THE EFFECT OF CLEANING PROCEDURES ON CORROSION COUPON SURFACE TOPOGRAPHY

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SUMMARY: Several standardised procedures are available to corrosion researchers for preparing, cleaning, and evaluating corrosion test specimens in experimental investigations using coupon mass loss to measure corrosivity. These procedures may be mechanical, chemical or electrolytical in nature and are designed to remove corrosion products from coupons, ostensibly without significant loss of base metal. However, recent very detailed short-term corrosion experiments suggested that some of the procedures may interfere with the mass loss estimation and also may cause unexpected surface characteristics. The latter is problematic if the topography of the cleaned surfaces is of interest, for example in the investigation of the corrosion of mild steel surfaces exposed to marine immersion conditions for which, typically, corrosion is not uniform. This paper reports on a comparative study of the effect, on surface images, of the mechanical, chemical and electrolytic corrosion product removal procedures. It presents scanning electron microscopy images and the differences of final surface topography corresponding to each cleaning methods. This has implications for the selection of cleaning technique for specific investigations.

Keywords: Corrosion, coupons, cleaning, mass loss, surface topography.

1. INTRODUCTION

The present paper is concerned with the effectiveness of techniques commonly used for cleaning steel coupons after they have been exposed for some time to seawater immersion test conditions. In particular interest lies in the progression of mass loss over a relatively short period of time (say 1-28 days) in order to ascertain the corrosion loss trend during this time. The motivation for this work is three-fold: (i) comparison with the assumption of a constant corrosion rate for short-term exposures, (ii) comparison of the short-term corrosion loss trend for natural as compared with UV treated seawaters and (iii) examination of the changes in, or the development of, the corroded metal surfaces under these two exposure conditions (Melchers and Jeffrey 2014). Standard methods for coupon cleaning are available (e.g. ASTM 2011). These have been developed over many years and are considered to give, if properly applied, near-negligible corrosion losses occasioned by the cleaning process, low enough to be ignored in practical corrosion experimental work. However, preliminary investigations by the authors have shown that these methods may have some side-effects, sufficient to cause concern if examination of the corroded surfaces is of interest. The earlier investigations showed what appeared to be deposits on the surface but this was not always the case. For examination of the corroded surfaces remaining after corrosion cleaning such deposits obviously are not desirable.

The present paper reports on a controlled set of experiments in which identical coupons, all exposed for the same exposure time periods at the same location were cleaned using different techniques. The surfaces were then immediately examined. The next section outlines the materials used and the methods employed for coupon cleaning and for examination. This is followed by a description of typical observations for each technique, followed by discussion of the results and the implications of the test results.

2. MATERIALS AND METHODS

Mild steel coupons 25 mm by 25mm and 3mm in thickness (composition % by weight: 0.08 C; 0.21 Mn; 0.017 S; 0.03 N; 0.059 Al; 0.03 Cu; 0.02 Sn; <0.001 Nb; <0.001 Cr; <0.001 Mo; <0.001 P; <0.001 Ti; balance Fe) were exposed vertically to natural seawater at a constant immersed depth of 50 mm at the corrosion test site at Taylor’s Beach, NSW Australia. The natural seawater chemistry (Table 1), velocity and temperature conditions and the general environment have been documented previously (Melchers et al. 2010).

The coupons were mirror polished clean using a series of fine silicon-carbide abrasives, finishing with a 1 micron polishing paste, then washed in distilled and deionised water, dried with methanol (methyl alcohol) and stored in sterile containers with dessicant prior to exposure. Care was taken to ensure there was no corrosion product on the surface at the time of exposure (Fig. 1a). The coupons were suspended from plastic CTMP1000 Smart Tube UV resistant cable ties and coded for
Replicate sets of 8 exposed coupons were recovered at 1, 3 and 4 weeks, wire brushed cleaned of gross marine growth and major rust components and then subjected to the final cleaning process in the laboratory.

Table 1. Typical seawater chemistry at Taylor’s Beach Research facility.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Typical value</th>
<th>Parameter</th>
<th>Units</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity(CaCO₃)</td>
<td>ppm</td>
<td>409 – 419</td>
<td>Nitrite</td>
<td>ppm</td>
<td>&lt; 0.003 – 0.011</td>
</tr>
<tr>
<td>Ammonia</td>
<td>ppm</td>
<td>0.017 – 0.090</td>
<td>pH</td>
<td></td>
<td>8.1 – 8.3</td>
</tr>
<tr>
<td>Calcium</td>
<td>ppm</td>
<td>374 – 409</td>
<td>Salinity</td>
<td>ppt</td>
<td>25.7 – 31.8</td>
</tr>
<tr>
<td>Chloride</td>
<td>ppm</td>
<td>21,000</td>
<td>Sulphate</td>
<td>ppm</td>
<td>1600 – 2750</td>
</tr>
<tr>
<td>Diss. Oxygen</td>
<td>%</td>
<td>90</td>
<td>Total Phosphorus</td>
<td>ppm</td>
<td>0.003 – 0.07</td>
</tr>
<tr>
<td>Nitrate</td>
<td>ppm</td>
<td>0.017 – 0.050</td>
<td>Water Temp.(annual mean)</td>
<td>°C</td>
<td>20.0</td>
</tr>
</tbody>
</table>

![Figure 1. (a) Typical surface of a coupon before exposure showing the cleanliness of the surface and (b) coupon immediately after recovery being stored in sterile container filled with natural seawater for transportation to laboratory.](image)

Immediately after recovery of each set of 8 coupons, each coupon was placed in a labelled sterilized plastic container that was filled with the natural seawater from the site (Fig. 1b). This procedure was used to allow for the transportation time back to the laboratory (about 1 hour).
In the laboratory, the four cleaning methods (Table 2) were each applied to two replicate coupons. For acid cleaning, chemical cleaning and electrolysis, different exposure periods were used also. To ensure correct identification in subsequent analysis, the coupons were identifiable using coloured cable ties with alphanumeric coding: A1, A2 (Acid cleaning); C1, C2 (Chemical cleaning); T1, T2 (Tap water cleaning); E1, E2 (Electrolysis cleaning) (Fig. 1b). The tap water used in the water jet cleaning process was Newcastle tap water, a ‘soft’ water with chemistry as shown in Table 3. Immediately following the cleaning process, all coupons were thoroughly rinsed with deionised water, then immediately dried and placed in sterile containers. These were then taken for SEM examination.

Table 3. Water chemistry of tap water used for coupon cleaning.

<table>
<thead>
<tr>
<th>Ammonia</th>
<th>Chloride</th>
<th>O₂</th>
<th>Nitrate</th>
<th>Nitrite</th>
<th>pH</th>
<th>Salinity</th>
<th>Sulphate</th>
<th>Sulphite</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/L</td>
<td>mg/L</td>
<td>%</td>
<td>mg/L</td>
<td>mg/L</td>
<td></td>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td></td>
</tr>
<tr>
<td>0.017</td>
<td>34</td>
<td>96.3</td>
<td>0.013</td>
<td>0.002</td>
<td>7.18</td>
<td>0.1</td>
<td>27</td>
<td>&lt;0.05</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Both surfaces of each coupon were examined using a Scanning Electron Microscopy (SEM) (Philips XL30 SEM with Oxford ISIS EDS and Gatan MiniCathodluminescence Detector). Coupons were mounted individually on 30 mm diameter sized aluminium stubs and gold coated. Analytical energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) was used for elemental analysis of features on the surfaces of the coupons. The replicate coupons for these were coated with carbon.

3. RESULTS

Little difference was observed between the results of the cleaning methods for different lengths of seawater exposure. Here only the observations on coupons exposed for 4 weeks are reported. Figs. 2-9 show SEM images representative of the surface topography of the coupons resulting from each of the cleaning processes. It was observed that for most coupons the edges showed atypical corrosion patterns compared with much of the surface of the coupons. This was presumed to be due to incomplete removal of rust product layers at the edges. For this reason the regions (roughly 1 mm) near the edges were not considered in the comparison between cleaning methodologies in the analysis given below. Each figure shows the surface of the steel and the deposits on the surface at two different magnifications, with the scale bar on each showing 200 microns (left) and 20 microns (right). The Figure on the right is an increased magnification of part of the image on the left. In all cases the left hand image is representative of the entire coupon surface area.

Figure 2. Coupon A1 after 10 minutes of ‘Acid’ cleaning method (Table 2). The background is the steel surface. The doughnut-shaped and smaller features were identified by EDS as predominantly Fe. Scale bars: left = 200 µm, right = 20 µm.
Figure 3. Coupon A2 after 30 minutes of ‘Acid’ cleaning method (Table 2). The steel background is entirely covered by a conglomerate of doughnut-shaped and smaller features. These were identified by EDS as predominantly Fe. Scale bars: left = 200 µm, right = 20 µm.

Figure 4. Coupon C1 after 10 minutes of ‘Chemical’ cleaning method (Table 2). A few areas of the background steel can be observed. The doughnut-shaped features are more numerous and conglomerated compared to ‘Acid’ cleaned coupons. There is some evidence of remaining hard marine growth (top centre). Scale bars: left = 200 µm, right = 20 µm.

Figure 5. Coupon C2 after 30 minutes of ‘Chemical’ cleaning method (Table 2). The steel background is entirely covered by a conglomerate of doughnut-shaped features which are now 2-3 times larger compared to similar formations in Figure 4(b). These were also identified by EDS as predominantly Fe. Scale bars: left = 200 µm, right = 20 µm.
Figure 6. Coupon E1 after 1 hour of ‘Electrolysis’ cleaning method (Table 2). The background is the steel surface depicting pitting and a few peculiar shell-like features. The features shown at left were identified by EDS as predominantly CaCO\(_3\). Microstructure is also visible (right). Scale bars: left = 200 µm, right = 20 µm.

Figure 7. Coupon E2 after 2 hour of ‘Electrolysis’ cleaning method (Table 2). The background is the steel surface. No features observed. Microstructure is also visible (right). Scale bars: left = 200 µm, right = 20 µm.

Figure 8. Coupon T1 after gentle stream ‘Tap water’ cleaning method (Table 2). The background is the steel surface. The features shown at left and the magnified feature at right are predominantly CaCO\(_3\). Scale bars: left = 200 µm, right = 20 µm.
Figure 9. Coupon T2 after strong jet of ‘Tap water’ cleaning method (Table 2). The background is the steel surface. The features shown at left and the magnified feature at right were identified by EDS as predominantly CaCO$_3$. Scale bars: left = 200 µm, right = 20 µm.

Table 4 shows the mass loss of each coupon after cleaning using one of the methods in Table 1 and a comparison to the original mass of that coupon. The derived mass loss information is summarized in Fig. 10. Coupons cleaned with a jet of tap water showed the lowest mass losses, consistent with the observations that not all rust products were removed even with a strong water jet stream. Coupons cleaned by ‘acid’ or ‘chemical’ methods show higher mass losses compared to the electrolytical method. Coupons A1 and C1 that were given a 10 minute cleaning, show lower mass loss compared to coupons A2 and C2 which were exposed for longer periods (30 min) of cleaning. There is little difference in mass loss for 1 hour and 2 hours of electrolytic cleaning (compare E1 with E2).

<table>
<thead>
<tr>
<th>(Grams)</th>
<th>A1</th>
<th>A2</th>
<th>C1</th>
<th>C2</th>
<th>E1</th>
<th>E2</th>
<th>T1</th>
<th>T2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loss</td>
<td>0.0871</td>
<td>0.0960</td>
<td>0.0866</td>
<td>0.0980</td>
<td>0.0825</td>
<td>0.0850</td>
<td>0.0598</td>
<td>0.0663</td>
</tr>
</tbody>
</table>

Figure 10. Comparison of coupon mass losses estimated after application of different cleaning techniques.
4. DISCUSSION

On the basis that the cleaning methods used here are all accepted procedures for removal of rust products, it was expected that they all would show complete removal of rust products, independent of the cleaning methodology implemented. However, microscope (SEM) observations showed that in the case of acid, chemical and tap water cleaning some materials were present on the surfaces after application of these procedures (Figs. 2-5 and 8 and 9). Overall, in both cases the amount of surface material increased with increasing acid and chemical exposure (compare Figs 2a and 3a and also 4a and 5a respectively). This shows that the materials observed are not the original rust products that were to be removed but rather that they are in whole or in part the result of the acid and chemical cleaning processes. Although Figs. 2a and 3a and to a lesser extent Figs. 4a and 5a show that rusts were removed over parts of the coupon surface, it is feasible that not all rusts were removed and that subsequently the cleaning process formed new rusts that deposited over the original marine rusts. The possibility of new rusts forming on older rusts has been proposed before (Jeffrey and Melchers 2007). Further, the geometry of individual parts of the deposits is similar for these two types of cleaning – for convenience let them be termed ‘doughnuts’. The surfaces of these doughnut shaped rusts also are similar in appearance. In both cases the doughnut features are larger in size for the longer exposure periods. This supports the proposition that the visible deposits are, in part of not wholly, the result of each of the two cleaning processes.

For the acid cleaning, the short-duration exposures show evidence of metal surface structure (Fig 2b) partly obscured by the surface deposit. However, metal surface structure is less evident for the longer duration exposure (Fig. 3b), even though there are large areas without surface deposits (Fig. 3a). The observations are similar for the coupon surfaces subject to chemical cleaning except that the coverage of deposits appears to be thicker and cover most of the surface, even for the short exposure period (Fig. 4a).

In contrast, the surfaces of the water-cleaned samples show, apart from isolated raised features, surfaces on which metal grain structure and surface feature can be recognized (Figs. 8a, 9a), indicating that the water cleaning method was effective, at least for these parts of the surfaces. The isolated raised features seen on the surfaces of the water-cleaned samples (Figs. 8 and 9) appear to be similar in shape and characteristics and although somewhat different in number do not appear to be dependent on the velocity of the applied water stream. These raised features have a fragile appearance in contrast to the bulky nature of the majority of the deposits seen on the metal surfaces subject to acid and chemical cleaning processes. However, closer examination of Figs. 2b - 5b shows the presence of some of the fragile-looking features also in these cases.

EDS examination of the fragile-looking features showed presence of Ca and C suggesting they are CaCO₃. The presence of these is not atypical in rusts formed in seawater (LaQue 1975). It is possible also that they are remnants of shells or other hard marine growth that were attached to the surface of the coupons. For both possibilities their presence is surprising in view of the acid and chemical treatments applied, although it may be speculated that the inhibited solutions were insufficient to completely remove the carbonates.

Figs. 6 and 7 show that the electrolysis cleaning method was very effective in removing rust products, particularly after 2 hours of continuous application (Fig. 7). There is no presence of the bulky doughnut shaped features seen for the acid and the chemical cleaning procedures. The features seen after only one hour application (Fig. 6a) are similar in appearance to the fragile-looking features noted for the other cleaning methods. This supports the contention that the fragile-looking features are the hard remnants of marine organisms that had attached to the coupons during the field exposures. This is consistent with their presence being much lower for the longer application of the electrolysis procedure. Both after one hour and after 2 hours the metal surface reveals clear metal grain structure.

The water-jet cleaning procedure was effective in removing rust products but not in removing what appeared to be the fragile-looking features similar to those noted above as the hard remnants of marine organisms. Again, EDS identified these to contain Ca and C, consistent with marine shells. It is clear from Fig. 9 that even a hard water jet does not remove all rusts and other deposits.

Comparing the surface areas of metal exposed by the different cleaning methods, it is seen that although the ‘acid’ and ‘chemical’ cleaning methods are less time consuming they are not so effective in removing rust products compared to the electrolysis method. It removed 100% of rust products with a 2 hour electrolytic clean (coupon E2). In contrast both the acid and the chemical cleaning methods produced rust deposits as a result of the cleaning process, in the case of coupon C2 with 30 minutes exposure, with rust formations on almost the entire surface. Overall, it is evident that the electrolytic method provides both consistent results and a high degree of surface cleaning, without adding corrosion products originating from the cleaning process.

The results given herein are for coupons that were exposed for 4 weeks, all at the same site. The overall results for the effectiveness of cleaning and the various observations of surface deposits are very similar for the coupons exposed for only one week and for 3 weeks and are therefore not reported herein. It is noted that the surface features identified as CaCO₃ were less numerous for the one week exposure coupons, as might be expected.

A matter of some (scientific) interest is the shape of the ‘doughnut’ features seen in the case of acid and of chemical cleaning but not elsewhere. Without going into details here, it is considered that they represent the surface topography of rusts.
associated with a corrosion pit under the centre of the doughnut, and the rust products (Fe(OH)\(_2\) and subsequent oxyhydroxides) formed at the edges of the pit mouth. It is noted also that the rust products at the centre of the doughnut are less dense in appearance (Figs 2b-5b), consistent with the venting of gaseous H\(_2\) and possibly diffusion of FeCl\(_2\) from a pit beneath (Wranglen 1974). That this interpretation has some validity is supported by the doughnuts being larger and more bulbous for the longer period (30 min.) of acid and chemical cleaning (Figs. 3b and 5b). It has support also in observations of the form of rust products noted adjacent to the edges of pits formed on otherwise uncorroded steel surfaces (Papé 2009). The matter remains for further clarification.

Finally, it is observed in Fig. 2a that the doughnuts appear to follow short chain-like patterns. This is not inconsistent with the chain-like pitting patterns often observed for localized corrosion (pitting) of mild steel coupons (Evans 1960), presumably following some grain boundaries. This is a further matter for clarification, although neither this nor the previous point affect the present results.

5. CONCLUSION

Cleaning techniques conventionally used for corrosion mass loss estimation were considered herein for their effectiveness in removing all rust products necessary for microscopic examination of the remaining steel surfaces. Mild steel coupons exposed to seawater immersion for up to 4 weeks were used in all cases. The results show that both the conventional ASTM Acid cleaning and the Chemical cleaning methods left deposits of material identified as corrosion products resulting from the cleaning process. The deposition was found to increase with longer exposure time to the cleaning chemicals.

An alternative procedure, water jetting with tap water, was found to remove most of the 4 week old seawater corrosion products. High pressure water jetting was found to be more effective than low pressure removal. Whether water jetting is effective for marine corrosion products formed after much longer exposure periods is an open question.

The most effective cleaning process for removing the seawater corrosion products was found to be electrolytic cleaning. This procedure took a considerable time to remove all the corrosion products but if not applied for long enough left some features identified as calcium carbonate presumably the hard remnants of marine organisms. However, when applied for a sufficient period of time this procedure clearly revealed the metal grain structure.

6. ACKNOWLEDGMENTS

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7. REFERENCES


8. AUTHOR DETAILS

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