Paper
04418

CORROSION2004

PERFORMANCE AND TESTING OF VAPOR PHASE CORROSION INHIBITORS

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ABSTRACT

Vapor Corrosion Inhibitors (VCIs) possess the appreciable pressure of saturated vapors under normal atmospheric conditions. These vapors enrich the metal surface and provide corrosion protection by adsorption on it.

Corrosion testing can be performed in the laboratory under controlled conditions and in the field under natural or service conditions. In both the laboratory and field tests, corrosion rate can be evaluated by the direct determination of the metal loss or by measuring of corrosion current, corrosion potential, polarization resistance, and other electrochemical corrosion characteristics with electrochemical instruments.

Many standards and special tests and testing programs are utilized for evaluation of VCIs performance. For evaluation of the performance under natural conditions, special testing programs can be created. The paper presents the example of such a program and the data of this study. Corrosion protection provided by VCI vs. distance from its source was evaluated by corrosion monitoring, utilizing metal coupons and Corrosometer with special probs.

Keywords: Vapor corrosion inhibitor, corrosion tests, corrosion rate, corrosion protection, monitoring, coupons.

INTRODUCTION

Vapor Corrosion Inhibitors (VCIs) are organic compounds with vapor pressure about 10^{-7}–10^{-2} mm Hg [1-5]. They are transported by diffusion through the gas phase and adsorbed onto the metal with a thickness of a few monolayers, thereby protecting it from corrosion. VCIs are especially useful for protecting metals in cavities and other hard to reach places.

Amine-based corrosion inhibitors have been in use since the 1940s when the United States Navy used them to protect boilers and piping systems. Commercial use of VCIs (emitters, packaging products, coatings, and water treatment and process applications) began in the 1970s.

Vapor corrosion inhibitors can be incorporated in:

- Packaging materials - VCI treated paper, films, cardboard, foam pads, emitters, tablets and pouches with VCI, which can be inserted in the packaging
- Lubricants
- Metalworking liquids
- Cooling agents
- Water treatment and process liquid additives
- Cleaners
- Rust removers
- Paint strippers
- Oil- and water-based coatings
- Surface treatment and admixtures for concrete

Evaluation of the performance of vapor corrosion inhibitors can be done in the laboratory under controlled conditions and in the field under natural or service conditions. Both the laboratory and field testing can be performed by utilizing direct metal loss measurements, by electrochemical tests of the corrosion process and determining such parameters as corrosion current, corrosion potential, polarization resistance, electrochemical impedance spectra, etc., and by electrochemical noise measurements

Resistance probes (Corrosometer) can also be used to detect the rate of the corrosion process by measuring the change in the resistance of a wire as the wire corrodes and loses cross section [6]. Monitoring of the corrosion process by using a Corrosometer follows the kinetics of the corrosion/protection-developing processes.

Usually laboratory testing includes not one but several procedures to evaluate the effect of different conditions on the VCI performance.

In general, laboratory tests of VCI products consist of:

- Preconditioning the metal specimen. The VCI emitter is placed in a testing chamber by normal conditions to obtain the VCI's adsorption-desorption equilibrium at the metal surface.
- Subjecting a 'control' and the VCI protected specimens to various corrosive atmospheres. Variations include: elevated temperatures and relative humidity levels; cycling of condensation and evaporation of the moisture; corrosive salt solutions and industrial contaminants (sulfur dioxide, hydrogen sulfide, hydrogen chloride, ammonia, etc.).
- Evaluation of the test results.

Majority of the state and industrial standards for evaluation of the performance of vapor corrosion inhibitors use the Federal Standard No. 101C, Method 4031, (Corrosion Inhibiting Ability of VCI Vapors). This test can be applied for testing of the VCI films, papers and powders, and is included in the Japanese Industrial Standards JIS Z 1519, JIS Z 1535, JIS K 2246 **[7-9]**, and others. According to this test, the VCI material (film, paper, etc.) is placed (suspended in case of a film or paper) inside a jar that serves as a test chamber. The jar contains a water-glycerin solution, which produces a relative humidity of 90%. There is also a metal specimen inside the jar. This specimen does not contact the VCI material. After a conditioning period the metal is chilled hi a manner that causes condensation on the surface. For non-VCI materials this condensation will cause corrosion. If the material contains an adequate amount of VCI, adsorbed VCI molecules will protect the metal surface.

Several tests of vapor corrosion inhibition were developed in Germany. One of them, Testing of Corrosion Inhibiting Effect of VCI Packing Aids, is included in German Military Standard TL-8135 **[11]**. According to this procedure, the VCI paper is attached to the stopper of an Elmer Flask. The test assembly is stored for 20 hr. at room temperature. At the end of the conditioning time the rubber stopper is removed from the Elmer flask and a glycerin/water mixture is poured into the Elmer flask. The flask is immediately resealed. After 2 hours the test assembly is placed in an oven set for 40°C for 2 more hours. Corrosion protection provided by the VCI material is graded by visual inspection of the metal specimens according to a rating scale given.

According to the Eschke Test [19] VCI film or paper insulates the moisture on the bottom from the rest of the vessel. The lid with attached metal samples seals the vessel. This arrangement provides the conditions, that the metal panels are surrounded with air containing VCI vapors and moisture transmitted through the VCI product. The temperature cycle of the test includes a rise in temperature from 15°C to 40°C and dropping back to 15°C in 4 hours. The cycles are repeated over a duration of 14 days.

Multimetal Corrosion Test [12] evaluates the protection provided by a packaging material against galvanic corrosion. Carbon steel, copper, galvanized steel, aluminum, brass or other metals are attached to a star-shaped holder. These metal panels are connected with conductive wire and are kept inside the VCI film or paper bag. The temperature cycle uses 20 hours at room temperature (conditioning), 0.5 hour at 80°C, 1.5 hours at room temperature, and 0.5 hour at 80°C. Humidity inside the bag is provided by a piece of paper saturated with water, inserted inside this package. The results of the test shall be presented using the scale:

- No corrosion promoting effects
- Slight/Strong corrosion promoting effect
- No protective effect
- Slight/average/good protective effect

EXPERIMENTAL PROCEDURES

Standard Testing Program

The standard testing program for quality control purposes, for evaluation of unknown and newly formulated VCI materials, consists of easy-to-perform accelerated procedures.

Many manufactures and end users of VCI materials use single tests for evaluation of the quality of VCI products [13,14]. For this purpose, we suggest the use of a testing program consisting of several methods which provide detailed evaluation of VCI products.

Examples of such a program include:

VIA test- modified German Military Standard TL-8135[11], F-12 Cyclic Corrosion Test, SO_2 Test, Razor Blade Test and 'H_2S Corrosion test' [15,16], etc..

The above-mentioned tests can be performed on different metals. The first three procedures and also the 'H_2S Corrosion test' are designed to evaluate the ability of the VCI-containing products to protect metal in the vapor phase, while the 'Razor Blade Test' evaluates corrosion protection of the packaging materials when they are in direct contact with the metal.

F-12 Cyclic Corrosion Test evaluates the corrosion inhibiting abilities of VCI products in conditions of elevated temperatures and humidity. A beaker with aqueous salt solution is placed inside a sealed vessel. A temperature cycle consists of 16 hours in an oven set at 50°C and 8 hours at ambient temperature. It creates the conditions of cyclic evaporation and condensation of water vapors. VCI papers, emitters, foam products, powders, and tablets are subjected to four cycles; VCI films - to eight cycles.

SO_2 Corrosion Test evaluates protective properties of a VCI film or paper in the presence of SO2 and it is usually performed in sealed 1 gallon jars.

Panels, wrapped in a VCI film or paper, a small beaker containing 0.04g of sodium thiosulfate and a 50-mL capacity beaker containing a 30 mL of an aqueous blend, consisting of 1% ammonium chloride and 1% sodium sulfate solution, are placed inside the jar. Finally, 0.5mL of 1N sulfuric acid is added directly to the sodium thiosulfate beaker. The jar is immediately capped. Usually the duration of the test is 24 hours. The temperature cycle is 50°C for 16 hours, followed by 8 hours at ambient temperature.

H;S Corrosion Test evaluates protective properties of VCI packaging materials in the presence of hydrogen sulfate. It is very similar to the SO2 Corrosion Test. The only difference is that in the testing vessel an atmosphere of H_2S is created by using the chemical reaction between iron sulfide (FeS) and HCl, introduced in the testing vessel (1 gallon jar) in sufficient amounts.

Razor Blade Corrosion Test for films and papers evaluates the inhibiting abilities of VCI films or papers in contact with metal samples. According to the procedure a drop of de-ionized water or aqueous salt solution (depends on the metal) is placed on a clean and dry metal panel and quickly covered with a VCI film or paper. A similar panel is covered with untreated film or paper (control). The metal under the VCI product should not corrode, while the 'control' metal panel should. The duration of the test and the salt solution will vary depending on the metal used for evaluation.

Special Testing Programs

The case histories of successful protection of the bottom of gasoline tanks were presented in the paper "Storage Tank Bottom Protection Using Volatile Corrosion Inhibitors" [17].

The factor, which wasn't investigated in this work and is of big interest to end-users is the maximum distance of the source of VCI from the metal construction which has to be protected. To clarify this matter two additional experiments were performed.

Outdoor Experiment. At the ground level a box space, filled with sand, was prepared. The dimensions of this box space were: 3'(L)x3(W)'x2'(D) (90x90x60cm).

A plastic pipe with cuts, containing the corrosion inhibitor, served as the VCI source. This pipe was buried at the depth of 1 ft. in sand and preconditioning was achieved over a 30 day period.. Thirty days after that test coupons were placed in the sand box along the length at distances from the pipe ranging from 0 to 60inches (0 - 150cm), at a depth of 3-5 inches (7.5 -10.5cm) **(Figure** 1). Corrosion rate was determined according to the formula **[18]:**

Corrosion rate (mils/year) = (K x 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.Δ

At the same time corrosion was monitored with a Corrosometer (CK-3, manufactured by Rohrback Cosasco System, Inc.).

A set of two Corrosometer probes was buried thirty days after the pipe was set underground. The probes were buried 4-6 inches deep, at distances of 2 and 5 feet from the pipe **(Figure** 1). The area was covered with a plastic film for the prevention of loss of the corrosion inhibitor.

Readings of the resistance rates were obtained on a regular basis. These measurements were used to calculate the instantaneous corrosion rate with a formula provided by the manufacturer of the probes:

Corrosion rate (mils/year) = (change in dial reading/# of days which have passed) x0.365 x probe span

For probe type B span =5.

The duration of this experiment was 260 days.

<u>Laboratory (indoor) test:</u> For this test four ClearView (high-density polyethylene) containers were used (Figures 5). The volume of the container was ~96 qt. (100 L).

Carbon steel, aluminum and cast iron were cleaned with methanol, air-dried and positioned in the containers as follows:

2.5 in (6.35 cm) from the VCI source
5 in (12.7 cm) from the VCI source, and
10 in (50.8 cm) from the VCI source.

To provide 80 -90% Relative Humidity inside the container, four beakers, each containing 400 mL of de-ionized water, were placed in its corners.

Conditions in containers were as follows:

1. Without VCI powder, at room temperature and 80 - 90% Relative Humidity ('Control').
2. With VCI powder, at room temperature and 80 -90% Relative Humidity
3. Without VCI powder, at 50°C and 90-100% Relative Humidity ('Control').
4. With VCI powder, at 50°C and 90-100% Relative Humidity.

Containers were sealed during the test and panels were evaluated on a regular basis. The duration of the test was two weeks. The date of the appearing of the first sign of corrosion was recorded and tested panels were visually evaluated and graded according to the scale below:

- Extremely severe corrosion: 0;
- Very severe corrosion: 1;
- Severe corrosion: 2;
- Moderate corrosion: 3;
- Slight corrosion: 4;
- Very slight corrosion: 5;
- No visible corrosion: 6.

RESULTS AND DISCUSSION

Outdoor test results:

- The coupons situated closer to the VCI source experienced a lower corrosion rate **(Figure** 2) One can see that corrosion rate of the coupon placed at the distance of 48inch (125 cm) from vapor 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 corrosion inhibitor migrates through the sand at the distance: 45inch(125cm)< L< 60inch (150cm).
- Figure 3 and Figure 4 show that the corrosion rate decreased over time for both probes.
- The average corrosion rate for probe 1, which was closer to the VCI source, was significantly lower than that of probe 2 (Table 1).

Indoor test results: Table 2, Figures 6-11

- Vapor corrosion inhibitor, placed in the center of container, provides corrosion protection for all the panels inside the container.
- Vapor corrosion inhibitor protects from corrosion carbon steel, cast iron and aluminum.
- Vapor corrosion inhibitor inside the container significantly delayed offset of corrosion of metals at room temperature and 80-90% relative humidity and/or at 50°C and 90-100% relative humidity respectively.
- Corrosion of the metal started to develop more slowly in the container with the corrosion inhibitor than in the "control" container.

These data confirm that VCIs provide effective protection to carbon steel, cast iron and aluminum, both at room temperature and at 50°C and 90-100% humidity, for the metal samples positioned at all three locations of the testing container.

CONCLUSION

- Use of Vapor Corrosion Inhibitors is a relatively new and is considered as a very effective corrosion protection technology.

- For performance evaluation of VCI containing products manufactures and end-users have to develop the testing program, which can include standard procedures and special tests, related to the service conditions as well.

- Results of outdoor and indoor study of a VCI Powder given in this work, situated at different distances from the metal, confirmed the effectiveness of VCI in corrosion protection for different metals under different set of conditions: buried in sand, exposed to atmosphere, at high humidity and temperature ranges.

ACKNOLEDGMENTS

Authors would like to thank Catherine Mackiewicz for her participation in this investigation.

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TABLE 1: AVERAGE CORROSION RATES CALCULATED FROM CORROSOMETER DATA

Material	Average Corrosion Rate (in mils/year)
Probe 1	2.41 (0.061 mm/year)
Probe 2	3.23 (0.082 mm/year)

TABLE 2: TIME FOR ONSET OF CORROSION, DAYS

Material----> Exposure conditions	Carbon Steel		Cast Iron		Aluminum	
	VCI	Control	VCI	Control	VCI	Control
Room Temperature, Humidity	>14	4-5	>14	4.5	>14	5-7
50°C, 90-100% R.H.	>14	1-2	8-11	1-2	8-14	3-4

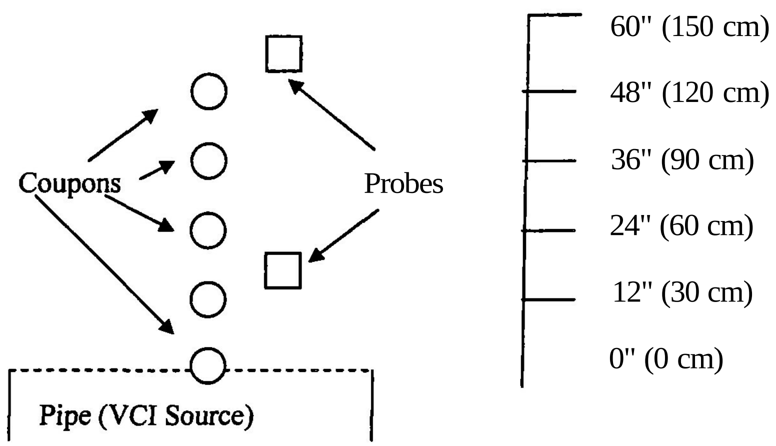

FIGURE 1: Setup of outdoor investigation of VCI performance

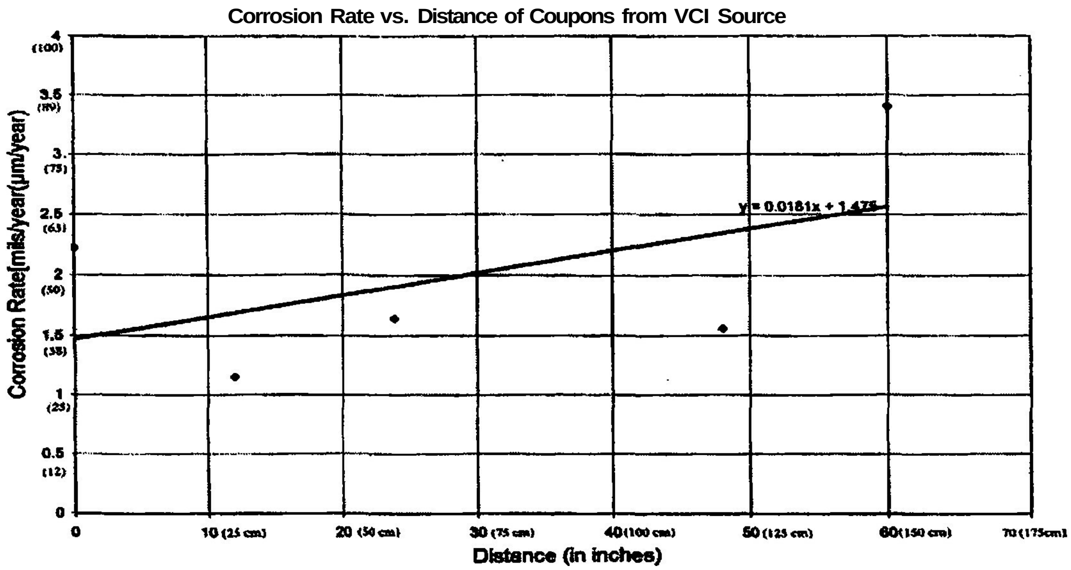

FIGURE 2: Corrosion Rate vs. Distance of Coupons from VCI Source

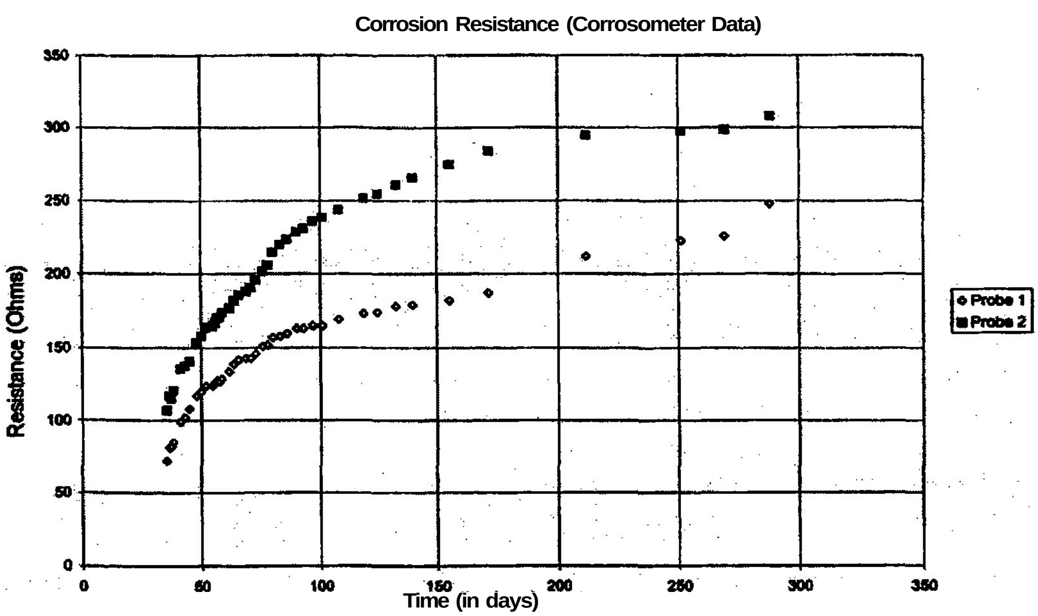

FIGURE 3: Corrosion Resistance (Corrosometer Data)

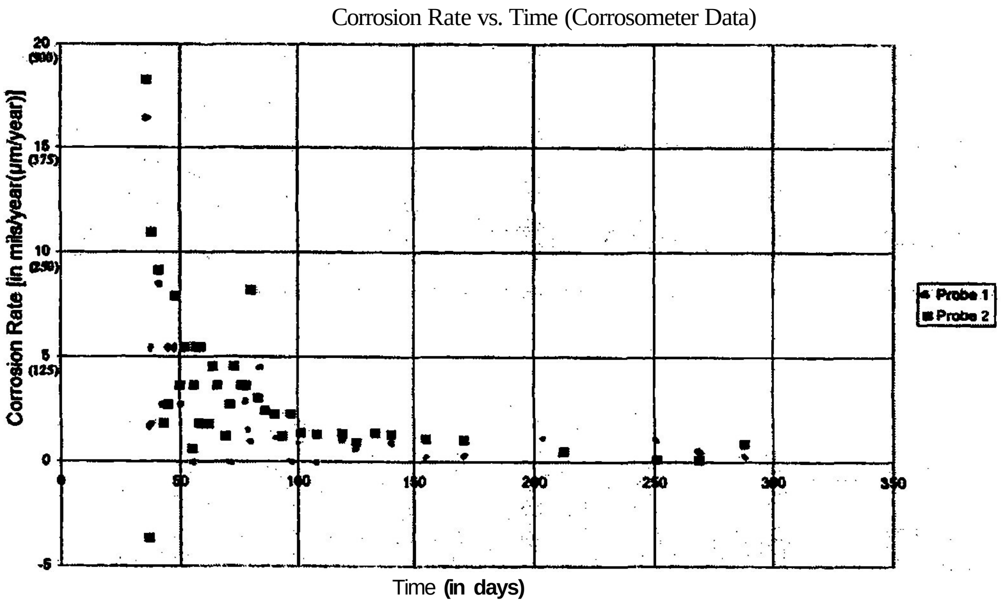

FIGURE 4: Corrosion Rate vs. Time (Corrosometer Data)

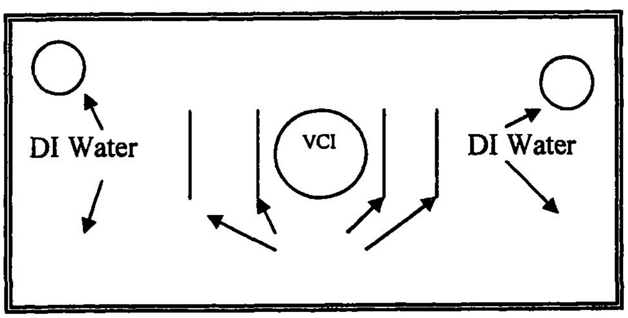

FIGURE 5: Indoor test diagram

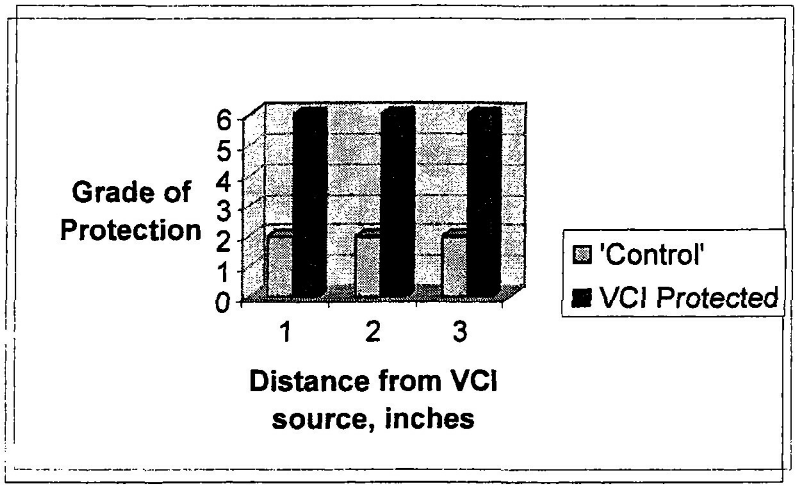

Figure 6: Protection of Steel at Room Temperature

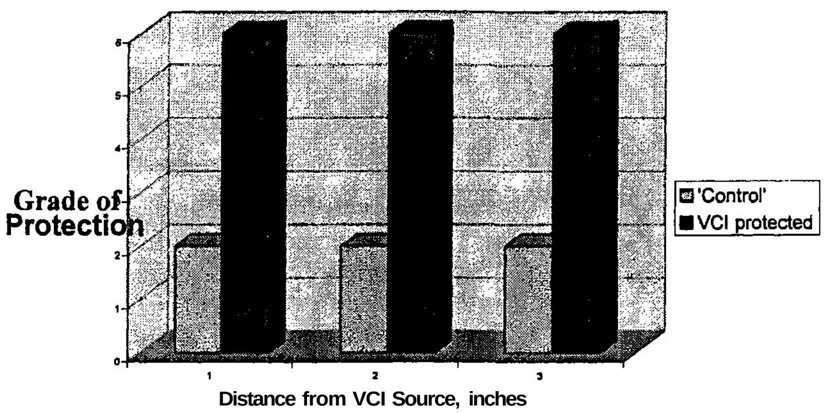

Figure 7: Protection of Cast Iron at Room Temperature

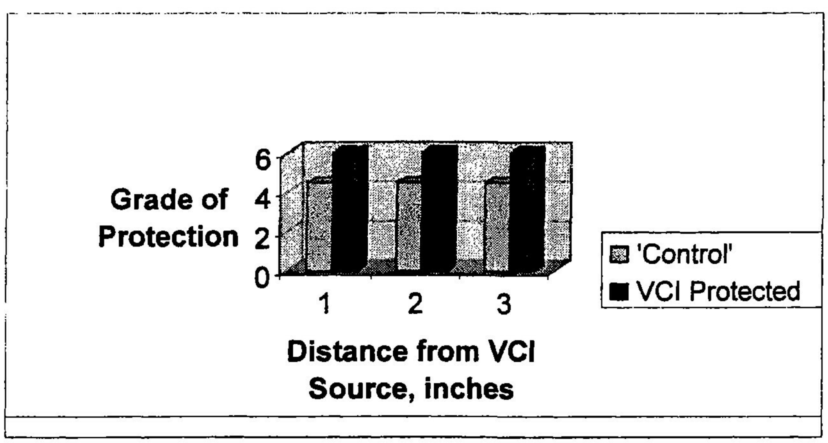

Figure 8: Protection of Aluminum at Room Temperature

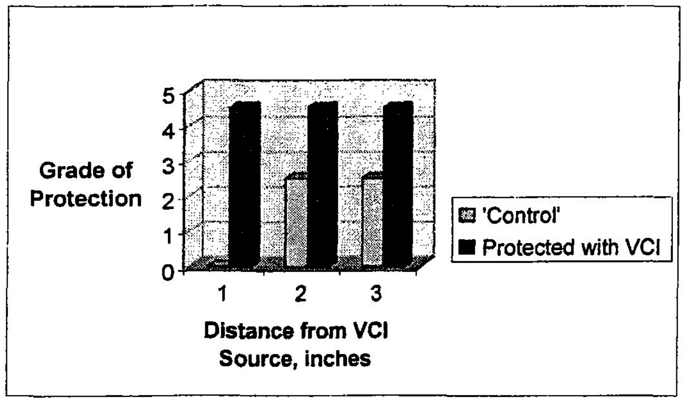

Figure 9: Protection of Aluminum at 50°C

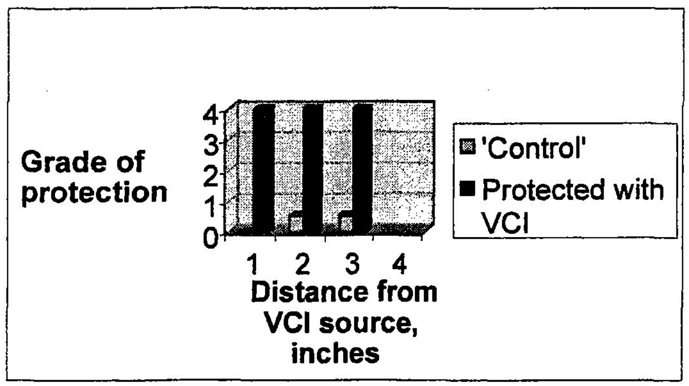

Figure 10: Protection of Cast Iron at 50°C

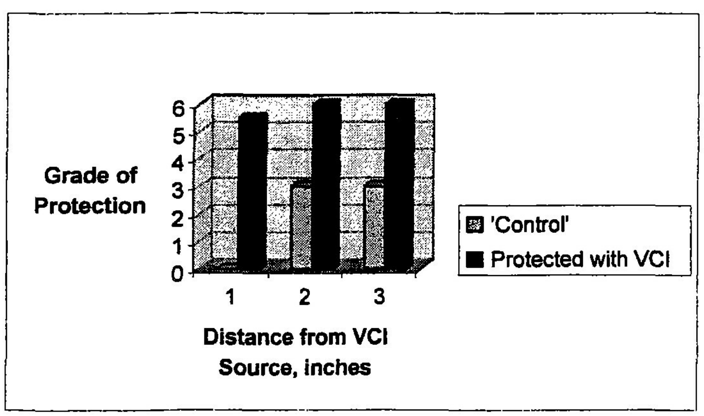

Figure 11: Protection of Carbon Steel at 50°C