Metal Corrosion: A Qualitative Analysis

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Abstract

The use of metal corrosion as a determining factor in forensic analysis has been an ongoing practice for many years. A more focused interpretation of subsequent damaged from water intrusion can be an indispensable factor in a water loss investigation. Although the use of corroded materials in a building can be used for structural interpretation, corrosion as a "duration of loss" tool can add a new perspective previously overlooked. This paper offers qualitative insight into the duration of exposure associated with different types of materials such as copper pipe and galvanized metals. It also includes the materials and methods, litigation support for the Daubert standard, photographs for visual representation, inherent error, and similar research.

Introduction

The forensic engineer recognizes the effects of corrosion in a building investigation because of the ubiquitous use of metal components in construction such as structural framework, plumbing, mechanical equipment, and electrical hardware. The visible condition of these components reflects the moisture exposure circumstances of their installation. Corrosion studies provide a tool to establish a timeline of events following moisture exposure. This qualitative investigation attempts to advance the scientific community's use of research to substantiate opinions of the duration of free water exposure to common building materials.

Customary approaches to studying metal corrosion are the loss in weight technique, accelerated testing, electrochemical processes and the percentage coverage of corrosion on visible surface areas. The approach presented in this paper is intentionally qualitative and offers a day by day documentation of metal degradation when exposed to fresh (tap) water, salt water and elevated humidity. In conformance with previous metal corrosion research, we focused on the ASTM standards for use of a salt spray apparatus (B117); preparing, cleaning and evaluation of test specimens (G1); exposure of metals by immersion in sodium chloride (G44); exposure and evaluation of metals in seawater (G52); conducting cycling humidity exposure (G60); conducting and evaluating galvanic corrosion in electrolytes (G71); and modified salt spray testing (G85).

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Materials and Methods

A four-chambered Plexiglas test apparatus was constructed that featured isolated and independently controlled environmental conditions. These conditions were exposure to fresh water, salt water, elevated humidity, and a control environment at ambient conditions. Each chamber was equipped with 6 shelves located above one another to serve as mounting points for the specimen arrangement and secondarily to divert water away from the specimens located on the shelves below. This arrangement helped to maintain the integrity of each shelf environment by decreasing the likelihood of chemical interaction from one sample to another during drainage.

The corrosion tests were conducted on six materials: five galvanized metal products (metal lath, nail guard, conduit, sill plate and corner bead) and one copper pipe product (½" copper pipe). The materials were exposed to fresh or salt water in fog spray as prescribed by ASTM B117. Three specimens of each material were placed inside each of four chambers and exposed to fog spray (**Illustration 1**). The water supply (fresh and salt) was fed from a reservoir then filtered and misted onto the test materials. A 30-gallon capacity re-circulatory system was used for both the salt water and fresh water. Water was pumped from the reservoir using two identical 1½ hp pumps (Pacific Hydrostar, Model 69304). The pumps delivered approximately 6.8 ounces per minute during active misting. The final misting sequence of 15 minutes "on" and 45 minutes "off" was selected to provide good exemplar wetting and maintain the water temperature inside the test chambers below 82°F.

Fresh water (City of Tampa) was provided by tap. Salt water was created by using salt crystals (Coralife Marine Salt) mixed with tap water. Approximately 9 lbs of salt were used to prepare a 30 gallon salt solution. The test apparatus was equipped with grooved 10-micron filters (3M Filtrete, 3WH-STDGR-F02) that were positioned between the reservoirs and the fogging spray heads to maintain the integrity of the water mixture and prevent clogging.

The salt and fresh water pH (Etekcity pH-2011, Oakton Instruments 35624-22, and Aquarium Pharmaceuticals Product#27), salinity (Strom Store RHS-ATC10), temperature (Coralife 96300232) information was recorded on every photograph day. Fresh water conductivity (General Tools CO-502) was measured at the same intervals. Similarly, tap water was measured periodically to serve as a control. The control and elevated humidity chamber temperature and humidity (Taylor 1523) were measured periodically, as were total dissolved solids (HM Digital TDS-3) in both water samples. The dissolved oxygen content in the salt and fresh water samples, and the conductivity of the salt water were measured twice over the 30-day period (YSI Professional Plus 10J100927 and Horiba W22). Lastly, supply water pressure was also periodically monitored (Orbit 91130).
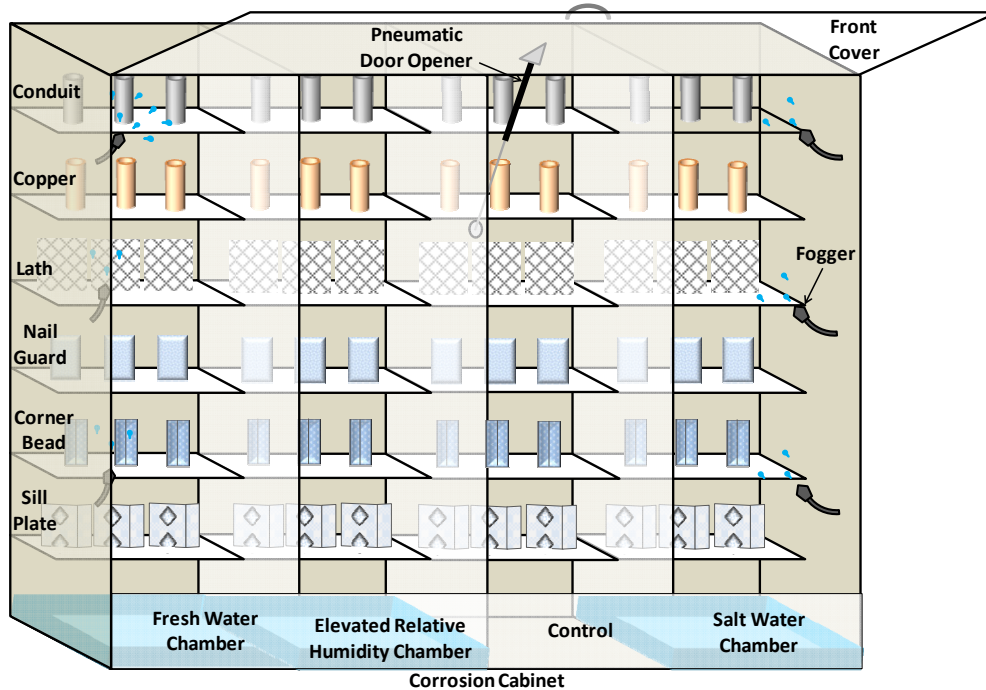
Illustration 1: Four-chamber corrosion test cabinet

Test Specimen Preparation

Test specimen preparation adherence to ASTM Method (G1) was a primary concern. Initially, the test specimens were cut to size to fit on their respective shelves. Using an angle grinder, 3 inch sections were cut (12 total) of each type of test material. One of the most frequently reported modes of failure for galvanized steel materials was on the cut edges (Yildiz, 2012). The edges that were cut with the angle grinder required sealing to assure proper testing. During the first set of tests (discussed below) polyurethane was used to seal the cut ends and resulted in an almost immediate sealant failure and visible corrosion. In subsequent tests a metal primer (Rust-Oleum) was applied on the cut edges to a height of three millimeters. After the primer dried the test specimen surfaces were cleaned with acetone to remove any surface contaminates such as fingerprints or manufacturing oils. Nitrile gloves were worn during specimen handling to deter against accelerated corrosion where skin oils contacted the specimen surface (UL, 2010).

First Set Test Methods (Proof of Concept)

During our first test, specimens were placed upright on the shelves with a plastic supportive leg to provide additional stability. Independent pumps, filters, plumbing, and reservoirs were used to recirculate the fresh and salt water supply into their respective chambers. The fresh and salt chambers were equipped with 6 spray nozzles, one for each shelf. A timer controlled pump supplied water every 30 minutes for every 1½ hours. Flow rates were not measured and the pumps served the purpose of simply wetting the specimens. Individual five gallon fresh and salt water reservoirs cooled by a copper coil ambient temperature heat exchanger proved to be insufficient. Heated

water from the bypass house promptly elevated the 5 gallon reservoir's water temperature and resulted in overheating the pump and reservoir water. Eight strip lights (led) were mounted to illuminate the chamber walls. This initial design was operated for 29 days and proved useful in identifying errors and unforeseen circumstances that altered the test specimen's corrosion rates.

Second Set Test Methods

Several refinements were employed to improve the second test. Metal specimens were suspended from plastic clips attached to the shelves above. The fresh and salt water chambers were equipped with 3 fogger nozzles (TEFEN, Model 5NPF-L) positioned at equal heights. A timer controlled pump operation supplied the fresh and salt water into their respective chambers every 45 minutes for a 15 minute duration. The same model pumps were used for both water systems (Pacific Hydrostar, 69304). Pressure gauges were tied into each water supply line before the fogger manifold. The fresh and salt water flow rates were calculated by measuring pressure specific mass flow rates, and were ultimately regulated to approximately 3.2 gallons per hour. The fresh and salt water reservoirs were increased to 30 gallons each and the previously discussed strip lights remained mounted to the interior walls of each chamber. Color wheels were placed on the exterior surfaces of the corrosion cabinet for each shelf as a control reference for photographic purposes. With the exception of the chamber door, the exterior surfaces were draped with a white fabric to provide a neutral background. A continuously operating portable fan (Lasko, Model 3520) was employed to cool both water pumps.

Fresh water was used to dissolve the salt water solution to achieve a 1.024 specific gravity (31 ppt). The water for both 30-gallon reservoirs was changed weekly to maintain water quality. Water quality measurements were taken when the photographs were taken to document changes during the course of the study. Uniformity in photographic documentation was maintained by using a tripod-mounted camera positioned at a predetermined height and distance away from each set of specimens.

Previous Research

Although corrosion adheres to the basic laws of thermodynamics; predictability and corrosion uniformity diminish with variations in temperature, pH, and stress (Schweitzer 2006). According to Schweitzer, a metal progresses through three stages in an atmospheric corrosion process. The first stage (induction period) occurs when the metal experiences formation of a semi-protective layer around the material. The second stage (transition period) occurs when this layer becomes a fully developed corrosion coating. The final stage (stationary period) occurs when the material transitions toward a constant chemical composition and corrosion rate (Fundamentals of Metallic Corrosion, 2006).

There are two generally accepted methods for assessing corrosion rates. The first method employs monitoring specimen weight over time. The "loss in weight" rate of

corrosion was reduced to a formula that evaluated millimeter per year (mm/y) or meter per year (mpy) reduction depending on the material type, weight loss, and density. Good, satisfactory, and unsatisfactory corrosion rates are less than 0.15 mm/y, 0.15 to 1.5 mm/y, and greater than 1.5 mm/y, respectively (Revie 2008). Significant usefulness of this test is limited to circumstances when the corrosion is not uniform. Extensive localization of corrosion creates an error rate that underestimates the maximum corrosion rate (ASTM, 2006).

Due to the inherent electrochemical nature of the corrosion process (Schweitzer 2006), the second popular method for determining corrosion rates involves recording changes in the material's electrical properties. One application of this concept uses polarization data, which involves measuring the electrical potential of a corroding surface in an electrolyte under open-circuit conditions relative to a reference electrode (*i.e.,* corrosion potential) (Revie 2008; NACE/ASTM 2009). Understanding the different approaches to quantifying metal degradation provided insight and background on which to base this qualitative study.

Results

Two sample sets were examined; the first set (proof of concept) was run for 29 days while the second set (test) was run for 43 days. Each sample type was subjected to conditions previously discussed. The first occurrences of gradual changes in appearance are discussed below.

The specimens in the first set were prepared with exposed cut ends (see Materials and Methods). This condition prompted earlier corrosion than the second sample set. The corrosion gradually progressed from the cut ends to the face section of the specimens in the majority of the first sample set. The corrosion progressed at a slower rate in the second sample set; however, the ends appeared to be the location where the majority of the corrosion began. These observations indicated that the unsealed cut ends encouraged earlier corrosion than unaltered portions of the same material.

A second sample set photographs noted white rust (fresh water) and minor black pitting (salt water) on day 4 of the study. The black pitting became noticeably greater on day six. Based on the observations in this study was assumed that white rust occurs quickly (within the first few days) of free water exposure.

The subsequent corrosion of the materials was photographically documented with visual observations made each day. A log was maintained for record keeping (water quality, visual observations) and was converted to a visual representation noted in Tables 1 and 2. The photographs provided comparative documentation of the exemplars for use in forensic reports when establishing the duration of moisture exposure (ASTM E860).

First Set (Proof of Concept) Observations

All of the observations detailed in this section are listed in Table 1. The conduit developed white rust (zinc oxide) on the first day of photographs in both water chambers. Black discoloration began on day three and on day five black pitting began. Rust (red iron oxide) began at the cut ends of the fresh water conduit on day six and on the salt water specimens on day nine. On day 29, rust was observed at the cut end surfaces of the elevated relative humidity (RH) conduit.

A general darkening of the copper salt water specimens occurred on day three followed on day 13 by a general lightening of the specimens. Patina (copper nitrate, copper sulfate, copper acetate, copper hydroxide, copper carbonate) spots began on the elevated RH specimens on day six (Richardson). On Day 12 patina spots were documented on the face surface of the fresh water specimens along with the cut ends of the salt water specimens. Soon after on day 17 patina spots were observed on the salt water face surface.

On day one of the fresh and salt water tests white rust was observed on the metal lath, nail guard, corner bead and sill plate. On day 27, rust was documented on the cut ends of the fresh water metal lath. Additional changes were not associated with the metal lath specimens. White rust occurred on the elevated RH nail guard, corner bead and sill plate on day 9. Rust occurred on the cut ends of the fresh water corner bead on day 13 and on day 22 for the salt water. Rust occurred on the cut end of the fresh water sill plate on day 21 and day 27 for the salt water.
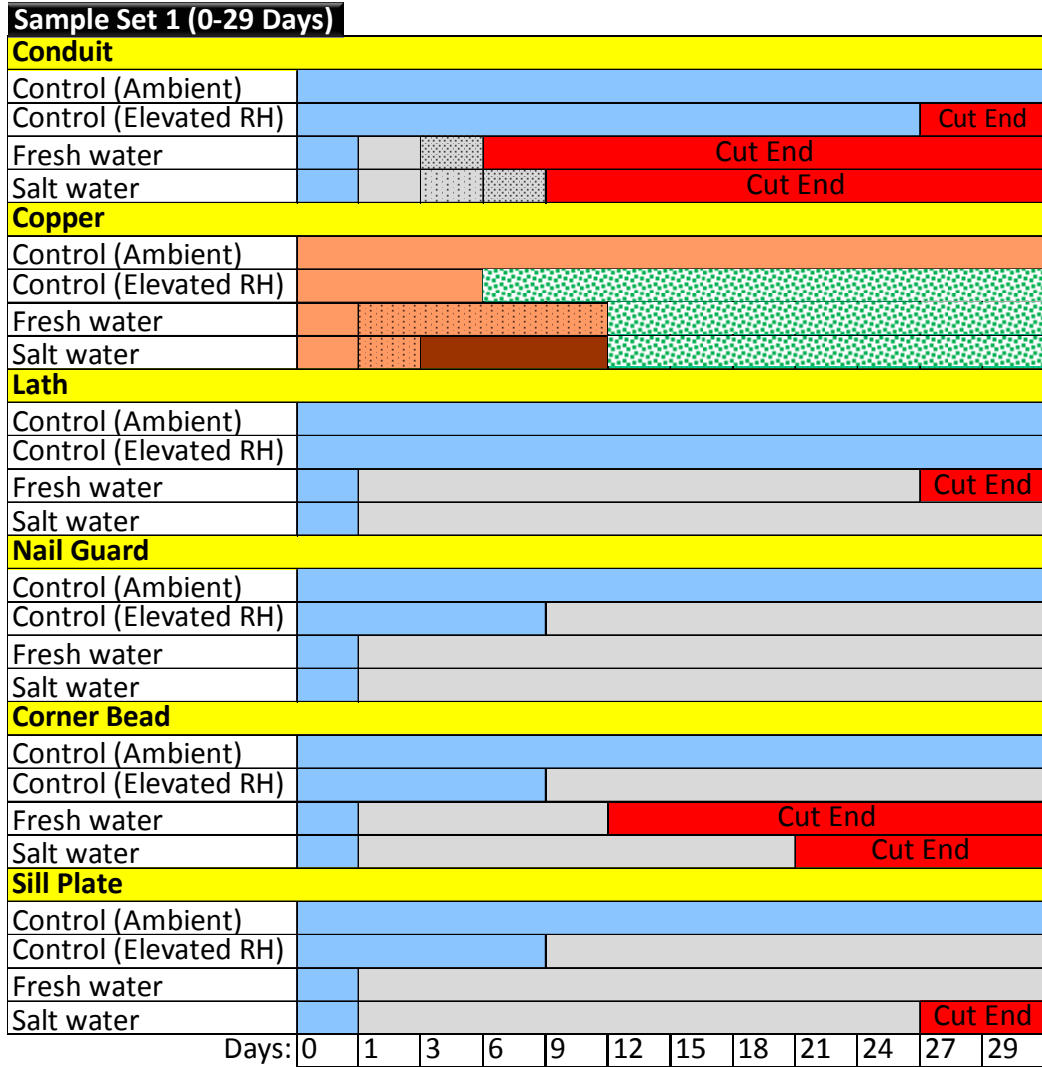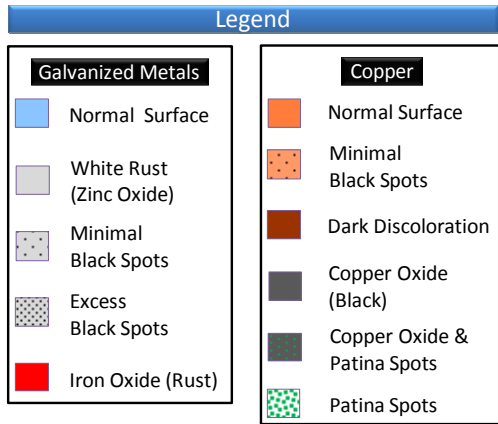
Sample Set 1 (0-29 Days)

Conduit										
Control (Ambient)										
Control (Elevated RH)										Cut End
Fresh water				Cut End						
Salt water				Cut End						

Copper										
Control (Ambient)										
Control (Elevated RH)										
Fresh water										
Salt water										

Lath										
Control (Ambient)										
Control (Elevated RH)										
Fresh water										Cut End
Salt water										

Nail Guard										
Control (Ambient)										
Control (Elevated RH)										
Fresh water										
Salt water										

Corner Bead										
Control (Ambient)										
Control (Elevated RH)										
Fresh water						Cut End				
Salt water							Cut End			

Sill Plate										
Control (Ambient)										
Control (Elevated RH)										
Fresh water										
Salt water										Cut End

Days: 0 1 3 6 9 12 15 18 21 24 27 29

Table 1: Sample Set 1; Color coded changes on the surfaces of the different materials over time.

Legend

Galvanized Metals
- Normal Surface
- White Rust (Zinc Oxide)
- Minimal Black Spots
- Excess Black Spots
- Iron Oxide (Rust)

Copper
- Normal Surface
- Minimal Black Spots
- Dark Discoloration
- Copper Oxide (Black)
- Copper Oxide & Patina Spots
- Patina Spots

Second Set Observations

All of the observations described in the second set are listed in **Table 2**. A general darkening occurred on day three of the salt water conduit specimens. Rust was visible on the interior of the salt and fresh water specimens on day 21 and day 33, respectively.

The copper specimens noted in the photographs show the most significant color change occurred in the salt water chamber. The first change was a tarnished copper surface, eventually a patina covered most of the surface area sprayed directly by the foggers. An unanticipated result occurred when the copper specimens were rotated to evaluate the unseen reverse side. Characteristic patina "spots" developed where the foggers did not spray the surface directly. A general darkening of the salt water copper specimens occurred on day nine. Black and green patina spots began on the salt water specimens on day 10. The elevated RH, fresh and salt water copper specimens became discolored on day 14. General surface darkening occurred in the fresh water specimens on day 18 followed by black spots on day 19. Patina spots of the fresh water and salt water specimens occurred on day 33 (**Photo 2**).
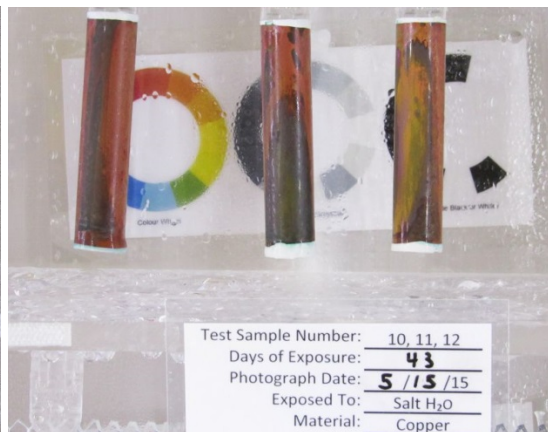
| Photo 1: Copper in salt water Day 0 | Photo 2: Copper in salt water on Day 43 |

| Photo 3: Nail guard in fresh water Day 0 | Photo 4: Nail guard Day 36 in fresh water |

| Photo 5: Sill plate in salt water Day 0 | Photo 6: Sill plate on Day 43 in salt water |
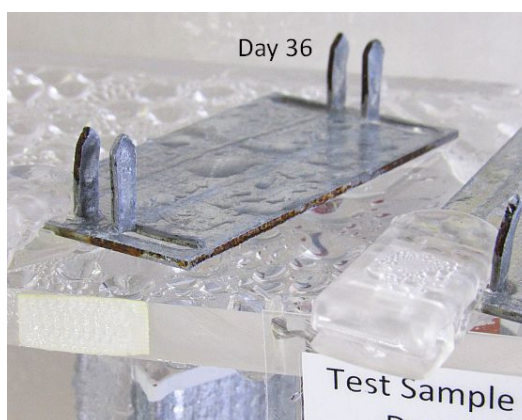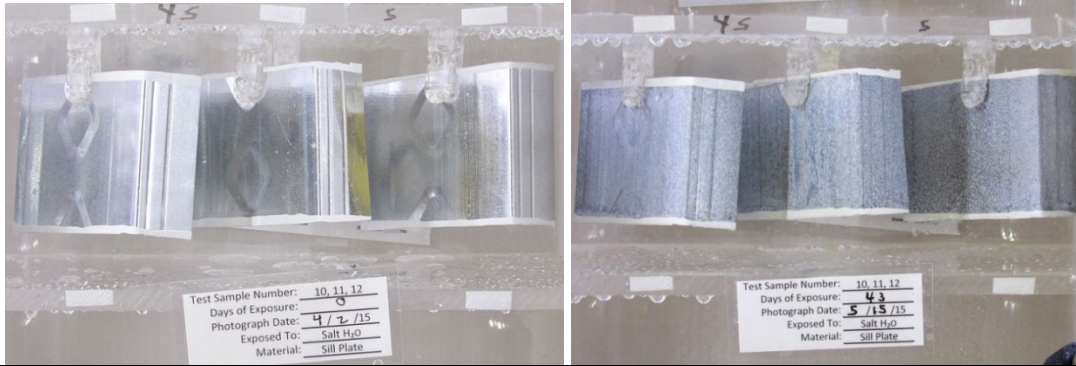
The white rust was observed on day four of the fresh and salt water samples of conduit, lath, nail guard, corner bead, and sill plate. Black pitting of the salt water corner bead and sill plate specimens along with the fresh water metal lath specimens occurred on day 14 (**Photo 6**). The corner bead and sill plate fresh water specimens became dull in appearance on day 14. The rust at the edges of the nail guard appeared by day 33 but only occurred on the edges (fresh water); there was limited migration of the rust to the face surfaces (**Photo 4**).

Table 2: Sample Set 2; Color coded changes on the surfaces of the different materials.

Legend		
Galvanized Metals		
	Normal Surface	
	White Rust (Zinc Oxide)	
	Minimal Black Spots	
	Excess Black Spots	
	Iron Oxide (Rust)	

Copper	
	Normal Surface
	Minimal Black Spots
	Dark Discoloration
	Copper Oxide (Black)
	Copper Oxide & Patina Spots
	Patina Spots

Lessons Learned

The investigation revealed several unforeseen variables. The first test results effectively reduced variables that may have increased or decreased the second test rate of corrosion. Some design flaws were noted and corrected during the second test as listed below.

  i. Horizontal shelves caused the accumulation of stagnant water around the base of the test specimen's in-between system cycles.
  ii. Insufficient cut edge sealing of the test specimens accelerated the corrosion rates due to bypassing the protective zinc coatings.
  iii. Close proximity of the fresh and salt water chambers lead to accidental cross contamination.
  iv. The spray heads used for test specimen saturation were not fogging, in accordance with ASTM B117.

During the redesign of the corrosion chamber after the first test, modifications reduced the error rates and closely aligned with ASTM Method criteria.

Both fixed and variable sources of error existed in this experiment and mitigation efforts were employed to minimize their effect wherever possible. The accuracy of the measuring equipment used was a fixed error source. This included the conductivity meter and pH meter. The variable sources of error involved human interpretation of the refractometer readings, duration of specimen exposure to uniform environmental conditions during photography, and the deterioration of corrosion cabinet components not including the tested specimens (i.e., pump hardware, translucence of the Plexiglas). Aside from errors, variations existed in photography focus and framing, and the measured water properties.

Monitoring the pH, salinity, temperature, conductivity, and dissolved oxygen provided a means for broadly assessing the water quality and its corrosive agents. Gaseous constituents that contribute to atmospheric corrosion such as sulfur dioxide, nitric acid, and formaldehyde were not explicitly monitored because collective influence would

be accounted for by changes in pH (Schweitzer, Fundamentals of Metallic Corrosion, 2006). Additionally, the corrosive contribution from organic matter and microbiological forms were not accounted for due to the design of the corrosion cabinet's artificial environment (Roberge, 2008). Salinity was monitored because it encompassed chloride content, a known corrosive agent (Roberge, 2008). Temperature was monitored because corrosion rates typically increase with temperature (Davis, 2000; Roberge, 2008). The conductivity was measured to see if the recirculated water sources were distinctly influenced by corrosive precipitants not captured by the filter, or by a change in the water's ionic properties.

Summary

There are few published metal corrosion investigations that can benefit the forensic engineer attempting to determine the duration of water loss without disturbing the material in its environment. Efforts to display and defend images of metal corrosion are difficult to substantiate in the absence of established exemplars and peer-reviewed research. The Daubert standard for expert witnesses in federal courts and most state courts requires the introduction of scientifically-based studies to substantiate admittance of expert testimony. The Daubert standard promotes the testing of different materials when the duration of a water loss is a critical factor in the acceptance or denial of a property loss disagreement. To that end, research was conducted on various metal materials found in the construction industry to establish the time necessary for visible corrosion to occur. We propose that comparative research photographs can guide the investigation and decisions of real world circumstances of corrosion.

Conclusion

Our qualitative approach rendered the following results.

1. By reducing the amount of variables during the testing process the time lapse images of metal deterioration provide exemplars that characterize the gradual development of oxidized surfaces and rust.

2. Testing the recirculated water each day (pH, TDS, conductivity, etc.) indicated the use of a fine filter media ($\leq$10 microns) was sufficient enough to maintain water quality.

3. After exposure to fresh and salt water for approximately 33 days the copper test specimens experienced characteristic corrosion or blue-green patina appearance.

4. After exposure to fresh and salt water for approximately 43 days galvanized steel test specimens had not experienced characteristic corrosion such as the iron oxide (red-orange) on any of the face (unaltered) surfaces.

5. The surface photographs after 3 days showed the zinc alloy layer and copper surface layer converted to zinc oxide (white rust) and copper oxide (black layer), respectively.

References

Yildiz, R. "Investigation of the cut-edge corrosion of organically-coated galvanized steel after accelerated atmospheric corrosion test". Adana, Turkey. 2012. Sciencedirect.com

Baboian, R. ASTM International. Corrosion Test and Standards. Application and Interpretation. 2nd Edition. Library of Congress. Baltimore, MD. 2005

University of Leicester. "Forensic metal fingerprinting: Simple, handheld device which can measure corrosion on machine parts". *ScienceDaily*. 22 October 2010. <www.sciencedaily.com/releases/2010/10/101020084229.htm>.

Cornell University Law School. "Daubert Standard". Legal Information Institute. Ithaca, NY. 1993

Davis, J. R. 2000. Corrosion: Understanding the Basics. Materials Park: ASTM International.

NACE/ASTM. Standard Terminology and Acronyms Relating to Corrosion. Engineering Standard. West Conshohocken: NACE International/ASTM International. 2009

Revie, R. Winston. 2008. Corrosion and Corrosion Control. Hoboken: John Wiley & Sons, Inc.

Roberge, P.R. 2008. Corrosion Engineering: Principles and Practice. New York: McGraw-Hill.

Schweitzer, P.A. 2006. Corrosion Engineering Handbook, Second Edition. Boca Raton: CRC Press.

Fundamentals of Metallic Corrosion. Hoboken: Taylor and Francis. 2006

Richardson, H. W. "Handbook of Copper Compounds and Applications". New York, NY: CRC Press, Jan 16, 1997.