Corrosion Protection by coatings – how to figure out the best systems for practice?

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Abstract
What is the best method for finding out appropriate corrosion protection systems for steel structures? Coated hydraulic structures for example undergo stresses in form of impacts, abrasion provoked by transport, erection and use as well UV-aeration, osmoses and cathodic protection current. The selection criteria generally are reduced to check the coatings by defined laboratory test procedures especially by measuring the rusting of the substrate at an artificial scribe after a certain time of corrosion loads in cabins. The advantage is obvious: short time of testing and getting a definite value of rusting for comparing it with the threshold value or forming ranking. By that a further question arises: which real stresses for coated steel structures there are and how they may be reproduced in laboratory test procedures. With the help of a variation diagram the rusting measurements of diverse coating systems may be checked for the correlation between field and laboratory results. A first step for that is to compare rusting at a scribe and by that it is necessary to get rusting values from different protection systems from both the test procedures mentioned above (salt spray or cycle test procedures e.g. and long term trials in nature i.e. field test). It is advantageous to subdivide the field test trials in immersion, water changing and splash water zone! The research carried out by BAW sometimes show significant positive correlations with a certain statistic security. The results also show, that field test results are more reliable than laboratory tests and that protection systems work at best with special formulated primers.

This benefit also can be observed when protective coatings are tested to the resistance to electric protection currents: Systems with special primers generally show better results, which can be measured by the uptake of protection current and the grade of blistering. It should be mentioned that cathodic corrosion plants work especially in the immersion zone, where otherwise the corrosion stresses are low as shown.

Hydraulic and offshore steel structures often suffer by mechanical stress reasoned by transport and erection of the buildings. This kind of damages can be imitated by impacts to the coated panels. To make the damages by resulting micro fissures visible the panels in addition to the falling weight test where loaded by the salt spray test. The first results shows the positive effects of zinc-dust primer systems in combination with elastic binders, mainly single pack polyurethanes.

Key words: corrosion protection; test methods; long term trails in nature; cathodic corrosion protection
1 Introduction
With the revision of the corrosion protection standard ISO 12944 (“Paints and varnishes —
Corrosion protection of steel structures by protective paint systems”) especially the parts 5 and
6 (corrosion systems and corrosion test procedures respectively) are in discussion. Furthermore
the ISO 20340 also is in revision and will be introduced as the new part 9 of this standard.
By that the general questions of ideal testing procedures and durability of coatings should be
answered. Generally there are two ways to propose coating systems for heavy duty corrosion
protection immersed steel structures:
- using or even creating test procedures to figure out best corrosion systems by performance or
  in contrary to that
-  choosing coating systems in advance and allow to introduce them by appropriating or even
  lowering the threshold values of test procedures.
These are also immediately the point of views of an owner of a structure and of a producer re-
spectively. The Federal Waterways Engineering and Research Institute (BAW) has done a lot
of tests to search for good coating systems for hydraulic steel structures as well for wind gener-
ating structures in the Northern and  in the Baltic Sea. In addition the  German Federal Maritime
and Hydrography Agency (BSH) has formulated “minimum requirements” (Standard de-
sign [1]) which describe the measures to be taken for German offshore wind energy structures
concerning their integrity, i.e. ensuring their function and stability, for a lifetime of 25 years. In
both the fields, hydraulic steel structures as well offshore wind energy structures, the challenges
for corrosion protection are nearly the same: Long durability under extreme climate and other
very special loads. Special loads often mean mechanical or electrochemical stress. The overall
aim of corrosion tests is to figure out and certificate usable coating systems for these high de-
mands and to list them for announcement in the public area.

2 Different Types of Corrosion Stresses on Coatings in Marine Environments
In corrosion standards, the common tests used are generally based on laboratory testing
procedures and it is important to know that these test procedures cannot often determine the
true corrosion prevention potential of a coating system. No overall laboratory test exists which
considers all the different stresses. Also there is a lack of appropriate corrosion factors or
rates, in order to relate an accelerated test to lifetime in real file.

Within a structure erected in a maritime environment (sheet pile walls, oil platforms or wind
energy structures), there are various zones with different intensities of corrosive attack: bottom
or sea floor, immersion and low water zone, tidal and splash zone and last but not least, the at-
mospheric zone. Therefore, it is necessary to consider different intensities of corrosion along a
structure. But the relation of a laboratory test procedure to a specific corrosion zones in nature
is not yet worked out.

Moreover there is continuous mechanical stress from waves, floating matter and ice movement
in winter that can attack coatings and coatings also commonly suffer from mechanical impact
during transport and erection, which can lead to localized damage, coating detachment result-
ing in heavy rusting. The wet, high-salt environment is a constant danger that leads to corro-
sion; especially the splash zone is the area of highest corrosive stress. Furthermore failure of a
coating by osmotic blistering may be caused by condensation and diffusion of water. UV-
radiation and biological growth in addition are phenomena that can weaken coatings by deteri-
oration of the binder.
Often forgotten is the stress applied to coatings from the electric current produced by a combination of different metals (galvanic cell), as well as by cathodic corrosion protection systems (which should actually prevent any corrosion of the steel) in the immersion zone. Both circumstances cause an acceleration of the corrosion cell’s cathodic reaction and propagation of hydroxyl ions that eventually attack the coating binder at the steel/primer boundary-area.

3 Methods of determination of protection properties of coatings

The relatively short duration of accelerated laboratory weathering tests (e.g. ISO 20340 or ISO 9227 and ISO 11997) may not produce significant deterioration of the coating system as a whole. Therefore, the use of selection criteria to determine best performance is often limited to the post-test determination of underlying rusting at an artificial scribe. With this method, the rusted area may be easily determined and fixed threshold values, i.e. the pass/fail criteria, can be used. In contrary, coating defects, deterioration of the coating or even rusting of the substrate are not always found, or can be differentiated after accelerated testing. These circumstances have forced BAW to carry out Long Term Trials (LTT; according to the criteria of the Guidelines of Testing of Coatings (RPB, [2]) in different types of waters and in different zones over a long period of time (five years) to allow corrosion of coated steel to occur, as well as to expose the coated panels to multiple stresses at the same time. This report shows that a large part of these individual single stresses can be tested by a combination of Long Term Trials (LTT, i.e. field tests) in nature (and was recently proposed by members of the WG 6 of ISO preparing the update of the ISO 12944) with common laboratory test procedures. But on the other side observations also show that even in LTT in nature, virtually no critical damages comparable to the ones usually caused by impact, abrasion and galvanic action, occurred to the exposed panels. Therefore in addition more specified laboratory test procedures are necessary.

4 Results of test procedures

Generally there is a lack of equalization of laboratory test methods with reality. Variation diagrams are useful tools to detect dependencies between two different series of test results. Comparisons of laboratory test results to those of trials in nature are seldom done and therefore correlations are really rare ([3], [4]).

4.1 LTT in Nature — Comparison to Laboratory Test Results

To check the validity of laboratory test results a comparison must be made with the results of rusting in LTT in nature. To avoid uncertainties due to application effects, the couples/pairs of the statistical population must be prepared in the same time and manner. In this way, statistical dependencies can be checked for by calculating a correlation coefficient ($r=0.8$), which shows the confidence level depending on the number of pairs ($n=10$), as presented in Figure 1. The statistical probability that field test results of rusting in the tidal zone and the salt spray test are dependent on each other is higher than 99 percent. When one compares the threshold values in the correlation curve (1 mm salt spray test), there is a point of intersection at 9 mm (LTT) and this is virtually almost identical to the respective threshold values there (10 mm according [2]). The significant dependency shown in Figure 1 is the only one found between rusting in laboratory test results and LTT tests in various zones. It means on the other side that both of the common laboratory test procedures (ISO 20340 aging test and ISO 9227 salt spray test) are unable to mirror results obtained in the immersion and splash zone in nature exactly.

BAW publishes a list of approved coating systems for application on structures in seawater
twice a year based on the results of standardized corrosion test procedures in the laboratory [5].
Over the last decade, a certain trend was observed: an increasing number of corrosion protection, primer-free coating systems have passed the salt spray test (ISO 9227; 1,440 hours, with rusting at the scribe of less than 1.0 mm). It seems that primers such as zinc-rich ones can be substituted by these new systems — mainly one- or two-coat systems based on epoxy resins. But according to the BAW guidelines [2] a long-term trial test in nature must follow any laboratory accelerated test in order to be fully conforming. After the evaluation of the long-term trial test results, a huge discrepancy was found: more than half of the approved coating systems did not confirm to the good performance of the laboratory test. This poor result was due to the very high values of rusting seen at the scribe within the tidal and splash zones after the more relevant stresses in the field test (e.g. location of Kiel, Baltic Sea). As an example figure 2 shows test panels with rusting at the scribe after the five-year field test. While in the laboratory salt spray test the panels showed a mean rusting value of less than 1.0 mm (i.e. threshold value), the panel in this figure (left) shows a rusting at the scribe of 25 mm after natural exposure. This is far above the required threshold value of 6 mm according [2] after natural weathering. On the other hand, figure 2 (right) shows a far better result: This System is built up by diverse layers with a primer. Immediately the variation diagram of figure 1 gives that impression according the distribution of the data points.

Figure 1: Variation diagram of rusting at the scribe in the tidal zone of field test (LTT) and salt spray test in laboratory

\[
y = 3.3427x + 5.9536 \\
R^2 = 0.6354 \\
n = 10 \quad R = 0.797 \quad \text{stat. sec. > 99%}
\]
The clear tendency is that coating systems without specially formulated inhibitive primers (single- and two-coat systems) tend to fail in the most corrosive zones in LTT. The explanation of this phenomenon is at first simple: the rusting of the substrate along an artificial scribe is prevented by the zinc rich primer systems. Zinc-rich primers are able to avoid chloride-induced corrosion, and by that underlying rusting, independent of the generic type of binder of the primer. Their action is manifold: sacrificial behavior as mentioned above as well binding of OH- and Cl-ions, decreasing the primer’s “porosity” and increasing its barrier protection.

**Corrosion rates and acceleration factors**

The calculated corrosion rates (µm/h) of the rusting at the scribe in the previously described test procedures are listed in Table 1, in relation to the threshold values of different standards and guidelines. It can be seen that the salt spray test (ISO 9772) has practically the same corrosion rate value (0.69 versus 0.71 µm/h) as the aging test (ISO 20340) with however the more stressing cycles (see UV-radiation and thermal shock!). It is concluded that the threshold value of 3 mm for the very good systems is too high a claim and this value should be raised to 4 mm.

**Table 1: Corrosion rates [µm/h] of different standards and test results (um/h)**

<table>
<thead>
<tr>
<th>Testing procedures</th>
<th>Corrosion rates</th>
<th>Zn-rich primer</th>
<th>Zn-free systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt spray test (lab., 1,440 h; 1.0mm*)</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aging test (lab., 4,200 h; 3.0mm*)</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Immersion zone (LTT, 43,200 h; 2.5mm*)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>Tidal zone (LTT, 43,200 h; 10mm*)</td>
<td>0.23</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>Splash zone (LTT, 43,200 h; 6mm*)</td>
<td>0.14</td>
<td>0.11</td>
<td>0.52</td>
</tr>
</tbody>
</table>

1) ISO 9772; 2) ISO 20340; 3) RPB [2], LTT test = long term trial test in nature (BAW, 2008-2013); * threshold values

The results also indicate that in the immersion zone all the different coating systems show little corrosion at the scribe. In contrast to that, in the tidal zone there is a lot more corrosion and the values allow for a degree of discrimination between systems, as can also be seen in the splash zone. When the corrosion rates of the different test procedures are compared, one can calculate the acceleration factors, for example, the aging test against the immersion zone in nature: 0.71/0.06 = 12. Generally the corrosion rates of laboratory tests are higher, whereas the differ-
ence with that of tidal or splash zone in nature is lower, what confirms the high aggression in these zones! The values of the corrosion rates of threshold values of the LTT are within the area of very good (zinc-rich systems) and the average systems (single and two-coat systems; table 1).

4.2 Tests of cathodic corrosion protection

The Cathodic Corrosion Protection Plant (CCP) by impressed current is a well-known method for protecting structures in seawater against corrosion. Generally, this method is to be preferred over galvanic anodes as it doesn’t release dangerous metals like zinc or aluminium into the maritime environment, does not change the milieu so completely and gives the possibility to observe the function by measuring the electric protection potential. Nevertheless both the methods cause stress to the coatings due to the protection current that delivers electrons, which, in combination with diffusing water and oxygen may form hydroxyl ions at the boundary of the steel surface and the primer. This in turn attacks the polymer, finally formation of blisters or even causing disbondment. A very important quality of a coating under these conditions is the possibility of incorporating, or neutralizing, the propagated harmful hydroxyl ions.

Figure 3 shows graphs of the required electric current per test panel along the time of fifteen months according the test method of guidelines ([2], [6]). This development sometimes also changes strongly: less good coating system generally demand for higher protection current – often after the testing time of six month. This on the other hand is the testing time of ISO 15711(Determination of resistance to cathodic disbonding) and it is shown, that this time is far too short. Also one should recognize that the observation of protection current during the test could be an addition and a more susceptible method than counting blistering and measuring the disbondment after the test!

![Graph showing CCP-test need of protection current along the testing time (15 months); primer free systems show demand for higher current](Image)

4.3 Further laboratory tests – mechanical loads

As mentioned above there are many applied stresses to be considered when mild steel has to be protected in sea water, especially in offshore regions. Some tests may be carried out in laboratory. In addition there is a need of the knowledge of the abrasion resistance (see [2]) of a coating material. In combination with the falling weight test (ISO 6272) this enables a good characterization of the mechanical quality, i.e. of attributes like hardness
and elasticity, of a coating system. These properties can help to avoid disbondment or effects of impact during transport or erection of a structure that would result in the rusting of the substrate. The effects of impact can be clearly shown when this damage is followed by a rusting stress, e.g. salt spray cabin: By that the area of rusting of the substrate may be measured that is more definite than other counting rates (e.g. testing for pores and cracks by high-voltage test, DIN 55670) and it makes clear the true deterioration! Up to now there are not enough results for exact conclusions because the results are somewhere individual according the coating system. But there is a tendency that zinc-rich primer based coating systems show less rusting of the substrate than zinc-free systems (56 mm² for zinc-primer and 119 mm² for systems without primer in average). Both the results of twelve different coating systems are shown in a variation diagram with the values of the rusting after the field test (water changing zone, Baltic Sea) and after the impact test with following salt spray test (fig. 4). When combined in this matter both the parameters give a more complete impression of good functioning protection systems because of the appropriate input of practical stresses. The distribution of the rusting values shows, that best results in both the tests were achieved with zinc-rich primer systems in accordance with universal laboratory test procedures.

**Figure 4: Rusting areas after impact test and salt spray load**

It is often argued that high adhesion values of a coating help to prevent corrosion. But the reason why high pull-off values are advantageous hasn’t yet been proved, also in this work. High adhesion values for example are not enough to prevent creep, rusting of the substrate or at the scribe, nor are they ever high enough to prevent osmotic effects which are important for underlying rusting. A statistical calculation at BAW showed that zinc-rich primers have an average value of 6.7 MPa in the (single side) pull-off test while the two- or one -coat systems show an average value of 7.6 MPa. Both the values are comparable and don’t give hints for significant positive protective properties of coatings.

5 Discussion and Conclusion
The laboratory testing procedures depend essentially on the values of the rusting at the scribe.
Generally threshold values for that should be aimed at the performance and should not prefer certain systems. For the aging test of ISO 20340 (4,200 hours), a threshold value of 4 mm for rusting at the scribe for all systems of full renewal is recommended while for the salt spray test (ISO 9227) 1 mm for 1,440 hours (immediately 1.5 mm for 2,160 hours) of duration are proposed as threshold values.

The most critical zones for structures of maritime offshore environments are the tidal and the splash zone. Coating systems such as the zinc-free systems do not show good performance in the field test in these zones, even when they pass the laboratory salt spray test (ISO 9227) or the aging test (ISO 20340). This is in agreement with the observations of sometimes large values of underlying rusting areas on existing offshore structures. The reason may be that they have no special active layer to prevent rusting at the substrate, as well-formed primer-based systems do. Also, high adhesion values are not suitable to prevent rusting of the substrate. A statistical calculation showed that zinc-rich primers have only a slight lowered pull-off value than other coating systems and there is at all no breaking between substrate and primer! To shorten the discussion of this aspect it should be recognized that even very high pull-off values don’t protect the coating systems against rusting at the scribe or osmosis. The osmotic pressure is always much higher than the coating strength. Also high adhesion values do neither prevent the infiltration of aggressive ions (SO₄²⁻, Cl⁻, OH⁻) nor can suppress the crystallization pressure of new formed rusting phases.

Are there any other advantages of primer-free coating systems as often reclaimed by producers? To reduce or prevent rusting at the scribe, the coatings must be insensitive to impact and other damage that leads to deterioration of the coating during transport or erection, however single-coat systems tendentious are more sensitive to falling weight tests than primer-based coating systems and show significant failure after the test and a weathering stress in a salt spray cabin. If a coating system shows signs of damage, there is a high demand for self-protection against rusting. This can be achieved with specially formulated primer systems as proven in laboratory and field tests, as well as on existing structures. Guidelines for corrosion protection should help to figure out the best systems available by defining proper threshold values in corrosion test procedures compared to the results of long term trials in nature. In addition laboratory test methods for corrosion protection coatings should include further mechanical test procedures such as abrasion and falling weight tests.

Within the immersion zone the difference of underlying rusting of primer-based systems and single- or two-coat systems is low. Generally very little corrosion will happen there, but at the same time, this is the zone where Cathodic Corrosion Protection system works and this means that due to cathodic polarization, hydroxyl ions are produced by delivering electrons to the polarized areas in order to protect the steel in sea water. The results over decades of measurement have shown a constant result, that zinc-rich primer based coating systems can bear or withstand hydroxyl attack and this way disbondment and blistering of the coating can be avoided. As a further conclusion, there is a need to observe the behavior of a coating with a protection current under field conditions (~950 mV versus Ag/AgCl-electrode in sea water) for at least 15 months. Most of the coatings have a limited resource to resist the propagating of hydroxyl at areas with cathodic polarization. In addition it is recommended to introduce a current density of about 2 mA/m² for the whole area of the front side of a testing panel (coated area including holiday area), which results in a maximum current of 50 µA.

Generally there is a lack of known correlations between different test procedures detecting rust-
ing at the scribe. Consequently also comparisons of corrosion rates from different test methods are missing. Therefor ultimately the results of a long-time exposure in nature should determine how a system can work in avoiding corrosion under extreme circumstances and conditions on site. In the field test about half the coating systems failed and only systems with zinc-dust primers passed the test. Existing laboratory test procedures are useful to a certain extent — for example, as a pre-qualification test for the protection quality of coatings or to complete the determinations of useful properties.

References
[5] List of certified protection systems; www.baw.de