## VAPOR PHASE CORROSION INHIBITORS

# Evaluation of Impressed Current Cathodically Protected Tank Bottoms in the Presence of Vapor Phase Corrosion Inhibitor

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This work aims to assess the effectiveness of an amine carboxylate-based vapor phase corrosion inhibitor (VCI) on the protection of storage tank bottoms against soil-side corrosion, as standalone and in combination with an impressed current cathodic protection (ICCP) system. It also attempts to determine the effect of VCI on instant-off potential. Lab-scale tanks simulating the environment of single bottom storage tanks sitting on washed sand with a high-density polyethylene (HDPE) liner and ICCP system were considered. The corrosion rate for each tank was monitored using an electrical resistance probe corrosion monitoring system. Natural and instant-off potentials of tank bottom steel plates were also monitored throughout the experiment using a temporary copper/copper sulfate (Cu/CuSO,) reference electrode. Corrosion rate data from electrical resistance probes indicated that amine carboxylate VCI slurry is effective in mitigating corrosion on carbon steel bottom plates. The corrosion rate was reduced by 82.5% and 89.7% as standalone and in combination with ICCP, respectively. The study also indicated a



FIGURE 1. Section view of lab-scale tank.

shift of the instant-off potential, which might need to be considered by CP operators in the case of using a VCI in supplementing ICCP for protection of storage tank bottoms.

**Soil-side corrosion is a principal cause** of storage tank failure and imposes a major environmental and operational challenge worldwide. Several techniques have been adopted to mitigate soil-side corrosion of aboveground storage tank (AST) floors, such as bituminous sand, impressed current cathodic protection (ICCP), and coatings. However, the total effectiveness of these techniques, as standalone or combined, have been questionable in providing the required protection, especially against pitting corrosion.

Al- Sulaiman1 discussed the possibility of a bituminous layer trapping moisture and corrosive species between the underside of the tank floor and construction pad, resulting in a corrosive environment. The author also highlighted the likelihood of the bituminous layer when combined with CP to shield protection current and render the CP system ineffective, at least partially. Yu<sup>2</sup> concluded that inevitable air gaps between the construction pad and tank bottom plates block CP current at that location and consequently prevent its uniform distribution on the underside surface of the tank bottom. Chatterjee<sup>3</sup> emphasized that underside coating of bottom plates alone cannot prevent corrosion due to unavoidable defects during its application and deterioration during tank operation.

There is a growing industrial awareness

about the importance of finding a viable solution to supplement the performance of the aforementioned techniques in an attempt to achieve a comprehensive corrosion protection scheme for the tank bottom. One promising solution is the use of amine carboxylate-based vapor phase corrosion inhibitors (VCIs). An amine carboxylate VCI is a chemical substance that 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 includes adsorption, dissolution, and hydrophobic effects on metal surfaces, where the rate of soil-side corrosion of bottom plate surfaces is thereby inhibited.

VCI material comes in a powder form composed of fine white crystalline amine carboxylate-based material infused with silica to eliminate clumping and ensure smooth fogging application through the tank floor. It also comes 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 enclosed in a pouch constructed from a breathable membrane is used. 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 that provides soilside corrosion protection.4

One of the first publications that confirmed the potential of using VCI material for soil-side corrosion protection, including pitting, of AST bottoms was written in 1993 by Rials et al.<sup>5</sup> Since then, several other published technical articles have recommended and/or confirmed the viability of VCI as a potential solution for this chronic industrial problem.<sup>4-12</sup> The use of VCI in protecting tank bottoms against soil-side corrosion has been classically coupled with the use of electrical resistance (ER) probes to monitor their impact on the corrosion rate data before and after injection. Unlike other indirect corrosion monitoring systems, ER probes are designed to evaluate and continuously monitor the corrosiveness of the surrounding





FIGURE 3. Electrical resistance probe used for the experiment.

environment under the tank floor. In most cases, ER probes are used as the primary corrosion rate monitoring technique. They are usually installed away from the inhibitor injection point to confirm inhibitor diffusion and evaluate the overall effectiveness of VCI material.<sup>4,7,8,11-12</sup> However, to our best knowledge, the interaction and effect of introducing such chemicals under the tank floor on the instant-off potential of an ICCP-protected storage tank bottom and soil-side corrosion haven't been investigated.

An experiment was designed to assess the effectiveness of amine carboxylate-based VCI slurry in protecting single storage tank bottoms against soil-side corrosion. The experiment also looked into the effect of VCI slurry on the instant-off potential when installed in combination with the ICCP system.

### **Experimental Procedures**

Six lab-scale tanks simulating the environment of single bottom storage tanks sitting on sweet sand with a high-density polyethylene (HDPE) liner and ICCP system were constructed and examined

for 120 days. Plastic tanks 1 m in diameter were cut off their tops and filled with washed sand having an average resistivity of 35,000  $\Omega$ ·cm. Each tank was fitted with a 35-mm in diameter perforated VCI slurry dispensing ring positioned 100 mm above the tank bottom. A mixed metal oxide (MMO) anode grid was placed 270 mm below the steel plate. An ER probe was placed about 100 mm below the steel plate. Slotted monitoring polyvinyl chloride (PVC) pipe 50 mm in diameter was also installed in each tank. After compacting and leveling, a 4-mm thick sandblasted round steel plate was placed over the sand. The plates were weighted down with cement blocks and sealed with caulking. Figures 1 and 2 show an illustration of the test tank design.

Figure 3 shows the ER probe selected for this experiment. This probe configuration was chosen for compatibility with the PVC access pipe, which was installed under the steel plate of each tank. Data from the probes were taken on a daily basis by connecting to a data logger supplied by the probe manufacturer.

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FIGURE 4. Natural potential of unprotected tanks during pre-injection phase.



TK-01 (Probe# 9666) TK-02 (Probe# 9673) ▲ TK-03 (Probe# 9670)

FIGURE 5. Total metal loss of ER probes installed in unprotected tanks during pre-injection phase.



FIGURE 6. Underside steel plate of unprotected tanks at the end of pre-injection phase.







FIGURE 8. Total metal loss of ER probes installed in ICCP-protected tanks during pre-injection.



FIGURE 9. Underside steel plate of ICCP-protected tanks at the end of pre-injection phase.





FIGURE 10. Comparison between total metal loss of ER probes installed in unprotected tanks before and after injection of VCI slurry.





TABLE 1. CORROSION RATE DATA RESULTS				
Tank Category	Tank Tag # and Probe ID	Corrosion Rate Before VCI Application (mpy)	Corrosion Rate after VCI Application (mpy)	Percentage of Corrosion Rate Reduction After VCI Application
Unprotected Tanks	TK-01 (probe # 9666)	15.44	6.39	58.6%
	TK-02 (probe # 9673)	10.73	0.91	91.5%
	TK-03 (probe # 9670)	15.44	0.40	97.4%
ICCP Tanks	TK-04 (probe # 9665)	2.52	0.29	88.4%
	TK-05 (probe # 9668)	3.80	0.29	92.3%
	TK-06 (probe # 9672)	3.50	0.40	88.5%





The natural potential of the six tanks was measured and recorded using a copper/copper sulfate (Cu/CuSO4) reference electrode. The six tanks were randomly split into two groups; three tanks had their ICCP system activated and the other three hadn't. The input current for the ICCP tanks was adjusted to 29 mA until -850 mV instant-off potential was achieved.

The experiment was divided into two phases; pre-injection and post-injection of VCI slurry. During the pre-injection phase, corrosion rate data were collected and the natural potential for unprotected tanks and instant-off potential of ICCP tanks were monitored for 45 days. When steady state was achieved, the tanks were opened and the status of each steel plate was photographed. Plates were put back into their original place and sealant was reapplied. VCI slurry was injected through the preinstalled dispensing ring in all tanks. The effect on metal loss of the ER probes and the instant-off potential of the steel plates was monitored for 75 days.

## Results

## Pre-Injection Phase

The natural potentials of the unpro-

Instant-off Potential (ICCPtanks)





tected tanks (TK-01, TK-02, and TK-03) continued to shift in the negative direction until it stabilized at an average of -551 mV after approximately 20 days (Figure 4). Corrosion rate data from the ER probes installed in non-CP protected tanks showed an average corrosion rate of 15.5 mpy as calculated per Equation (1) from the data in Figure 5.

$$\frac{\text{CR} = \text{M2} - \text{M1}}{\Delta \text{T}} \times 365 \tag{1}$$

where  $\Delta T$  is the lapse time in days between total metal loss between M1 and M2.

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The high corrosion rates from the ER probes were confirmed by the actual status of the steel plates. Upon removal of the steel plates from the unprotected tanks, it was observed that the internal surfaces were covered with sand and corroded, especially at the center area (Figure 6). ICCP protected tanks (TK-04, TK-05, and TK-06) showed an average instant-off potential of -1,024 mV (Figure 7), satisfying the -850 mV instant-off protection criteria. Corrosion rate data from ER probes installed in control tanks showed an average corrosion rate of 3.2 mpy as calculated per Equation (1) from the data in Figure 8.

The low corrosion rate is in line with the fact that protection criteria were achieved. However, visual inspection of the underside surface of the plates revealed considerable levels of corrosion (Figure 9). Despite meeting the -850 mV instant-off protection criteria, the actual status of the underside surfaces showed otherwise. The corrosion morphology looked similar to the unprotected tanks.

This might be attributed to the fact that the CP system was not commissioned during and after the construction of tanks for a period of about two weeks. Similar challenges, even on a larger scale, exist in real life, where tanks take from several months to years to be boxed up and their CP systems commissioned. Tank bottom plates are usually left without any protection during this time. In other cases, lack of availability of a power supply hinders activation of the CP system for several years at the job site.

### Post-Injection Phase

After injection of VCI slurry through the dispensing ring, a noticeable effect was observed on the metal loss of ER probes in both unprotected (Figure 10) and ICCP protected tanks (Figure 11). The average corrosion rate of ER probes installed in TK-02 and TK-03 reduced from 13.1 mpy to 0.66 mpy, with an average percentage reduction of 95%. However, the corrosion rate in TK-01 didn't reflect the same level of effect after VCI application where the corrosion rate was reduced from 15.44 to 6.39 mpy, a 59% reduction only. For ICCP-protected tanks, the average corrosion rate of ER probes went from 3.2 mpy to 0.3 mpy, with an average percentage reduction of 90%. It is worthwhile to note that the introduction of VCI

slurry under the tank plate helped maintain an average corrosion rate under 1 mpy in all tanks, excluding TK-01. Table 1 summarizes the corrosion rates of the individual ER probes before and after VCI application. It is worthwhile to note that the reduction in the corrosion rate of all ER probes not only confirmed the ability of VCI molecules to diffuse through a compacted sand layer over a short period of time and protect the underside of the tank floor, but also diffused through the corrosion product layer on the tank floor and hence reduced the corrosion rate of pre-rusted steel.

It was noticed that VCI slurry shifted the average potential of unprotected tanks from -550 mV to -500 mV (Figure 12). For ICCP tanks, each tank reacted differently to the VCI slurry (Figure 13). In TK-05, the average instant-off potential shifted temporarily from -1,020 mV before injection, to -1,205 mV for the first 19 days before it started to go back to the original value through the end of the experiment. TK-06 also showed a transient behavior, where its instant-off potential shifted in the negative direction from an average of -1,000 mV to reach a value of -1,300 mV on day 16 after injection. However, the instant-off potential shifted in the positive direction to stabilize at an average of -1,200 mV until the end of the experiment.

Prior to injection of VCI slurry, TK-04 showed an average instant-off potential of -1,004 mV for about 36 days. A sudden shift in the negative direction of the instant-off potential was noticed on day 37 and continued for seven days before injection of VCI slurry to reach -1,318 mV. After the introduction of VCI slurry, no clear change was noticed until the end of the experiment. However, if the average instant-off potential for all tanks was considered before and after injection in Figure 13, it can be concluded that an overall shift of 150 mV in the negative direction occurred. Although the findings might not be conclusive in terms of an exact value of the potential shift and whether this shift is permanent or transient, the CP operator can expect a shift in the instant-off potential of the protected tank. Therefore, a longer study should be conducted to answer such queries.

### Conclusions

Soil-side corrosion on ASTs, including those protected by CP, can present a chronic

challenge to operating companies. There is a growing industrial awareness about the importance of finding a viable solution to supplement the performance of the aforementioned technique. One promising solution is the use of an amine carboxylate-based VCI. This experiment was designed to assess the effectiveness of an amine carboxylate-based VCI system on the protection of AST bottoms against this type of corrosion as standalone and in combination with an ICCP system. The experiment also looked into the effect of VCI slurry on the instant-off potential and in turn the protection criteria of an ICCP system. The obtained results led to the following conclusions:

- Despite having a CP system satisfying the protection criteria of -850 mV instant-off potential, the tanks showed signs of soil-side corrosion. This might be partially attributed to the CP system not being commissioned as soon as the tanks were constructed, allowing the corrosion process to start. Due to the spontaneous protection mechanism of an amine carboxylate VCI system, it might be advantageous to introduce amine carboxylate VCI material into the tank sand pad to provide protection of the underside of tank bottom plates during construction and until the CP system gets commissioned.
- ER corrosion rate probes can be used to evaluate the corrosiveness of the environment under an AST and indicate the effectiveness of VCI in reducing and controlling soil-side corrosion.
- VCI slurry can be effectively introduced and distributed through a designed online injection system under existing and new ASTs.
- VCI slurry alone showed the ability to reduce the corrosion rate by 82.5%, which makes it a viable solution to protect against soil-side corrosion, especially for tanks without a CP system or when the existing CP system is deficient.
- VCI slurry in combination with ICCP showed a synergetic effect on the corrosion rate and helped maintain it below 0.5 mpy, with an average reduction of 89.7%. This suggests that supplementing new and existing CP systems with VCI material is therefore advantageous to operating companies. The introduction of VCI slurry may have

an effect on instant-off potential and this might need to be considered by CP operators in the case of using VCI slurry in supplementing an existing ICCP system. However, an experiment for longer duration or actual field trials is required to confirm the value of this effect and whether it is transient or permanent.

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