

CORROSION IN UNDERGROUND TANK AND ITS PREVENTION BY CATHODIC PROTECTION PROCESS

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ABSTRACT

Cathodic protection is the important process to all approaches of corrosion control by means of externally applied electric current, and metal surface can be maintained in corrosive environment for along time safe from corrosion attacks deterioration of metal taking place after along time until the material of electrochemical process is lost. Mechanism of prevention depends on external current polarizing cathodic elements of localized cell to the open circuits of anodic potential. If the surface become equally potential and corrosion current could not flow for along time Cathodic protection is mainly applicable where metals such as steel, copper, lead are present. On the basis of salt water. Copper can be successfully protected against corrosion by coupling it to zinc and iron, themselves or in combination. Cathodic protection can be used for the protection of the bottoms of the above ground storage tanks and the material which is emerge in land made up of mild steel or Raw Iron.

Keywords: *Potential, Corrosion, Cathodic Protection, Deterioration, Copper, Mild Steel, Inhibition*

INTRODUCTION

Cathodic protection was incidental to the mechanism of protecting steel sheet coated by dipping in molten zinc. This method was firstly implemented in France in 1836 and in England in 1837 (Wilson, 1951). Practice of zinc coating in France early to these dates 1742 (Burns *et al.*, 1967) impressed electric current for protection of underground structure was observed in England and United State, about 1910-1912. The potential of zinc is less than that of Magnesium (ϕ_H in sea water = -0.8V) and hence current output per anode is also less. High purity zinc is usually specific in order to avoid maximum polarization along with resultant reduction of current output caused by accumulation of adherent insulating zinc reaction products on commercial zinc. In sea water passivity is best avoided by alloying additions for example, alloying aluminum with 0.1% Sn followed by heat treatment at 620 °C for 18 hrs and water quenching to retain tin in solid solution very much decreases in anodic polarization in chlorine solution.

The corrosion potential of the 0.15% Sn alloys in 0.1N NaCl is -1.2V. Some sacrificial aluminum anode contain about 0.1% Sn and 5% zinc (Lennox *et al.*, 1968) about 25 million pound of aluminum consumed each year in the United State (Shepsis *et al.*, 2001). Another method of corrosion prevention is pulsed plasma polymerization it is a use to prepare a wide range of polymer film, including the conducting polymers polyaniline (Gong *et al.*, 1998; Olayo *et al.*, 2006) polypyrrole (Morales *et al.*, 2000) and polyacetylene (McConnell *et al.*, 2008). It is mainly used to increase the thickness of thin film over the surface of the metal. Cathodic protection is the usual methods to control corrosion in storage tanks as well as vacant tanks. Commercially available corrosion inhibitors are investigated for their performance in combination with cathodic protection. Corrosion inhibition studies by aliphatic amine, salicylic amines and their salts used as corrosion inhibitor in various industries (Andreev *et al.*, 2001). However, investigations bearing oxygen, Nitrogen or sulphur atoms in ring have received little attention. Benzotriazole has been reported as effective inhibitor for copper metal and its alloys (Batidas *et al.*, 2005; Sastry *et al.*, 1998) have studies morpholine and its salt carbonate, borate and phosphate. In practice, the corrosion rate of copper sheathing was maximum reduced, as Davy has predicted but unfortunately, cathodic protected coppers fouling by marine organization.

Metallic corrosion cost the United States in about \$276 billion a year approximately one third of the cost of corrosion (\$ 100 billion) is avoidable can not controlled by using corrosion resistant materials and the application of state of the art corrosion control technicalities.

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Vapor phase corrosion inhibition process or volatile corrosion inhibitors VCI belong to the organic material. They absorb on the metal surface and suppress metal dissolution and reduction reactions. These affect both anodic and cathodic processes. Organic alanin carboxylates are typical examples of this class. Vapor phase corrosion inhibitors needs moderately high vapor pressure and can prevent corrosion without applying VCI directly to the metal surface. Advantage of VCIs is that the vaporized molecules easily reach hard-to-reach spaces. When reaches the metals VCIs attaches to it by the active group (Gao *et al.*, 2007). Vapor pressure is a critical parameter in VCI effectiveness the most favorable range of the pressure is 10^{-3} - 10^{-2} Pa at the room temperature. If pressure is low slow rate of establishment of the protective layer have been reported. If the pressure is very high VCIs working processes will be limited to very short time. The affectivity end of VCIs also depends on their adsorption power on the metal. It was observed that amine type of VCIs have capability to form the protective layer for up to three months and as a rule low molecular amines are more inclined to disruption than branch high molecular weight amines. Vapors phase corrosion inhibitors are best known to protect metallic articles and equipments during storage and transportation. There are numerous investigations are reported as corrosion inhibitor properties of amines and its derivative inhibited 90 to 95% protection have been observed.

Volatile corrosion inhibitors are able to protect from corrosion not only when used as a packing aids, or in electrical and electronic assemblies but also in many situation when metal equipment is exposed to the hot atmospheric conditions.

For example VCIs can be successfully used for protection under the thermal insulation. For this investigation a section of carbon steel pipe covered with wet calcium silicate thermal insulation material was treated by mixing of VCIs in the metal/insulation interface. The test conditions were 200^o F surface temperature and 5 psig steam pressure, Maintained by continuous water injection at 5ml/hr. After 6 months the following results were found control pipe was approximately 8% corroded at the low of the water injection points. Investigation show that 20 precipitators, treated with VCIs and then wrapped in thermo insulation together with associated assembly had been transport by river and stored for I year with no or minimum corrosion.

Corrosion protection of fuel storage tanks is a very costly, incaution loss of the fuel tank filled or vacant can additionally contaminate the environment high repair cost, and effect on protection which depend on prompt fuel. Cost effective and dependable long-term corrosion protection has been provided by volatile corrosion inhibitor or cathodic protection processes and above ground storage tanks.

Most of the cases were found to preventing bottoms of the storage tanks may be field or vacant from corrosion by adding volatile corrosion inhibitors. For single bottom tank VCIs were added to sand on which storage tank was fitted and for double tanks in the space between bottoms. Different application methods were developed for the protection of new and used tanks. The result of application has been reported.

The most vulnerable part of the storage tanks is the bottom on the basis of VCIs were used for the protection of the bottoms storage tanks powder was mixed with gravel and sand. Corrosion was monitored over 2 year's period. It was later confirmed that VCIs protected the bottoms of those tanks against corrosion till 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 bottom. Here treatment of VCIs working by forming layer but here technique is change cathodically it protect by displacement method for new tank after sub base of sand and gravel spread. VCIs powder is applied at the rate of 5-10 kg. /5 m. sq. It is mixed into the base with simple hand tools. The tanks bottom is then laid out and fabricated as normal.

When tanks are being refurbished and new bottom plates are in VCIs are spread under the plate. When it is possible. VCIs should be distributed in the adjacent areas. Another approach is to inject a 5% solution of VCIs in the under bottom section of the storage tanks. For the new installation double bottom tanks it is recommended to spread VCIs powder at the rate of 500 gm. per 5 m². The spaces and the second bottom are then welded in place. For protection of existing tanks. VCIs power should be carefully blown into the voids to proved uniform distribution. Alternately VCIs solution may be pumped into the voids

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and either left there or drained. Recent experience of using of VCIs for the protection of the above ground storage filled and vacant tank described in the paper published before this section.

Another case is corrosion protection of 17 large diameter double-bottom tanks with VCIs slurry. VCIs was installed 10 to 11 year ago (2004-2005) and measurements indicate very good corrosion protection and no significant depletion of inhibitors have been observed. In this application VCI slurry was injected into interstitial space. The space was filled with the VCIs slurry and held full for about 60 days. The telltale pipe is then uncapped and the slurry was allowed to drain to the level to the telltales pipes.

Cathodic protection 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.

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 sources 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 anodes (s).

In oil/natural gas production cathodic protection play an important role. Sometime this technique takes place, this is used to protect external surfaces of buried and submerged piping as well as casting tank bottoms, offshore structures and the internal surfaces of liquid handling tanks and vessels were untouched by VCIs.

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 - 0.78V, - 0.80 V and -0.25V vs., saturated KCl calomel silver/silver chloride, and high purity zinc, respectively. The common caused 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 VCIs along with CP for the bottom protection in addition to VCI instead of, cathodic protection. By this method layer formed by corrosion can not take place till time of working this process after that corrosion takes place.

Field Work

This experiment was performed to find maximum range of Cathodic protection..

At the ground level a box space, filled with sand, was prepared. The dimensions of this box space were 2' (L) x 2' (W) x 2' (D) (60x60x30 cm)

A plastic pipe with cuts, containing the corrosion inhibitor, served as the VCIs source. This pipe was buried at the depth of 1 ft. (30 cm) in sand and pre conditioning was achieved over a 30 days period. After 30 days pre conditioning the test coupons were placed in the sand box along the length at distances from the pipe ranging from inches (0-150 cm) at a depth of 3-5 inches (7.5-10.5 cm) . Corrosion rate was determined according to the formula. This is given below.

Corrosion rate (mills/year) = $(K \times W) / (A \times t \times \Delta)$, where K = constant, 3.45×10^6 , W mass loss, grams:

A = area of the metal coupon. Centimeter squared, t = time, hours, A= density of the metal, grams per centimeter cubed.

Analytical Observation-I

Sand Test Two corrosion inhibitors, a VCIs 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	30 %
Tap water	20.4%
Sodium Chloride	0.05%
VCI	0.25%

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

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between steel and zinc panels was measured by Multimeter. After 12 days panels were removed from the sand and their weight loss was determined.

Electrochemical Evaluation

Combination of the VCI and CP action, when CP is provided by impressed current. as studied using the following methodology.

Potentiostat Versastate manufactured by EG&G with software '352 Soft Corr 111, these electrodes in 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, 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 1% 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.

Analytical Observation-II

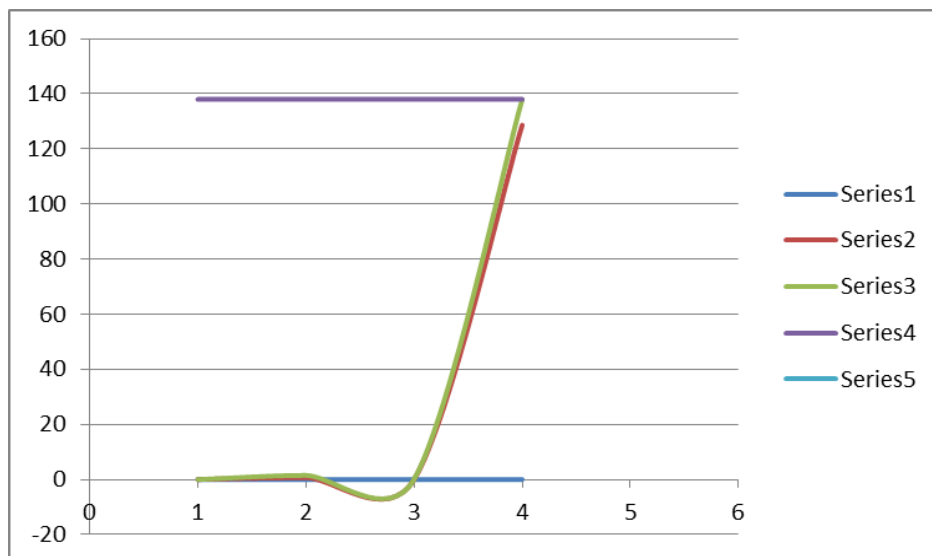
The reduction in corrosion rate achieved by application of VCIs technology for the corrosion protection of the existing tank bottoms on underside of a double-bottom tank upper floor and on a single-bottom tank with an HDPE secondary containment liner is described.

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

For this experiment, VCI slurry was prepared by mixing of 60 pounds of VCI powder with 90 gallons of water. A manifold assembly was built to allow flow of the slurry into talltail pipes. The distribution of the slurry during application was thoroughly controlled.

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

Results



*Inhibitor was not added to sand

Figure 1: Controlled Data for Analytical carbon steel

Field Work Test

The coupons situated closer to the 'VCI source experienced a lower corrosion rate One can see that corrosion rate of the coupon placed at a distance of 44 inches (125 cm) from volatile corrosion inhibitor

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source is lower than that of the coupon located at the distance of 60 inches (150 cm). Probably, under the described conditions, the volatile corrosion inhibitor migrates through the sand for a distance.

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

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 with Zinc couple. At the same time VCI lowers corrosion rate of electrically connected zinc and steel.

Electrochemical Evaluation: The result presented in the Analytical observation figure 2 was obtained in 1% NaCl solution with and without inhibitor added. Electrochemical potential of the working electrode made from Mild steel (wt %): 0.14% C, 0.35%Mn, 0.17%Si, 0.025%S, and 0.03 % P.

These results show that the level of current which corresponds to this potential depends on the type of the inhibitor in solution. VCI when added to the solution inhibits the cathodic reaction. Raised to prevent the corrosion process. Potential of working electrodes made up of mild steel was -900 mV vs calomel saturated reference electrode.

Results

Analytical Observation Weight Loss by VCI

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 Zn couple. At the same time VCI lowers corrosion rate of electrically connected zinc and steel.

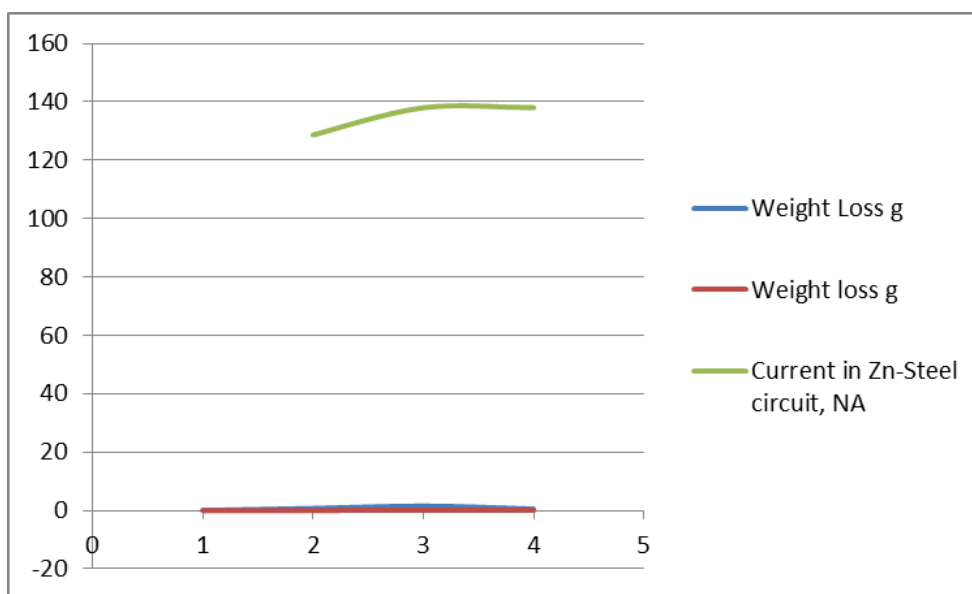


Figure 2: Wieght loss by VCI processes

Potential of the working electrode made from Mildsteel was -900 mV vs. calomel saturated reference electrode.

Table 1: Potentiostatic Test

Material	Current at - 900 mV, uk/cm ³
0.5%	22.9
0.5% Conventional Corrosion Inhibitor	38.80
Control (1% NaCl)	35.2

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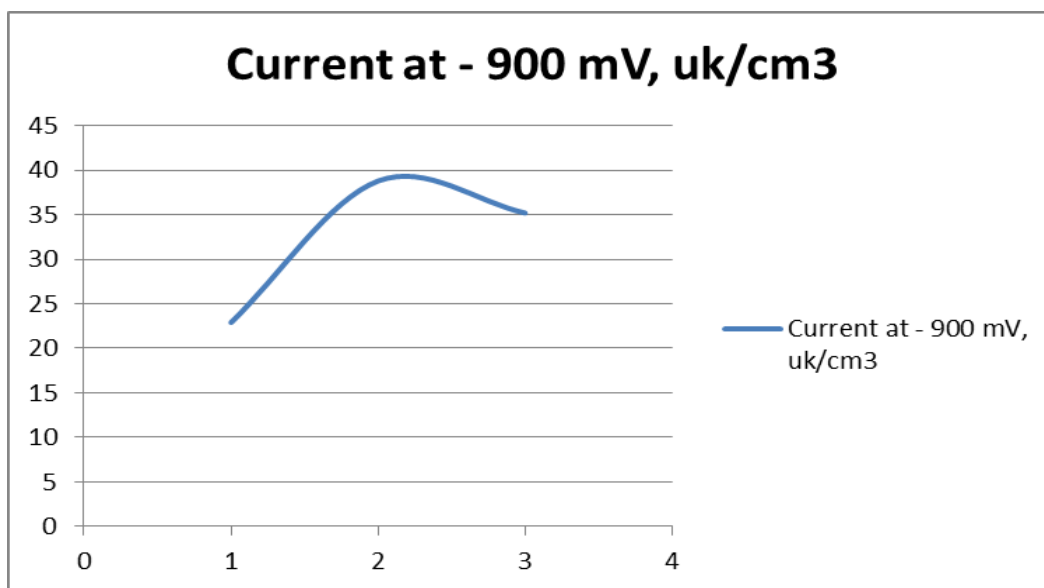


Figure 3: Potentiostatic Test at -900mV,uk/ cm³

Table 2: Corrosion Potential of Carbon steel and Zinc in % NaCl Solution Containing Corrosion Inhibitors

Material	E _{corr} , mV, Carbon Steel	E _{corr} .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	759	435
Control (3% NaCl)	-535	-995	460

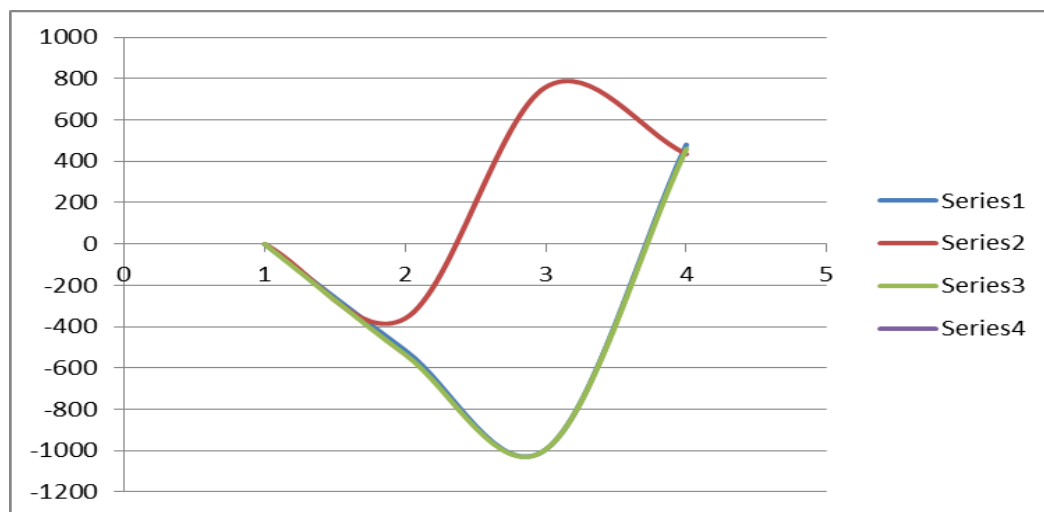


Figure 4: Corrosion Potential of Carbon steel and Zinc in % NaCl Solution Containing Corrosion Inhibitors

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From the figure it is clearly show that the level of current which corresponds to this potential depends on the type of the inhibitor in solution. VCI 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 rises the current corresponding to this potential.

Data presented in Figure 5 show that corrosion potentials of carbon steel and zinc in 1% NaCl electrode containing VCI and in the control are close. It confirms film-forming mechanism of corrosion protection of VCI inhibitors. According to this mechanism adsorption of VCI 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.

RESULTS AND DISCUSSION

The results of analytical testing are in a good agreement with the experimental results reported in. They show that VCI 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 VCI is 2-3 times lower comparing to non-protected this processes is also implemented in mild steel material in analytical testing.

In combination with cathodic protection, different corrosion inhibitors act differently. According to analytical testing corrosion test data. VCI improves the condition of both metals in studied galvanic couple: carbon steel and zinc. At the same time in the presence cathodic protection of steel is less effective and causes noticeable higher corrosion rate of sacrificial anode.

Cathodic current at the potential of 450 mV vs. calomel saturated reference electrode is lower than 'control' in the presence of VCI and higher in the presence of conventional corrosion inhibitor.

Inhibitors based on their chemical nature can affect positively or negatively the effectiveness of cathodic protection. Analysis of the obtained data show that combination of VCI and cathodic protection provided better corrosion protection than cathodic protection by itself both type of corrosion inhibition processes provided better corrosion protection of carbon steel tank.

However, not every inhibitor can be successfully used in combination with cathodic protection. Also are several reasons for non-compatible of cathodic protection with certain inhibitors:

CP provided 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 very specific category of VCI is used with cathodic processes due to higher temperature of vaporization.

Conclusion

Its derivative shows good inhibitor efficiency. Inhibition of corrosion is by the formation of physical barrier between metal and corrosive environment by the interaction The volatile corrosion inhibitor of mild steel carried out by using piperzine of metal and inhibitor molecules is more effective.

Investigation shows that CP & VCI provides very effective corrosion protection processes for the single and double bottom storage tanks. VCI can be applied in the powder form or as slurry by mixing it with sand used at the time of the installation of the tanks.

It is confirmed that VCI & CP provides protection to the metal located at least 1 feet from the VCI source. As per to the testing data. VCI is compatible with cathodic protection and when used in combination with it lowers the corrosion rate of both steel and zinc. VCI can also lower the usage of the electric power

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necessary for the cathodic protection. All types of the inhibitors can be used in combination with cathodic protection.

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