Compatibility & Interactions between Cathodic Protection and a Vapor Phase Corrosion Inhibitor

Calvin R. Pynn
AEGIS Technical Systems LLC
Dubai, United Arab Emirates
Email: Calvin.Pynn@eim.ae

Khalil Abed
CORTEC Middle-East
Dubai, United Arab Emirates
Email: kabed@cortec-me.com

ABSTRACT

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 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 injection 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 cathodic protection and a vapor phase corrosion inhibitor where applied together in a liquid-phase environment.

The work comprised of laboratory experiments to quantitatively evaluate the effects of a particular amine carboxylate based inhibitor and cathodic protection, when applied individually and jointly on an oxygen concentration corrosion macro-cell in a salt water solution.

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

Keywords: tank bottom, AST, air gaps, voids, corrosion inhibitor, cathodic protection, polarization, absorption, soil-side corrosion, macro-cell, vapor phase, liquid phase, corrosion current

INTRODUCTION

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 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 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 cathodic protection or other corrosion prevention measures

The objective of this work was to evaluate the mutual compatibility and interactions between cathodic protection and a particular vapor phase corrosion inhibitor where applied together.

TEST SET-UP AND PROCEDURE

The test method objective was to provide a quantitative evaluation of the effectiveness of cathodic protection and an amine carboxylate based vapor-phase inhibitor 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 electrodes was deemed representative of the prevalent macro-cells that exist on tank bottoms. A salt water solution (3.6 litres @ 35g NaCl per litre) was used. A variable-output air pump forced air though a diffuser positioned below one of the carbon steel electrodes to encourage a cathodic (reduction) reaction and create a potential difference with respect to the un-aerated steel electrode. An MMO/Ti rod anode was positioned mid-way between the steel electrodes and powered by a variable DC power supply. The schematic and physical arrangement of the test apparatus is depicted in Figures 1 and 2.
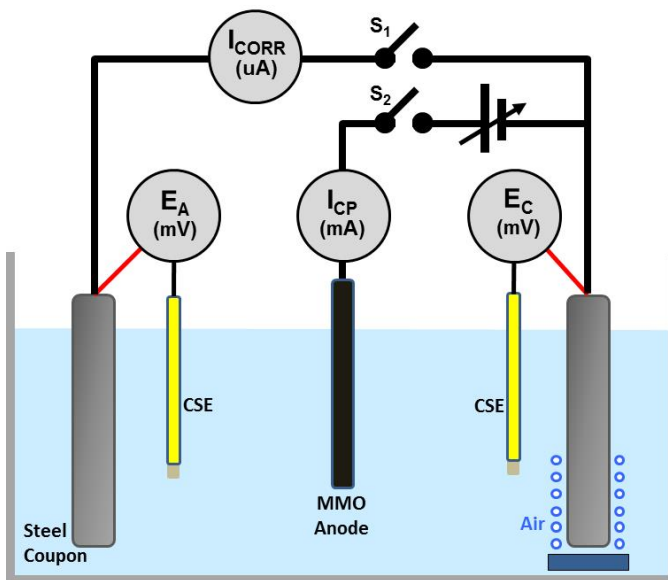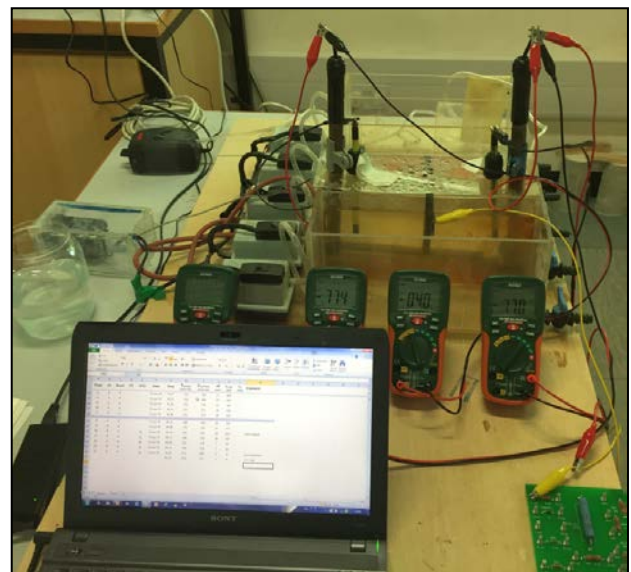

Figure 1: Test Setup - Schematic

Figure 2: Test Setup – Physical Arrangement

Preparatory Procedure

A preliminary preparatory procedure to reliably produce the macro-cell consisted of the following steps.

1. Test container was cleaned and rinsed
2. Salt water solution (3.6 litres with 35g NaCl per litre) was prepared and placed in test container
3. Test rod metal surfaces were cleaned and sanded to Sa 3 / NACE #1 finish.
4. Test rods were placed in solution, without bond, and allowed to soak for at least 16 hours for each to reach a stable open-circuit potential.
5. Copper-sulfate reference electrodes were freshly prepared, tested to verify <1mV difference between them, and placed in the test apparatus.
6. Open circuit potential of each test rod was measured and monitoring to ensure their stability
7. Test rods were bonded, and the bond current and potentials 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 40mV was achieved along with an associated corrosion current (i.e. I_{CORR}) of 350 to 400µA.

Test 1 – Effect of Vapor phase Inhibitor on Active Cathodic Protection System

Following the Preparatory Procedure above, this test consisted of the following steps.

1. The cathodic protection arrangement was energized, and the cathodic protection 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. First 3g 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. Inhibitor concentration was increased by adding another 3g and 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. Inhibitor concentration was increased by adding another 3g and 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. Cathodic protection was de-energized and I_{CORR} 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 Vapor phase Inhibitor prior to application of Cathodic Protection System

Following the Preparatory Procedure above, this test consisted of the following steps.

1. First 3g of inhibitor was added to the solution. The effect on the I_{CORR} was monitored until a steady state was reached.
2. Inhibitor concentration was increased by adding another 3g and the effect on I_{CORR} was monitored until a steady state was reached.
3. Inhibitor concentration was increased by adding another 3g and the effect on I_{CORR} was monitored until a steady state was reached.
4. The cathodic protection arrangement was energized, and the cathodic protection current (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. Cathodic protection was de-energized and I_{CORR} 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 1 - Effect of Vapor phase Corrosion Inhibitor on Active Cathodic Protection System

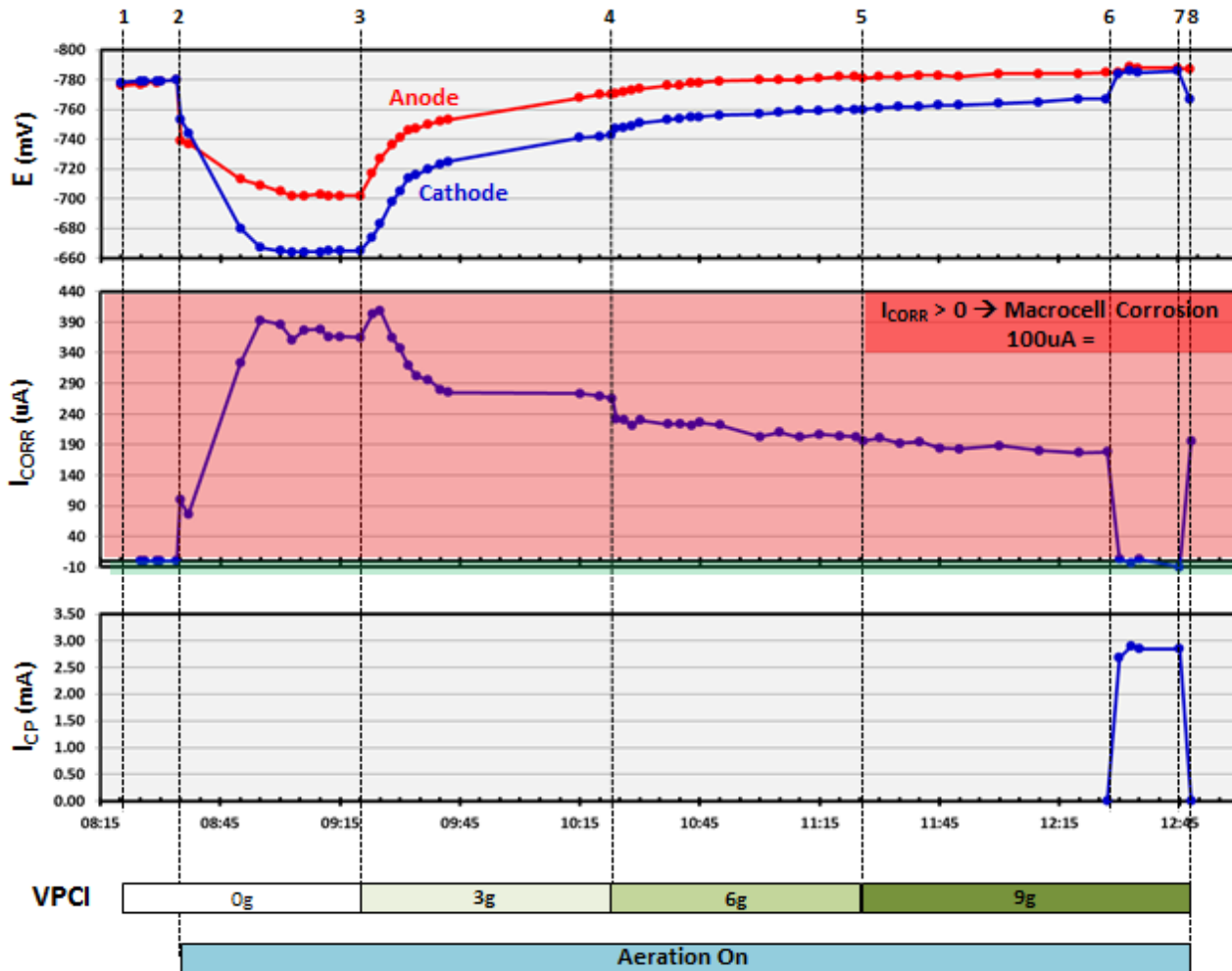The test results are illustrated in Figure 3 below..
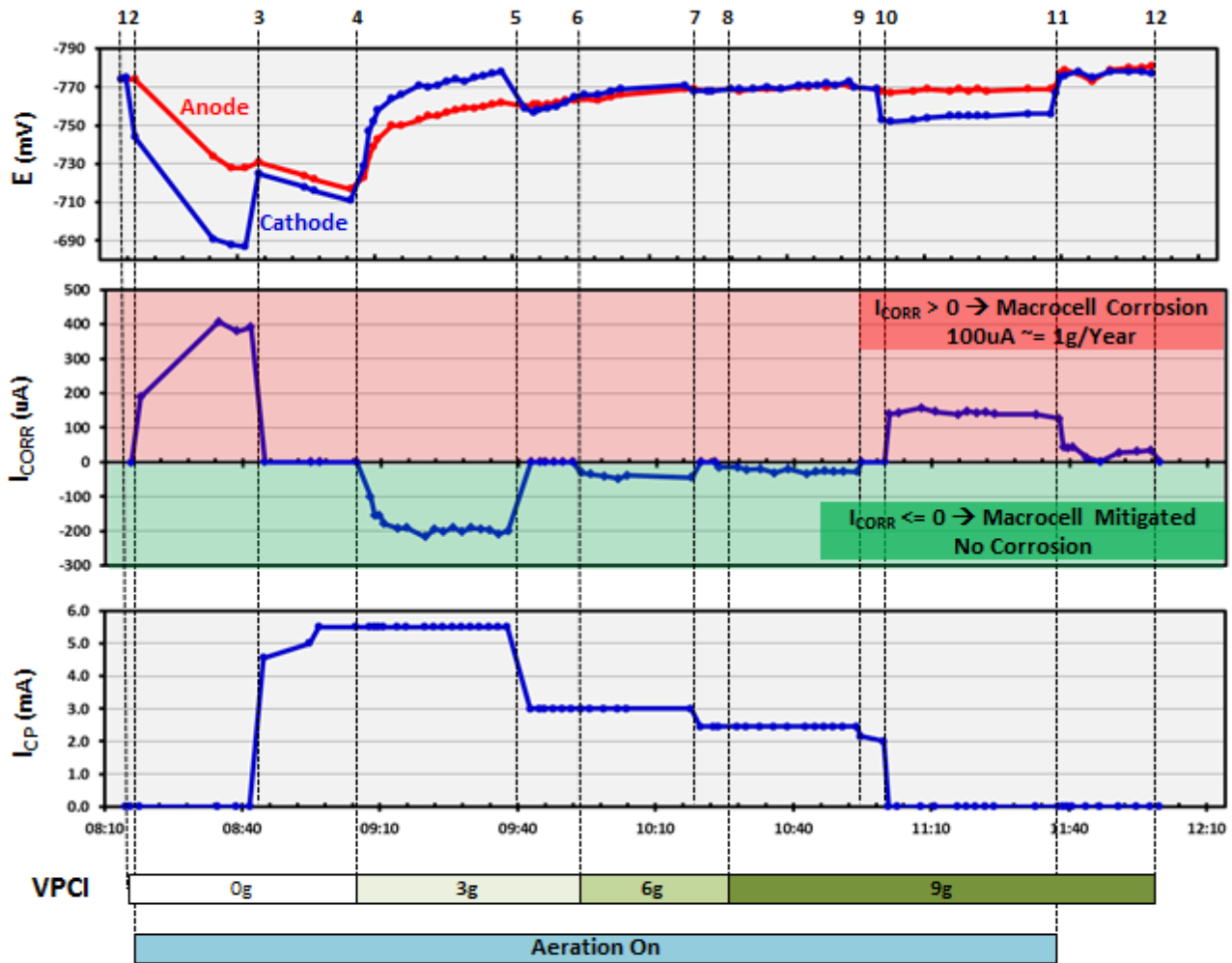
Test Procedure Events
1. Test Start - Steady state coupon potentials following Preparatory Procedure
2. Aeration started to create stabile macrocell with potential difference of ~40mV between coupons and I_{CORR} of ~400uA
3. Cathodic Protection output current energized and adjusted to reduce I_{CORR} to 0uA
4. 3g VCI(x) inhibitor added to solution
5. Cathodic Protection output reduced to maintain I_{CORR} at 0uA
6. 3g VCI(x) inhibitor added to solution
7. Cathodic Protection output reduced to maintain I_{CORR} at 0uA
8. 3g VCI(x) inhibitor added to solution
9. Cathodic Protection output reduced to maintain I_{CORR} at 0uA
10. Cathodic Protection de-energized
11. Aeration stopped
12. Test End

Figure 3: Test 1 Results – Effect of Vapor phase Corrosion Inhibitor on Active Cathodic Protection System

Test 2 - Effect of Vapor phase Corrosion Inhibitor in absence of Cathodic Protection

The test results are illustrated in Figure 4 below.

Test Procedure Events
1. Test Start - Steady state coupon potentials following Preparatory Procedure
2. Aeration started to create stabile macrocell with potential difference of ~40mV between coupons and I_{CORR} of ~375uA
3. 3g VCI(x) inhibitor added to solution
4. 3g VCI(x) inhibitor added to solution
5. 3g VCI(x) inhibitor added to solution
6. Cathodic Protection output current energized and adjusted to reduce I_{CORR} to 0uA
7. Cathodic Protection de-energized
8. Test End

Figure 4: Test 2 Results – Effect of Vapor phase Corrosion Inhibitor in absence of Cathodic Protection

DISCUSSION OF RESULTS

Test 1 - Effect of Vapor phase Corrosion Inhibitor on Active Cathodic Protection System

The Test 1 results show the following

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

Test 2 - Effect of Vapor phase Corrosion Inhibitor in absence of Cathodic Protection

The Test 2 results show the following

Event	Observation
1	Both coupons at $-777V_{CSE}$ following Preparatory Procedure
2	A macrocell was created by the aeration to achieve a steady state potential difference of ~40mV between coupons and an I_{CORR} of ~375µA. The aeration caused potentials of both coupons to shift electropositive as a result of cathodic depolarization.

3   Initial 3g of VPCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~275µA.

4   Further 3g of VPCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~205µA.

5   Further 3g of VPCI(x) was added to the solution. Both coupons shifted electronegative, indicating they were being cathodically polarized, and I_{CORR} decreased to ~180A.

6   The application of cathodic protection with I_{CP} = 2.85mA caused the cathode coupon to cathodically polarize towards the potential of the anode coupon, thereby reducing I_{CORR} to 0µA to effectively mitigate the macrocell.

7   The CP system was de-energized and the cathode potential shifted electropositive and I_{CORR} increased back to ~200µA.

SUMMARY OF CONCLUSIONS

The results indicate a beneficial synergistic effect between the VPCIx inhibitor tested and cathodic protection, where the inhibitor enhances cathodic polarization to reduce cathodic protection current requirement, and the cathodic protection reduction reaction appears to enhance the absorption & 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 VPCIx inhibitor tested

   a. The VPCI(x) inhibitor tested is a 'cathodic polarizer'.

   b. As a cathodic polarizer, the VPCI(x) inhibitor tested reduced cathodic protection current requirement – and could thereby also enhance cathodic protection current distribution. Specifically, the cathodic protection current requirement of 5.5mA to mitigate the corrosion cell before addition of inhibitor was reduced by 45% with first 3g addition, 55% with further 3g addition, and 60% with final 3g addition.

   c. At the concentrations tested, the VPCI(x) inhibitor substantially reduces, but does not completely mitigate the corrosion rate (i.e. I_{CORR}) in a liquid-phase macro-cell. Specifically, original corrosion rate of 375µA was reduced by 27% with first 3g addition, 45% with further 3g addition, and 52% with final 3g addition.

2- With respect to cathodic protection

   a. Cathodic protection can completely mitigate liquid-phase macrocell corrosion.

   b. Cathodic protection appears to enhance the absorption & 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 vapor phase corrosion inhibitor 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 vapor phase

corrosion inhibitor 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 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 cathodic protection 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.

ACKNOWLEDGEMENTS

REFERENCES

1. S. Al-Sulaiman, H. Sabri, R. Rahim, "Evaluation of Cathodic Protection System criteria On Constructed Tanks Over Bituminous Sand Mix Layer," 14th Middle East Corrosion Conference, paper no. 63-CP-10 (Manama: NACE,2012)

2. Xiaming (Andy) Yu, "Evaluation of the Tank Bottom Corrosion and CP Effectiveness at a Saudi Aramco Crude Oil Tank Farm," 13th Middle East Corrosion Conference, paper no. 10043 (Manama: NACE, 2013)

3. B. Chatterjee, "Prevention of External (Soil Side) Corrosion on Storage tank Bottom Plates by Cathodic Protection System." CORROSION/08, paper no. 8058 (Houston TX: NACE, 2008)

4. A. Meroufel, M. Al-Hajri, K. Abed "Mitigation of Soil-Side Corrosion on Storage Tank Bottoms in the Absence or Deficient of CP System", 16th Middle East Corrosion Conference, paper no. MECCFEB16-7995 (Manama: NACE,2016)

5. T. Whited, "Mitigation of Soil side corrosion on double contained aboveground storage tank floors", MP (2011), p. 7-10.

6. S. R. Rials, J.H. Kiefer, "Evaluation of Corrosion Prevention Methods for Aboveground Storage Tank Bottoms," MP 32, 1 (1993): p. 20-25

7. A. Gandhi, "Storage Tank Bottom Protection Using Vapor-phase Corrosion Inhibitors", MP 1 (2001): p. 28-30.

8. T. Whited, "Corrosion Slowed On Tank Bottoms: Vapor Corrosion Inhibitors Used To Mitigate

9. Corrosion Rate of a Double-Tank Interstitial Space," Pipeline & Gas 32, 6 (2005): p. 49-50

10. B. A. Miksic, A. Y. Furman, M. Kharshan, "Storage Tank Protection Using Volatile Corrosion Inhibitors," MP, 6 (2006): p. 34-37

11. I. Y. Barnawi, "Comparison of corrosion attack on tank bottoms with and without cathodic protection" MP 51, 8 (2012): p. 31-35.

12. T. Whited, X. Yu, R. Tems, "Mitigating Soil-Side Corrosion on Crude Oil Tank Bottoms Using Volatile Corrosion Inhibitors," CORROSION/13, paper no. 2242 (Houston TX: NACE, 2013)

13. K. Abed, P. Panchal, A Gandhi, "Evaluation of Impressed Current Cathodically Protected API 650 Tank Bottoms in the Presence of Vapor Phase Corrosion Inhibitor", Corrosion 2016, paper no. 7600 (Vancouver: NACE,2016)