# A Laboratory Study of the Cathodic Protection Afforded by 55-percent Al-Zn Coating in Comparison with a Galvanized Coating

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This paper reports studies of the galvanic protection afforded to the base steel by a 55-percent Al-Zn coating\* in comparison with a galvanized coating. Both types of coatings are obtained by a continuous hot dip process in a bath containing the coating in a molten state. Results are presented for laboratory tests using solutions (distilled water and 5-percent sodium chloride) to evaluate the influence of different variables (electrolyte, cathode-toanode surface ratio and anode-cathode separation distance) involved in the galvanic corrosion process. The conductivity of the electrolyte and the cathode (steel) anode (coating) surface ratio influence the degree of cathodic protection (CP) afforded by the coating. The conclusions reached in this study agree with field data previously obtained by the authors in relatively unpolluted (rural and urban) and marine atmospheres.

The literature contains very few studies dealing with research into the degree of CP of the base steel provided by a 55percent Al-Zn coating.<sup>1-6</sup> Field studies have generally been limited to visual evaluations of the appearance of the materials at the cut edges of specimens, or at scratches made on the material with the coating locally removed.<sup>1-4</sup> Electrochemical considerations of the galvanic process involved have been addressed in a few cases,<sup>2.5,6</sup> although some questions remain.

In this research, an electrochemical study was made to analyze the effect of different variables affecting the galvanic corrosion process: electrolyte, cathode-to-anode separation and cathode-to-anode surface ratio.

Different tests have been performed in an attempt to simulate situations (cut edges, scratches) in which galvanic corrosion cells are frequently generated in practice.



*Fig.* 1—*Specimens for study of CP without separation between cathode (steel) and anode (coating). Surface ratios: (left) 1:1 and (right) 14:1.* 

#### Experimental Procedure

Cold-rolled steel sheet, coated with  $25 \,\mu m$  of 55-percent Al-Zn alloy (Galvalume) or with  $20 \,\mu m$  of a galvanized coating (Sendzimir) was used. The electrolytes consisted of distilled water and 5-percent sodium chloride, in an attempt to simulate to a certain degree the behavior of the materials in rural or moderate urban atmospheres and in marine atmospheres, respectively. Tests were conducted at room temperature.

Two types of tests were carried out: one without separation between the anode and cathode and another with separation, at two different distances. The aim of the first test, which reflects to a greater extent the normal galvanic corrosion process in practice, was to observe the time that coatings kept the steel protected without the appearance of consistent rust.

The aim of the second test was to obtain information in the laboratory about the electrochemical process (galvanic current, corrosion potential, etc.), to analyze and compare the galvanic behavior of the two coatings. The second type of test was also of interest to assess the effect of the cathode-toanode surface ratio and the cathode-to-anode separation distance. The surface ratios selected were chosen to represent, as far as possible, the conditions arising in practice at the cut edges of the sheet and at scratches accidentally caused during handling.

Two cathode-to-anode surface ratios were selected—14:1 and 1:1. In the case of the cut edges of a plate 0.6 mm thick and 20  $\mu$ m of coating thickness, the steel surface exposed is approximately 14 times that of the coating. In the case of scratches, the selected cathode-to-anode ratio was 1:1; the reason is as follows. If the coating is removed by creating a longitudinal scratch 1 mm in width, it may be seen, after a certain period of exposure of the material in a polluted

atmosphere, that the width of the closest damaged coating, visibly the most sacrificed to protect the base steel, is similar to the width of the corresponding scratch.

## Tests without Separation between Anode and Cathode

Circular specimens of steel coated with the 55-percent Al-Zn or galvanized coating were prepared. Specimens of two different diameters were used. In the central zone of the specimens, a standard area of the metallic coating, in concentric form, was removed by dissolving it in concentrated hydrochloric acid. In this way, a circular steel area, 4.7 mm in diameter, was obtained. Depending on the initial diameter of the specimen, the cathode-

<sup>\*</sup> Made in Spain by CSI Planos under the trademark Algafort which has been licensed by BIEC International, Inc. This product is commercially available in U.S.A. under the trademark Galvalume.

# Table 1 Conductivity Values of Solutions Without Anode-Cathode Separation for Galvanized Steel $\mu S/cm$

## Table 3 CP of Steel in Atmospheric Tests (months)

μS/cm				Rural	Urban	Marine
Electrolyte	Initially	After 30 days	55% Al-Zn	0.5	0.5	>18
Distilled water 5% NaCl	9.4 68,000	29.5 72,000	Galvanized	2	2	>18

to-anode surface ratio was 14:1 or 1:1 (Fig.1).

The edges and reverse face of the specimens were covered with an isolating film. The specimens were then submerged, in duplicate, in vessels containing the two electrolytes. Oxygen was periodically insufflated into the solutions and any water evaporated was restored.

Tests with Separation between Anode & Cathode

Rectangular specimens of uncoated steel and steel coated with the 55-percent Al-Zn or galvanized coatings were cut. The dimensions of the specimens were 4.5 x 4.5 cm and they were all provided with a tail for the electrical contact. Each specimen was entirely covered with tape, except for the central zone of one of the faces where a circular area remained uncovered. For a cathode-to-anode surface ratio of 14:1, the diameters of the uncovered surfaces were 19 mm (steel) and 5 mm (coating). When the surface ratio was 1:1, the diameters of both steel and coating surfaces were 17 mm (Fig. 2a).

Once the steel and coating specimens were prepared, they were placed facing each other at separation distances of 1.7 and 4.5 mm, using plastic spacers (Fig. 2b), to ensure that the anodic and cathodic zones were always at the same distance. The couples thus formed were submerged in beakers containing the different solutions. Oxygen was periodically insufflated into the solutions and any water evaporated was restored.

The current intensity of the galvanic couples was measured by contacting the tails to a zero-resistance ammeter and waiting for the value obtained to stabilize. The

Table 2
Galvanic Currents of Coated Steel Galvanic Couples in Distilled Water
μA

S.:S.	d <sub>ea</sub> , mm	1 d	1 day		ays	14 days	
t a	t-a	Α	G	Α	G	Α	G
1:1	1.7	22.5	30.3	32.9	27.2	31.8	28.8
	4.5	15.9	22.5	16.8	26.9	22.8	36.4
14:1	1.7	6.4	6.7	7.0	5.7	7.0	6.5
	4.5	6.4	5.3	7.0	5.9	5.8	3.8

A: 55% Al-Zn

G: Galvanized

S<sub>c</sub>:S<sub>a</sub> cathode-to-anode surface ratio

(a)

d cathode-to-anode separation

c C Cathode (steel) A: Anode (coating) d: Distance (1.7, 4.5 mm) s: Spacer

Fig. 2—Arrangement for study of CP with separation between cathode (steel) and anode (coating). Separation (d) between anodic and cathodic plates was with rectangular plastic spacers (s).

(b)



μΑ							
$S_c:S_a$	d <sub>c-a</sub> , mm	1 day A G		3 days A G		7 days A G	
1:1	1.7	32.5	30.7	31.2	28.4	25.9	28.0
	4.5	35.6	39.4	36.3	35.8	40.4	34.2
14:1	1.7	39.6	40.3	35.8	29.7	33.7	35.9
	4.5	39.8	41.9	35.0	43.7	38.2	40.4
A: 55% Al-Zn G: Galvanized $S_c:S_a$ cathode-to-anode surface ratio $d_{c-a}$ cathode-to-anode separation							

measurements of galvanic potentials were made by placing a saturated calomel electrode in the device shown in Fig. 2b, then connecting a millivoltmeter to the tails and waiting for the measurement to stabilize.

# Results and Discussion

#### Distilledwater

With the 14:1 surface ratio, the steel remained protected for only three hr with the 55-percent Al-Zn coating and one day with the galvanized coating. With the 1:1 surface ratio, the duration of the protection was one day with the 55-percent



41 days

Fig. 3—Results obtained without separation (in distilled water).

Al-Zn coating and approximately 40 days with the galvanized coating (Fig. 3).

The reason for the considerable degree of protection afforded by the galvanized coating when the cathodic and anodic surfaces are equivalent is that the attack initially suffered by the zinc gives rise to a sufficient concentration of Zn+2 ions in the vessel to make the medium appreciably conductive (Table 1). This increase in the conductivity of the medium would not occur in the layer of

electrolyte existing on the metal during atmospheric exposure, and would explain why galvanized steel is not capable of providing effective and lasting CP in rural and moderate urban type atmospheres.<sup>2</sup>

The galvanic currents obtained in the steel-coating galvanic couples (Table 2) are notably greater in the tests carried out with a 1:1 surface ratio. The low values obtained for the 14:1 surface ratios agree with the fact that the protection provided by the anodic material was insufficient. The considerable difference found in the current magnitudes in the two situations is easily understandable, bearing in mind the high

resistivity of the medium and the geometry of the test. When the surface ratio is 1:1, the whole anodic surface is completely face to face with the cathodic surface, there then being a uniform distribution of the current lines. With the 14:1 surface ratio, however, which involves a circular anode of 5 mm diameter facing a cathode with a greater surface area (19 mm diameter), it would be more difficult for the anodic protection current to reach the rest of the cathodic surface (the opposite facing area). The high resistivity of the medium would dissipate the current lines that would otherwise "connect" the anode with the peripheral cathodic zones.

With reference to the current values displayed in Table 2 for the 1:1 cathode-to-anode surface ratio, it is possible to detect a certain effect of the cathode-anode separation on the magnitude of the galvanic current. These differences are most predominant in the case of the 55-percent Al-Zn coating, and could be attributed to a certain passivation of the coating in this medium with time. With the galvanized-steel couple, however, this effect decreases with time, a fact which may be attributed to the aforementioned dissolution of zinc, which would make the medium progressively more conductive during the test.

To facilitate the comparison of the galvanic current measurements, and taking into account

Table 5					
Galvanic Currents of Steel-55% Al-Zn Galvanic					
Couple in Conductive Solution*					
uδ					

Anode diameter, mm	Cathode diameter, mm	3 hr	1 day	3 days
5	5	6.8	21.0	18.8
5	13	35.0	41.8	39.4
5	19	55.5	57.1	53.3
13	19	71.0	65.9	49.3
19	19	74.2	56.7	54.0

\* 0.4%  $(NH_4)_2SO_4 + 0.5\%$  NaCl (Prohesion solution) Separation: 4.5 mm

the different anode and cathode surfaces considered in the study, it has been decided to express the magnitude of the galvanic currents in intensity units instead of current densities.

#### Five-percent Sodium Chloride

Visual evaluation of the submerged specimens, with continuity between the cathode and the anode, shows that the 14:1 surface ratio is insufficient to protect the steel with either material, the presence of abundant rust being found on the

cathode after two days of testing. When the cathode-to-anode surface ratio is 1:1, however, the CP afforded by the two types of coatings is maintained throughout the entire test (more than 40 days; Fig. 4). The results obtained with the 1:1 surface ratio confirm conclusions reached by the authors in a previous publication<sup>2</sup> (Table 3), where both coatings afford effective CP to the base steel from scratches. The salinity of this medium makes it possible for chloride ions to break the passive layer, which the 55-percent Al-Zn coating spontaneously develops upon contact with the atmosphere.<sup>7</sup>

When analyzing the galvanic current data (Table 4), it is seen that the values for the 14:1 surface ratio are generally slightly greater than those corresponding to the 1:1 ratio. This implies that the 1:1 ratio would be close to the surface ratios corresponding to the maximum drainage of current that the anodic material is capable of providing. The 14:1 surface ratio is therefore so high that it causes the anodic material to act by providing the maximum possible current, but not enough to achieve effective and lasting CP. On the other hand, for the 1:1 surface ratio, the anode output current has values somewhat lower, but sufficient to provide lasting CP to the steel.

To justify the relative similarity between the current values obtained for both surface ratios in a conductive solution, a study was carried out, in which, for a separation distance of 4.5 mm between the steel and the 55-percent Al-Zn coating, galvanic currents of this galvanic couple were measured, modifying the cathodic surface for a similar anodic surface and vice versa. Table 5 lists the values, in  $\mu$ A, recorded for times of 3 hr, 1 day and 3 days. From the analysis of these data, a clear cathodic control can be inferred in this medium, as the most notable differences between the currents are found when the cathodic surface is varied and the anodic surface kept constant.

In highly conductive media, the ohmic resistance of the electrolyte is negligible, and given that the polarization resistance of the anode is much lower than that of the cathode, it is reasonable to conclude that the process should be controlled by the polarization resistance of the cathode, and therefore by its surface area.

In a resistive medium, such as distilled water, the ohmic resistance of the

electrolyte would be the fundamental part of the circuit's resistance and, therefore, in principle, the value of the galvanic current would be controlled by the anode-cathode separation distance, although as has been argued above, the surface ratio is also an influencing factor.

In 5-percent sodium chloride, the separation distance between the cathode and anode is not seen to affect the degree of protection that both coatings afford to the steel, although the current magnitude is slightly higher when the distance is 4.5 mm. The values of the galvanic potentials of the steel-

$$S_{C}: S_{A} = 1:1$$

$$S_{C}: S_{A} = 14:1$$

36 days Fig. 4—Results obtained without separation in 5% NaCl.

Table 6
Galvanic Potentials of Coated Steel Galvanic Couples in 5% NaCl
mV

mV <sub>sce</sub>	
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S.:S.	d <sub>ea</sub> , mm	1 day		3 days		7 days	
t a	c-a	Α	G	Α	G	Α	G
1:1	1.7	-1016	-1039	-983	-1043	-949	-1036
	4.5	-1017	-1040	-1009	-1030	-967	-1026
14:1	1.7	-939	-1021	-936	-1009	-917	-989
	4.5	-933	-1016	-908	-996	-828	-890
	A: 55% Al-Zn						

G: Galvanized

S<sub>2</sub>:S<sub>2</sub> cathode-to-anode surface ratio

d<sub>a</sub> cathode-to-anode separation

coating galvanic couples (Table 6) indicate that, at least during the testing time shown in this table, both types of coating are cathodically protecting the steel by maintaining it within the zone of immunity (E<sub>SCE</sub><-860 mV, critical potential). These potentials can also be seen to be more negative in the case of the 1:1 surface ratio, which seems to indicate greater duration of CP in this case than the 14:1 surface ratio.

The shift in galvanic potential toward more negative values than the critical potential, which would move the steel in the immunity zone, is more pronounced for the galvanized coating than for the 55-percent Al-Zn coating.

The galvanic potentials of the steel-coating galvanic couples increase with time, and are generally to be found in the immunity region of the steel. These results agree with those obtained by Dalledone et al.5 For the 14:1 surface ratio, however, evidence of rust was already seen after two days of testing. Although the test with separation between the cathode and anode does not exactly reproduce the results obtained in the test with continuity (as the cathode and anode areas in the former are always at the same distance), greater concordance was to be expected between the appearance of rust observed for the 14:1 surface ratio and the corresponding values of the galvanic potential. Accordingly, although these values indicate CP offered by both coatings, the existence of some points of corrosion on the cathodic surface is not excluded. Globally, the cathodic surface would be protected; however, this protection would not reach the entire surface.

# Conclusions

1. The surface ratio of the galvanic couple is a determining factor in the effectiveness and duration of the CP afforded by the coatings.

a. In a conductive medium (5-percent NaCl), and for a 1:1 cathode-to-anode surface ratio, both coatings provide effective CP. The galvanic potentials are situated within the immunity region of steel and the values of cathodic current density are greater than those corresponding to distilled water, where the anodic action of the coatings is more restricted.

b. For a 14:1 cathode-to-anode surface ratio, the steel does not receive complete CP in either of the two media studied.

c. The conclusions reached in this study agree with field data previously obtained by the authors in relatively unpolluted (rural and urban) and marine atmospheres.<sup>2</sup> 2. The cathode-anode separation distances considered in the study, 1.7 and 4.5 mm, do not affect the galvanic behavior of the coatings in 5-percent sodium chloride. They acquire a certain importance only in the case of the 55-percent Al-Zn coating in distilled water and for a 1:1 surface ratio.

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