Surface Adsorption: Overcoming 'Water-Soluble' Salts

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Not all "water-soluble" salts may be removed by water washing because various salts adsorb on the steel surface. If a surface salt analysis indicates salts, extra surface preparation—in addition to traditional cleaning—is necessary to ensure good coating performance.

To the corrosion control industry, the phrase "water-soluble salts" generally refers to an ionic chemical compound that dissolves in water. Yet, when preparing a steel surface for coating, ion-specific surface analyses show that water alone may remove only a portion of the salt ions from the surface. Water may not solubilize and wash all the "water-soluble" salts from the surface in the time allotted for washing. Remaining salts can effectively catalyze future corrosion reactions. To understand how this happens, one must understand the steel surface and the salt contaminant.

Steel Surfaces

Steel is an alloy of iron. It also may contain varying amounts of carbon, molybdenum, phosphorous, sodium, calcium, magnesium, nickel, zinc, etc. Various mixtures give steel its characteristics: ductility, malleability, corrosion resistance, etc. These ingredients, disbursed throughout the steel matrix, make the steel surface heterogeneous. A heterogeneous (two or more solids mixed together) surface has a diverse composition throughout; in contrast, a homogeneous surface has the same composition throughout. Because of the mixture of ingredients, steel surfaces possess many anodes and cathodes per square centimeter.

Liquid Water Mixtures

TYPES OF MIXTURES

Liquid water mixtures are divided into four types: solutions, colloids, suspensions, and emulsions.[1] Salt mixed with water becomes a solution. Solution particles are ions or molecules. Colloidal particles consist of small clumps of molecules while suspension particles consist of large clumps of molecules. Emulsions are two or more liquids mixed together. If they dissolve in each other, they are "miscible." If they do not mix together, they are "immiscible."[1]

PARTICLE SIZE

Solution particles (salt ions) are the smallest liquid water mixtures. Colloidal particle sizes are measured in nanometers (1 nm = 0.000000001 m, or one millionth of a millimeter) and range from 1 to 100 nm. Suspension particles are larger than 100 nm and solution particles are smaller than 1 nm.[1] Ions, the smallest of the solution particles, are measured in atomic mass units. For example, 5 micrograms of chloride ions (Cl^-) equal ~40 quadrillion ions while 5 micrograms of nitrate ions (NO_3) equal ~3 quadrillion ions and 5 micrograms of sulfate ions (SO_4) equal ~2 quadrillion ions. Yet, even this amount of contaminant cannot be seen with the unaided eye.

ADSORPTION

Adsorption is defined as the property of holding substances to a surface.[1] Lint or dust on a television or computer screen illustrates this property. Turning the screen face-down does not break the attraction force of the particles to the screen. This force of attraction (electrical charge) is similar to the force of attraction that salts have on a steel surface. The salt particles are dipoles (having a positive end and a negative end) and are attracted to the anodes and cathodes on the steel surface. If only water is used to wash a salt-contaminated surface, some of the salts may remain. This is so because the very small size of the salt molecule, coupled with the adsorption forces, overcome the solubility of water.

SURFACE-REACTED SALTS

The greatest factor causing corrosion to continue is the presence of negative ions (salts) and the forces concentrating them to the metal surface. Numerous salts form in the corrosion process; some of them may be chloride ions (Cl^-), iron chlorides ($FeCl_2$, $FeCl_3$), and hydrogen chlorides (HCl), but all require removal from the surface. In this case, the chloride ions and the hydrogen chlorides are not reacted with the steel surface and may be removed by their solubility with water. The chloride attached to the iron now is considered a surface-reacted salt (SRS). Though iron chloride by itself is water-soluble, when it becomes an SRS it is very difficult for water solubilization to occur because of the electrochemical forces attaching them to the steel surface. Note that boiling a steel coupon (requiring a tremendous amount of external energy), contaminated with SRS and using deionized (DI) water for 1 h, removes only ~90 to 95% of the salts. In the field, tepid potable water (low external energy) washed onto the metal surface may remove only a minor amount or none at all.

In the corrosion cycle, iron transforms through numerous chemical changes—depending on its environment—until it is passivated or oxidized. If it is not passivated, the corrosion process from iron (Fe) through to the iron oxide (Fe_2O_3) (orange, red, or brown rust) may take as little as a millisecond to minutes or even hours. It is important to realize that quadrillions of these reactions—all at various steps—may be occurring at the same instant.

BOND BREAKAGE-COLLISIONS

For molecules to react, they must first collide. This collision does not guarantee a reaction as most collisions result in simple rebounding. For a reaction to occur, however, the colliding molecules must contain enough potential energy for bond breakage. An important factor is that often the molecules must be correctly oriented to each other for a reaction to take place. If the collision contains enough potential energy, the point is reached where it is energetically more favorable for the new bond to form rather than the old bond to exist. The temporary passage between the two states is fleeting and has a high potential energy relative to the reactants and the products.

TIME

The movement of the molecules in their environment is expressed as kinetic energy. Not all molecules will pose the same amount of potential and kinetic energy. One speaks of average energy as the total energy of a reaction. Because the energies of all molecules (salts) are not the same, a certain amount of time is required to produce product. How fast the reaction takes place is called the rate of reaction.

Before reaching the product state, the potential energy required can be visualized as an old car being driven up a long, steep hill. Does the car have enough energy to reach the top, or will it stall and slide back down the hill? Upon reaching the top, which way will it go—back the way it came or down the other side? Descending the far side, the choice is easy—relax and let the car roll to the bottom. The required maximum energy to reach the transition state (top of the hill) has been overcome.

Salt Removal

A stronger "external force" or energy than possessed by water alone must be applied to remove or overcome the salt adsorption force to the steel surface. This extra or added force may be derived from chemical energy, electrical energy, or kinetic energy. Conventional methods of surface preparation such as abrasive blast cleaning, power or hand tool cleaning, and water washing do not impart sufficient energy to break the salt adsorption force bond.

Conclusion

This article highlights the misconception that water alone will remove all "water-soluble" salts. Supported by surface salt analysis data, water alone—with no added external force or energy—would not remove all soluble salts from steel surfaces. In reality, a soluble-salt-contaminated steel surface must be tested for salts—and not just chloride salts. If salts are found, the surface must receive additional surface preparation in addition to the traditional cleaning methods. This extra effort is essential to ensure that the level of soluble salt contamination is low enough to mitigate premature coating failure caused by relatively low levels of these catalyzed salts.

Reference

1. G.I. Sackheim, D.D. Lehman, 4th ed., Chemistry for the Health Sciences (1981).

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