UNCLASSIFIED

AD 428513

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

64-8

428513

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF RECLAMATION

LABORATORY INVESTIGATION OF THE EFFECT OF CATHODIC PROTECTION ON THE CORROSION OF THE GALVANIZED COATING ON GALVANIZED STEEL

CATALOGED BY DDC
AS AD No.

Chemical Engineering Report No. SI-35

DIVISION OF RESEARCH

FEB 6 1964
TISIA B

428513

OFFICE OF CHIEF ENGINEER
DENVER, COLORADO

July 1, 1963

The information contained in this report may not be used in any publication, advertising, or other promotion in such a manner as to constitute an endorsement by the Government or the Bureau of Reclamation, either explicit or implicit, of any material, product, device, or process that may be referred to in the report.

CONTENTS

	Page
Introduction	1
Summary and Conclusions	2
Test Apparatus and Procedure	3
Results	4
Discussion	5
Electrochemical Reactions Tending to Promote Corrosion of the Galvanized Coating	5
Significance of Specimen-to-electrolyte Potential Measurements on Galvanized Steel	6
Application of Cathodic Protection to a Galvanized Steel Structure	6
Selected References	7

	Figure
Galvanized steel test specimens prior to testing	1
Galvanized steel test specimen with magnesium anode attached	2
Test of cathodically protected specimen	3
Test specimens after 90-day testing in saline solution	4

	Table
Degree of corrosion of galvanized plates	1
X-ray analysis of typical corrosion and encrustation products on cathodically protected galvanized specimens	2

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF RECLAMATION

Office of Chief Engineer
Division of Research
Chemical Engineering Branch
Physics and Chemistry Section
Denver, Colorado
July 1, 1963

Laboratory Report No. SI-35
Written by: T. E. Backstrom
Reviewed by: W. Y. Holland
W. A. Pennington
Submitted by: L. O. Timblin, Jr.

Subject: Laboratory investigation of the effect of cathodic protection on the corrosion of the galvanized coating of galvanized steel

INTRODUCTION

Zinc is used extensively as a coating on iron and steel to protect these underlying metals from corrosion. The composite, i.e., galvanized iron or galvanized steel, is employed in small piping, sheet metal fabrications, well casings, and many other ways.

There are two ways in which the zinc offers protection: (1) it has a lower corrosion rate than any ordinary ferrous material in many environments and (2) it offers a galvanic (sacrificial) protection to any exposed iron or steel which may develop because of the corrosion of the zinc layer. This galvanic protection leads to less severe pitting of the ferrous metal.

The corrosion rates of a single metal are dependent upon two factors: (1) its solution tendency and (2) the protection afforded by its own corrosion products.

Zinc has a very high solution tendency, much higher than iron or steel. In certain environments it forms a dense impervious, adherent corrosion product which protects the metal from attack. Zinc, in protecting itself, serves to protect the base metal.

If a galvanized structure is placed in an environment in which the zinc corrosion products are freely soluble, no protective film is formed and the galvanized coating is rapidly corroded.1/ Solubility of the protective film is dependent upon the pH of the electrolyte in the immediate vicinity of the metal. Rapid corrosion would be expected in the acid pH range from zero to 6 and in the basic pH range from 12.0 to 14.5.1/

References listed at end of report

Since the primary function of the galvanizing process is the formation of a protective coating on the steel base, any procedure which reduces the corrosion of the coating by preserving the protective film on the coating metal, in effect, extends the service life of the base metal. Application of cathodic protection to a galvanized structure reduces the corrosion of the zinc by reducing or eliminating the current demand of exposed steel on the zinc and by direct cathodic protection of the zinc. Cathodic protection also tends to promote scale formation in slightly scale-forming waters because of the increased pH at the cathode.

SUMMARY AND CONCLUSIONS

A laboratory investigation was made to determine the possible benefit of cathodic protection to the service life of galvanized iron or steel. The study was performed using sacrificial magnesium anodes producing structure-to-electrolyte potentials of -1.04 to -1.20 volts with an average value of -1.05 volts with reference to a copper-copper sulfate half cell.

Controlled laboratory tests showed that cathodic protection will reduce significantly the corrosion of galvanized metal at structure-to-electrolyte potentials produced by magnesium sacrificial anodes.

It is concluded, on the basis of tests performed at current densities necessary to impress a structure-to-electrolyte potential of -1.05 volts, that:

1. Cathodic protection reduces general corrosion of the galvanized coating significantly.

2. Cathodic protection does not eliminate corrosion of the galvanized coating entirely, as local pitting corrosion occurs to some extent.

3. The equilibrium concentration of alkali at the cathode is too low to promote alkali corrosion of the cathodically protected coating.

It is believed that properly adjusted and maintained cathodic protection can be used to extend the service life of a galvanized structure by extending the life of the coating protecting the base

metal. An outdoor exposure test is being installed to correlate the laboratory results with actual field performance.

TEST APPARATUS AND PROCEDURE

Tests were performed to determine whether corrosion of the galvanized coating could be expected if the coating were cathodically protected, and whether, in the event the galvanized coating did corrode, the service life of the coating would be extended by the cathodic protection.

Six 5-1/2-inch-square specimens were fabricated from 1/4-inch galvanized steel (Figure 1). A square approximately 1-1/2 inches on a side was acid etched through the coating to the steel in each plate. This square was made to permit current flow from the magnesium anode through the electrolyte directly to the steel to demonstrate whether adequate cathodic protection was being provided to the steel. The steel in the acid-etched area would be expected to be easily corroded without cathodic protection. Magnesium anodes were connected to three of the specimens in such a way that electrical contact was made with both the steel and the coating. These specimens were labeled 1A, 2A, and 3A (Figure 2). Three other specimens, labeled 1B, 2B, and 3B, were tested as control. No cathodic protection was provided to these latter specimens.

All specimens were tested in a saline solution containing 1.9 pounds of sodium chloride per gallon of solution, a standard solution used for testing in the Protective Coatings Laboratory. Specimens were placed in 4-liter beakers and the solution was added until the upright specimen was submerged to within 1/2 inch of the top (Figure 3).

The specimens were tested in three environments to determine the effect of environment on the relative rates of corrosion of the cathodically protected galvanized coatings as compared to the corrosion rate of the unprotected control coating. Specimens 1A and 1B were submerged in the static test solution. Specimens 2A and 2B were tested in the same solution, but oxygen was added continually by bubbling air through the solution. Specimens 3A and 3B were placed in the test solution, and air was bubbled through the solution at a high rate in order to agitate the solution and to provide oxygen.

All specimens were tested for 90 days. The test water was changed each week.

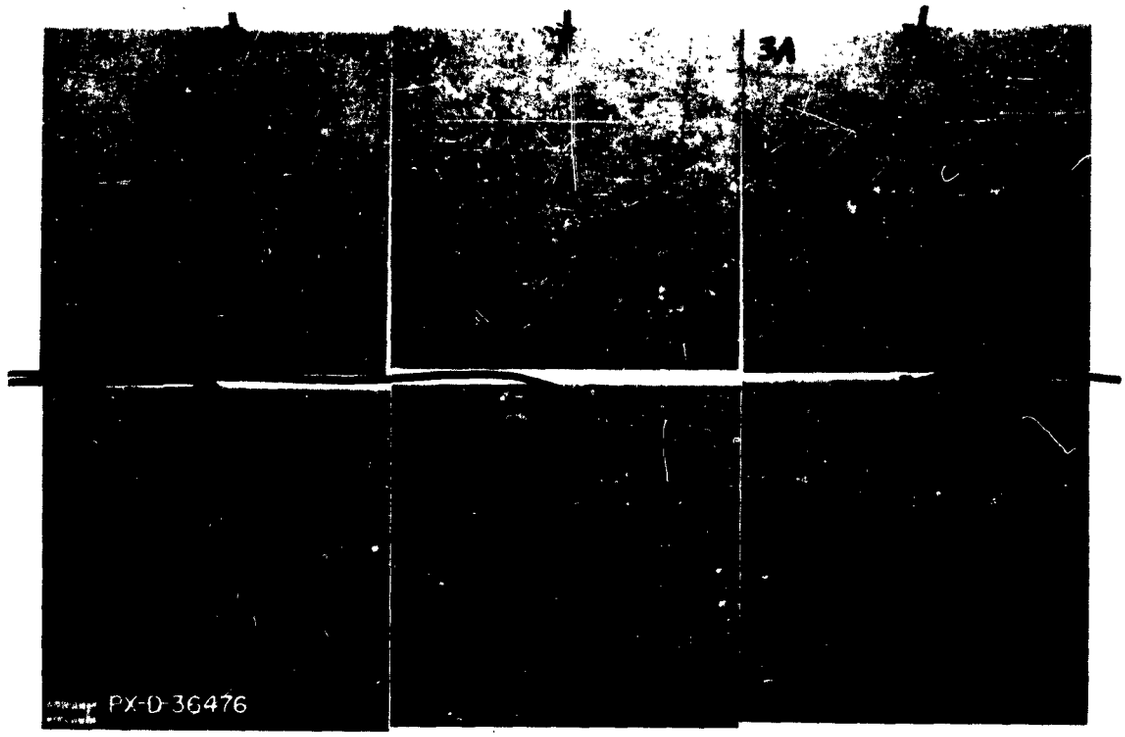

Figure 1. Galvanized steel test specimens prior to testing. Specimens in the top row were cathodically protected by magnesium anodes. Approximately 2/5 natural size.

metal. An outdoor exposure test is being installed to correlate the laboratory results with actual field performance.

TEST APPARATUS AND PROCEDURE

Tests were performed to determine whether corrosion of the galvanized coating could be expected if the coating were cathodically protected, and whether, in the event the galvanized coating did corrode, the service life of the coating would be extended by the cathodic protection.

Six 5-1/2-inch-square specimens were fabricated from 1/4-inch galvanized steel (Figure 1). A square approximately 1-1/2 inches on a side was acid etched through the coating to the steel in each plate. This square was made to permit current flow from the magnesium anode through the electrolyte directly to the steel to demonstrate whether adequate cathodic protection was being provided to the steel. The steel in the acid-etched area would be expected to be easily corroded without cathodic protection. Magnesium anodes were connected to three of the specimens in such a way that electrical contact was made with both the steel and the coating. These specimens were labeled 1A, 2A, and 3A (Figure 2). Three other specimens, labeled 1B, 2B, and 3B, were tested as control. No cathodic protection was provided to these latter specimens.

All specimens were tested in a saline solution containing 1.9 pounds of sodium chloride per gallon of solution, a standard solution used for testing in the Protective Coatings Laboratory. Specimens were placed in 4-liter beakers and the solution was added until the upright specimen was submerged to within 1/2 inch of the top (Figure 3).

The specimens were tested in three environments to determine the effect of environment on the relative rates of corrosion of the cathodically protected galvanized coatings as compared to the corrosion rate of the unprotected control coating. Specimens 1A and 1B were submerged in the static test solution. Specimens 2A and 2B were tested in the same solution, but oxygen was added continually by bubbling air through the solution. Specimens 3A and 3B were placed in the test solution, and air was bubbled through the solution at a high rate in order to agitate the solution and to provide oxygen.

All specimens were tested for 90 days. The test water was changed each week.

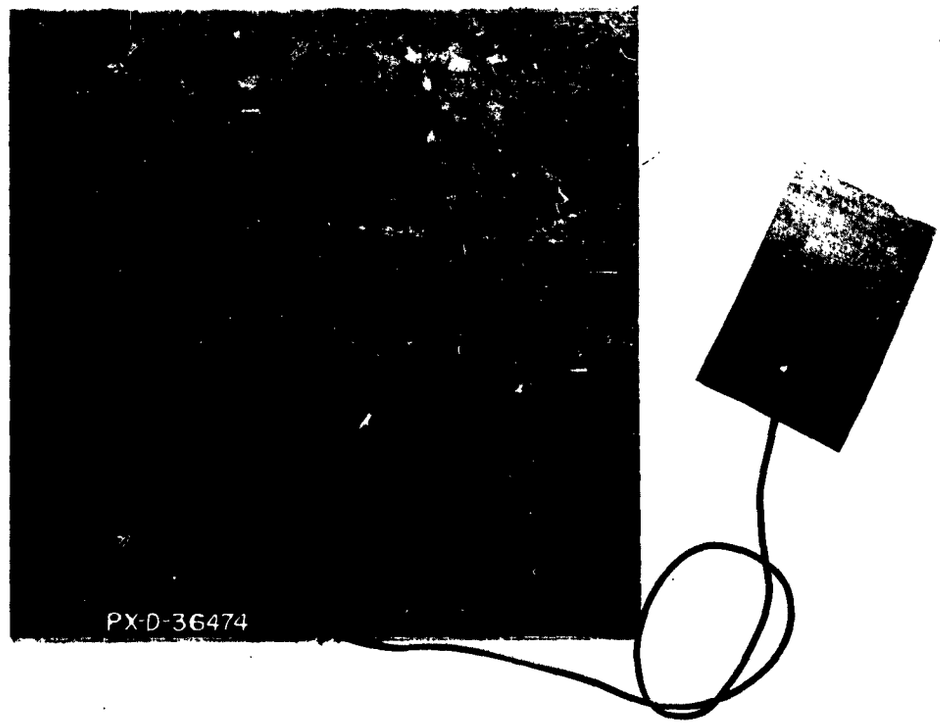

Figure 2. Galvanized steel test specimen with magnesium anode attached. Approximately 3/4 natural size.

Figure 3. Test of cathodically protected specimen. Note bubbles of hydrogen gas evolved on both the specimen (cathode) and the magnesium (anode). Approximately 1/3 natural size.

The potentials between the specimens and a copper-copper sulfate reference cell were measured weekly to determine the range of protection offered by the magnesium anodes.

RESULTS

Examination of the specimens at the conclusion of the test shows that cathodic protection reduces the rate of corrosion of the galvanized coating (Table 1). The galvanized coating on the 3-control specimens was entirely removed on approximately one-half of the specimens' surfaces and considered as failing on the remainder of the surfaces. Severe attack on the control specimens was evident after less than 1 month in the salt solution. Deep etching of the coating was evident after less than 1 month in the salt solution, although no steel corrosion was observed even in the etched areas. Deep etching of the coating was evident in control Specimen 2B in Figure 4.

Table 1

DEGREE OF CORROSION OF GALVANIZED PLATES

Plate No.	Cathodic protection	Percent total area corroded
1A	Protected	15
1B	Unprotected	100
2A	Protected	5
2B	Unprotected	100
3A	Protected	15
3B	Unprotected	40

Localized areas of the galvanized coating of the cathodically protected specimens were corroded as shown by the black areas associated with the white corrosion products (Figure 4). The large dark areas at the lower left and lower center of Specimen 1A in Figure 4 are discolored sections with the galvanized coating still intact. Some severe corrosion of the coating was evident in the region of the waterline (the top 3/4 inch of the specimens). This region is protected only intermittently by the anodes and is subject to accelerated corrosion due to the oxygen concentration cell formed in the waterline region.

X-ray analysis of the encrustation and corrosion products on the plates showed brucite and zincite to be the major constituents (Table 2). The

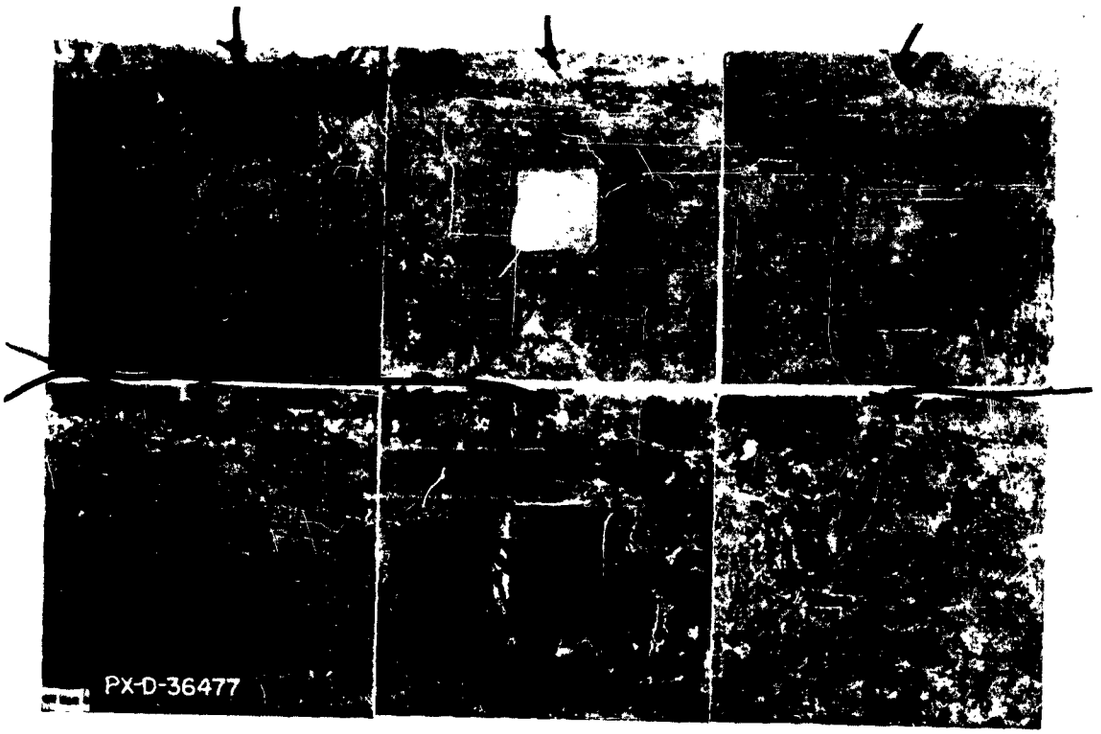

Figure 4. Test specimens after 90-day testing in saline solution. Cathodically protected specimens are shown in the top row. Approximately 2/5 natural size.

brucite is an insoluble corrosion production of the magnesium anode and the zincite is the normal corrosion product of zinc.

Table 2

X-RAY ANALYSIS OF TYPICAL CORROSION AND ENCRUSTATION PRODUCTS ON CATHODICALLY PROTECTED GALVANIZED SPECIMENS

Cathodic protection specimen	X-ray analysis: Major constituents	X-ray analysis: Minor constituents	Remarks
2A	Brucite $Mg(OH_2)$	Zincite ZnO Unidentified phase	Brucite is a corrosion product of the magnesium anodes

No significant acceleration of the corrosion of the galvanized coating due to concentration of hydroxyl ion at the cathode was observed. Corrosion of zinc in a concentrated chloride-containing solution would be a spreading-type corrosion which would be present over most of the surface of the plate.[2]

DISCUSSION

Electrochemical Reactions Tending to Promote Corrosion of the Galvanized Coating

Zinc corrosion is greatly increased in the presence of chloride ions. This acceleration of zinc corrosion restricts the use of galvanized steel in sea water, as zinc may be considered a heterogeneous zinc-steel alloy with a composition ranging from pure zinc on the surface to steel at the galvanized coating-steel interface.

Evans[3] says that this accelerated corrosion of zinc is caused by destruction of the protective zinc oxide film by the chloride ion to form a soluble zinc chloride. This destruction of the protective film exposes bright metal to the corroding solutions, and corrosion continues.

By application of cathodic protection to a galvanized structure, the structure is made the cathode of the system and the galvanized coating is available for corrosion by the byproducts of the typical concurrent cathode reactions:

$$(1) \quad H_2O = H^+ + (OH)^-$$

$$2H^+ + 2e = H_2 \uparrow$$

$$(2) \quad O_2 + 4e + 2H_2O = 4\,(OH)^- \downarrow$$

As shown by the equations, the main byproducts of the cathode reaction are the formation of $(OH)^-$, which then becomes available for reaction with the Zn. The rate of formation of the hydroxyl ion is proportional to the current density; thus the pH in the vicinity of the cathode is determined primarily by the current density at the cathode in a static electrolyte. The pH in the neighborhood of the cathode is known to reach a value of 11 by the above mechanism. Corrosion of amphoteric materials such as zinc is accelerated by highly basic solutions above a pH value of about 12.

The low corrosion rate experienced by the cathodically protected test specimens shows that current density necessary to produce a structure-to-electrolyte potential of -1.05 volts is not sufficient to raise the pH in the neighborhood of the cathode to a value high enough to promote corrosion of the galvanized coating.

Significance of Specimen-to-electrolyte Potential Measurements on Galvanized Steel

Specimen-to-electrolyte potentials measured in the tests showed that the electrode potential of the unprotected galvanized steel plate was approximately that which would be expected from a pure zinc plate. The values determined averaged -1.05 volts referenced to a copper-copper sulfate half cell. The results of the test indicate that the steel in the test specimens is under galvanic cathodic protection from the galvanized coating.

Specimen-to-electrolyte potentials for cathodic protection specimens ranged from -1.04 to -1.20 volts, well above the cathodic protection level required to protect steel.

Application of Cathodic Protection to a Galvanized Steel Structure

Cathodic protection of galvanized steel, using a sacrificial magnesium anode, would provide protection to the zinc as well as to the steel. If the value of the solution potential difference between magnesium and zinc (1.6v)[2] is compared with the solution potential difference between magnesium and steel (1.9v)[2], it is seen that the magnesium would provide zinc and steel approximately the same degree of protection.

SELECTED REFERENCES

1. Uhlig, H. H., The Corrosion Handbook, 1948, John Wiley and Sons, Inc., New York, page 335.

2. Evans, U. R., The Corrosion and Oxidation of Metals, 1960, Butler and Tanner Ltd., London, pages 99 and 116.

3. Ibid, page 116.

4. Ibid, page 310.

5. Office of the Chief of Civil Engineers, "Corrosion Prevention, Part M," Maintenance and Operation of Public Works and Public Utilities, December 7, 1956, page M-26.

GPO 836-245