Measuring Surface Salts: Conductivity vs. Ion Specific Testing


Testing and identifying residual surface salts is an integral part of proper surface preparation; their removal is pivotal to the long-term performance of industrial coatings. Consequential risk reduction translates to lower life-cycle costs. Two commercial field methods are discussed to provide the user guidance on the method most suited to identifying the presence of salts where salt contamination is suspected.
To complete a satisfactory protective coatings project, accurate testing is required during the process to ensure everyone is engaged in a complete, quality procedure that will achieve the desired outcome. Specifically, the challenge facing the coatings industry is to have a repeatable, quantitative test method for measuring the ion-specific salt that may be present.

Knowing that salts are an important or even leading cause of premature coating failure, salt limits have been reduced in specifications to threshold or even nondetectable levels to reduce the risk of premature coating failure. This reduces maintenance costs during the life of the asset.

The two common commercial methods used for testing the presence of surface soluble salts are conductivity and ion-specific testing. The differences in results obtained from each challenge the notion of correlating or comparing the two. It is very important for the asset owner, specifier, or other interested parties to have a good understanding of the capabilities of each method. The method used should be documented, and the input records used to achieve the final results should be kept. Providing the details for each can help the user decide what to use and how to use the results obtained.

The details of surface salt testing have been misunderstood, or forgotten or overlooked in some cases. This article compiles what is known about the various methods to allow the user or specifier to decide what method is suitable or desired.

**Surface Salts Testing Basics**

Commercially available field-testing methods for surface soluble salts have two basic parts: extraction and measurement. The essence of every test method is the ability to extract the surface salts with sufficient accuracy to give a fair assessment of what is actually on the surface.

To reflect what is experienced with weathered steel, comparative tests of extraction efficiency should be made on surfaces that duplicate this morphology. Without actual samples of weathered steel to use, steel exposed in a salt fog cabinet or prohesion cabinet may provide comparable morphology. Testing on weathered steel has shown that using deionized (DI) or demineralized water as an extraction solvent will remove only a fraction of the actual surface salts present; this can be attributed to the fact that the salt anions are adsorbed, or bonded, to the substrate metal.

For the measurement part of the test, either conductivity or an ion-specific titration is done. Conductivity meters have evolved over the years into a convenient design so they can be easily carried and used in the field. Ion-specific chemical titration using drops of chemicals and chemical indicators has been replaced with a convenient ion selective titration or ion selective electrodes with an associated electronic readout device.

**Considerations for Conductivity**

The notion that a certain conductivity reading can be translated to a defined measurement of an ionic species of a water-soluble molecule must be held with great reservation. Key assumptions must be made, and even then any number written down should be asterisked for qualification. The key assumptions are that all the soluble salts from the surface will be removed during the extraction step and that all or the vast majority of the conductive species is chloride. Realistically, this is highly unlikely, making this method of measurement semi-quantitative, as stated in SSPC-Guide 15.

Inputting chloride levels from a correlation chart, such as that provided in ISO 8502-9, may have some relevance if the surfaces to be tested have been exposed solely to marine environments, where ~55% of the salt ions can be expected to be chlorides. In taking a measurement, one would need to assume the data to be total dissolved salts (TDS). It is a challenge to translate that into chloride equivalents when the test is taken after an abrasive blast. There are other ion species known to be present in salt water, including possible free metal ions from the surface. These other conductive species may or may not have any bearing on substrate corrosion as it relates to coating failure or performance. After dry abrasive blasting, micronic particles may be left even after a blow-down. These particles can be charged, which elevates the level of conductivity of an extracted surface sample.

Discussing the effects of the chloride ion has merit because of the reactivity and the corrosion-inducing effect that chlorides can have on a metal surface. Yet, the presence of sulfate ions, which is not insignificant in seawater, generates a higher level of conductivity than a similar concentration of chloride ions but has a lower corrosion-inducing effect in both marine and atmospheric environments. Conductivity and reactivity cannot be directly correlated.

The salt content of seawater is approximately 3.5%. From the molecular weight percentages of significant salt ions in salt water and their relative conductivities, the conductivity of the TDS calculates to be within 1% of the conductivity of a salt solution, which is 3.5% sodium chloride (NaCl) alone. Considering the corrosion-inducing effect of sulfate, the impact is mitigated by 8 to 13% relative to a 3.5% NaCl solution. This presupposes that steel weathered in marine environments experiences the same level of contamination as the salts identified in seawater itself. Acceptance of conductivity alone as a criterion in surface cleanliness may lead to unnecessary expenditures of time and money.

With no direct relationship between conductivity as μS/cm and the concen-
Measuring Surface Salts: Conductivity vs. Ion Specific Testing

Prescribed conductivity levels offer a rough estimate of salts concentration because there is no way to obtain the exact concentration due to the interaction between ions. Table 1 reflects various sources that calculate chloride concentration from conductivity, assuming the use of 3 mL of extraction DI water solution for obtaining the values other than the theoretical comparative basis. The variations are not insignificant because the desired outcome is a single digit for a specific anionic species.

At a laboratory in Houston, Texas, comparative conductivity and ion specific testing was done to determine any pattern or relationship between them. Clean metal coupons were placed in a salt fog cabinet, according to ASTM B11711 for 144 h, using a 5% solution of NaCl. The panels were then blast cleaned to a near white NACE No. 2/SSPC-SP 1012 standard. Conductivity was done following the ISO 8502-6 and 8502-9 procedures. The Cl\(^{-}\) ion-specific testing was done with a chloride ion-selective electrode. Table 2 shows the results for the 20 panels.

Unfortunately, no correlation could be found between conductivity levels and ion-specific levels on panels, which simulated weathered steel.

### Considerations for Extraction

The extraction efficiency is of key importance to the accuracy of any commercially available field test. ISO 8502-6 details a method of extraction using a blister patch cell (Bresle) with a hypodermic needle to inject DI water and facilitate circulation within the patch. This process assists the extraction of a sample of surface soluble salts, which may be present. Boocock\(^6\) shows that extraction of abrasive blasted weathered panels using the Bresle method ranged from 26 to 53%, with an average of 35% for the limited data presented. The challenges of extracting salts from weathered steel are also addressed by S. Flores, et al.\(^{14}\) ISO 8502-2\(^{15}\) states the difficulty of removing salts from corroded surfaces, even after white metal blasting, in more technical terms. Uhlig and Revie provide details of the adsorption of salts to substrates, making their dissolution with water difficult.\(^7\)

Another variable, confirmed by participants working on NACE International Task Group (TG) 392 in 2008 that led to NACE Standard SP0508,\(^{16}\) was the addition of conductivity imparted by the Bresle patch itself in the range of 5 to 7 µS/cm. Boocock\(^6\) outlined the higher level of extraction, and thus, greater accuracy of measuring the level of surface salts that may be present on weathered panels when using an acidic solution. Others have reported the same conclusion.

### Specified Ionic Species Limits

The amount of data relating to recommended numeric limits of chlorides to achieve optimal or full coating life performance is quite impressive. A literature search by Alblas, et al.,\(^{17}\) enumerates the levels of chlorides recommended for various service types and coating systems. Many coating manufacturers state in their
Challenges in Calculating Chlorides from Conductivity

Seo, et al., in their work related to the marine industry’s adoption of the IMO Resolution MSC.215(82), challenge the use of the ISO conductivity method to arrive at specific levels of surface chloride contamination limits because of “shortcomings” of that method. This white paper is a good example of how extrapolation of a conductivity reading to an ion-specific value is a mathematical estimation and not chemically accurate.

Example Calculation

The following is an example of the methodologies available for inputting chloride concentration levels from surface conductivity readings. These calculations confirm that conductivity simply provides an indication of surface salt concentration.

- The specification says to take a sample immediately after abrasive blasting a steel surface to determine the level of residual chlorides that may be present. A Bresle patch is used with 3 mL of DI water as an extraction solution. The DI water has been tested and shown to read 5 µS/cm after calibration of the conductivity meter.
- The DI water is injected as instructed in ISO 8502-6, and the hypodermic needle is used to agitate the solution inside the patch.
- The DI water is then removed and a conductivity reading of the solution is taken. The reading is 35 µS/cm. Subtracting the 5 µS/cm from the extraction solution, the net reading is 30 µS/cm.
- If it is assumed that a high proportion of the extracted salt is NaCl, an estimate can be made of chlorides from the conductivity reading.
- To convert the field reading of conductivity to a theoretical chloride concentration value: 584 mg/L (ppm) NaCl is equivalent to 1,156 µS/cm (from Table 1); (354/584) × 1,156 is equivalent to 700 µS/cm chlorides [Cl⁻ = 35.4 g/mole; NaCl = 58.4 g/mole]. That is, 354 mg/L Cl⁻ is equivalent to 700 µS/cm.
- Returning to the example with a reading of 30 µS/cm, the proportion is 30/1,156 × 584 mg/L or 15.2 ppm.
- Using the Bresle patch: 15.2 ppm × (3/12.5) = 3.6 µg/cm² of TDS (3 mL DI; 12.5 cm² is the average Bresle surface area).
- The theoretical chloride level, again assuming the extracted salt is all NaCl: 3.6 × (354/584) = 2.2.
- 30 µS/cm is equivalent to 2.2 µg/cm² Cl⁻.
- To compare with the above: Using the ISO 8502-9 chart, comparing 3 mL of solution vs. 10 mL (since there is no 3 mL line):
  - 3/10 = 0.3
  - Extrapolating 30 µS/cm (assuming all of the salt is NaCl): 30 × 0.3 × 0.4 = 3.6 µg/cm² of TDS (0.4 is the result from the chart correlation multiplied by the empirical constant).

Why the Continued Use of Conductivity?

Given the facts provided, this seems a reasonable question especially when technology has evolved to allow for convenient field testing of ion-specific species. The vast laboratory testing and published information of ion-specific limits provide a safeguard for the optimal long-term performance of a coating. These data also provide a valid basis for using numeric ion-specific limits in specifications. Eliminating one important risk for potential failure can help drive down long-term coating maintenance costs.

There may be niche uses for surface conductivity testing to provide guidance on surface preparation. As addressed earlier, in marine environments, where the single largest salt is NaCl, conductivity specified levels may be instructive and facilitate a way to reduce risk in maintenance coatings projects. Yet, what is the conductivity level that is acceptable given the numerous variables involved?
Surface Salts Testing for the 21st Century

Published data have not been found that provide a definitive relationship between conductivity levels and life-cycle coating performance. Certain companies may have proprietary multi-year performance test data using specific conductivity measurements to arrive at a level of conductivity that relates to an effective coating service life. It is recognized that long-term testing is costly and would need to be service or environment specific to minimize the impact of conflicting variables. If companies have undertaken this effort, the information has not been made available in the public domain. The literature in the public domain states salt limits by ionic species and offers a cost-effective and very possibly a lower-risk way to control one variable in corrosion prevention and asset protection.

References
12 NACE No. 2/SSPC-SP 10, “Near-White Blast Cleaning” (Houston, TX: NACE International).
19 IMO Resolution MSC.215(82); “Performance Standard for Protective Coatings for Dedicated Seawater Ballast Tanks in All Types of Ships and Double-Side Skin Spaces of Bulk Carriers” (London, UK: IMO, 2006).

HAP PETERS is the managing director at CHLOR-RID International, Inc., PO Box 908, Chandler, AZ 85244, e-mail: hpeters@chlor-rid.com. The company is a global supplier of surface preparation products that include field test kits for ion-specific identification of contaminating salts and remediation chemicals for their removal and surface treatment. His educational background includes an undergraduate degree in chemistry and an M.B.A. He has over 30 years of experience in the chemical, refining, petrochemical, and capital equipment industries and has served in various U.S. and global assignments including sales, business development, marketing, and business management. He is a member of NACE, SSPC, and ASTM. He has authored numerous papers on international chemical marketing, business development, and technical issues, and has been a speaker at industry conferences including NACE and SSPC and annual conventions. RP®

The 2011 MP Media KIt Is Now Available

Plan your 2011 advertising schedule by visiting the Publications area of the NACE Website: www.nace.org, or request a hardcopy of the kit from Brenda Nitz at +1 281-228-6219 or brenda.nitz@nace.org.