Paper No.
11030

NACE INTERNATIONAL CORROSION Conference & Expo 2018

A study on the Effect of Volatile Corrosion Inhibitors on Impressed Current Cathodic Protection

Khalil M. Abed
CORTEC Middle-East
Sheikh Zayed Road
Dubai, P.O. Box 115133
United Arab Emirates

Calvin R. Pynn
AEGIS Technical Systems LLC
26th Street - Al Quoz 4
Dubai, P.O. Box 37894
United Arab Emirates

ABSTRACT

The physical and electrolytic contact between the bottom plate of an aboveground storage tank and the underlying soil typically varies over the area of a tank bottom plates. External tank bottom plates are exposed to both electrolytic and vapor-phase corrosive environments. Cathodic Protection (CP) requires direct electrolytic contact between the tank floor and the underlying soil to effectively mitigate corrosion; hence it is ineffective in a vapor-phase environment.

There is a growing trend to supplement cathodic protection with Volatile Corrosion Inhibitors (VCI) beneath tank floors to specifically address vapor phase corrosion and enhance overall protection of tank bottom plates against soil-side corrosion. The objective of this experimental work is to expand on the study done by Pynn & Abed[1] and investigate mutual compatibility and interactions of three different volatile corrosion inhibitors and cathodic protection when applied jointly on an oxygen concentration corrosion macro-cell setup.

The test results varied significantly between the three volatile corrosion inhibitors. One showed it had cathodic polarization effect and resulted in reduction of CP current requirement by 48%. Another had an anodic polarization effect and resulted in reduction of CP current requirement by 2%. Third had no polarization effect, and resulted in an increase of CP current requirement by 10%.

Key words: tank bottom, AST, volatile corrosion inhibitor, cathodic protection, polarization, absorption, macro-cell, vapor phase, corrosion current, air gaps, chime area, soil-side corrosion

INTRODUCTION

Effective control of soil-side corrosion on aboveground storage tank bottoms during the complete life cycle of the tank is critical both operationally and environmentally. Different foundation construction methods and corrosion protection techniques have been implemented over the last several decades in attempts to mitigate and control soil-side corrosion, including the use of asphalt pad, bituminous sand, cathodic protection and coating. Despite these measures, field experience and inspection activities indicate that soil-side tank floor corrosion persists in some cases.[2-3]

Underside surfaces of tank bottom plates are typically exposed to a combination of electrolytic and vapor-phase corrosive environments. While cathodic protection can be an effective corrosion mitigation technique where there is an electrolytic contact between the tank bottom surface and the underlying soil, it is ineffective in a vapor-phase environment. Air gaps or where there is intermittent moisture in the soil contacting the tank bottom surface are typical examples of vapor-phase environments under a tank floor. Published technical articles have discussed the practical limitations of the different protection methods, including cathodic protection systems, that are ineffective in providing protection in air gap areas or where cathodic current is shielded.[2,4]

There is a growing trend to supplement cathodic protection with volatile corrosion inhibitors beneath tank floor to specifically address vapor phase corrosion and enhance overall protection of tank bottom plates against soil-side corrosion. There are several studies and field applications that confirmed and/or recommended the use of volatile corrosion inhibitors as a potential solution for this chronic industrial problem.[5-11] However, 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. For example, a study done by *Abed, Panchal & Gandhi*.[12] showed that an amine carboxylate based volatile corrosion inhibitor has synergistic effect on corrosion rate when combined with CP and outperformed each system when implemented as standalone. The findings of this study were further confirmed by another work done by *Pynn & Abed.*[1] which showed an amine carboxylate based corrosion inhibitor worked as a cathodic polarizer and resulted in reduction of corrosion current and cathodic corrosion current. The study also suggested a synergistic effect of cathodic protection reduction reaction in enhancing the absorption & effectiveness of the inhibitor at the cathodic metal surface.

The objective of this work was to expand on the previous study done by *Pynn & Abed.*[1] and investigate mutual compatibility and interactions between cathodic protection and three volatile corrosion inhibitors, when jointly on an oxygen concentration corrosion macro-cell in a salt water solution.

EXPERIMENTAL PROCEDURE

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 (35g NaCl per litre) was used. The schematic and physical arrangement of the test apparatus is depicted in Figure 1.

A preliminary preparatory procedure to reliably produce the macro-cell consisted was followed, where the test container was cleaned and rinsed, salt water solution (35g NaCl per litre) was prepared and placed in test container and test rod metal surfaces were cleaned and sanded to Sa 3 / NACE #1 finish.

The test rods were placed in solution, without bond, and allowed to soak for at least 24 hours for each to reach a stable open-circuit potential. Copper-sulfate reference electrodes were freshly prepared, tested to verify <1mV difference between them, and placed in the test apparatus. Open circuit potential of each test rod was measured and monitored using automatic data logger to ensure stability. The Test rods were bonded, and the bond current and potentials were monitored using automatic data logger until they stabilized. Once stable open circuit potential was achieved, aeration was started to cause a potential difference between the test rods – and adjusted until a steady state potential difference of 30 to 40mV was achieved along with an associated corrosion current (i.e. I_{CORR}).

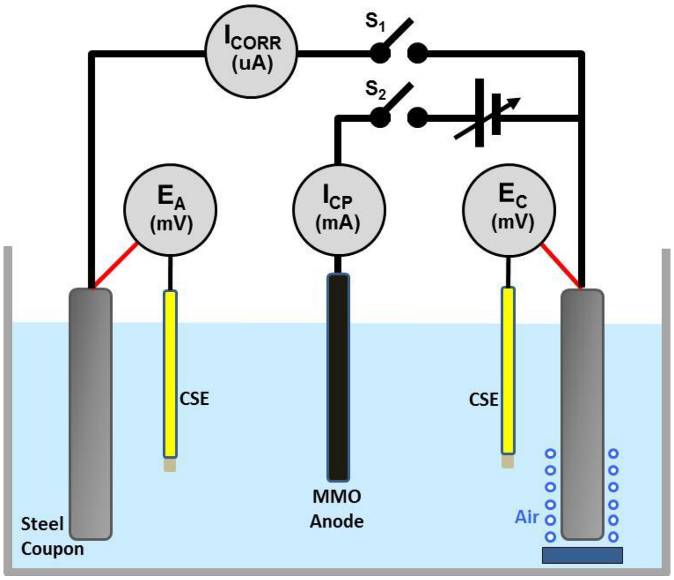

Figure 1: Test Setup Schematic

RESULTS

In the three following tests, 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. The volatile corrosion inhibitor was added to the solution at a dosage rate of 1 gram and the effect on the I_{CORR} was monitored. After 20 hours, another 1 gram was added and the effect on I_{CORR} was monitored. A third dose of 1 gram of the inhibitor was added and the effect on I_{CORR} was monitored, and I_{CP} was adjusted to maintain I_{CORR} at zero.

Volatile Corrosion Inhibitor (A) Test Results

Figure 2 shows the following:

1. Both coupons were bonded and left to stabilize to -790 mV
2. A macrocell was created by 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} = 8 mA caused the cathode coupon to cathodically polarize towards the potential of the anode coupon, thereby reducing I_{CORR} to 0µA and effectively mitigate the macrocell. Cathodic protection current was left to stabilize for 20 hours.
4. Cathodic protection current was adjusted to I_{CP} = 12.5 mA maintain zero I_{CORR}
5. One gram of VCI(A) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. Both coupons' potentials 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. ~ -100µA).
6. Cathodic current was reduced to I_{CP} = 9.5mA and I_{CORR} was brought back to zero.
7. Another gram of VCI(A) was added to the solution and I_{CP} and I_{CORR} were monitored over 70 hours. Both coupons' potentials 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. ~ -350µA).

8 Cathodic current was reduced to I_{CP} = 5.9mA and I_{CORR} was brought back to zero.
9 A third gram of VCI(A) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. Both coupons' potentials 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).
10 Cathodic current was reduced to I_{CP} = 6.4mA and I_{CORR} was brought back to zero.
11 At the end of experiment, cathodic protection system was turned off

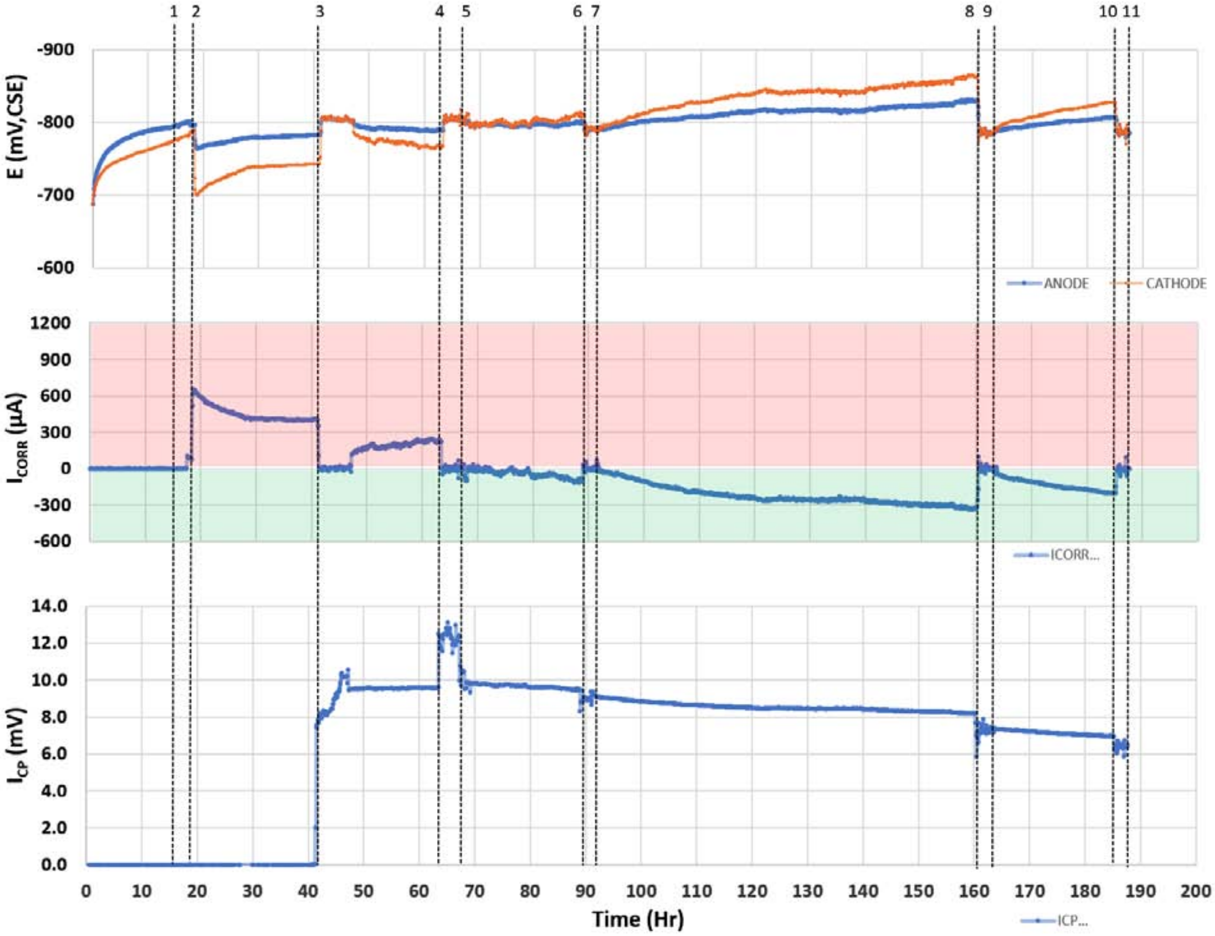

Figure 2: Test Results for volatile corrosion inhibitor VCI(A)

Volatile Corrosion Inhibitor (B) Test Results

Figure 3 shows the following

1 Both coupons were bonded and left to stabilize to -795mV
2 A macrocell was created by aeration to achieve a steady state potential difference of ~40mV between coupons and an I_{CORR} of ~360µA. The aeration caused potentials of both coupons to shift electropositive because of cathodic depolarization.
3 The application of cathodic protection with I_{CP} = 6.9mA caused the cathode coupon to cathodically polarize towards the potential of the anode coupon, thereby reducing I_{CORR} to 0µA and effectively mitigate the macrocell. Cathodic protection current was left to stabilize for 20 hours
4 Cathodic protection current was adjusted to I_{CP} = 7.9mA to maintain zero I_{CORR}

5 One gram of VCI(B) was added to the solution and I_{CP} and I_{CORR} were monitored over 18 hours. Both coupons' potentials shifted in the electropositive direction, indicating they were being anodically polarized. However, the anodic polarization rate of the anode coupon was more than the cathode coupon, resulting in a '-ve' I_{CORR} value (i.e. ~ -68µA).

6 Cathodic current was reduced to I_{CP} = 7.5mA and I_{CORR} was brought back to zero.

7 Another gram of VCI(B) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. Both coupons were anodically polarized. However, the polarization happened for both coupons at the same rate resulting in minimal difference between the potential of the cathode coupon and the anode which consequently resulted in a very small '+ve' I_{CORR} value (i.e. ~ 12µA).

8 Cathodic protection current was kept at I_{CP} = 7.7 mA as I_{CORR} remained at zero.

9 A third gram of VCI(B) was added to the solution and I_{CP} and I_{CORR} were monitored over 22 hours. Similar to the behavior in step 7, both coupons were anodically polarize at the same rate resulting in minimal difference in potential and hence I_{CORR} remained around zero value.

10 Cathodic protection current was kept at I_{CP} = 7.7mA and I_{CORR} at zero. At the end of Experiment, cathodic protection system was turned off

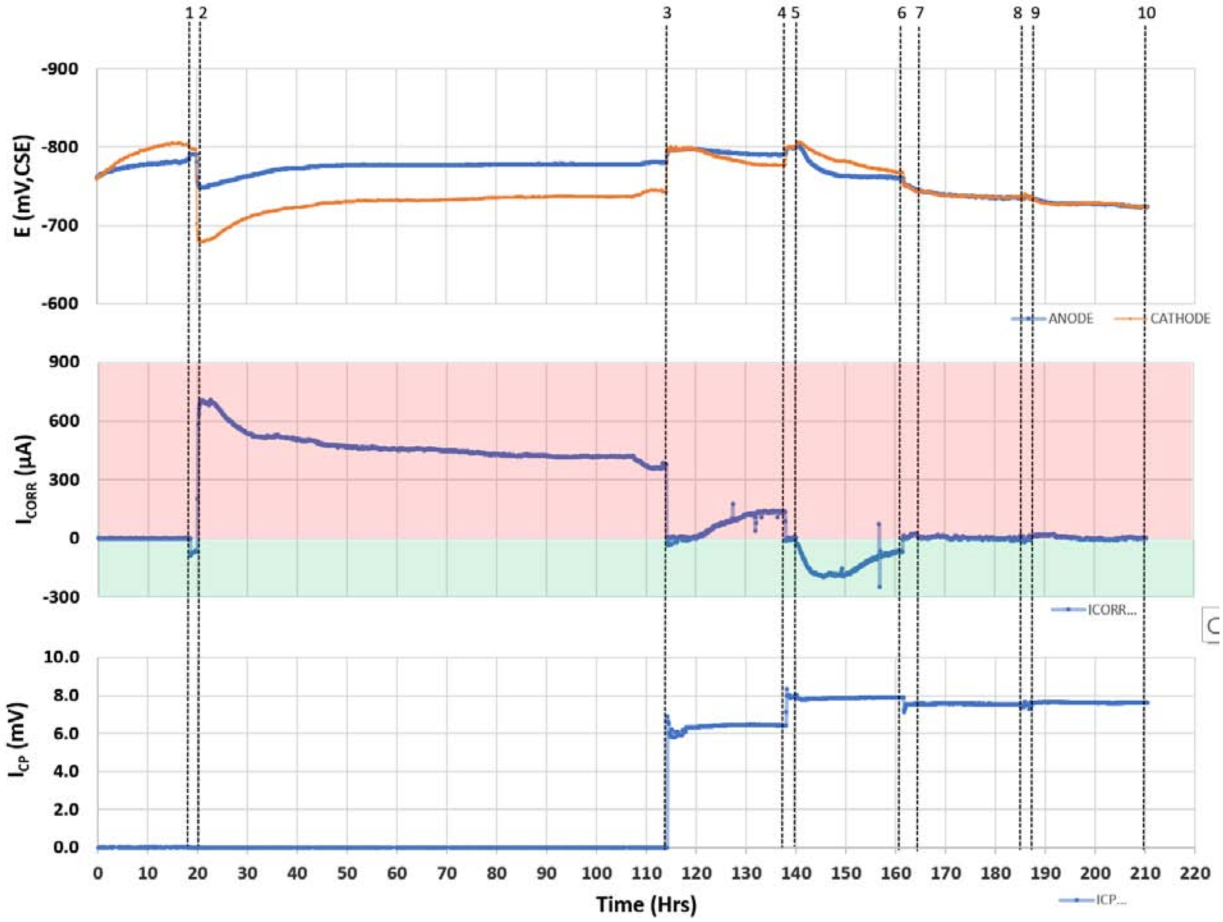

Figure 3: Test Results for volatile corrosion inhibitor VCI(B)

Volatile Corrosion Inhibitor (C) Test Results

Figure 4 shows the following

1 Both coupons were bonded and left to stabilize to ~ -790 mV

2 A macrocell was created by aeration to achieve a steady state potential difference of ~30mV between coupons and an I_{CORR} of ~300µA. 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 and effectively mitigate the macrocell. Cathodic protection current was left to stabilize for 20 hours and

4 Cathodic protection current was adjusted to I_{CP} = 5.7mA to maintain zero I_{CORR}

5 One gram of VCI(C) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. The inhibitor didn't seem to have any cathodic or anodic polarization effect. However, it resulted in small '+ve' ICORR value (i.e. ~ +20µA).

6 Cathodic current was increased to I_{CP} = 6mA and I_{CORR} was brought back to zero.

7 Another one gram of VCI(C) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. The inhibitor continued not to show any anodic or cathodic polarization and resulted in a small '+ve' I_{CORR} value (i.e. ~ +25µA).

8 Cathodic current was further increased to I_{CP} = 6.2mA to bring back I_{CORR} to zero.

9 A third gram of VCI(C) was added to the solution and I_{CP} and I_{CORR} were monitored over 20 hours. Similar to the behavior in step 5 and 7, the inhibitor didn't seem to have any cathodic or anodic polarization effect and resulted in small '+ve' I_{CORR} value (i.e. ~ +25µA).

10 Cathodic protection current was further increased to I_{CP} = 6.3mA to bring back I_{CORR} value to zero.

11 At the end of Experiment, cathodic protection system was turned off

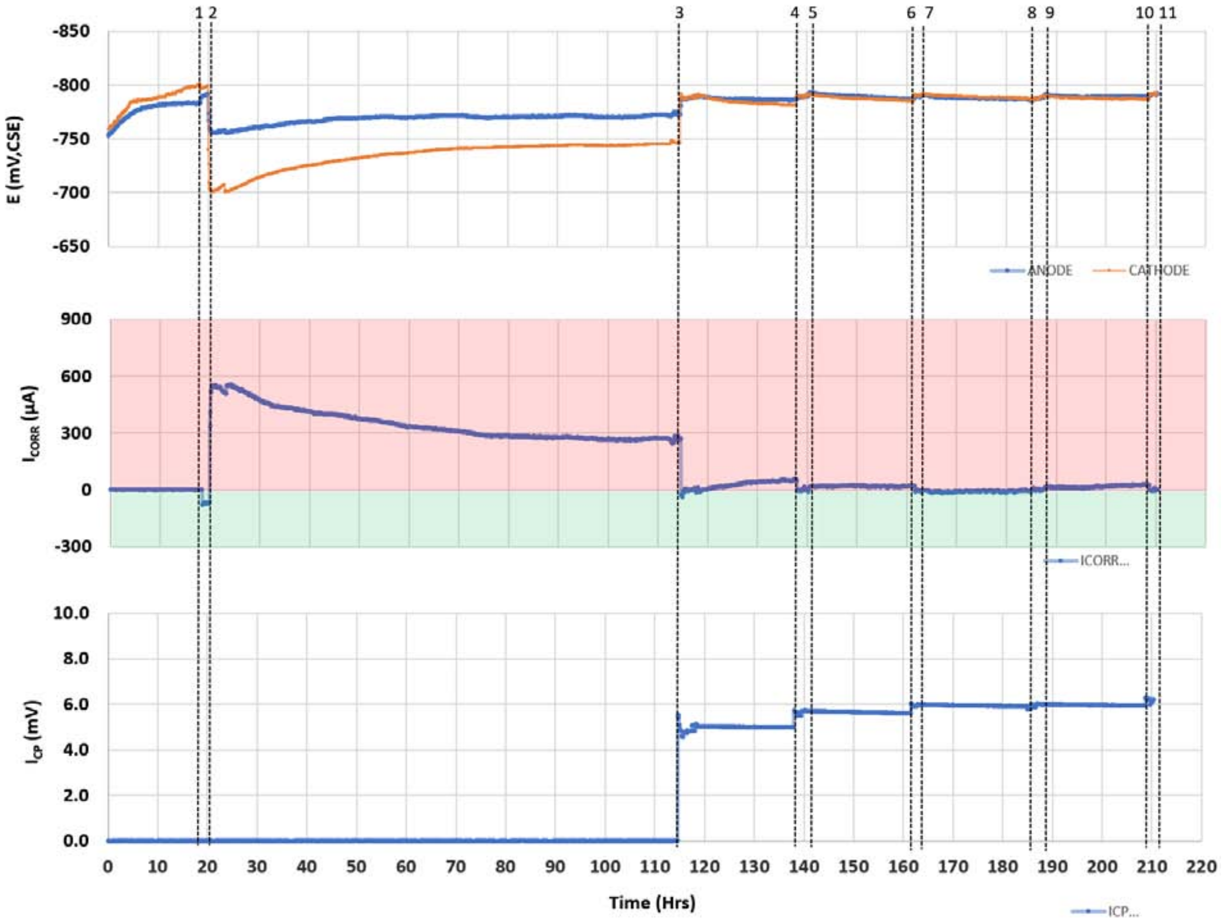

Figure 4: Test Results for volatile corrosion inhibitor VCI(C)

CONCLUSIONS

The results demonstrate that different volatile corrosion inhibitors types interact with cathodic protection in substantially different ways. Some have beneficial effects while others can have adverse effects, as follows:

1. Volatile corrosion inhibitors types such as VCI(A), have a substantial beneficial and synergistic effect with cathodic protection, where the inhibitor enhances cathodic polarization and reduces cathodic protection current requirement. VCI(A) results show that it caused cathodic polarization by at least -60mV and reduced cathodic protection current requirement by 48%.
2. Volatile corrosion inhibitors types such as VCI(B), cause anodic polarization and may or may not affect cathodic protection current requirement. VCI(B) results show an anodic polarization of +75mV and had no substantial effect on cathodic protection current requirement.
3. Volatile corrosion inhibitors types such as VCI(C), do not affect polarization potentials and while increasing cathodic protection current requirement. VCI(C) results showed no effect on cathodic potential, but increased the cathodic protection current requirement by 10%.

In summary, the electrochemical interaction characteristics of a volatile corrosion inhibitor must be evaluated and verified before it is applied in conjunction with cathodic protection to both avoid risk of incompatibility and maximize the benefit of compatibility.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the assistance of Andreas Skapoulli at Cortec Middle East and Dr. Mohamad Nagi at the American University of Dubai for the test facilities.

REFERENCES

1. C. Pynn, K. Abed “Compatibility & Interactions between Cathodic Protection and a Vapor Phase Corrosion Inhibitor” CORROSION/17, paper no. 9232 (New Orleans, LA: NACE, 2017)

2. 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)

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. 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)

5. 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)

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

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

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

9. T. Whited, “Corrosion Rate Slowed On Tank Bottoms: Vapor Corrosion Inhibitors Used To Mitigate Corrosion 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 Volatile Corrosion Inhibitor”, Corrosion 2016, paper no. 7600 (Vancouver: NACE,2016)