Storage Tank Protection
Using Volatile Corrosion Inhibitors

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ABSTRACT

Research and fieldwork show that vapor phase corrosion inhibitors (VpCIs) by themselves or in combination with cathodic protection can be used for the protection of the bottoms of the above ground storage tanks (AST's) [7].

Vapor phase corrosion inhibitors are compounds which are transported in a closed system to the site of corrosion by volatilization or diffusion from a source. Protection occurs by the adsorption of the VpCI molecules at the metal surface. VpCIs are especially useful in protecting metal surfaces that are difficult to reach.

Cathodic protection is the traditional method of the corrosion control of the storage tanks. Two commercially available corrosion inhibitors were investigated for their performance in combination with cathodic protection. The result of this study was analyzed and a product for that application was suggested.

The performance of this product was confirmed by several corrosion and electrochemical methods.

1. INTRODUCTION

Metallic corrosion cost the United States is about $276 billion a year [1]. Approximately one third of the cost of corrosion ($100 billion) is avoidable and could be saved by using corrosion resistant materials and the application of state-of-the-art corrosion control technologies.

Vapor phase corrosion inhibitors or volatile corrosion inhibitors (VpCIs) belong to the organic type inhibitors. They adsorb on the metal surface and suppress metal dissolution and reduction reactions. These affect both anodic and cathodic processes. Organic amines and carboxylates are typical examples of this class. Vapor phase corrosion inhibitors posses moderately high vapor pressure and can prevent corrosion without applying VpCI directly to the metal surface [1-3].

The advantage of VpCIs is that the volatilized molecules can reach hard-to-reach spaces. When reaches the metal VpCI attaches to it by the active group. Vapor pressure is a critical parameter in VpCI effectiveness. The most favorable range of the pressure is 10^{-3} -10^{-2} Pa at the room temperature. Too low pressure leads to the slow establishment of the protective layer; if the pressure is too high, VpCI effectiveness will be limited to a short time [1-3].

The effectiveness of VpCIs also depends on their adsorption energy on the metal. It was found that amine type of VpCI are capable of forming the protective layer for up to three months, and, as a rule , low molecular weight amines are more inclined to desorption than high molecular weight amines.

Vapor phase corrosion inhibitors are able to protect from corrosion not only when used as a packaging aids, or in electrical and electronic enclosures, but also in many situations when metal equipment is exposed to the harsh atmospheric conditions. For example, VpCI can be successfully used for protection under the thermal insulation [4]. For this investigation a section of carbon steel pipe covered with wet calcium silicate thermal insulation material was treated by injection of VpCI in the metal/insulation interface. The test conditions were 200°F (93°C) surface temperature and 5psig steam pressure, maintained by continuous water injection at 5ml/hr. After 6 months, the following results were found: control pipe was approximately 80% covered with build-up of corrosion whereas pipe treated with VpCI was approximately 5% corroded at the two of the water injection points. Field results show that 20 precipitators, treated with VpCI and then wrapped in thermo-insulation together with associated equipment, had been transported by river and stored for 1 year with no or minimal corrosion [4].

Corrosion protection of fuel storage tanks is a very important task - failures are extremely costly, including loss of the fuel tank, which can additionally contaminate the environment, high repair cost, and effect on projects which depend on prompt fuel delivery. Cost effective and dependable long-term corrosion protection has been provided by VpCI technology for single and double bottom above-ground storage tanks.

Starting from 1986 there were many cases of preventing bottoms of the storage tanks from corrosion by adding Vapor phase Corrosion Inhibitors. For single bottom tanks, VpCIs were added to sand on which storage tanks were positioned, and for double bottom tanks - in the space between bottoms. Different application\ methods were developed for the protection of new and used tanks. The results of applications have been reported in [6].

The most vulnerable part of the storage tanks is the bottom [6]. According to [6], VpCIs were used for the protection of the bottom storage tanks operated by Conoco Oil Co. VpCI powder was mixed with gravel and sand. Corrosion was monitored over a 2 years period. It was later confirmed that VpCI protected the bottom of those tanks against corrosion for over 15 years after application. A special dispensing system for this application was developed, and this type of protection was incorporated into standard for corrosion control of new and existing tank bottoms.

For new tanks, after a sub-base of sand and gravel is spread, VpCI powder is applied at the rate of 10 - 20 kg/100 m² (2 - 4 lb/100 ft²). It is mixed into the base with simple hand tools. The tank bottom is then laid out and fabricated as normal [6].

When tanks are being refurbished and new bottoms plates are welded in, VpCI are spread under the plate. When it is possible, VpCIs should be distributed in the adjacent areas. Another approach is to inject a 5% solution of VpCI in the under bottom section of the storage tanks. For the new installation double bottom tanks it is recommended to spread VpCI powder at the rate of 1 to 2 kg/10 m² (2 to 4 lb/100 ft²). The spacer and the second bottom are then welded in place. For protection of existing tanks, VpCI powder should be carefully blown into the voids to provide uniform distribution. Alternately, VpCI solution may be pumped into the voids and either left there or drained [6]. Recent

experience of using of VpCI for the protection of the above ground storage tanks is described in the paper [6].

Another case is corrosion protection of 17 large diameter double-bottom ASTs with VpCI slurry. VpCI was installed four to five years ago (2000-2001) and measurements indicate very good corrosion protection and no significant depletion of inhibitor. In this application VpCI slurry was injected into interstitial space. The space was filled with the VpCI slurry and held full for about 60 days. The telltale pipes were then uncapped and the slurry was allowed to drain to the level of the telltale pipes.

Cathodic protection (CP) is a technique to control the corrosion by making the surface of the metal a cathode of an electrical cell. Since corrosion takes place at the anode of an electrical cell, cathodic surfaces stay protected.

Presently cathodic protection (CP) is applied to prevent corrosion of those tanks.

Cathodic protection can be accomplished in two ways: by using the sacrificial metal (zinc, aluminum, magnesium) anodes or by applying a cathodic potential to metal equipment from the power source - impressed current cathodic protection. In both cases, corrosion control is achieved by keeping the electrochemical potential of the metal at a level when corrosion transferred from the corroding structure and moved to an anode(s).

In oil/ natural gas production, CP is used to protect external surfaces of burred and submerged piping, well casing, tank bottoms, offshore structures and the internal surfaces of liquid handling tanks and vessels.

The criteria of the successful cathodic protection are either the level of the electrochemical potential, which should be: -0.85V vs. copper/copper sulfate, or -0.78 V, -0.80 V and -0.25 V vs. saturated KCl calomel, silver/silver chloride, and high purity zinc, respectively [8-9]. The common causes of failures of CP are bad connections or passivation of the surface of sacrificial anodes.

The goal of this paper is to show the advantages of the use of VpCI for the bottom tank protection in addition to, pr instead of, cathodic protection.

2. EXPERIMENTAL

2.1. Outdoor Experiment

This experiment was performed to find maximum distance of VpCI action.

At the ground level a box space, filled with sand, was prepared. The dimensions of this box space were: 3' (L) x 3' (W) x 2' (D) (90 x 90 x 60 cm).

A plastic pipe with cuts, containing the corrosion inhibitor, served as the VpCI source. This pipe was buried at the depth of 1 ft. (0.3048 m) in sand and preconditioning was achieved over a 30 day period. After 30 days preconditioning, the test coupons were placed in the sand box along the length at distances from the pipe ranging from 0 to 60 inches (0 – 150 cm), at a depth of 3-5 inches (7.5 –10.5 cm) (Figure 1). Corrosion rate was determined according to the formula [11]:

Corrosion rate (mils/year) = (K × W) / (A × t × Δ),

where K = constant, 3.45×10^6

W = mass loss, grams;

A = area of the metal coupon, centimeter squared;

t = time, hours;

Δ = density of the metal, grams per centimeter cubed.

2.2 Indoor Experiment

2.2.1 Sand Test Two corrosion inhibitors, a VpCI and a conventional anodic inhibitor, were tested in presence of cathodic protection. The results were compared to control data, where measurements were conducted under the action of the cathodic protection but without corrosion inhibitor.

Mixture was prepared:

Play ground sand	- 70.0%;
Tap water	- 29.4%
Sodium Chloride	- 0.3%;
VpCI	- 0.3%;

Plastic containers were filled with this mixture. Pre-weighted panels made from carbon steel (SAE 1010) 5 cm x 9 cm by size, and zinc (99.9% Pure) 1 cm x 5 cm by size were inserted into the sand at the distance of 10 cm apart. In each container steel and zinc panels were electrically connected. The current in between steel and zinc panels was measured by Multimeter DM-8600, manufactured by A.W. Sperry Co. After 12 days panels were removed from the sand and their weight loss was determined (Table 1).

2.2.2 Electrochemical Evaluation Combination of the VpCI and CP action, when CP is provided by impressed current, was studied using the following methodology.

Potentiostat 'Versastat' manufactured by EG&G with software '352 SoftCorr 111,' three electrode electrochemical cell, saturated Calomel electrode (SCE) as a reference; high density graphite as a counter electrode, and carbon steel SAE 1018 working electrodes were utilized for the study.

Based on normal practice [10], a cathodic potential of –900 mV (SCE) was applied to carbon steel electrode and current corresponding to this potential was measured.

To evaluate the difference in the behavior of different inhibitors applied in combination with CP, potentiodynamic polarization curves and corrosion potentials of zinc and carbon steel were measured. All electrochemical measurements were conducted in 3% sodium chloride electrolyte; corrosion inhibitors were added at concentration level of 0.5% by weight. The scan rate of the potential in potentiodynamic studies was 0.5 mV/s.

2.3 Field Application

The reduction in corrosion rate achieved by application of VpCI technology for the corrosion protection of the existing tank bottoms on underside of a double-bottom tank upper floor and on a single-bottom tank with an HDPE secondary containment liner are described in [7].

The results of the treatment were measured by electrical resistance corrosion rate probes.

For this experiment, VpCI slurry was prepared by mixing of 600 pounds of VpCI powder with 900 gallons of water. A manifold assembly was built to allow flow of the slurry into telltale pipes. The distribution of the slurry during application was thoroughly controlled.

Corrosion rate data were measured before application of the VpCI and then each 2 weeks after application until stabilization of rate was achieved. It was found that application of VpCI gradually reduced the corrosion rate and finally after 56 days the reduction reached 67-76% of the initial corrosion rate.

3. RESULTS

3.1. Outdoor Test

The coupons situated closer to the VpCI source experienced a lower corrosion rate (Figure 2). One can see that corrosion rate of the coupon placed at a distance of 48 inches (125 cm) from vapor phase corrosion inhibitor source is lower than that of the coupon located at the distance of 60 inches (150 cm). Probably, under the described conditions, the vapor phase corrosion inhibitor migrates through the sand for a distance (L):

45 inches (125 cm) < L < 60 inches (150 cm).

3.2. Indoor Test

3.2.1. "Sand Test" The results are presented in the Table 1.

This test shows that the presence of the corrosion inhibitor affects the corrosion rate of both metals. Conventional corrosion inhibitor raised corrosion rate of zinc sacrificial anode almost two times and the corrosion rate of steel in more than three times comparing to the 'Control'. At the same time VpCI lowers corrosion rate of electrically connected zinc and steel.

Table 1 - Corrosion Rate of Electrically Connected Carbon Steel and Zinc

Material	Weight loss, g	Weight loss, g	Current in Zn-Steel circuit, nA
	Zn	Steel	
VpCI	0.5	<0.01	131.7
Conventional anodic Inhibitor	1.3	0.1	137.5
Control*	0.7	0.03	135.0

*Inhibitor was not added to sand

3.2.2. Electrochemical Evaluation The results presented in the Table 2 were obtained in 3% NaCl solution with and without inhibitor added. Electrochemical potential of the working electrode made from carbon steel SAE 1018 was -900 mV vs. calomel saturated reference electrode.

Table 2 - Potentiostatic Test

Material	Current at -900 mV, $\mu k/cm^3$
0.5% VpCI	22.9
0.5% Conventional Corrosion Inhibitor	38.80
Control (3% NaCl)	27.2

These results show that the level of current which corresponds to this potential depends on the type of the inhibitor in solution. VpCI when added to the solution inhibits the cathodic reaction and

subsequently lowers the level of cathodic current at given potential. Addition of the conventional anodic inhibitor causes the opposite results – it raises the current corresponding to this potential.

Table 3* - Corrosion Potential of Carbon Steel SAE 1018 and
Zinc in 3%NaCl Solution Containing Corrosion Inhibitors

Material	Ecorr, mV, Carbon Steel	Ecorr., mV, Zn	Difference in the electrochemical potentials of Carbon Steel and Zinc, mV
0.5%VpCI	-515	-995	480
0.5% Conventional Corrosion Inhibitor	-360	-795	435
Control (3%NaCl)	-535	-995	460

*Obtained from the polarization curves

Data presented in Table 3 show that corrosion potentials of carbon steel and zinc in 3% NaCl electrolyte containing VpCI and in the control are close. It confirms film-forming mechanism of corrosion protection of VpCI inhibitors. According to this mechanism adsorption of VpCI on the metal does not cause the shift of corrosion potential because it effects both anodic and cathodic reaction. It also shows that the difference in the electrochemical potentials of carbon steel and zinc remain sufficient for use of the zinc as an effective cathode in that system. At the same time presence of the conventional anodic corrosion inhibitor in the system affects the corrosion potentials of metals in a way when electrical connection with zinc will not polarize carbon steel to the cathodic potential sufficient for its protection [8, 9, 10].

3.3. Field Test [7]

Table 4 - Application of VpCI to a Double-Tank Interstitial Space

Date	Probe #	Calculated Mils/Year Corrosion Rate	Decrease in Corrosion Rate
Original corrosion rate after 13 days (control)			
12/16/04	P1	21.2	
	P2	16.5	
	P3	28.5	
	P4	17.3	
Corrosion rate 21 days after inhibitor installation			
1/6/05	P1	12.4	42%
	P2	9.5	42%
	P3	10.7	62%
	P4	5.9	66%
Corrosion rate 56 days after inhibitor installation			
2/10/05	P1	7.0	67%
	P2	3.9	76%
	P3	9.4	67%
	P4	4.8	72%

4. DISCUSSION

- The results of outdoor testing are in a good agreement with the field results reported in [6,7]. They show that VpCI protects metal from corrosion when the source is more than 4 ft (1.2m) from the metal surface. Corrosion rate of carbon steel protected by VpCI is 2-3 times lower comparing to non-protected.

- In combination with cathodic protection, different corrosion inhibitors act differently. According to indoor corrosion test data (Table 1), VpCI improves the condition of both metal in studied galvanic

couple: carbon steel and zinc. At the same time in the presence of the conventional anodic inhibitor cathodic protection of steel is less effective and causes noticeably higher corrosion rate of sacrificial anode.

Cathodic current at the potential of -900 mV vs. calomel saturated reference electrode is lower than 'control' in the presence of VpCI and higher in the presence of conventional corrosion inhibitor (Table 2).

- Inhibitors based on their chemical nature can affect positively or negatively the effectiveness of cathodic protection. Analyses of the obtained data show that combination of VpCI and cathodic protection provides better corrosion protection than cathodic protection by itself.

    However, not every inhibitor can be successfully used in combination with cathodic protection.

    Below are several reasons for non-compatibility of cathodic protection with certain inhibitors:

    - CP is provided by sacrificial anode, but inhibitor protects anode metal more effectively than it protects steel; in such a case CP is less effective.

    - CP is provided by impressed current; the level of the corrosion potential in the presence of inhibitor can be a factor. In case of strictly anodic inhibitors, (potential of carbon steel in their presence is shifted to more positive numbers), to maintain the required for CP level of potential can take higher level of impressed current than without inhibitor.

    - For both types of CP it is important that used inhibitor is stable under applied polarization conditions and doesn't undergo hydrolyses/electrolyses causing the generation of aggressive ions.

5. CONCLUSION

1. It is confirmed that VpCI provides very effective corrosion protection for the single and double bottom storage tanks. VpCI can be applied in the powder form or as slurry by mixing it with sand used for the installation of the tanks.

2. It is confirmed that VpCI provides protection to the metal located at least 1m from the VpCI source.

3. According to the testing data, VpCI is compatible with cathodic protection and when used in combination with it lowers the corrosion rate of both steel and zinc. VpCI can also lower the usage of the electric power necessary for the cathodic protection.

4. Not all types of the inhibitors can be used in combination with cathodic protection. Film-forming and cation-active types of inhibitors have a better chance for successful use with cathodic protection.

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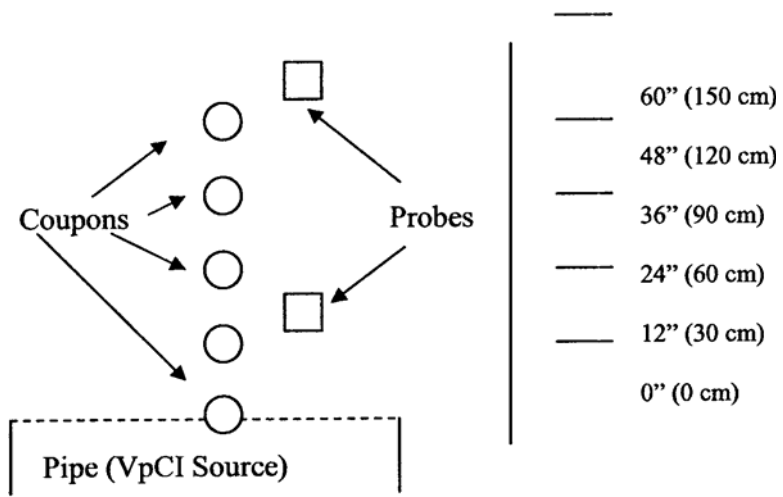
FIGURE 1 - Setup of Outdoor Investigation of VpCI Performance
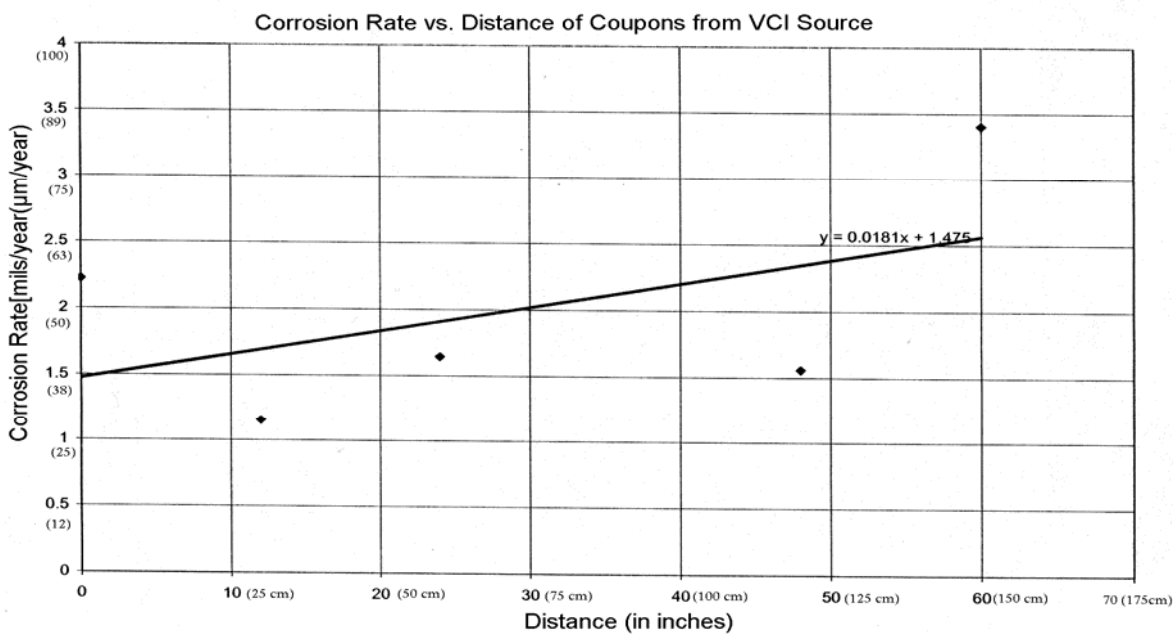
FIGURE 2 - Corrosion Rate vs. Distance of Coupons from VpCI Source