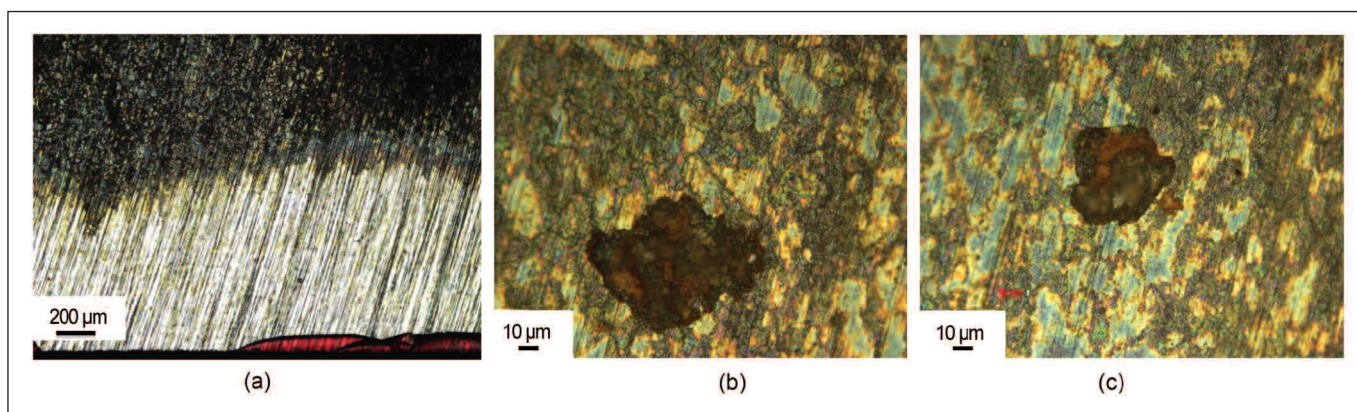


Figure 10: Optical microscope images of the crevice wall of Type 410 SS after the crevice test in 3.5 % NaCl solution.

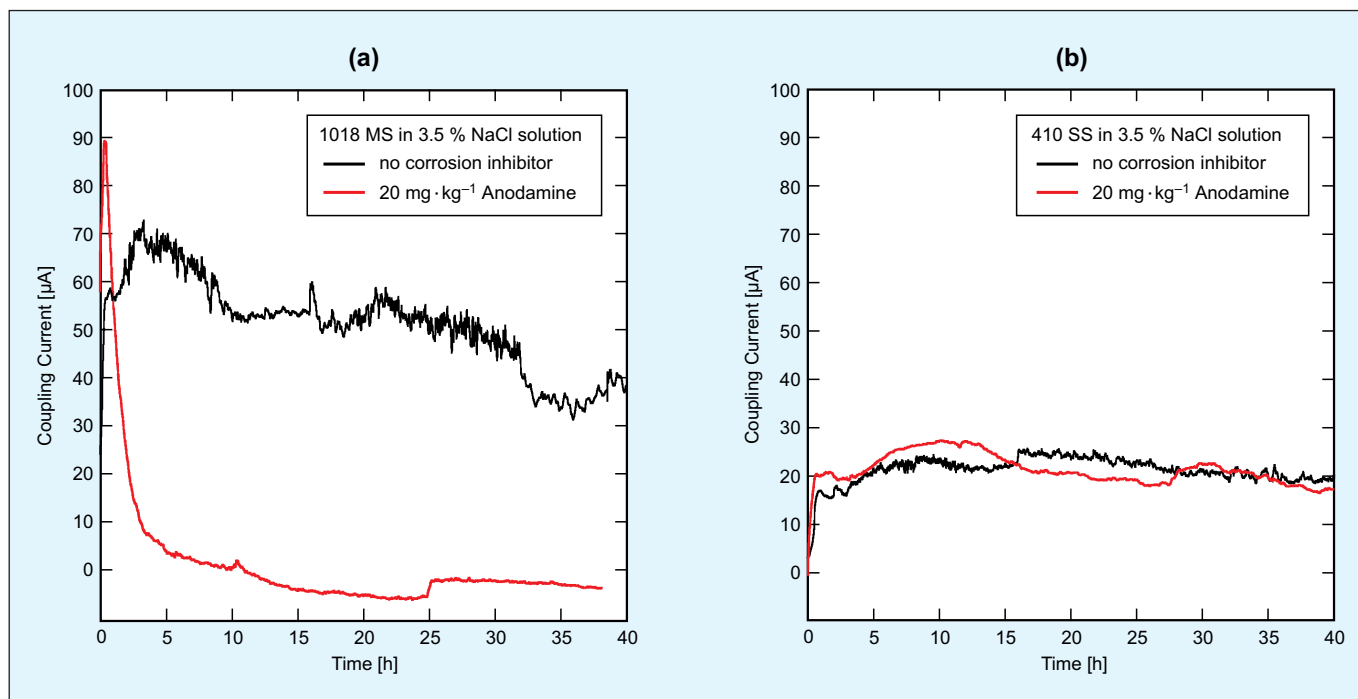


Figure 11:

Plots of the coupling current measured with (a) 1018 mild steel (MS) and (b) Type 410 SS at ambient temperature in 3.5 % NaCl solution and 3.5 % NaCl solution containing 20 mg · L<sup>-1</sup> of polyamine corrosion inhibitor.

Figure 12 shows the coupling current measured on Type 410 SS in 3.5 % NaCl solution with various concentrations of polyamine corrosion inhibitor. It was recognized that the coupling current of Type 410 SS in the solution without corrosion inhibitor had the trend of gradually decreasing toward a steady state, while in the solution with the polyamine corrosion inhibitor, the coupling current, while being lower, especially at the highest concentration, tended to increase over the experimental period. Thus, for any given time, as the concentration of polyamine increased, the coupling current in the steady state decreased. In particular, in the solution with 500 mg · L<sup>-1</sup> of polyamine, the coupling current increased after about 2 h, as shown in the inset of Figure 12, and after the crevice corrosion test of 6 days, we could not observe significant corrosion attack by visual inspection. When a sufficient amount of polyamine exists in the solution, crevice corrosion of Type 410 SS can be effectively inhibited by the formation of a protective inhibitor film, thereby inhibiting the cathodic reaction occurring on the external surface. This results in a decrease in the magnitude of the coupling current, and hence a reduction in the incurred rate of damage accumulation.

The effect of the polyamine corrosion inhibitor on the ongoing crevice corrosion was also studied. A Type 410 SS crevice specimen with a 0.6 mm gap was first immersed in 3.5 % NaCl solution without any corrosion inhibitor. During the test, 18.4 mL of 1 000 mg · L<sup>-1</sup> poly-

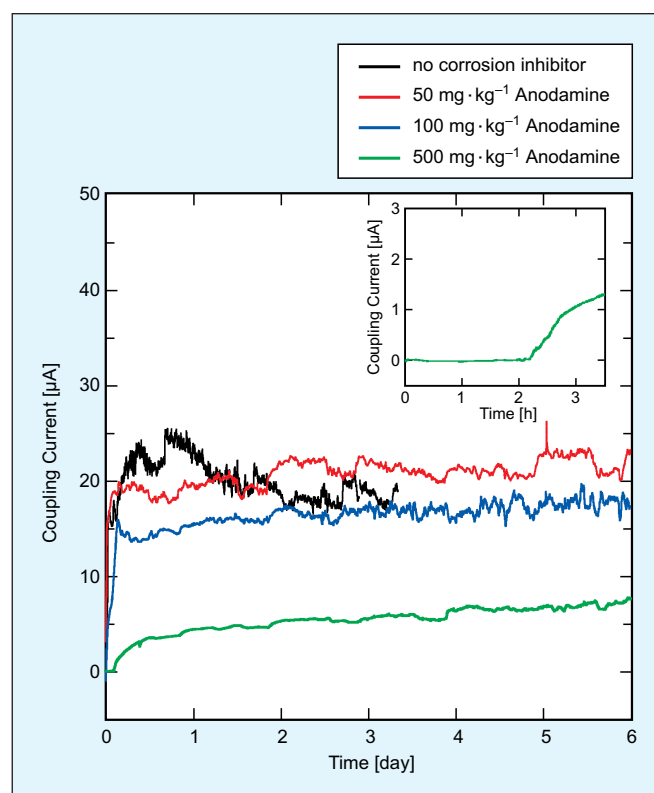


Figure 12:

Plots of the coupling current measured on Type 410 SS at ambient temperature in 3.5 % NaCl solution containing different concentrations of polyamine corrosion inhibitor.



amine was injected into the solution to yield a concentration of around  $50 \text{ mg} \cdot \text{L}^{-1}$ . As shown in Figure 13, right after the injection, the current increased instantly and then relaxed to a value that is much lower than the previous steady current. It seems that the film-forming amine is notably effective in suppressing the ongoing crevice corrosion. At the second injection to give a total inhibitor concentration of  $100 \text{ mg} \cdot \text{L}^{-1}$ , the same phenomenon occurred, although the resulting steady-state current only changed a little. As mentioned before, the polyamine could inhibit crevice corrosion by suppressing the cathodic reaction on the external surface.

From these observations, we conclude that the film-forming amine is an effective inhibitor of crevice corrosion in both mild steel and ferritic stainless steels, provided a sufficiently high concentration is present in the solution. Furthermore, monitoring the coupling current provides a "real time" method of monitoring crevice activity and represents the most reliable method for determining the efficacy of an inhibitor of crevice corrosion.

## SUMMARY AND CONCLUSIONS

In this paper, we have demonstrated a simple crevice corrosion monitor. It employs the electron coupling current that flows between the crevice and the external surface, where it is annihilated with the positive ion current flowing through the solution in the same direction by a charge transfer reaction, such as oxygen reduction or hydrogen evolution, as a means of monitoring crevice activity and inhibition in "real time." This monitor has been used to follow the development of crevice corrosion in 1018 mild steel, Type 304 SS, and in Type 410 SS in DI water and in sodium chloride solutions of varying NaCl concentrations with and without a chemical corrosion inhibitor being present. The principal findings of this study are as follows:

1. The monitor accurately follows the evolution of crevice activity in a manner that can be understood in terms of the cathodic process that occurs on the external surface (oxygen reduction) and that develops within the crevice due to the accumulation of  $\text{H}^+$ , thus providing a "real-time" method of monitoring crevice activity and inhibition.
2. The crevice initiation time is typically very short (less than 2 h for the experiments reported here), but appears to depend upon the chloride concentration and possibly on the inhibitor concentration.
3. The coupling current increases with time after initiation, passes through a maximum and then decreases, eventually changing sign to mark crevice inversion. The inversion is attributed to the gradual build-up of  $\text{H}^+$  in the crevice to the extent that proton reduction

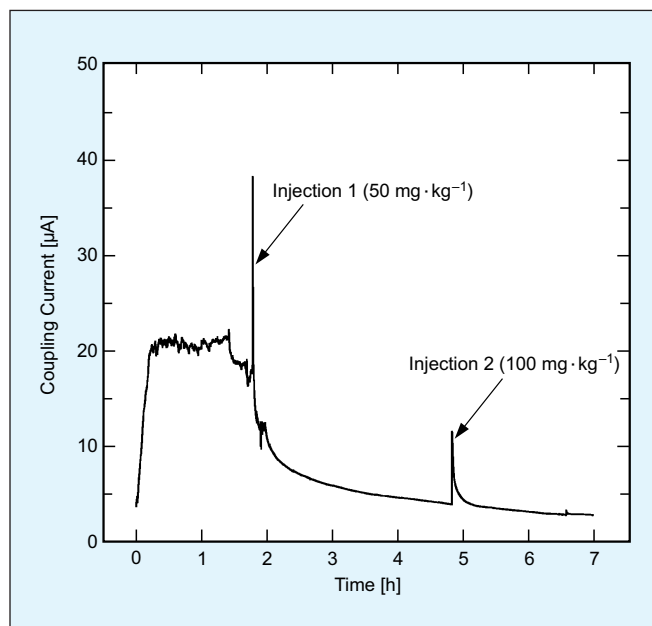


Figure 13:

Plot of the coupling current measured on Type 410 SS at ambient temperature in 3.5 % NaCl solution with injections of polyamine corrosion inhibitor.

within the crevice becomes the principal cathodic reaction in the system, while the anodic reaction moves to the external surfaces.

4. In the absence of a charge-compensating anion (chloride, in this case), crevice corrosion does not initiate, as there is no means of balancing the positive charge being injected into the crevice by metal dissolution.
5. Anodamine is an effective corrosion inhibitor of crevice corrosion of both mild steel and ferritic stainless steels in sodium chloride solutions, provided that it is present at a sufficiently high concentration.

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## REFERENCES

- [1] Karush, W., *Journal of Applied Physics* **1952**, 23(4), 492.
- [2] Karlberg, G., Wranglen, G., *Corrosion Science* **1971**, 11(7), 499.
- [3] Vicentini, B., Taccani, G., Sinigaglia, D., *Werkstoffe und Korrosion* **1971**, 22(11), 916.

- [4] Vicentini, B., *Werkstoffe und Korrosion* **1974**, 25(8), 593.
- [5] Vahdat, N., Newman, J., *Journal of The Electrochemical Society* **1973**, 120(12), 1682.
- [6] Alkire, R., Nicolaidis, G., *Journal of The Electrochemical Society* **1974**, 121(2), 183.
- [7] Alkire, R., Nicolaidis, G., *Journal of The Electrochemical Society* **1975**, 122(1), 25.
- [8] Alkire, R., Siitari, D., *Journal of The Electrochemical Society*, **1982**, 129(3), 488.
- [9] Galvele, J. R., *Corrosion Science* **1981**, 21(8), 551.
- [10] Gravano, S. M., Galvele, J. R., *Corrosion Science* **1984**, 24(6), 517.
- [11] Walton, J. C., *Corrosion Science* **1990**, 30(8–9), 915.
- [12] Jones, D. A., *Principles and Prevention of Corrosion*, **1992**. McMillan. Inc., New York.
- [13] Gartland, P. O., *Proc., 12th International Corrosion Congress*, **1993** (Houston, TX, U.S.A.). NACE International, Houston, TX, U.S.A., Volume 3B, 1901.
- [14] Frankel, G. S., *Journal of The Electrochemical Society* **1998**, 145(6), 2186.
- [15] Nocedal, J., Wright, S., *Numerical Optimization*, **2006**. Springer, New York, NY, U.S.A., 2nd edition.
- [16] Ijsseling, F. P., *Survey of Literature on Crevice Corrosion (1979–1998) – European Federation of Corrosion Series 30*, **2000**. Maney Publishing, London, United Kingdom.
- [17] Vankeerberghen, M., Abdulsalam, M., Pickering, H., Deconinck, J., *Journal of The Electrochemical Society* **2003**, 150(9), B445.
- [18] Vankeerberghen, M., *Corrosion* **2004**, 60(8), 707.
- [19] Pickering, H. W., Frankenthal, R. P., *Journal of The Electrochemical Society* **1972**, 119(10), 1297.
- [20] Frankenthal, R. P., Pickering, H. W., *Journal of The Electrochemical Society* **1972**, 119(10), 1304.
- [21] Pickering, H. W., *Corrosion* **1986**, 42(3), 125.
- [22] Pickering, H. W., *Corrosion Science* **1989**, 29(2-3), 325.
- [23] Shaw, B. A., Moran, P. J., Gartland, P. O., *Corrosion Science* **1991**, 32(7), 707.
- [24] Xu, Y., Pickering, H. W., *Journal of The Electrochemical Society* **1993**, 140(3), 658.
- [25] Nystrom, E. A., Lee, J. B., Sagüés, A. A., Pickering, H. W., *Journal of The Electrochemical Society* **1994**, 141(2), 358.
- [26] Cho, K., Abdulsalam, M. I., Pickering, H. W., *Journal of The Electrochemical Society* **1998**, 145(6), 1862.
- [27] Abdulsalam, M. I., Pickering, H. W., *Corrosion Science* **1998**, 41(2), 351.
- [28] Wang, M., Pickering, H. W., Xu, Y., *Journal of The Electrochemical Society* **1999**, 146(8), 2853.
- [29] Al-Khamis, J. N., Pickering, H. W., *Journal of The Electrochemical Society* **2001**, 148(8), B314.
- [30] Pickering, H. W., *Journal of The Electrochemical Society* **2003**, 150(5), K1.
- [31] Engelhardt, G., Strehblow, H.-H., *Corrosion Science* **1994**, 36(10), 1711.
- [32] Engelhardt, G. R., Macdonald, D. D., Urquidi-Macdonald, M., *Corrosion Science* **1999**, 41(12), 2267.
- [33] Anderko, A., McKenzie, P., Young, R. D., *Corrosion* **2001**, 57(3), 202.
- [34] Chen, Z. Y., Cui, F., Kelly, R. G., *Journal of The Electrochemical Society* **2008**, 155(7), C360.
- [35] Macdonald, D. D., Urquidi-Macdonald, M., *Corrosion Science* **1991**, 32(1), 51.
- [36] Manahan, M. P., Macdonald, D. D., Peterson, A. J., *Corrosion Science* **1995**, 37(1), 189.
- [37] Zhou, X., Balachov, I., Macdonald, D. D., *Corrosion Science* **1998**, 40(8), 1349.
- [38] Gomez-Duran, M., Macdonald, D. D., *Corrosion Science* **2003**, 45(7), 1455.
- [39] Gomez-Duran, M., Macdonald, D. D., *Corrosion Science* **2006**, 48(7), 1608.
- [40] Engelhardt, G. R., Macdonald, D. D., *Electrochimica Acta* **2012**, 65, 266.
- [41] Abella, J., Balachov, I., Macdonald, D. D., Millet, P. J., *Corrosion Science* **2002**, 44(1), 191.
- [42] Kennell, G. F., Evitts, R. W., *Electrochimica Acta* **2009**, 54(20), 4696.
- [43] Lu, L., Li, X., *International Journal of Minerals, Metallurgy and Materials* **2011**, 18(3), 320.
- [44] *Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*, **2011**. ASTM International, West Conshohocken, PA, U.S.A., ASTM G48-11.
- [45] Shu, H.-K., Al-Faqeer, F. M., Pickering, H. W., *Electrochimica Acta* **2011**, 56(4), 1719.
- [46] Stockert, L., Böhni, H., *Materials Science Forum* **1991**, 44–45, 313.

- [47] Shinohara, T., Mascko, N., Tsujikawa, S., *Corrosion Science* **1993**, 35(1-4), 785.
- [48] Sridhar, N., Dunn, D. S., *Corrosion* **1994**, 50(11), 857.
- [49] Laycock, N. J., Stewart, J., Newman, R. C., *Corrosion Science* **1997**, 39(10-11), 1791.
- [50] Dunn, D. S., Cragolino, G. A., Sridhar, N., *Corrosion* **2000**, 56(1), 90.

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