

Compatibility and Interactions Between Cathodic Protection and a Vapor Phase Corrosion Inhibitor

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The nature of the physical contact between the bottom plate of an above-ground storage tank and the underlying foundation/soil varies considerably over the area of a tank bottom and from tank to tank. This may vary from direct electrolytic contact between the plate and moist underlying soil to void spaces between the plate and the soil due to floor buckling and/or soil settlement. Cathodic protection (CP) is a proven corrosion mitigation technique where the target metal surface is in contact with a conductive electrolyte such as moist soil, but it will not be effective in void spaces where there is no electrolyte contact with the tank floor. Consequently, there is increasing application of vapor phase corrosion inhibitor (VCI) in-

jection beneath tank bottoms to ensure corrosion is mitigated in the void spaces. The objective of this work was to evaluate the mutual compatibility and interactions between CP and a VCI where applied together in a liquid-phase environment. The work comprised laboratory experiments to quantitatively evaluate the effects of a particular amine carboxylate-based inhibitor and CP, when applied individually and jointly on an oxygen concentration corrosion macrocell in a salt water solution. The results indicate a beneficial synergistic effect between the particular inhibitor tested and CP, where the inhibitor enhances cathodic polarization to reduce CP current requirement, and CP reduction reaction appears to enhance the

absorption and effectiveness of the inhibitor at the cathodic metal surface.

The nature of the physical contact between the bottom plate of an above-ground storage tank and the underlying foundation/soil varies considerably over the area of a tank bottom and from tank to tank. This may vary from direct electrolytic contact between the plate and moist underlying soil to void spaces between the plate and the soil due to floor buckling and/or soil settlement.

Cathodic protection (CP) is an effective corrosion mitigation technique where there is an electrolytic contact between the tank bottom surface and the underlying soil (i.e., liquid-phase environment), but it cannot provide protection in the absence of an electrolyte, as is the case where there are gaps or voids between the tank bottom and soil, or where there is intermittent moisture in the soil contacting the tank bottom surface (i.e., vapor-phase environment).

Increasingly, vapor phase corrosion inhibitors (VCIs) are being injected beneath tank bottoms to mitigate the vapor-phase corrosion aspect. There are many types and chemistries of corrosion inhibitors that affect the electrochemical reactions at the metal-electrolyte interface. Each of these has specific properties that may or may not be compatible with CP or other corrosion prevention measures.

The objective of this work was to evaluate the mutual compatibility and interactions between CP protection and a particu-

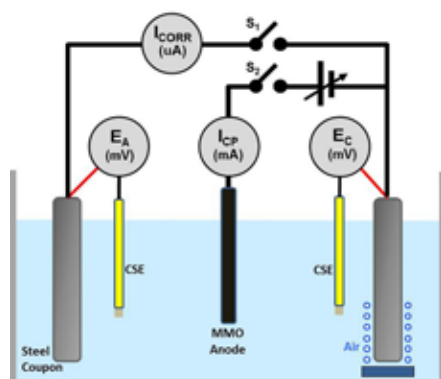


FIGURE 1 Test setup—schematic.

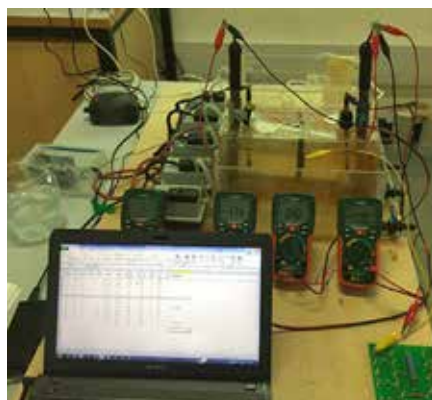


FIGURE 2 Test setup—physical arrangement.

lar VCI where applied together.

Test Setup and Procedure

The test method objective was to provide a quantitative evaluation of the effectiveness of CP and an amine carboxylate-based VCI when applied individually and jointly to mitigate the corrosion current in a liquid-phase corrosion “macro-cell.”

An oxygen concentration cell between two carbon steel (CS) electrodes was deemed representative of the prevalent macro-cells that exist on tank bottoms. A salt water solution (3.6 L at 35 g sodium chloride [NaCl] per L) was used. A variable-output air pump forced air through a diffuser positioned below one of the CS electrodes to encourage a cathodic (reduction) reaction and create a potential difference with respect to the unaerated steel electrode. A mixed metal oxide Ti rod anode was positioned midway between the steel electrodes and powered by a variable direct current power supply. The schematic and physical arrangement of the test apparatus is depicted in Figures 1 and 2.

Preparatory Procedure

A preliminary preparatory procedure to reliably produce the macrocell consisted of the following steps:

1. The test container was cleaned and rinsed.
2. Salt water solution (3.6 L with 35 g NaCl per L) was prepared and placed in the test container.
3. Test rod metal surfaces were cleaned and sanded to NACE No. 1/SSPC-SP 5/Sa 3¹ finish.
4. Test rods were placed in solution, without bond, and allowed to soak for at least 16 h for each to reach a stable open-circuit potential (OCP).
5. Copper/copper sulfate (Cu/CuSO₄) reference electrodes (CSEs) were freshly prepared, tested to verify a <1 mV difference between them, and placed in the test apparatus.
6. The OCP of each test rod was measured and monitored to ensure their stability.
7. The test rods were bonded, and the bond current and potentials were monitored

until they stabilized.

8. Aeration was started to cause a potential difference between the test rods, and adjusted until a steady state potential difference of 35 to 40 mV was achieved along with an associated corrosion current (i.e., I_{CORR}) of 350 to 400 μ A.

Test 1—Effect of VCI on Active CP System

Following the preparatory procedure, this test consisted of the following steps:

1. The CP arrangement was energized, and the CP current (I_{CP}) was adjusted to mitigate I_{CORR} (i.e., reduce I_{CORR} to zero). As cathodic polarization increased, I_{CP} was further adjusted to maintain I_{CORR} at zero until a steady state was reached.
2. The first 3 g of inhibitor was added to the solution. The effect on the I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
3. The inhibitor concentration was increased by adding another 3 g, the effect on I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
4. The inhibitor concentration was increased by adding another 3 g, the effect on I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero until a steady state was reached.
5. CP was de-energized and I_{CORR} was monitored until a steady state was reached.
6. The aeration was turned off and I_{CORR} was monitored until a steady state was reached.

Test 2—Effect of VCI Prior to Application of CP System

Following the preparatory procedure, this test consisted of the following steps:

1. The first 3 g of inhibitor was added to the solution. The effect on the I_{CORR} was monitored until a steady state was reached.
2. The inhibitor concentration was increased by adding another 3 g and the effect on I_{CORR} was monitored until a steady state was reached.
3. The inhibitor concentration was increased by adding another 3 g and

the effect on I_{CORR} was monitored until a steady state was reached.

4. The CP arrangement was energized, and the I_{CP} was adjusted to mitigate I_{CORR} (i.e. reduce I_{CORR} to zero). As cathodic polarization increased, I_{CP} was adjusted further to maintain I_{CORR} at zero until a steady state was reached.
5. CP was de-energized and I_{CORR} was monitored until a steady state was reached.
6. The aeration was turned off and I_{CORR} was monitored until a steady state was reached.

Test Results

The results for Test 1 are illustrated in Figure 3. The results for Test 2 are illustrated in Figure 4.

Discussion of Results

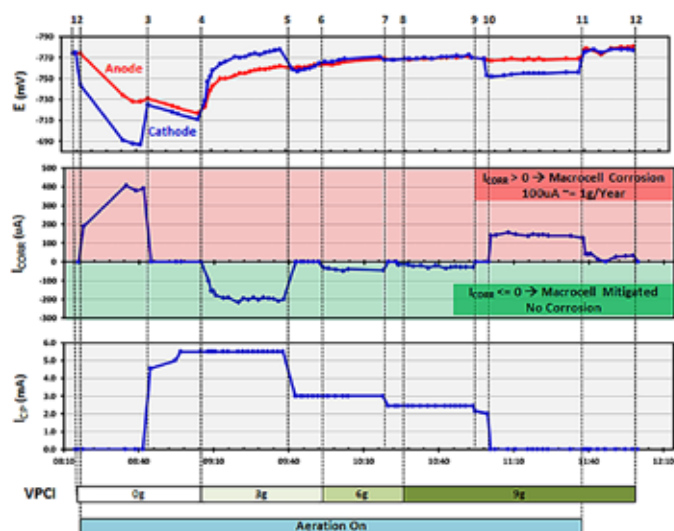
The Test 1 results are shown in Table 1. The Test 2 results are shown in Table 2.

Conclusions

The results indicate a beneficial synergistic effect between the VCI(x) tested and CP, where the inhibitor enhances cathodic polarization to reduce CP current requirement, and the CP reduction reaction appears to enhance the absorption and effectiveness of the inhibitor at the cathodic metal surface.

The following is a point-form summary of the conclusions drawn from this testing.

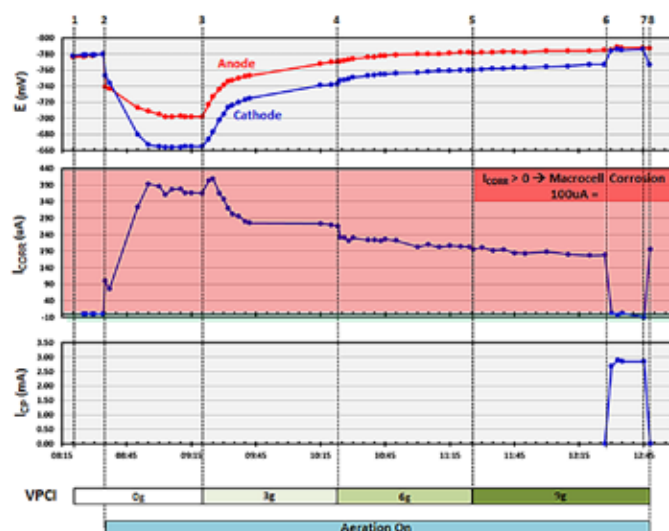
1. With respect to the VCI(x) tested:
 - a. The VCI(x) tested is a “cathodic polarizer.”
 - b. As a cathodic polarizer, the VCI(x) tested reduced CP current requirement, and could thereby also enhance CP current distribution. Specifically, the CP current requirement of 5.5 mA to mitigate the corrosion cell before the addition of inhibitor was reduced by 45% with the first 3 g addition, 55% with further 3 g addition, and 60% with the final 3 g addition.
 - c. At the concentrations tested, the VCI(x) substantially reduces, but does not completely mitigate the corrosion rate (i.e., I_{CORR}) in a liquid-phase macro-cell. Specifically, the original corrosion



Test Procedure Events

1. Test start—steady state coupon potentials following preparatory procedure
2. Aeration started to create stable macrocell with potential difference of -40 mV
3. CP output current energized and adjusted to reduce I_{CORR} to 0 μA
4. 3 g VCI(x) added to solution
5. CP output reduced to maintain I_{CORR} at 0 μA
6. 3 g VCI(x) added to solution
7. CP output reduced to maintain I_{CORR} at 0 μA
8. 3 g VCI(x) added to solution
9. CP output reduced to maintain I_{CORR} at 0 μA
10. CP de-energized
11. Aeration stopped
12. Test end

FIGURE 3 Test 1 results—effect of VCI on active CP system.



Test Procedure Events

1. Test start—steady state coupon potentials following preparatory procedure
2. Aeration started to create stable macrocell with potential difference of -40 mV between coupons and I_{CORR} of -375 μA
3. 3 g VCI(x) added to solution
4. 3 g VCI(x) added to solution
5. 3 g VCI(x) added to solution
6. CP output current energized and adjusted to reduce I_{CORR} to 0 μA
7. CP de-energized
8. Test end

FIGURE 4 Test 2 results—effect of VCI in the absence of CP.

rate of 375 μA was reduced by 27% with the first 3 g addition, 45% with further 3 g addition, and 52% with the final 3 g addition.

2. With respect to CP:
 - a. CP can completely mitigate liquid-phase macrocell corrosion.
 - b. CP appears to enhance the absorption and effectiveness of the inhibitor at the cathodic metal surface.

Caveats to Conclusions— Limitations of Testing

1. The test results revealed in this work apply to the specific VCI type and concentrations tested and are definitely not indicative of all inhibitors. For example, completely different results would be expected for “anodic inhibitor” chemistries.
2. There are many types and chemistries of corrosion inhibitors with varying application concentrations on the market having specific properties that differ

from the VCI tested in this work. Each of these should undergo similar testing as that performed in this work to specifically evaluate their effectiveness and compatibility.

3. It must be emphasized that this work evaluates the effectiveness and compatibility in the liquid-phase exposure. It does not in any way reflect the effectiveness of the inhibitor to reduce corrosion in the vapor-phase for which it is primarily intended.
4. As inhibitors generally affect the electrochemical reactions at the metal-electrolyte interface, and therefore their potentials, the presence of any inhibitor in the electrolyte would be expected to affect the potential stability of permanent reference electrodes used for CP performance evaluation, and similarly, the potential of any galvanic anodes in the same environment.
5. It is recognized that the time between test

stages was limited and therefore not sufficient for parameters to reach a true steady state before adjusting variables. These times should be extended in future work.

Acknowledgments

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TABLE 1. EFFECT OF VCI ON ACTIVE CP

Event	Observation
1	Both coupons were at -774 mV vs. CSE following the preparatory procedure.
2	A macrocell was created by the aeration to achieve a steady state potential difference of ~ 40 mV between coupons and an I_{CORR} of ~ 400 μ A. The aeration caused potentials of both coupons to shift electropositive as a result of cathodic depolarization.
3	The application of CP with $I_{CP} = 5.5$ mA caused the cathode coupon to cathodically polarize toward the potential of the anode coupon, thereby reducing I_{CORR} to 0 μ A to effectively mitigate the macrocell.
4	An initial 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 5.5 mA. Both coupons shifted electronegative, indicating they were being cathodically polarized. The cathodic polarization of the cathode coupon exceeded that of the anode coupon, resulting in a “-ve” I_{CORR} value (i.e., ~ -200 μ A).
5	I_{CP} was reduced to 3 mA to bring I_{CORR} to 0 μ A.
6	Further 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 3.0 mA. As was the case following Event 4, both coupons shifted electronegative, but not to the same magnitude as observed with the initial VCI(x) addition, resulting in a “-ve” I_{CORR} value (i.e., ~ -40 μ A).
7	I_{CP} was reduced to 2.45 mA to bring I_{CORR} to 0 μ A.
8	Further 3 g of VCI(x) was added to the solution while I_{CP} was maintained at 2.45 mA. As was the case following Event 6, both coupons shifted electronegative, but not to the same magnitude as observed with the initial VCI(x) addition, resulting in a “-ve” I_{CORR} value (i.e., ~ -20 μ A).
9	At Event 7, I_{CP} was reduced to 2.15 mA to bring I_{CORR} to 0 μ A.
10	The CP system was de-energized and the cathode potential shifted electropositive and I_{CORR} increased to ~ 140 μ A.
11	When the aeration was stopped, thereby eliminating the driving source for the macrocell, the potential of the cathode coupon approached that of the anode coupon (i.e., -774 mV vs. CSE), and I_{CORR} decreased to ~ 30 μ A.

TABLE 2. EFFECT OF VCI IN THE ABSENCE OF CP

Event	Observation
1	Both coupons were at -777 V vs. CSE following the preparatory procedure.
2	A macrocell was created by the aeration to achieve a steady state potential difference of ~ 40 mV between coupons and an I_{CORR} of ~ 375 μ A. The aeration caused potentials of both coupons to shift electropositive as a result of cathodic depolarization.
3	An initial 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~ 275 μ A.
4	Further 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~ 205 μ A.
5	Further 3 g of VCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~ 180 A.
6	The application of CP with $I_{CP} = 2.85$ mA caused the cathode coupon to cathodically polarize toward the potential of the anode coupon, thereby reducing I_{CORR} to 0 μ A to effectively mitigate the macrocell.
7	The CP system was de-energized, the cathode potential shifted electropositive, and I_{CORR} increased back to ~ 200 μ A.

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Electrochemical Polarization Measurements	ASTM G8 CC-030	Water based electrolytes
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Adhesion (Tape)	ASTM D3359	Coatings
Adhesion (Testers)	ASTM D 4541 (Test Method B); ASTM D7234 CC-034 CC-036	Coatings
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