



EXPLORING THE MECHANISM AND LONGEVITY OF CORROSION INHIBITORS IN INSULATION



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INTRODUCTION

ABSTRACT

Thermal insulation is an integral part of the petrochemical and refining industry used to conserve energy, maintain process control, and ensure operator safety. It is a key component to ensuring industrial operations run as efficiently and sustainably as possible. Insulation systems, comprised of thermal insulation, jacketing, mastics, and sealants, are designed to keep water out in order to maintain the integrity of the thermal insulation and limit corrosion under insulation (CUI). However, even the best designed and installed systems sometimes become compromised, resulting in the presence of water at the pipe surface and the potential for CUI. As such, it is important to understand how the chemistry of the thermal insulation affects the CUI potential.



The purpose of the analysis discussed in this paper is to better understand how CUI is impacted by the interaction between the thermal insulation chemistry and the metal surfaces that are routinely seen in industrial systems. The analysis is also intended to gain a better understanding of the longevity of the XOX Corrosion Inhibitor® in thermal insulations under compromised conditions.

Previous research has shown that the material properties and chemistries of thermal insulations can have an impact on the systems they are designed to interact with. Since there is no way to design an insulation system that is immune to liquid water penetration, it is imperative to understand the influence those material properties can have on CUI potential.

INTRODUCTION

Thermal insulation is an integral part of the industrial complex, and it offers a variety of benefits to industrial facilities. Using insulation helps decrease energy consumption by preventing heat loss through the piping systems, reducing overall production cost, and limiting environmental impacts of the processes. Insulation also provides personnel protection and improves safety by lowering the surface temperature of piping and equipment to “safe-to-touch” temperatures (140°F/60°C) as established by OSHA. Industrial processes are more consistent

and controllable with the use of insulation. Additionally, insulation can serve as passive fire protection by limiting damage to equipment and personnel during fires.

While insulation systems can provide significant benefits to the end user, systems that are not properly installed or maintained can result in conditions that promote CUI. Despite advancements in technology, CUI continues to plague the industry, causing substantial financial implications as a result of pipe or equipment replacement, system downtime, and inspection resources.

Most mitigation strategies for CUI have focused on removing of water from the CUI equation by inhibiting water intrusion. Insulation systems are jacketed and sealed to keep the weather and water out. Current strategies also promote insulations that have water-repellent properties; however, heat exposure degrades the efficacy of the water repellent additive, after which even water-repellent insulations will become saturated. The metal or the pipe surfaces are a second focus where end users rely on coatings. However, pipe surfaces that have been coated can be installed improperly and damaged during installation. Over time, this results in weak points where CUI can take hold.

A new CUI mitigation strategy based on the chemistry of the insulation has been developed. In this concept, a pipe coating or system metallurgy can be designed to better work in conjunction with a specific insulation, based on the chemistry of that insulation. An inspection program can be optimized based on known corrosion by-products or signatures. The first step in building this new mitigation strategy, and the basis for this research, is understanding the corrosion by-products of different insulation types based on their chemistries and investigating the longevity of properties such as the XOX Corrosion Inhibitor.



EXPERIMENT: CORROSION BY-PRODUCT ANALYSIS USING VARIOUS INSULATIONS

The first test protocol used in this study is based on ASTM C1617 *Standard Practice for Quantitative Accelerated Laboratory Evaluation of Extraction Solutions Containing Ions Leached from Thermal Insulation on Aqueous Corrosion of Metals*. Per the test method, the leachable content of the insulation is extracted via a boiling liquid extraction. The extractions are then dripped onto heated carbon steel coupons for a period of 96 hours to mimic accelerated wet-dry cycles.

In this study, after 96 hours of exposure, the surface corrosion and by-products on the carbon steel coupons were subjected to laboratory analyses via electron diffraction spectroscopy (EDS), optical microscopy, and scanning electron microscopy (SEM). The EDS analysis was used to determine the composition and relative amount of each element on the surface layer of the coupons. The enhanced optical and SEM analyses were used to visually inspect the surface of the coupons. The insulation samples tested in this study are listed below. They cover the CUI range and are designed for use in applications up to 1200°F:

1. Hydrophobic silica aerogel blanket
2. MinWool-1200®: Water-repellent mineral wool
3. Thermo-1200®: Water-resistant calcium silicate with XOX Corrosion Inhibitor
4. Sproule WR-1200®: Hydrophobic expanded perlite with XOX Corrosion Inhibitor

EXPERIMENT: CORROSION INHIBITOR LONGEVITY

In addition to the ASTM C1617 protocol, two sets of Thermo-1200 water-resistant calcium silicate insulation were also tested to determine the longevity of the XOX Corrosion Inhibitor. For this test, 12 samples were cut from two separate pieces Thermo-1200 (six samples each). The insulation samples underwent the ASTM C1617 test protocol after being cycled through a wet and dry cycle up to 40 times. The insulation samples were cycled between 8 hours of water submersion followed by 16 hours in a 450°F oven. One set of Thermo-1200 insulation samples was submerged in tap water that was replaced with fresh water after each cycle. The second set of Thermo-1200 insulation samples was submerged in an initially 1500 ppm chloride solution. This solution was filled daily with fresh water to a fixed volume to ensure the chloride concentration returned to 1500 ppm after water absorption and evaporation during the wet-dry cycling created a more highly concentrated chloride solution. At every 10 cycles, one insulation sample was pulled from the cycling process to undergo the ASTM C1617 test protocol. The sample was tested to determine whether the material lost its corrosion inhibiting properties over the course of repeated wet-dry cycling.

The cycling process completed for the analysis was intended to serve as an accelerated replicate of the possible conditions that could be encountered in a field application. In many applications during process upsets, cycling operations, or scheduled downtime, the insulation in a compromised system can cycle through saturation and dehydration repeatedly. Tap water was used to mimic an inert environment; whereas, the 1500 ppm chloride solution was used to represent exposure in a coastal region. This second set of tests was conducted to address questions regarding the longevity or lifetime of the XOX Corrosion Inhibitor under these conditions.

RESULTS & DISCUSSION

RESULTS & DISCUSSION: CORROSION BY-PRODUCT ANALYSIS USING VARIOUS INSULATION

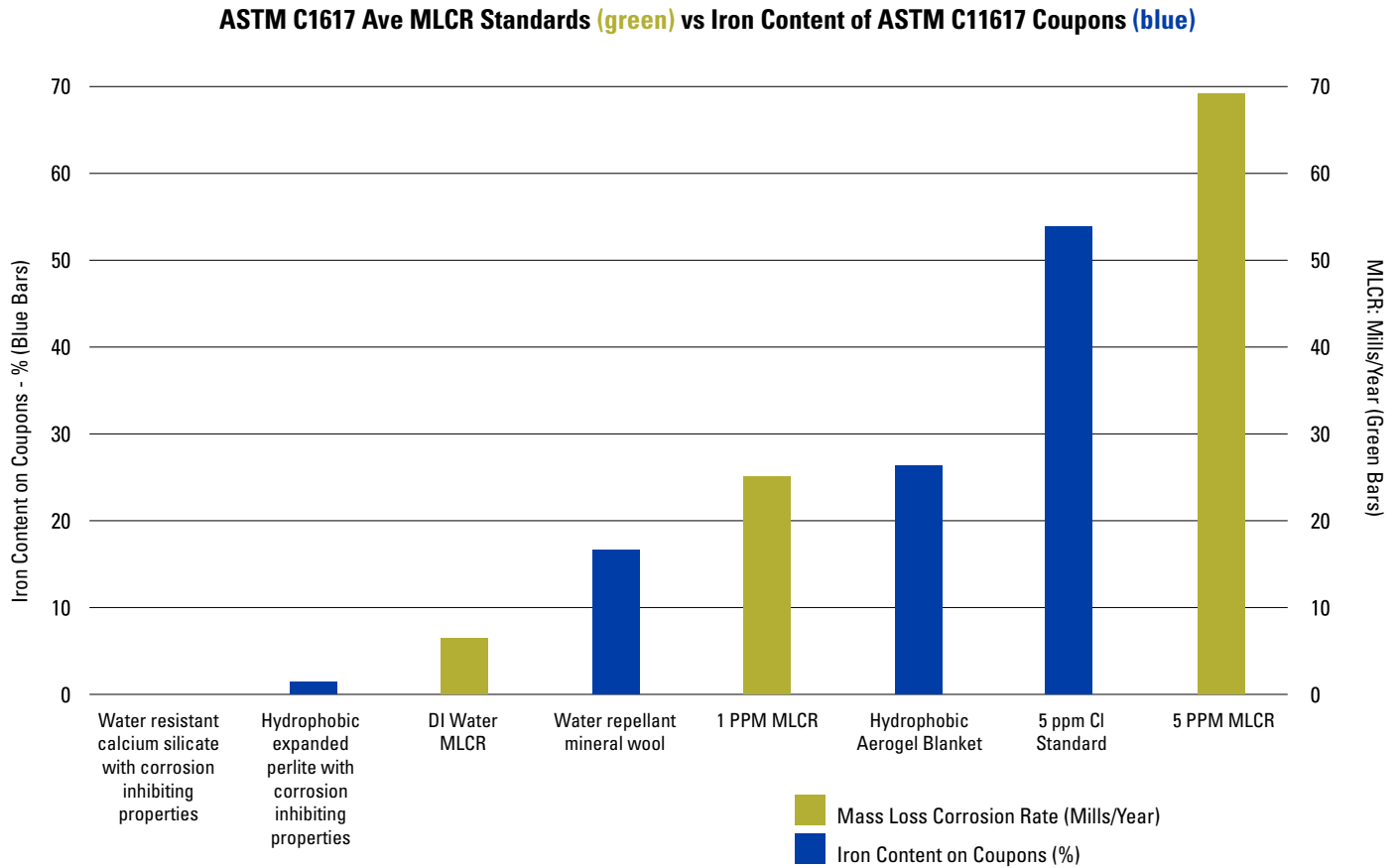
Results from EDS testing identified the composition of the corrosion surface layer on carbon steel coupons as well as the relative percentages of each component based on a specific insulation's leachate chemistry. The elements present in this study were predominantly metal oxides, including silica oxide, iron oxide, and calcium oxide, as well as sodium, magnesium, and chlorine. While some of the elements identified are known leachable ions from the insulation, each leachate from the insulation will impact the surface differently. In particular, the leachable silicates have been known to be an inert compound that have no negative corrosion implications; whereas, chloride ions are known to be corrosive and cause stress corrosion cracking on stainless steel. Iron oxide identified by the analysis indicates the presence of corrosion or rust on the surface of the coupon. Table 1 details the results of the analysis from the various insulation types.

Table 1: EDS Analysis of Corrosion Layer by Insulation Type

Sample ID	Composition (Atomic %)						
	O	Fe	C	S	Cl	Protective silicates & ions	Other leachable ion
Thermo-1200 w/ XOX Corrosion Inhibitor	51.1	0.0	8.3	2.7	0.0	36.9	1.0
Sproule WR-1200 w/ XOX Corrosion Inhibitor	49.1	0.9	6.0	0.0	0.0	43.1	0.9
MinWool-1200	50.8	16.9	9.2	0.0	0.0	5.6	16.5
Hydrophobic silica aerogel blanket	40.8	26.4	23.3	0.2	0.1	2.6	5.8
5 ppm Cl standard	42.9	54.0	0.0	0.0	0.1	1.6	1.4

For the various insulation types, the relative concentration of iron or iron oxide in the samples corresponds to the relative performance of the insulations using the ASTM C1617 corrosion test method. The iron oxide (column Fe) present in the analysis is the formation of rust or generalized surface corrosion. The ASTM C1617 test compares the relative corrosivity of the insulation leachate to three standards/controls: deionized (DI) water, 1 ppm chloride solution, and 5 ppm chloride solution. Figure 1 shows the representative relative average mass loss corrosion rate (MLCR) of the standards used in the testing protocol.

FIGURE 1: Mass Loss Corrosion Rate of Standards using ASTM C1617



Imaging Analysis

FIGURE 2: Enhanced imaging of metal coupons after ASTM C1617 test method using Thermo-1200 water resistant calcium silicate with XOX Corrosion Inhibitor sample.

Figure 2 shows there is no corrosion on the surface of the calcium silicate coupons. The buildup on the surface is consistent with the protective silicate and ion layer identified in the EDS analysis. The silicate and ion layer on the surface is acting to prevent the corrosion damage to the surface of the coupons.

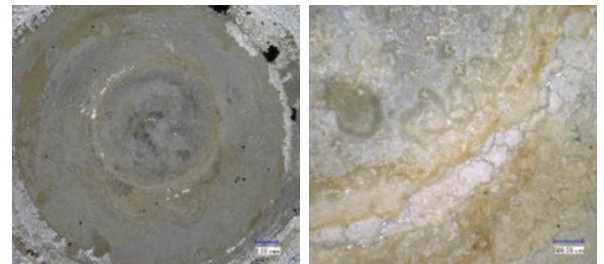


FIGURE 3: Enhanced imaging of metal coupons after ASTM C1617 test method using Sproule WR-1200 hydrophobic perlite with XOX Corrosion Inhibitor sample.

Figure 3 shows there is no corrosion on the surface of the perlite coupons. The buildup on the surface is consistent with the silicate and ion layer identified in the EDS analysis. Again, this layer on the surface is acting to prevent the corrosion damage to the surface of the coupons.

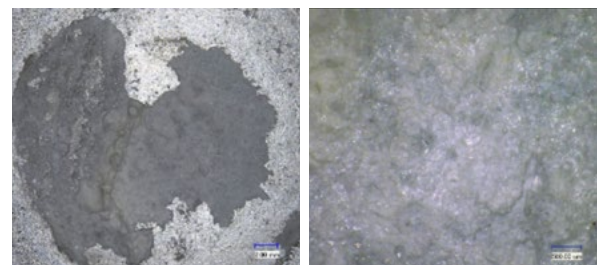


FIGURE 4: Enhanced imaging of metal coupons after ASTM C1617 test method using hydrophobic silica aerogel blanket sample.

Figure 4 shows a layer of iron oxide or rust on the surface of the coupon. No protective sodium silicate layer or carbon buildup is present.

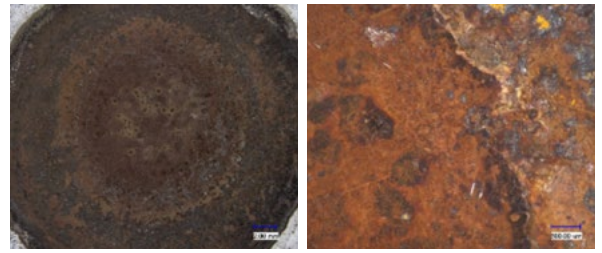
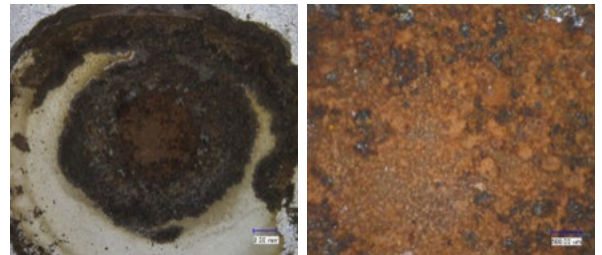


FIGURE 5: Enhanced imaging of metal coupons after ASTM C1617 test method using MinWool-1200 water repellent mineral wool sample.

Figure 5 shows a layer of iron oxide or rust on the surface of the coupon. No protective sodium silicate layer or carbon buildup is present.



The EDS analysis of the samples of the Thermo-1200 and Sproule WR-1200 with the XOX Corrosion Inhibitor revealed that the calcium silicate had no iron on its surface (0.0%) and the expanded perlite had a negligible amount of iron (0.91%). Additionally, both materials exhibited less corrosion than DI water in the ASTM C1617 analysis. In contrast, the MinWool-1200 and hydrophobic silica aerogel blanket samples had the highest relative concentrations of iron, 16.9% and 26.4%, respectively. As a comparison, the 5 ppm chloride standard tested had a relative iron concentration of 54%.

Insulations with the XOX Corrosion Inhibitor left a higher total protective silicate and ion concentration on the surface of the coupon than the other insulations. The Thermo-1200 and Sproule WR-1200 samples had concentrations that made up 36.9% and 43.1%, respectively, of the elements deposited on the surface of the coupon; whereas, all other insulation samples had protective silicate and ion concentrations of less than 10%.

The total ratio of the protective silicates and ions relative to the chloride and fluoride content in an insulation has been determined by ASTM and the NRC to limit the amount of corrosion that occurs on stainless steel. ASTM C795 Standard Specification for Thermal Insulation for Use in Contact with Austenitic Stainless Steel provides an acceptability curve, determined through empirical means, that shows the acceptable limits required of the sodium and silicate content of the leachable solution to limit the corrosion potential of a determined chloride and fluoride ion presence.

The carbon content measured from the Thermo-1200, Sproule WR-1200, MinWool-1200, and silica aerogel blanket sample surfaces are likely due to residual organics in the insulations from either the binder or hydrophobic treatment.

RESULTS & DISCUSSION: CORROSION INHIBITOR LONGEVITY

The EDS analyses of the Thermo-1200 samples with the XOX Corrosion Inhibitor that were cycled in tap water and 1500 ppm salt water are shown in Table 2. As discussed in ASTM C795, the total protective silicate and ion content were the focus of this analysis as they are the variable most correlated with reducing the occurrence of corrosion. The insulations were tested after submersion at 0, 10, 20, 30, and 40 wet-dry cycles. As shown in Table 2, the total silicate and ion content of the calcium silicate does not diminish over the number of cycles tested. The initial uncycled Thermo-1200 tap water set (0 Cycles in Table 2) had a total surface composition of 32.1% protective silicates and ions while the material that was cycled 40 times had a total surface composition of 32.2%. Throughout the test, it is clear that the protective silicate and ion composition remains relatively consistent.

For the salt water set, the initial uncycled sample (Salt Water 0 Cycles in Table 2) had a total surface composition of protective silicates and ions of 39.2% while the material that had been cycled 40 times had a total surface composition of 34%. Although the relative amounts of silicates and ions in the protective layer vary over the course of the testing, they do not diminish over time for either environmental condition. The minor variations we do see in silicate and ion composition are attributed to variations in the base chemistry of the insulation, and not to the material gaining or losing its corrosion inhibiting properties as a result of wet-dry cycling.

Table 2: EDS Analysis of Corrosion Layer of Cycled Calcium Silicate Insulation

Sample ID	Composition (Atomic %) Protective Silicates & Ions	Sample ID	Composition (Atomic %) Protective Silicates & Ions
DI Water	0.0	DI Water	3.2
0 Cycles	32.1	Salt Water 0 Cycles	39.3
10 Cycles	38.7	Salt Water 10 Cycles	39.9
20 Cycles	37.7	Salt Water 20 Cycles	38.7
30 Cycles	39.4	Salt Water 30 Cycles	39.1
40 Cycles	32.2	Salt Water 40 Cycles	34.0

CONCLUSION

In this study, analysis of surface corrosion layers on carbon steel show that different chemical compositions will form depending on the insulation material in contact with the metal surface. Most significantly, the relative amount of iron oxide present in the surface layer correlated well with the typical mass loss corrosion rates determined by the ASTM C1617 testing protocol (Figure 1). The hydrophobic silica aerogel blanket sample and water-repellant mineral wool sample had the highest relative surface concentration of iron oxide, and they also exhibited the highest typical mass loss corrosion rates when undergoing the ASTM C1617 testing protocol. The Sproule WR-1200 (hydrophobic perlite with XOX Corrosion Inhibitor) sample, and Thermo-1200 (water-resistant calcium silicate with XOX Corrosion Inhibitor) sample had little or no iron oxide present on the surface while also typically exhibiting the lowest mass loss corrosion rates during the ASTM C1617 test protocol.

Insulation materials with the XOX Corrosion Inhibitor were shown to decrease the proliferation of corrosion on metal surfaces by depositing a protective coating layer onto the metal surface. This layer was present when testing the Sproule WR-1200 with XOX Corrosion Inhibitor sample and the Thermo-1200 with XOX Corrosion Inhibitor sample. The surface layer that developed from the corrosion inhibiting properties had a chemical composition that was consistent with documented standard ASTM C795 requirements for limiting stress corrosion cracking of stainless steel.

Concerns with corrosion inhibitors in insulation are typically related to the longevity of the inhibitor activity; however, it was shown in this study that the protective attributes of the XOX Corrosion Inhibitor does not appear to decrease over time when cycled between wet and dry states with either tap or salt water. This is evident by the sustained presence of the protective surface layer after 40 wet-dry cycles of the insulation.

In summary, components leaching from different insulation chemistries interact with pipe surfaces in different ways. By analyzing the CUI surface layer (or absence of a CUI layer), engineers can understand how the insulation chemistry can influence the long-term corrosion prevention strategy. Understanding the influence of the insulation chemistry allows for an inspection program to be optimized based on known corrosion by-products or signatures. Most importantly, the study shows that insulation with the XOX Corrosion Inhibitor can limit corrosion by forming a protective surface layer, which does not disappear over repeated wet-dry exposures. Utilizing these findings can be the first step in building a comprehensive corrosion mitigation strategy and prolonging the life of the pipe and insulation systems.



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