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## Soluble Salts and Specifications

By James R. Johnson

**S**oluble salts are at the forefront of discussion regarding corrosion. In an effort to provide the industry with comprehensive information about corrosion prevention, CoatingsPro and ChlorRid are pleased to present the second article in an on-going series.

### Soluble Salts and Flash Rust

Virtually all rust on metallic surfaces is influenced or induced by salt contamination. We have been taught to believe that whenever there is bare steel and humidity, there will be flash rust. This is so ingrained into our thinking that some have a hard time believing that bare steel can be wetted and not rust. Take a clean uncontaminated steel coupon, abrasive blast it to White Metal, hold it at a 45 degree angle, and pour deionized (DI) water over it. Even though it will be thoroughly wetted, it will not rust! Take the same piece of steel and pour tap water over it, and then watch a light flash rust form, caused by the ions in the tap water. Add salt to the water and pour it over the same panel, it will flash rust much more heavily. As stated in the executive summary by Dr. Gerald Soltz in his research work for the National Shipbuilding Research Program, "Clean uncontaminated steel will not rust, even in 100% humidity, for thousands of hours."

The old habit of "blast it and paint it quick before it flashes" now has been found to be inappropriate. If flash rust occurs to any great degree, the substrate should be tested for contamination, because the rust is probably the result of non-visible soluble salt contamination. Without some ionic species present, there will not be rust. Even very low soluble salt levels can cause an appreciable amount of flash rust.



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### Identifying And Testing For Salts

There are several common field methods to test for and assess contamination levels. None of the field test methods can quantitatively measure the contaminants directly on the surface. The contaminants first must be extracted from the surface into a solution where they can be measured in parts per million (ppm). The ability of a certain method to perform this extraction is called the extraction efficiency, typically stated in the percentage of contaminants extracted from the surface versus the total on the surface. No method provides 100% extraction and the efficiency differs greatly from one method to another. Once the contaminant is in solution, a variety of methods can be used to measure the parts per million

(ppm) of a particular ion. This also varies from method to method, with differing degrees of difficulty, accuracy and other limitations, such as the minimum detection limit. The chosen test method is, therefore, a combination of two separate critical steps blended in a single methodology. Whichever methodology is chosen, in order to have useful information, the ppm must be converted to micrograms per square centimeter ( $\mu\text{g}/\text{cm}^2$ ), meaning a specific amount of salt over a specific area, a prime concern for adequate surface preparation. To perform this conversion, multiply the concentration of salts in solution (ppm) by the volume of extract liquid (milliliters) and divide that by the surface area sampled (square centimeters). The result is micrograms per square centimeter, expressed as  $\mu\text{g}/\text{cm}^2$ .

*The Society for Protective Coatings SSPC-Guide 15, Field Methods for Retrieval and Analysis of Soluble Salts on Substrates*, provides information on the commonly used field methods. It explains the swab method, the adhesive cell method, and the adhesive sleeve method. It also describes the advantages and disadvantages of each method. Unfortunately, the Guide does not provide any information as to efficiencies of the different extraction methods. The primary differences between the test methods are the extraction efficiency, degree of accuracy, lower limit of detection, ease of use, and the degree of potential operator error. Errors usually occur because of complexity of procedures, accuracy in measuring, and cross-contamination from reuse of components. Several factors should be considered when choosing a test method. No matter how cautious an operator is or how accurately he measures, he cannot overcome the accuracy, efficiency, limit of detection, or other limitations of a particular test method.

Regarding extraction efficiencies, there is limited data available. Stated in an outdated document, SSPC-TU-4, retrieval efficiency of the swab method is between 25% and 35%, as determined under controlled laboratory conditions. The same document reports the retrieval efficiency of the adhesive cell as 45% to 60%. The manufacturer of the adhesive sleeve reports retrieval efficiency as 75% to 80%, as tested by an independent laboratory.

Specifying the correct test method is important. For example the swab method is extremely hard to execute on a vertical surface and all but impossible overhead. Conversely, the other two methods — adhesive cell and adhesive sleeve — can be performed in any direction. It is easy to see that when critical areas are vertical or overhead surfaces, good quality

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assurance requires that the appropriate method be used.

Another important variable that must be considered is the test limit of the kit, more specifically the lower limit of the method used to determine the concentration of salts in solution. Typically, this has been measured by titration strip or detection tube. One common titration strip has a lower limit of ~ 30 ppm, while a common titration tube has a lower limit of ~1 ppm. Since concern for soluble salts is generally in the lower concentrations, this lower limit comes into the equation, therefore, using certain kits can cause false negatives. Another method uses reagent chemicals which provide a result within a certain range, such as over 10 but less than 20.

Specifiers should also consider potential error from factors such as cross contamination from test to test, inaccurate measurement of liquids and area, and overall complexity of the test procedures. Directions for performing these tests are included in SSPC Guide 15. This same document can be very helpful and informative to the inspector or contractor so they may fully understand the requirements.

In view of the variables involved in testing for soluble salts, it is reasonable to say that a correctly written specification should require that a specific test method be used and it should indicate the maximum test result permissible by that method. A specification that simply says,

for example, “chlorides are not to exceed 5 ppm” leaves much to be interpreted. Does the specifier intend the test result to not exceed 5 micrograms per square centimeter? Can any method be used? It is easy to see how an inspector or contractor could be left in controversy by such a specification. A specification should stipulate a particular test method, an acceptable test result and/or a factor (multiplier) to be used for different test methods.

The real life situation is that any amount of soluble salt, particularly chlorides, sulfates, or nitrates, is probably detrimental to some degree to the overall lifespan of the coating. The cleaner the surface, the greater the potential for a successful life cycle performance of a coating. A literature review found that virtually every coating is formulated to be applied to a clean, uncontaminated surface. After NEPCOAT (a consortium of north eastern state DOTs) spent years testing coatings in the laboratory, these coatings were applied to salt-contaminated surfaces in the field and every one of them failed, even though they had passed testing in the lab.

Since salts are a relatively new subject to many people, it is easy to understand that people are also not aware of the costs or methods of salt removal. Many specifiers fail to specify low allowable concentrations of soluble salts for fear of cost; others simply do not want to spend any additional funds. When all costs of asset downtime, surface preparation, and coating application are factored into a cost analysis, the cost of a premature failure is exorbitant when compared to the cost of taking reasonable steps to identify and remove soluble





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salts. Costs of surface preparation and coating application are generally estimated in dollars per square foot, while reasonable costs of soluble salts testing and removal are generally estimated at only cents per square foot.

### Why Ion Specific Testing For Salts Versus Conductivity?

In a previous article, (“Notes From The Field,” *CoatingsPro*, March 08), we established the importance of even low levels of specific salt anions when considering the corrosive effect and impact to the performance of a protective coating. Conductivity was developed as a quick way to estimate conductive species on metallic surfaces in and around marine environments. The use of this estimation method in a marine environment for testing surfaces subject to sea water exposure only is a widely used indicator of the amount of chloride present.

In non-marine areas however, many other ionic species will interfere with the

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detection of corrosion-inducing salts because not everything that is conductive is corrosion-inducing. A simple example is the dissolution of carbon dioxide in the atmosphere in moisture vapor to form carbonic acid. Carbonic acid is conductive, yet in and of itself, it does not have the same corrosion-inducing effects of salt anions. The EPA’s annual deposition maps verify this fact. Furthermore, in marine service, alkaline environments are beneficial in passivating surfaces (keeping them from corroding). Salt water is slightly alkaline (with a pH up to 8.1). This alkalinity is very slightly beneficial to the marine industry in mitigating corrosion because it operates in a highly salinic environment which is alkaline. In contrast, environments further

from the ocean are more acidic (acid rain fallout) which reverses surface passivation. In other words, in an acidic environment, subjecting steel to anion contamination will induce corrosion at a more rapid pace because the passivation process cannot occur. It is documented in SSPC 91-07, and referred to in SSPC’s TU4 that the adhesive cell method extracts somewhere around 50% of chlorides with DI water. The adhesive cell method is the prevalent way of obtaining samples for testing used in conductivity.

Conductivity assumes either that all the conductive species are chlorides (or converted to chlorides) or some major percentage is chlorides. From independent work done by a KTA-Tator Laboratory some years ago, little or no correlation was found between the levels of chlorides and conductivity. The results demonstrated that one can have low chlorides, yet high conductivity and vice versa.

This, then, raises the concern about cost. In testing with conductivity, high results would infer high levels of chlorides which may not be valid. Excess expenditures may be incurred which are not necessary. For example, Swedish research concluded that it takes several times the level of sulfates to get the same corrosion inducing effect of chlorides. Yet, conductivity cannot discern this difference.

Also, it is not just the anions (chlorides, sulfates, and nitrates) that are important in the corrosion cycle. The cations play a very important role. Conductivity is not ion-specific so measures them both. Chemically speak-





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ing, in the corrosion cycle, when the sodium of sodium chloride dissociates in the presence of moisture, and the chloride serves as the electrolyte of the corrosion cell, the sodium — because of size and reactivity — moves out of the corrosion cell to the periphery to form a hydroxide. Other cations such as calcium will do the same thing, although much more slowly, impeding the pace at which the chloride operates as an electrolyte in the corrosion

cell on the steel surface. If you measure everything that is conductive, how do you know how much of what species you are dealing with?

Conductivity seems to be a more engineer-oriented approach. Chemists will speak to ion-specific issues, most generally because one can test for ion-specific species in the laboratory. Conductivity measurements are actually the inverse of resistivity, which is what

is actually being measured. When you get to the inferred level of chlorides, yet another set of mathematical calculations take place. Chemists are big on math, but engineers thrive on it.

In summary, if only around 50% of the actual salts are extracted, and you get an indication of an assumed conductive species on a surface through conductivity testing, you can't expect very exacting results. Since salt anions, such as chloride, impact a coating's lifecycle performance so dramatically, accuracy in surface preparation becomes a matter of paramount importance. It is surface cleanliness prior to a coatings system's application that will help provide the desired lifecycle performance. **CP**

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