METHODS FOR MITIGATION OF CORROSION UNDER INSULATION (C.U.I.) AND OTHER CREVICE CORROSION

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INTRODUCTION

Corrosion of steel operating equipment and piping under insulation has been recognized as an important problem in the ammonia refrigeration, chilled water, chemical and petroleum industry. Insulation is a necessary component and there to function in three ways: save energy, control process temperatures, and protect workers from high wall temperatures. The environment under insulation, the CUI environment, can be hot, wet, and promotes aggressive corrosion. The American Petroleum Institute has directives that address the CUI problem and detail a program of identification, maintenance, and remediation. These directives, as well as efforts by professional societies (NACE and ASTM), promote the development of new solutions. The issue in achieving a good end result is that no clear solution exists for new installed piping as well as maintenance and remediation of existing installations.

NACE Standard RP0198-98 [1] is an excellent source of information for preventing corrosion under insulation, but many corrosion engineers would agree that electrolytes will eventually find their way into even the best system. Selecting the right coating is extremely important. The coating is the last line of defense for keeping the electrolyte from the metal surface and preventing corrosion. Recent coating innovations include a hydrophobic anti-corrosion gel that is tolerant of less than optimal surface preparation, is designed to keep the electrolyte away from the surface of the substrate, and also has the ability to neutralize the electrolyte if it breeches the vapor barrier and insulation.

TECHNOLOGY

The reactive anti-corrosion gel utilizes mineralization technology. Mineralization is the ability to grow very thin minerals on metal surfaces for useful purposes. The minerals are formed when reactants are delivered to the surface of the substrate as shown in Figure 1.



HOW THE REACTIVE GEL CORROSION TREATMENT WORKS:

When the ferrous (steel) surface (1) is covered with a layer of reactive gel (2), the metal surface reacts with components in the gel to form a mineral layer (3). This thin glasslike layer (3) acts as a barrier between chlorides and the metal surface, thus providing corrosion resistance.

The mineral layer (3) has a thickness of 50-200 angstroms, only 0.01% as thick as a piece of paper.

Although the thin mineral layer can be damaged by mechanical abuse, there is extra protection built into the system.

FIGURE 1- Mineral Formation

The presence and uniqueness of the mineralized layer can be confirmed by conventional analytical surface methods such as x-ray Photoelectron Spectroscopy (XPS) or Atomic Force Microscope (AFM) (Figure 2 and Figure 3).







FIGURE 3 – Mineralized Steel Surface

The anti-corrosion gel works in three basic ways:

- **1.** Barrier system The specially formulated products have great adhesion characteristics and are hydrophobic to help keep moisture away from the substrate.
- 2. Buffering system If moisture migrates through the gel, it is buffered to a high pH which is protective to steel piping.
- **3.** Mineralization Growing an engineered surface, or surface conversion creating a surface which resists corrosion even if moisture gets to it.

The anti-corrosion gel has a maximum service temperature of 350°F (177°C).

BACKGROUND

The mineralization technology in the anti-corrosion gel has a history of solving unique corrosion problems. The first application of the mineralization technology was by a major automotive supplier in a crevice corrosion application on the strand of brake cables. The strand in sleeve design of the brake cable combined with the cyclical environment of heat and moisture creates a severe crevice corrosion environment. The technology has been used for over 30 years in this application, which has resulted in an increased service life and greater reliability.

The first non-automotive industrial application was with the US Navy. Following successful laboratory, pier side, and shipboard demonstrations of the effectiveness of the gel in preventing crevice corrosion in anchor chain detachable link cavities, the US Navy in 1999 changed the Planned Maintenance System (PMS) to specify the use of a mineralizing gel as the replacement for white lead and tallow in all surface ship anchor chain detachable links. Also in 1999, following extensive testing, the Navy issued MACHALT 526 which changed the design of the internals of weather deck watertight and airtight door dogging mechanisms. The basis for the change is the use of a mineralizing lubricant inside the spindle sleeve in the door frame to stop the corrosion that had been the cause of dogging mechanism failure. The watertight door dogging mechanism corrosion problem was one of the top maintenance issues for the fleet. In May 2002 a second MACHALT, 544, was approved to apply the same technology to ballistic type dogs in three watertight doors in DDG-51 Class ships. These solutions represented a significant savings for the fleet.

The gel has years of history on Corrosion Under Insulation applications in the Food & Beverage Industry. It has also been used as an anti-corrosion coating in well head casings, on pig doors, structural steel, tank chimes, ammonia systems, vessels, and as flange filler. Field trials are currently underway to further evaluate this technology in areas where it is cost prohibitive to achieve optimal surface preparation.

TESTING

Laboratory Tests

<u>Aerated Salt Bath.</u> A test was conducted to determine the ability of the anti-corrosion gel to protect pipes in an aerated bath of 5% salt solution. Fifteen Black Iron pipes were used to measure the effectiveness of the gel in conditions similar to CUI. Fourteen pipes were coated with the gel, seven were glass-bead-blasted prior to the application, seven pipes were left as received with mil-scale, and one pipe was left uncoated to act as a control. All of the iron pipes were covered with fiberglass insulation and partially submerged in an aerated bath of 5% salt solution (Figure 4). One glass-bead-blasted and non-bead-blasted sample were pulled at 7, 31, 80, 138-day, and 1-year intervals.

The results of tests show a very distinct line separating the sections of the iron pipes that were treated with the anti-corrosion gel and the sections that were left untreated (Figure 5). The untreated pipe sections had significant corrosion at 7, 31, 80, 138-days, and 1-year intervals. There were no sign of corrosion on the coated sections of the pipes. Performance of the gel was good even with minimal surface preparation prior to the application.



FIGURE 4 – Aerated Salt Bath

FIGURE 5 – Pipe after 138 Days of Exposure

<u>Isothermal.</u> One such laboratory test was a simulated CUI cell under isothermal and wet/dry cycling test conditions [2]. The test conditions selected for the research program were (1) isothermal and (2) wet/dry cycling. The isothermal tests included maintaining the temperature at the ring surfaces at 150°F (65.5°C) continuously. The wet/dry tests included two cycles of maintaining temperature at 150°F (65.5°C) (wet) for twenty hours followed by at 250°F (121°C) (dry) for four hours. The samples were evaluated using electrochemical polarization resistance data per ASTM G59 and mass loss (ML) data per ASTM G1. The results of the test were that the anti-corrosion gel reduced the corrosion rate by a factor of ten (Figure 6) and was effective in four practical applications: on bare steel at isothermal (isothermal at 150°F, 65.5°C), on precorroded steel at isotherma⁻¹ (150°F 65.5°C) on bare steel in wet/dry environment (150/250°F, 65.5/121°C).



FIGURE 6 – Isothermal Test Results

<u>Weight Loss.</u> ASTM B117 Salt Spray protocol was used to evaluate the anti-corrosion performance. The ASTM B117 protocol simulates a severe corrosion environment using salt-water spray. The control coupons (bare steel) were tested alongside the coated samples to insure a predictable corrosion rate.

A total of 10 samples (1/2" X 3" X 0.062" 1020 steel coupons) were used for this test. The coupons were weighed prior to being coated or being placed in the ASTM B117 cabinet. 5 coupons were coated with approximately 20 mils of gel (Group #1) and 5 coupons were left uncoated to be used as controls (Group #2). The coupons were placed in an ASTM B117 corrosion chamber. Each coating system was inspected and photographed at 504 hour (21 day) increments until 2520 hours and then again at 5016 hours. One coupon from each group was removed at each 504 hour (21 day) increment until 2520 hours and then again at 5016 hours. Group #1 was removed, the gel was cleaned off with a citrus cleaner and the corrosion was removed by submerging the coupon in acid. After each sample from Group #2 was removed, the corrosion was removed to determine the amount of weight loss. The weight loss results are shown in Table 1 and Figure 7.

The gel samples showed significantly less corrosion than the control. After 5016 hours of exposure in ASTM B117 Salt Spray, the gel sample showed 5.67% weight loss versus 50.04% for the control sample. The gel was 90.2% more effective than the uncoated control after 2520 hours and 88.66% more effective than the uncoated control after 5020 hours of ASTM B117 testing. Much of the weight loss on the coated sample came from the corrosion that enveloped the hole used to hang the coupons in the test as shown in Figure 8. While this increased the corrosion rate on the coated coupons, there was no other feasible way to hang or suspend the coupon without further damaging the coating during the test.

Group #1 - Coated					
	Weight @	B117 Salt	Weight @ end	Weight Loss	
	start (grams)	Spray Hours	(grams)	(grams)	% loss
Panel #1	11.4722	504	11.4589	0.0133	0.12%
Panel #2	11.4920	1008	11.4766	0.0154	0.13%
Panel #3	11.3314	1512	10.9550	0.3764	3.32%
Panel #4	11.2317	2016	10.9215	0.3102	2.76%
Panel #5	11.5222	2520	11.1909	0.3313	2.88%
Panel #6	11.4718	5016	10.8210	0.6508	5.67%
Group #2 - Control					
	Weight @	B117 Salt	Weight @ end	Weight Loss	
	start (grams)	Spray Hours	(grams)	(grams)	% loss
Panel #1	11.3198	504	10.4278	0.8920	7.88%
Panel #2	11.2822	1008	9.5650	1.7172	15.22%
Panel #3	11.5520	1512	8.6714	2.8806	24.94%
Panel #4	11.3450	2016	8.2689	3.0761	27.11%
Panel #5	11.3753	2520	8.0336	3.3417	29.38%
Panel #6	11.4798	5016	5.7348	5.7450	50.04%



TABLE 1. ASTM B117 WEIGHT LOSS DATA

FIGURE 7 - Weight Loss Results



FIGURE 8 – Coupons used in Weight Loss Test

ENVIRONMENTAL

Testing

A 96-hour static acute toxicity screening test with the saltwater mysid (*Mysidopsis bahia*)" was conducted on this technology by Wildlife International Ltd. at the Wildlife International Ltd. aquatic toxicology facility in Easton, Maryland (Project Number 486A-106).

Groups of saltwater mysids (*Mysidopsis bahia*) (<24 hours old) were exposed to three concentrations of the test substance, a negative (dilution water) control and a solvent control for 96 hours under static test conditions. One replicate test chamber was maintained in each treatment and control group, with 10 mysids in each test chamber for a total of 10 mysids per test concentration. Test chambers were 2-L glass beakers containing 1000 ml of test solution. Nominal test concentrations were negative control, solvent control, 1.0, 10, and 100 mg of the anti-corrosion gel.

The solvent control and the 1.0, 10, *and* 100 mg anti-corrosion gel/L test solutions were prepared by adding the appropriate amounts of test substance along with 0.50 ml of DMF to 1000 ml of filtered salt water. Test solutions were stirred vigorously approximately 30 minutes each using Teflon-coated magnetic stir bars and stir plates. Once mixing was complete, mysids were added to the test chambers. The solvent concentration in all of the treatment groups and the solvent control was 0.50 ml/L. All control test solutions appeared clear and colorless. Test

solutions (1.0, 10, *and* 100 mg anti-corrosion gel) appeared clear and colorless with particles of test substance on the surface and on sides of test chambers, increasing in intensity with increasing concentration.

Cool-white fluorescent light tubes were used to illuminate the test and were controlled with an automatic timer to provide a photoperiod of 16 hours of light and 8 hours of darkness. Light intensity at test initiation was 285 lux at the surface of the water. The target test temperature was $25 \pm 1^{\circ}$ C. The test temperature, dissolved oxygen and pH were measured in each test chamber at the beginning and end of the test.

Observations of mortality and clinical signs of toxicity were made at approximately 3, 24, 48, 72, and 96 hours. Mortality data at 24, 48, 72, and 96 hours was used to estimate or calculate EC50 values. When possible, the EC50 values were calculated using the computer program of C.E. Stephan. The no-observed-effect-concentration (NOEC) was determined by visual interpretation of the mortality and clinical observation data.

Measurements of temperature ranged between 24.1°C and 25.2°C throughout the test. Dissolved oxygen concentrations remained $\geq 5.4 \text{ mg/L}$ (74 percent of saturation) and pH was 8.1 in all treatments and the control groups at the beginning and at the end of the test. At test initiation, the dilution water salinity was 20 parts per thousand (Table 1).

Mysids in the negative and solvent controls, and all treatment groups appeared normal and healthy throughout the test. Any moralities and clinical signs of toxicity in the treatment groups were considered to be incidental and not related to treatment. The 96 hour LC50 was determined to be > 100 mg anti-corrosion gel and the NOEC was 100 mg of the anti-corrosion gel. The test showed that the anti-corrosion gel was determined to have "No Toxicity At 100 ppm (96 Hours)."

The anti-corrosion gel is generally considered environmentally benign and has been accepted by industrial hygiene departments at companies in various industries including Food & Beverage, Oil & Gas, Chemical, and the US Military.

DELIVERY TECHNIQUES

Surface Preparation

Many coating require extensive surface preparation for optimal performance. The anticorrosion gel can be applied on new piping or pre-corroded surfaces with a minimum surface preparation of Steel Structures Painting Council (SSPC) SP-2 [3]. The anti-corrosion gel needs to "wet out" the substrate in order to react with the surface. This can be achieved on less than perfect surfaces that have tight rust as long as the loose scale is removed.

Application

The anti-corrosion gel can be glove, brush, or spray applied on in-service piping. Application methods have been developed for in service temperatures as low as -20° F (-29° C) and as high as 350° F (177° C). One advantage of the anti-corrosion gel versus paint type coatings is that the

gel can be applied on in-service systems that are expensive to shut down during the rehab process.

SUMMARY

The technology offers a non-hazardous and environmentally benign solution to CUI that offers versatile application methods and minimal surface preparation. The anti-corrosion gel is a cost effective alternative to solutions that require extensive surface preparation and require shutting down the system during the application.

Some of the benefits of the anti-corrosion gel are:

- Multiple delivery systems
- Multiple application methods
- Insensitive to surface preparation and application conditions
- Versatile
- Superior anti-corrosion performance
- Environmentally benign

Applications for the anti-corrosion gel

- Corrosion Under Insulation
- Crevice Corrosion
- Flange Filler
- Pig Doors
- Anti-Seize for Fasteners
- Casing Filler

REFERENCES

- 1. NACE RP0198-98, The Control of Corrosion Under Thermal Insulation and Fireproofing Materials A Systems Approach (National Association of Corrosion Engineers, 1998)
- N.G McGowan, Dr. D. Abayarathna, "Innovative and Environmentally Benign Solutions for Corrosion Under Insulation (C.U.I.) for Steam and Process Piping" CLI International, Inc., Test Report, March 2003.
- 3. Steel Structures Painting Council (SSPC) SP-2 "Hand Tool Cleaning Removal of all rust scale, mill scale, loose rust and loose paint to the degree specified by hand wire brushing, hand sanding, hand scraping, hand chipping or other hand impact tools or by a combination of these methods. The substrate should have a faint metallic sheen and also be free of oil, grease, dust, soil, salts and other contaminants."