Vapor Corrosion Inhibitors in Novel Applications in the Middle East

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Abstract: Vapor Corrosion Inhibitors (VCIs) are commonly used for preservation of equipment during transit and storage. Over the last five years, the use of VCIs has grown into multiple applications in both upstearm and downstream oil and gas industries in the Middle East. Applications tackled a wide range of corrosion challenges to include protection of aboveground storage tanks against soil side corrosion, offshore caisson leg internals and reinforced concrete structures. Monitoring of the treated environments was conducted utilizing electrical resistance (ER) probes and weight loss coupons. Collected data from these field applications provide valuable insights into the working mechanism, efficiency and performance of VCIs and confirm their effectiveness.

Keywords: VCI, caisson legs, aboveground storage tanks, steel bars, electrical resistance probes

Introduction

Vapor Corrosion Inhibitors (VCI) possess appreciable vapor pressure at atmospheric conditions, allowing significant vapor phase transport of the active inhibitor compound. They function by forming a bond with the metal surface and creating a barrier layer that helps prevent contact of corrosive species such as chloride. [1]

One category of VCIs is amine carboxylate based vapor corrosion inhibitors. They are organic salts produced from amines and carboxylic acids. They usually have relatively low saturation vapor pressure, often around 1×10^{-4} or 1×10^{-6} mmHg and can diffuse via vapor transport. VCI molecules are synthesized to be Small enough to be volatile, yet large enough to have a bulky hydrophobic tail to shield the metal from surrounding corrosive environment. They exhibit a strong physical adsorption potential to the metal between -5 to -20 kJ per mol. When the corrosion inhibitor molecule reaches metal surface, it gets adsorbed onto the surface. The inhibitor lines up in the same direction, molecule by molecule until a monomolecular film is formed. This film is hydrophobic in nature and causes a change in the kinetics of both anodic and cathodic corrosion reactions which results in reduction of corrosion rate. [2]

Traditionally, this type of corrosion inhibitors has been incorporated into emitting devices, packaging products and coatings to provide corrosion protection of metal parts and equipment caused by harsh climatic conditions associated with shipment and storage. Packaging products range from coated papers, impregnated foams, extruded films, cushions, emitter devices, inserts, and custom designed solutions. Amine carboxylate based VCIs have also been successfully integrated into fabrication and assembly processes in different delivery forms: powders to protect difficult-to-reach voids, water-based inhibitors to replace oily coatings, coolants to provide protection during machining processes and water soluble additives in hydrotest solutions to protect during and after draining.

In the Middle East, there has been recently a growing industrial awareness about innovative and unprecedented system-based solutions to corrosion challenges in a number of industrial applications, using amine carboxylate based VCIs and corrosion monitoring. Electrical Resistance (ER) probes have been adopted to monitor the effectiveness and uniform distribution of VCIs by comparing the corrosion rate before and after the introduction of the corrosion inhibitors. Unlike other indirect corrosion monitoring systems, ER probes are designed to provide online data regarding the corrosiveness of the surrounding environment.

Following is short description of some such applications with examples on successful implementation on a number of projects in different countries in the Middle East over the last 5 years.

Mitigating Soil-side Corrosion on Aboveground Storage Tank (AST) Bottoms

Aboveground storage tanks construction in the Middle East and especially tanks constructed in locations near the Arabian Gulf, present unique corrosion challenges compared to others constructed in other parts of the world.

Multiple methods, as standalone or in combination, have been adopted to control soil-side corrosion of bottom plates such as proper foundation design, placement of special backfills, construction using corrosion resistant alloys, coatings, and Cathodic Protection (CP) systems. Each one of these methods has its own performance and limitations. For example, in CP systems, electrical current flow between the anode and the cathode should be maintained to provide adequate protection. However, air gaps between the tank bottom plates and the tank foundation, often prevent the CP current from reaching the bottom plates in these areas. [3][4][5]

In the Middle-East, the first published recommendations to use VCI for underside AST bottom corrosion was in 2010 by Yu [5] and in 2012 by Barnawi. [6] When introduced under the tank floor, amine carboxylate VCI acts to reduce soil-side corrosion by a combination of volatilization from a VCI material, vapor transport in the headspace between floor plates and the tank pad atmosphere and condensation onto surfaces in the space. The condensation process is followed by adsorption, dissolution and hydrophobic effects on metal surfaces, where the rate of soil-side corrosion of bottom plates' surfaces is thereby inhibited. VCI products can be supplied in a variety of forms. Fine white crystalline amine carboxylate based material is infused with silica to eliminate clumping and ensure smooth fogging application through the tank floor. It is also supplied as a thin liquid solution, delivered into the interstitial spaces under the tank floor through injection pipes placed in the sand layer. During tank construction, VCI powder is enclosed in a pouch constructed from a breathable membrane. This breathable pouch allows the VCI molecules to sublimate through the membrane, diffuse through the sand layer and form a molecular layer on the tank bottom plates providing soil-side corrosion protection. [7]

Whited et al. [8] discussed a successful project on the use of powder VCI performed on a very large 107.4 meter in diameter crude oil AST located at a tank farm in the Arabian Peninsula in 2011. In this project six ER corrosion probes were installed inside slotted PVC pipes below the tank floor at locations where bottom plates showed severe corrosion. The probes were installed two months prior to the introduction of VCI powder to create a baseline corrosion rate. At the end of the two months, VCI powder was injected through 50 temporary injection ports distributed under all plates within 6 meter of the tank shell, plus all plates that had experienced severe corrosion. Chime area was sealed to prevent future ingress of corrosive species into the undertank environment and weekly corrosion data was taken for the next seven months. Corrosion rate data results showed an average percentage reduction of corrosion rate of 82.4% and an average absolute corrosion rate value of 0.26 mpy. The results concluded that amine carboxylate based VCI powder present an effective corrosion mitigation solution for ASTs.

In 2016, Meroufel et al. [9] published a successful implementation of online injection of VCI slurry in protecting a 15 meter in diameter water tank at a major desalination company near the Arabian Gulf. The AST was constructed on sweet sand resting on a concrete ring wall with an inoperative CP system. The concrete ring wall was cored to introduce six 25 mm perforated PVC pipes covered with geotextile into the sand pad under the tank for about 1.5 meters past the shell of the tank. Three pipes were dedicated for injection of VCI slurry and the balance were used to house the ER corrosion probes. The corrosion rate was monitored for about 160 days prior to the injection of the VCI slurry. The average corrosion rate for the three ER probes was 3.9 mpy. Post injection, the corrosion rate was monitored over a period of about 220 days and the data results showed an average percentage reduction of about 91.4% with an average corrosion rate value of 0.25 mpy. Post-injection average corrosion rate of this project coincides well with the average corrosion rate calculated from the results data of Whited et al [6]

Abed et al. [10] conducted a study to evaluate the effectiveness of amine carboxylate based VCI on the protection of storage tank bottoms against soil-side corrosion, as standalone and in combination with Impressed Current Cathodic Protection (ICCP) system. Six Lab-scale tanks simulating the environment of single bottom storage tank sitting on washed sand with High-density polyethylene (HDPE) liner and ICCP system were constructed. Corrosion rate for each tank was monitored using ER probe corrosion monitoring system. Natural and instant-off potentials of tank bottoms' steel plates were also monitored throughout the experiment using temporary Copper/Copper-Sulfate (Cu/CuSO4) reference electrode. Data from ER probes indicated that amine carboxylate VPCI reduced the corrosion rate by 82.5% and 89.7% as standalone and in combination with ICCP respectively. The study also indicated a shift of the instant-off potential in the negative direction, which suggested that VCI slurry acted as a cathodic polarizer. This confirms the synergistic effect of VCI and ICCP.

Offshore Platform Caisson Legs

The internals of aged platform caisson legs of offshore platforms at a major oil and gas producer in the Middle East were uncoated and filled with biocide-treated water and protected using suspended sacrificial anodes. After two decades of operation, the anodes had been depleted and gas generation led to a fatal accident in 2000 when an explosion occurred inside the confined compartment around a caisson leg of a platform. Board of inquiry recommended several actions including the removal of the sacrificial anodes, blasting grit and biocide treated water. A multidisciplinary team was assigned to investigate a methodology to maintain the integrity of the caisson legs and mitigate internal corrosion. Several options were considered and assessed for their effectiveness, ease of application, and environmental impact. The final recommendation was corrosion management utilizing amine carboxylate VCI. To assess the effectiveness of this approach, a pilot project was launched in 2009 whereby one caisson leg was emptied and preserved with VCI. [11] Carbon steel weight loss corrosion coupons were used to assess the effectiveness of this approach.

A caisson leg constructed of carbon steel with 1.80 m in diameter and 20.8 m in length was selected for the project. Three products with different delivery systems were chosen to achieve the desired result, product A, B, and C. Corrosion coupons were suspended in the void space of the pilot caisson legs. Similar corrosion coupons were installed in two control caisson legs that had not been emptied yet. Being full of water, one coupon was installed under the water line and one above the water line in the control caisson legs.

A pipe coater was used to apply Inhibitor A (liquid) on the internal diameter of the leg, Figure 9. This was chosen to provide both contact corrosion inhibition and biocidal treatment for the internal surfaces. Then Inhibitor B (pouch containing powder) was suspended on a stainless steel wire rope down the length of the leg. Inhibitor B is intended to provide a source of VCI to replenish any gaps in the surface protection. This was followed by fogging the leg internals with Inhibitor C (powder) which is intended to settle into the stagnant water and provide inhibition at that level. Application of all three products for a single structure was done within the same day. The adoption of three different products followed the philosophy of incorporating multiple protective methods to mitigate the risk of corrosion.

The results showed clear improvement in the amine carboxylate VCI-treated caisson leg where corrosion rates were maintained at low rates that were deemed acceptable, see table 1 below. The methodology was adopted for the treatment of all other caisson legs at the complex.

Table 1
Corrosion Rates in Pilot and Control Caisson Legs

Caisson Leg		**Monitoring Location**	**Corrosion Rate, MPY**				
USEAP			**Oct.11**	**Jan.12**	**Sep.12**	**Mar.13**	**Sep. 13**
4494-0034	PC-USEAP-4494 0034	Above Water			12.63	18.56	11.88
4494-0034	PC-USEAP-4494 0034	Below Water			0.88	0.29	0.36
4494-0036	SB-USEAP-4494 0036	Above Water			13.23	14.44	10.98
4494-0036	SB-USEAP-4494 0036	Below Water			1.05	2.05	0.40
USAAP							
4494-0052	SB-USAAAP-4494 0052	VCI, pilot leg	0.29	0.11	0.45	3.18	0.09

Conclusion

Corrosion control and its monitoring remains a constant challenge in many industrial applications, which in turn demands innovative system-based solutions to overcome. In the Middle East, there has been recently a continuous success in the implementation of amine carboxylate based VCI and ER corrosion monitoring probes to provide an unconventional solution to chronic corrosion problems.

References

1. B. Miksic, "Use of vapor phase inhibitor for the protection of metal parts. Corrosion 83, paper no. 308,(Anaheim California, NACE International, April 18-22,1983.

2. B. Bavarian, J. Zhang, L. Reiner, "Electrochemical and SCC Inhibition of Multi-alloy Systems using Vapor Corrosion Inhibitors", Corrosion 2013, paper number 2130, (Orlando, Florida, USA, NACE, 2013).

3. 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)

4. M. Ali, A.A. Al Beed, "Aboveground tank bottom corrosion due to inappropriate construction practices and corrosion control using cathodic protection", CORROSION/98, Paper N°596, (Houston, TX, NACE, 1998).

5. X. Yu, "Evaluation of the Tank Bottom Corrosion and CP Effectiveness at a Saudi Aramco Crude Oil Tank Farm," Paper N.O. 10043, 13th Middle East Corrosion Conference, Bahrain (2010).

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

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

8. T. Whited, X. Yu, R. Tems, "Mitigating Soil-Side Corrosion on Crude Oil Tank Bottoms Using Vapor-phase Corrosion Inhibitors", CORROSION 2013, Paper N°2242, (Houston, TX, NACE, 2013).

9. A. Meroufel, K. Abed, M. Al-Hajri "Mitigation of Soil-Side Corrosion on Storage Tank Bottoms in the Absence or Deficient of CP System", Paper No. MECCFEB16-7995, 16th Middle East Corrosion Conference, Bahrain (2016).

10. K. ABed, P. Panchal, A. Panchal "Evaluation of Impressed Current Cathodically Protected API 650 Tank Bottoms in the Presence of Vapor Phase Corrosion Inhibitor", CORROSION 2013, Paper N°7600, (Vancouver, Canada, NACE, 2016).

11. T. Al-Sayed, A. Eid, M. Al-Marzooqi "Protection of Offshore Platform Caisson Legs with a Vapor Corrosion Inhibitor- A Case Study", CORROSION 2014, Paper N°4200, (San Antonio, TX, NACE, 2014).