IT'S
A SALTY MATTER

Andrew Recker, Borchers ChlorRid, USA,
focuses on surface preparation and
corrosion reactions on steel surfaces,
with the understanding that these
corrosion reaction rates exist regardless
of the overlying applied coating.

The role of surface preparation with substrates for application of anti-corrosive coatings has been growing in importance since the early 1990s. The ability of a coating to provide a proper barrier with good adhesion started to become evident once lead and other heavy metal pigments that helped provide moisture resistance were determined to be toxic and banned from use in coatings. The barrier property of the coating needed to be that much better without these anti-corrosive pigments. Another regulatory change that challenged coating performance was the reduction in solvents used in coatings that contribute to VOCs, which took away from higher molecular weight thermoplastic resins from providing superior barriers with relatively high T_gs. The higher molecular weight and/or higher T_g of the polymer film provided for lower permeability to the corrosive reagents, water and oxygen. These challenges pushed for major development of new coatings technologies to increase barrier and adhesion properties through functionality and reactivity.

With the challenges being so great, it has also led to all aspects of the coating process being looked at, including the preparedness of the substrate to accept the coating. At some point, the cleanliness of the substrate was actually determined to be the most important part of the coating process, with the first surface preparation standards dating back to the 1960s with the Society for Protective Coatings (SSPC), but more commonly introduced as an ISO standard in 1988.

The first surface preparation standards were visible guides for comparison to the actual surface condition (SSPC-VIS 1). With this standard, the steel substrate is blasted and checked for shadowing or degree of white metal cleanliness. The steel could also be checked for oil-based contaminants by a water wet-out test. This process was fairly successful, with visible inspection adequate to determine proper surface cleanliness for the optimum coating performance. Over the next few decades, questions and frustrations started growing over the actual performance not matching the expected performance or the lab panel testing. Years of blaming the applicator or the coating chemistry as not being suitable for the environment for which it was applied would ensue. It was then determined that there was something invisible to the eye that was causing much of the premature failure of the coating. The invisible detriment was soluble salts.

Soluble salts

With the onset of identifying soluble salts on the surface, a reliable method to quantify salts needed to be developed. The Bresle patch was developed around 1995 as a reliable means to quantify the salts on the surface by extracting them with deionised water and using conductivity to determine salt concentration. This test method accounts for all ions soluble in deionised water, regardless of reactivity with the metal and resulting corrosion rates. The resulting surface density of salts can then be calculated with the following equation:

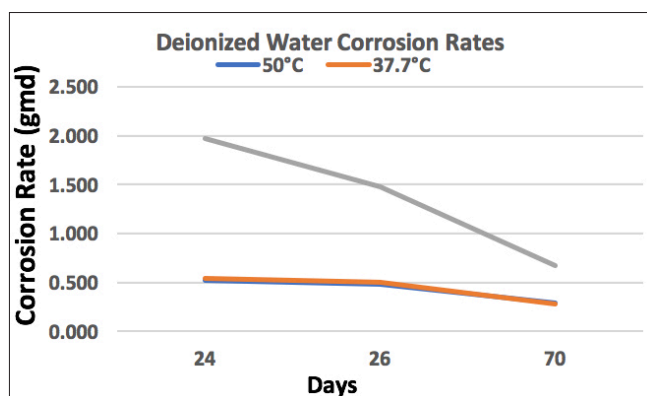$$\rho_A = \frac{c \cdot V \cdot \Delta\gamma}{A}$$

Figure 1. Corrosion rates for deionised water.

The constant (c) used is typically sodium chloride which is 5 kg/m^2 × S and is different for each salt based on ionisation and molecular weight. Consequently, there is some error in the calculation due to assumptions regarding the constant used, but more importantly this calculation assumes that all salt is sodium chloride. Other variables are as follows: pA is the equivalent surface salt density of the salts in mg/m^2, V = Volume of solution, dy = the change in conductivity, and A = the area of the test.[4] It also assumes that all salts and resulting ions have the same corrosion rate and should be of equal concern regarding surface preparation and coating performance. Should the corrosion rates be expected to be the same? What is the mechanism of the salt in the corrosion equation? Once the salts have been found on the surface, what is the best way to remove them?

Experimental procedure

The corrosion rates for different environments are varied and depend on environmental factors such as temperature, moisture levels, agitation, pH, and salt type/concentration. The experimental design constructed here attempts to isolate the variables so that their true impact on the corrosion rate is more evident. One of the main focal points of this paper is to determine the role of different anions in the corrosion process, which will help answer the question of the utility of using conductivity as a means of quantifying soluble salts on the surface or should the individual ions of interest be quantified through titration. Additionally, the experimental design then evaluates high-performance epoxy coatings from the market over the salt contaminated surface. The data generated will provide useful insight into what type of salts are most critical in terms of performance of the applied coatings, due to the pre-existing reactions at the steel surface.

For the general corrosion rate testing, the standard method of immersion in liquid media and measurement of mass loss over time is utilised. A standard panel size of 1 in. × 4 in. × 1/16 in. was used in all immersion testing. All of the panels tested for corrosion rates were unpolished cold rolled steel with no coating applied. The immersion containers used were 200 ml with an airtight screw cap closure. The container solution volume was controlled with 180 ml in each container. The solutions were left untouched as to not agitate the solutions – a significant variable not to be concerned with in this study. The only handling and movement of the containers was to remove them from the test for weight loss measurement, which terminates the sample. Also, the containers were not opened until time of removing the panel for mass loss measurement. The reason for this was to inhibit the introduction of more oxygen into the reaction. Starting with deionised water, these salt solutions were utilised in the study: DI water; 3.5% NaCl (neutral pH); 5% sodium nitrate (neutral pH); 5% sodium sulfate (neutral pH); and 1% sodium bicarbonate (8.5 - 9 pH). This range includes

the different salt anions of interest in the steel corrosion field.

After the baseline corrosion rates were established to illustrate the importance of the type of ions present, panels were aged for one week in 3.5% NaCl at room temperature to provide for a red ferric oxide adhered rust surface.

The panels were not rinsed, dried, and then tested for chloride ions with a surface extraction titration analysis (ISO 8502-15). Salt removal solutions were used with pH and proprietary chemistry providing the variables. An alkaline cleaning solution, an acidic cleaning solution, and potable water at neutral pH were lightly rinsed over the steel surface in a vertical position for one minute each. The chloride ion levels were then retested with titration analysis to determine the efficiency of the cleaning solution. This was carried out in triplicate.

Finally, the panels were coated with the performance coatings and boiled in deionised water for six hours then cooled for 18 hours, which equals one cycle. The panels were exposed for four cycles and evaluated with pull-off adhesion test (ASTM D 4541).

Results

Corrosion rates

The corrosion rates of the different salt ions proved to be quite different. Deionised water immersions with a 1 in. × 4 in. panel immersed in 180 ml in a 200 ml sealed container were conducted at three different temperatures and three different durations in duplicate. Each steel panel was in its own container and not agitated during the duration of the test. The corrosion rate at room temperature (21°C) was highest and as the temperature was increased the rates declined significantly (Figure 1). This is counterintuitive as it is not in congruence with the Arrhenius equation and simple kinetics, with the reasoning for this result discussed in literature, with detail regarding the formation of an iron oxide passivate on the surface (black oxide) which inhibits further corrosion of the steel.[1] At lower temperatures, the black oxide formation is not as quick and less ordered, and with higher temperatures, the oxide layer forms quickly and is more durable, as seen with a simple scratch resistance comparison. This black oxide passivate can be easily seen after a few days of immersion. Another key observation from the deionised water sample data is that with longer durations, the corrosion rates drop significantly. This is due to the consumption of oxygen in the closed container.

The introduction of chloride anions was provided by a 3.5% NaCl solution at neutral pH. The corrosion rates with sodium chloride were very different from the deionised water solution. As the temperature was increased, the corrosion rates increased significantly (Figure 2). This is in agreement with simple reaction kinetics and opposite to that of the deionised water rates. Again, with a longer duration of testing, the corrosion rates were lower due
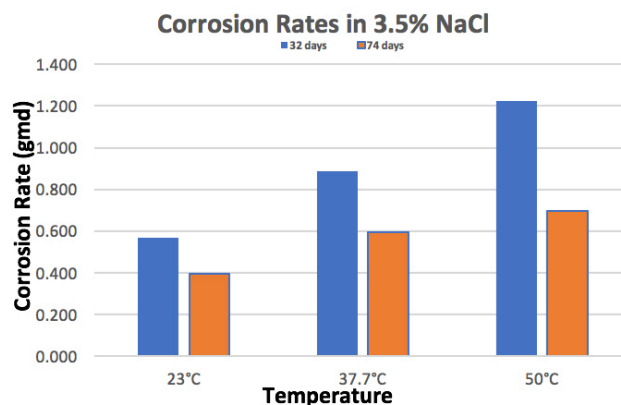

Figure 2. Corrosion rates for sodium chloride solution.
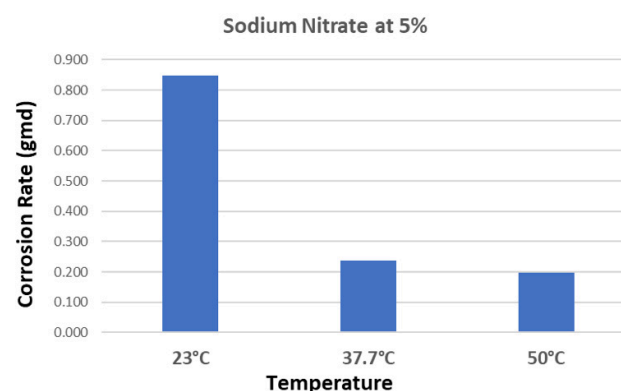

Figure 3. Corrosion rates of panels aged in sodium nitrate.
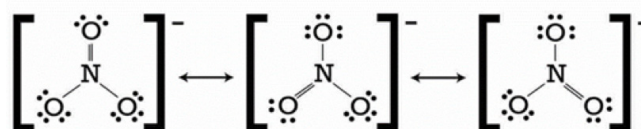

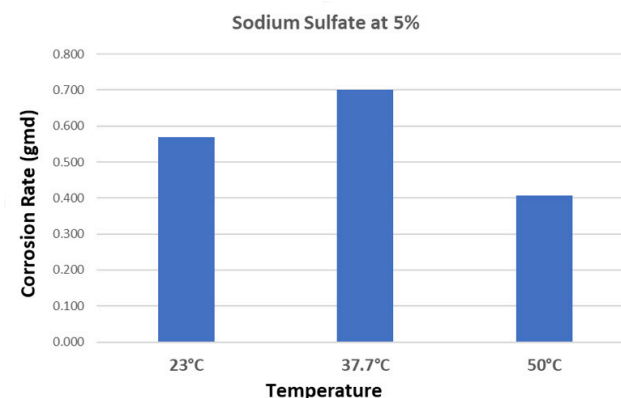Figure 4. Resonance structures of nitrate anion.

Figure 5. Corrosion rates of panels aged in sodium sulfate.

to the oxygen being consumed in the reaction. The panel surfaces were not black with these samples as in

the deionised water testing. The panels were etched with a dull grey appearance. The reason the black oxide layer did not form in this case is due to the chloride anion disrupting the passivate formation and integrity through adsorption to the steel surface and termination of the crystal lattice passivate layer. The chloride ion significantly inhibits the passivating oxide layer by its electronegative monovalent nature.[3]

Sodium nitrate solution corrosion rates again provided for different corrosion rates (Figure 3). The results are similar to deionised water but lower overall. Again, the corrosion rates declined as the temperature was increased. Visually, all of the panels formed a black oxide layer within 24 hours at each temperature. The integrity of the black oxide layers on the sodium nitrate panels was significantly greater than that of the deionised water panels which was easily determined with a metal to metal scratch evaluation. Similar to the deionised water immersion results, the oxide layer inhibited further corrosion of the steel and higher temperatures promote the formation of this film with greater efficacy. The nitrate ion is an anion with a negative charge similar to chloride, but there are key differences in the reactivity. The nitrate ion is less electronegative, but it is stable through valence resonance (Figure 4). This resonance does not allow the nitrate ion to adhere to the steel as well and prevents it from participating in blocking the black oxide formation. Instead, it promotes it.

Sodium sulfate solutions provided for yet another different corrosion rate and surface appearance. The corrosion rates were lower at room temperature, then increased as temperatures increased, and finally declined as the temperatures increased further (Figure 5). The room temperature panels showed some etching and black oxide which transitioned to more etching and a different greenish oxide layer, and finally at 50°C transitioned to a higher integrity, consistent greenish oxide passivate layer. This variability in the corrosion rates and passivation layer can be explained by the valence resonance structures available for the sulfate anion which is more extensive.

Salt removal and panel testing

New 2.5 - 3.5 mil profile blasted steel panels were placed in a 3.5% NaCl at neutral pH solution at RT for one week. The panels were then removed from the salt solution and dried without rinsing. The appearance of the panels was of a consistent red rust that was fairly well adhered to the surface as in NACE 4. The surface chlorides were then titrated using an ion specific titration tube specific for chlorides. Similar rusted panels were then treated with wash solutions and coated with high-performance coatings from the tank linings market. These coatings were highly crosslinked 2K epoxies with low permeation. The coatings were applied after the panels were washed and dried by drawdown application per the recommended dry film thickness stated in the product data sheets. The coatings were allowed to cure for seven days at room temperature before being evaluated for performance.

Conclusions

The corrosion testing of the individual salt ions showed clear differentiation between the different anions with regard to corrosion rates and visual corrosion products, which is confirmed in past literature and research from over 40 years ago. The results also confirm that using conductivity to analyse surface soluble salts assuming one type of salt, sodium chloride, is too limiting to provide a useful picture of the corrosive environment. For, example there are carbonates in the natural environment in non-metallic blast media which have been known to transfer to the steel surface during the blasting process. They provide conductivity, but they do not provide for a corrosive environment. There are other ways to analyse the salts on the surface through titration reactions that accurately analyse for the individual ions. These titrations allow little variation between tests and operators providing for a better understanding of the corrosive environment at the surface.

The results also show that an acidic solution will remove salts from the surface more effectively than an alkaline solution. Chloride anions are very electronegative and adhere to the steel surface strongly. The acidic anion displaces the salt, solubilises the chlorides that are complexed such as in akageneite, and removes them leaving no residue behind. An alkaline solution will remove salts that are not adhered to the surface and not complexed which is not effective enough for many specifications. Engineering standards for chloride levels versus corrosion rates confirm the need to provide for very low chloride levels to achieve the high performance desired from protective coatings.

Lastly, the results show how corrosion products and salt levels are detrimental to the coating performance. The significance is easy to see in the coating performance after the salts are removed by a mildly acidic solution. This supports much of the ongoing testing and case histories from the past few decades. Also, the results show that a non-corrosive salt that is alkaline such as sodium bicarbonate is not corrosive and not detrimental to the coating performance. This is not a surprise as soda blasting is a common cleaning practice in the protective coating market which has been used for decades. In conclusion, it is critical to determine the type of salt present on the surface along with using an efficient acidic solution to remove them, so that the highest performance of the overlying coating can be achieved. Ⓦ

References

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