NATURAL SURFACE PHENOMENA AND THE IMPACT OF CORROSION INDUCING SALTS

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Abstract: Corrosion and passivation are naturally occurring phenomena on metal surfaces. A passive film, or grain boundary, consisting of reaction products of metal oxide or other compounds, will form on the metal surface and separates the metal form from its environment, slowing the rate of reaction. These products are slightly alkaline to neutral in pH. The acidic environment and atmosphere and consequential contamination of metallic surfaces with salts will reverse the formation of the naturally protective surface boundary layer, exposing the surface to aggressive electrochemical corrosion induced by the salts.

INTRODUCTION

The corrosion inducing effect of soluble salts on metal surfaces is well known and documented (1-6). By now, the surface preparation industry is aware of the need to remove these surface-contaminating salts prior to coating. Why are surface residual salts such an issue now? We do not live in an environment in which steel can form a permanent passive film that provides a surface barrier to dissipate the formation of corrosion products (7). A metal is passive when it substantially resists corrosion in a given environment. Working against the natural formation of the surface barrier passive film is our naturally acidic environment. From numerous monitoring sites, the EPA reports rain water pH ranging from 4.3 to 6.0 across the U.S (8). A pH of 5.8 or less is defined as acid rain. CO_2, SO_2, and NO_X calculated emissions in the U.S. for 2001 were 2.39 billion tons, 10.63 million tons, and 4.69 million tons, respectively (9). The sources of these are well known, and their oxidation to form weak acids reverses the formation of the slightly alkaline to neutral passivation surface barrier layer on metals. Furthermore, the ban of leaded paint no longer allows the industry to take the potential presence of non-visible salts for granted during surface preparation. The benefit of lead reacting with the salt anion to form insoluble, unreactive solids, no longer exists.

Our attention is concentrated on very small amounts of surface reacted salts. We are focusing on angstrom or atomic layers because it is at these levels that corrosion will be induced. The challenge here is to expand on a subject that the existing glossary of definitions and terminology used by SSPC is unable to satisfactorily explain. As such, definitions will be provided to generate a better understanding of this topic.

NATURAL SURFACE PHENOMENA

We begin by looking at the metal surface. Adsorbed water, or water which comes into direct contact with the surface, over time and because of the polarity of water and presence of other ionic species, will produce products of metal hydrates, metal oxide and other compounds. Iron (Fe) and oxygen (O_2) both have uncoupled electrons, resulting in a strong affinity and covalent bonding. Fe is a transition metal containing uncoupled electrons and O_2 also has uncoupled electrons. Said another way, the high energy of adsorption of oxygen on the Fe corresponds to chemical bond formation.

At the interface between the adsorbed water and the metal, hydroxide (OH^-) ions form at cathodes:

$$1/2O_2 + H_2O \rightarrow 2OH^- - 2e^-$$

The anodic areas show the following reactions:

$$Fe \rightarrow Fe^{+2} + 2e^-$$

Steel which has a visual white metal appearance can be viewed under a microscope to show numerous minute dark spots (anodes) surrounded by clean white metal (cathodes).

The combination of the above two reactions is the formation of a stabilized layer of positively charged metal ions entering the adsorbed layers of negatively charged oxygen ions and molecules on the surface. The layer thickens as O_2 from atmospheric exposure is adsorbed. This creates a passive film, defined by some as a diffusion barrier layer (1). This agglomerated, and transitional chemical oxide layer is insoluble in water, separating the metal from its environment and slowing the rate of reaction (10). In distilled water, which has low conductivity, the hydroxide ion forms at cathodes and always in proximity to the ferrous (Fe^{+2}) anode (1). This provides an effective barrier layer.

$$Fe + 2OH^- \rightarrow Fe(OH)_2$$

The resulting hydroxide [$Fe(OH)_2$] film, which is adherent and immediately next to the metal surface has an observed pH around 9.5. This can be confirmed by testing a steel surface exposed to water in a container where the pH at the steel surface becomes slightly alkaline. As Fe^{+2} transitions to a more stable Fe^{+3} form in the continued presence of O_2, a more neutral $Fe(OH)_3$ is generated. The products of the passivation layer transition from slightly alkaline to more neutral in pH.

$$Fe(OH)_2 + 1/2O_2 + 1/2H_2O \rightarrow Fe(OH)_3$$

With time, the continuing presence of O_2 diffusing through the passive film forms more stable and chemically defined oxide layers. The properties differ dramatically from the earlier formed hydroxide layer, as confirmed by its greater resistance to cathodic reduction (11). For example:

$$Fe(OH)_2 \rightarrow FeO \cdot nH_2O$$

$$Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O$$

This more stable oxide layer, better known as rust, normally consists of three layers composed of $Fe_3O_4 \cdot nH_2O$ between FeO and Fe_2O_3. Pores, or imperfections can be found in the formed oxide layers where the passive film remains intact (1).

In the pH range of 4 to l 0, corrosion is independent of pH (12). In an acid solution with a pH of less than 4, the hydrous ferrous oxide passivation layer is dissolved, and the surface pH falls as iron comes into direct contact with the aqueous solution. Weak acids, such as carbonic and acetic, will dissolve the films at pH around 5 or 6. At this weaker acidic pH more free H^+ exist to dissolve the barrier than a strong acid. The rate of hydrogen evolution in a strong acid is so pronounced that oxygen has difficulty reaching the metal surface. This is why concentrated nitric and sulfuric acids can be contained in mild steel tanks without a coating.

The corrosion rate of iron is proportional to the oxygen concentration. The oxygen solubility in water decreases as the sodium chloride concentration is increased, which explains why the corrosion rate declines in saturated sodium chloride solutions. Reaction rates will be dependent on the sum of hydrogen evolution and oxygen depolarization.

$$2H^+ + 1/2O_2 \rightarrow H_2O - 2e^-$$

Above pH 10, the increase in alkalinity corresponds with the accelerated formation of hydroxide surface barrier layer, resulting in a decrease of corrosion because iron is denied ready contact with oxygen.

THE EFFECT OF HYDROXIDES AND SALTS

The surface becomes susceptible to aggressive electrochemical corrosion in the presence of salts. The most prevalent of these salts are chlorides, sulfates and nitrates (13). The salt anion penetrates the oxide film through the pores or defects of the passivation layer described earlier. In accordance with the adsorption theory the reactive anion is adsorbed to the metal surface, competing with the O_2 and OH^-. Once in contact with the metal, the metal salt formed favors the hydration of metal ions because of higher stability in the hydrated form. This increases the ease with which metals enter into solution. The opposite is true of the effect of adsorbed oxygen. The continued presence of oxygen and its formation of insoluble oxides decrease the rate of metal dissolution.

On the other hand, in the presence of a salt anion species, such as chlorides, the conductivity is greater and anodes and cathodes can be much further apart. The hydroxide does not react immediately with the ferrous chloride (FeCl2) formed at the anodes, and instead diffuse into solution and react to form ferrous hydroxide $Fe(OH_2)$ away from the metal surface. The ferrous hydroxide formed does not provide the protective barrier on the metal surface and iron will corrode more rapidly in the continuing presence of chloride metal salts because more dissolved oxygen can reach the surface.

THE EFFECT OF THE ENVIRONMENT

Hydroxides can provide an adequate surface barrier layer, but only if the salt anion presence is nil. In our inescapable acidic environment the alkaline surface barrier is neutralized and salt induced corrosion can follow. We remember that the chloride anion, defined as a halogen, is extremely reactive. Its presence will break down the passivation layer from above and below.

$$Fe(OH)_3 + 3H^+ \rightarrow Fe^{+3} + 3H_2O$$

$$Fe^{+3} + 3Cl^- \rightarrow FeCl_3$$

Over time and because metal typically has a greater affinity for oxygen than the salt anion, various oxides of the metal are formed (rust), displacing the anion. The breakdown of the passivated surface by anions occurs locally rather than generally, probably due to the existence of preferred surface sites (pores) where there are small variations in the passive-film structure and thickness. This creates what is commonly known as pitting corrosion. The presence of the metal salt and moisture form oxide rust products and an acid. The acid only furthers the corrosion cycle and creates the pitting effect we see on surfaces.

$$2FeCl_3 + 3H_3O \rightarrow Fe_2O_3 + 6HCl$$

The combination of hydrogen and salt anions accelerate the attack. It has been shown that a steel surface exposed to a neutral dilute solution of sodium chloride form a fluid in the crevices of that steel with 3 to 10 times as many chloride ions as the dipping solution and a pH of 4 rather than 7 (14).

The hydroxide barrier layer is potentially under attack from above and below. At the steel surface where the anode is producing an acid of the anion in the corrosion cycle, hydroxides convert to the more stable oxide rust layers. Exposure of the passive film surface to the acidic environment will break down the hydroxide layers.

$$Fe(OH)_2 + 2H^+ \rightarrow Fe^{+2} + 2H_2O$$

Most surface corrosion of concern to the surface preparation and coating industry can be identified as pitting corrosion, occurring deep within microscopic cells in the surface profile. In the case of immersed metals, deep pits or impingement attack is common when subjected to high-velocity liquids.

Corrosion and passivation are continuous processes where products formed on the surface are the result of chemical activity in the corrosion cells and on the metal substrate surface. The presence of the well known cathode, anode, metallic pathway and electrolyte will ensure the continuation of corrosion unless one of these is removed.

ARRESTING SURFACE CORROSION

Control of salt induced corrosion and consequential coating failures can be accomplished with the removal of the anionic corrosion inducing salt species. Acting as a semi-permeable membrane, all coatings will allow the transfer of moisture and O_2 through to the substrate. The osmotic pressure of salts, or affinity of salts to absorb moisture to form a more stable hydrated salt can exceed the adhesive strength of the surface coating. Moisture will migrate through the coating to the metal substrate because its vapor pressure as a solvent is greatly reduced compared to its normal state. In the absence of soluble salt anions, the transfer of moisture and oxygen through the coating is continuous and unimpeded. The coating, as a semi permeable membrane, permits water, only in its purest form, to reach the substrate metal. Without anions to induce electrolytic reactions and sequential surface oxidation, coating failure caused by surface corrosion will not occur.

One can reasonably conclude that salt anions adsorbed on and through the passivation layer eventually react with the metal cation and become imbedded in the surface barrier layer. A series of chemical reactions create the surface barrier, or grain, layer that is water insoluble. Their presence in the insoluble surface barrier layer may be the reason removal of these salts with water is ineffective or insufficient. Furthermore, as the salt anion generates electrolytic corrosion in cells in the metal profile, the formation of insoluble oxide layers, e.g., rust caps, above the corrosion cell can prevent their removal with water.

Certainly, the unreacted salt anions on the surface will dissolve more readily when in contact with water. Mitschke, in his study on the effects of chloride contamination and selected surface coatings, used both artificial (doped in a known chloride solution) and natural (salt fog cabinet to accelerate weathering) steel panels and found that naturally contaminated panels have slightly higher tolerance for chlorides at higher temperatures and longer times to failure (15). In comparison to weathered steel panels, doped panels most frequently used in laboratory testing probably have a higher incidence of salt anions merely lying on the surface. On the other hand, natural steel panels have been weathered so that contaminates can generate numerous chemical reactions to develop the electrochemical bonds which may limit the ability of water to remove them.

The salt anions which are diffused in the surface barrier layer and come in contact with the metal ion to eventually form hydrated metal ions in corrosion cells can lead to potentially debilitating pitting corrosion. The corrosion will continue unabated unless the salt anions are effectively removed.

The presence of the salt anions and their products of reaction exist in many forms through the mechanism of multiple chemical reactions. We are reminded of the definition of corrosion as the “destructive attack of a metal by chemical or electrochemical reactions with its environment (1).” If it is through the action of electrochemical forces that these products have been formed and bonded it is reasonable to expect that the most efficient way of disbonding the corrosion inducing salt anions is with chemical energy.

CONCLUSIONS

The removal of surface reacted salts by physical means, such as abrasive blasting, has limitations (3, 16). Further, in multiple test cases, wet blasting and hydroblasting have been found to be insufficient in removing residual soluble salts to threshold acceptance levels (17). The diffusion of the salt anion in the surface barrier layer and the presence of the anion underlying the steel/rust interface provide justification for the physical removal of the insoluble oxide layer with abrasives followed by a chemical treatment wash. The purpose of the chemical is to dissolve any remaining surface barrier layer unaffected by the abrasive and to react with residual salt anions.

More work and research is required to test the bond strength of the salt anion and its affinity to and within the surface barrier layer and in the surface profile electrolytic cells. We need a better understanding of the mechanism of the attachment of the salt anions to the substrate metal. A dedicated effort using sophisticated instrumentation available can certainly help in the understanding of this phenomenon.

In light of the industry trend to lower the limits of contaminating salts, scientific validation and measurement of the bond strengths of the contaminating metal salts will provide the answers on how best to disbond and decontaminate surfaces to be coated.

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