Electrochemical Study of Lap-Joint Corrosion of Steel with Metallic Coatings

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This paper analyzes the lap-joint corrosion susceptibility of steel with four different types of protective metallic coatings (hot-dip galvanized, galvannealed, electrogalvanized, and 55% Al-Zn). Measurements are made using electrochemical impedance spectroscopy (EIS) and current electrochemical noise with specially designed sensors. The results obtained indicate the importance of the crevice water retention for determining the risk of corrosion of lapped parts.

INTRODUCTION

The technology of precoated products in the steel industry has developed rapidly over recent decades, producing higher quality materials that have applications in the automobile and construction industries. In both of these industries it is common practice to overlap materials by different methods during the manufacturing of the final product. For instance, precoated steel is often used in lap or hem joints in manufactured vehicles, and the lapping of precoated steel plates (painted or not) is commonplace in the construction of large sheds and buildings. The premature failure of coated steel parts or structures when exposed to the atmosphere is often due precisely to corrosion processes that are initiated in the lap zone. However, very little research has been published in relation to this specific type of degradation.This research basically reports the results of accelerated natural exposure testing of different materials,[1-3] and there are gaps in basic knowledge about the corrosion processes that occur in the interior of these joints.

Electrochemical techniques, which are capable of offering quick and reliable information about the corrosion process, have been applied in a very limited way in lap joints,[4] probably due to the difficulty of accessing the lapped zone. Electrochemical impedance spectroscopy (EIS) has proven to be a valid tool for studying the degradation of metals with organic[5,6] and metallic coatings.[7] Recently, it has also been used to analyze the corrosion behavior of organic coatings in lapped zones.[8,9] However, the bilaminar sensors proposed for painted metals in the aforementioned studies cannot be directly used in the case of lap joints between bare metals or metallic coatings, since there will be a short-circuit between the two parts of the sensor.

This work studies the lap-joint behavior of steel with two types of metallic coatings frequently used in the construction industry (hot-dip galvanized and 55% Al-Zn) and two types of coatings frequently used in the automobile industry (electrogalvanized and galvannealed). For this purpose a new bilaminar sensor is proposed, which in fact is a modification of that previously used to study the lap-joint corrosion of unpainted metals.[9] This sensor is used to study the capacity of EIS to supply information about the corrosion of metallic coatings on steel in the lap zone, and a discussion is presented of the relative importance of the different factors intervening in the degradation process. The same type of sensor is also used to make current electrochemical noise measurements, whose capacity to provide interesting semiquantitative information about corrosion intensity has already been demonstrated in other systems.[10-12]

Multilaminar sensors (MS), previously used in studies of atmospheric corrosion,[13,14] confine in well-defined geometric areas the anodes and cathodes of the micropiles responsible for the corrosion. It was decided to test the possibilities of MS to study the driving force of the piles responsible for corrosion at lap joints.

EXPERIMENTAL

Four types of bare metallic coatings were studied: 55% Al-Zn (150 g m^{-2} and 20 µm nominal thickness), hot-dip galvanized (225 g m^{-2} and 20 µm nominal thickness), electrogalvanized (18 g m^{-2} and 5 µm nominal thickness), and galvannealed (56 g m^{-2} and 10 µm nominal thickness).

Specimens of 125 × 50 mm were constructed by overlapping two parts of 75 × 50 mm of the material under study (*Figure* 1). Thus, a lapped area of 25 × 50 mm was obtained, of which only 25 × 30 mm acted as testing area,

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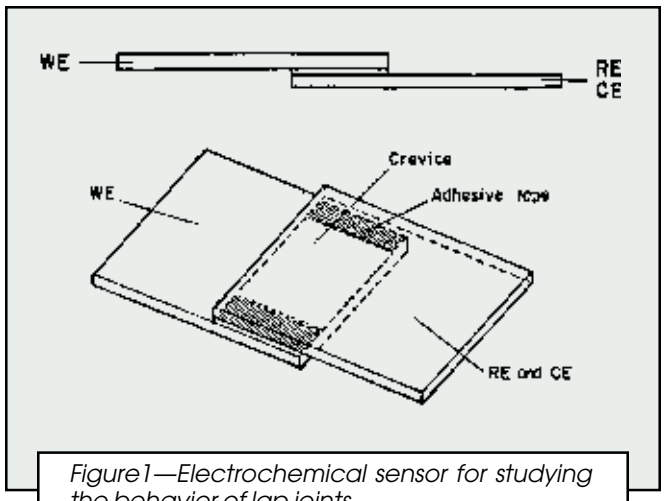

Figure 1—Electrochemical sensor for studying the behavior of lap joints.

due to the application of adhesive tapes at the sides to act as separators, to impede electrical short-circuits between the two parts of the lap joint. Crevices of 100 and 200 µm were obtained using separators of different thicknesses.

All the specimens were submerged for half an hour in distilled water, in order to ensure similar filling of the crevice to that produced by heavy rainfall, and were then exposed for one month in a humidity cabinet (atmospheric relative humidity (RH) of around 95%) and in the much drier laboratory atmosphere (RH about 50%). After one month of exposure, the specimens were once again submerged for half an hour in distilled water and then returned to their original atmospheres.

The response of the lap joints was monitored by EIS and electrochemical noise measurements (ENM). Impedance was recorded using a system comprised by a PAR 273A potentiostat and a Solartron 1255 transfer function analyzer. During the impedance measurements one part of the bilaminar sensor acted as working electrode and the other as counter electrode and reference electrode.

Spontaneous current oscillations between the two overlapped laminae of the sensors at their corrosion potential were recorded with a zero resistance microammeter, model AutoZRA by ACM Instruments. Data was acquired each 0.25 sec for 1024 sec, making four consecutive measurements whose results were then averaged for each type of sensor in each situation. Before making the statistical analysis of the data, a process was carried out to eliminate the tendency, when this existed, in order to correct the variation of the average current value during the data acquisition time. In these cases, the data obtained was adjusted to a straight line, and the difference at each moment between the measured value and the value of the adjusted straight line was considered as noise.

For reference purposes, EIS measurements were also made for steels with the same type of coatings but without lapping and totally submerged in distilled water. In this case an electrochemical cell with a traditional three-electrode configuration was used. A stainless steel wire was used as counter electrode, a saturated calomel electrode as reference, and coated steel specimens with a surface area of 133 mm^2 exposed to the distilled water as working electrode.

In the construction of MS, use was made of eight identical laminae of steel, of 80 × 30 × 3 mm. The laminae were juxtaposed, separated by isolating plastic sheets of 0.170 mm thickness. The laminae were short-circuited in two different blocks, one constituting the working electrode and the other the reference electrode. The assembly was set in a self-hardening resin, polishing one of the sides to be exposed to the environment. For lapped MS, the crevice was formed with a plastic sheet that shielded one block of laminae, while the other was directly exposed to the electrolyte.

RESULTS

Figure 2 reproduces the impedance results for the four different metallic coatings at the start of exposure, after only one hour in a humidity cabinet, for the case of crevices of 100 µm thickness. With crevices of 200 µm thickness, similar high frequency impedance measurements were initially recorded for each material, though the low frequency impedance was systematically higher than that detected in narrower crevices. In *Figure* 3 it can be seen that the initial low frequency impedance values of the lapped materials (which are inversely proportional to their corrosion rates) are comparable to those measured for fully submerged free surfaces of the same material.

For all the coatings, the impedance at all the measured frequencies increased with exposure time. The increase in impedance occurred very quickly in dry atmospheres (*Figure* 4) and more slowly in environments with a high RH (*Figure* 5). These increases in impedance with time were occasionally more pronounced for the coatings that initially presented lower corrosion resistance (minor low frequency impedance). The differences initially seen between the impedance values measured with specimens of different materials observed at the start ceased to be so clear (*Figure* 6).

With all the specimens, rehumidification of the lap joint led to a substantial drop in impedance, with responses similar in all cases to those initially obtained (see example in *Figure* 7).

The spontaneous current oscillations between the two laminae of the sensor have a noise whose standard deviation evolves in time inversely to the impedance, as can be seen in *Figure* 8. In all the sensors used in this research, irrespective of the material with which they were manufactured and the width of the crevice, a decrease in the current noise was detected as exposure time progressed, as well as a sudden rise in this parameter, approximately to the original values, after re-immersion.

When the sensors were dismantled after the electrochemical measurements, visual observation of the lapped surfaces of the specimens confirmed that the corrosion products were always much more abundant in the lapped zone that bordered the free surface, and that the lap was therefore a preferential attack zone. It was also seen that there were no significant differences in corrosion intensity between specimens of the same material, irrespective of width of the crevice. With the electrogalvanized and galvannealed specimens, in addition to the zinc corrosion products that appeared on all the sensors, reddish corrosion products characteristic of iron were also detected, mainly in this border zone.

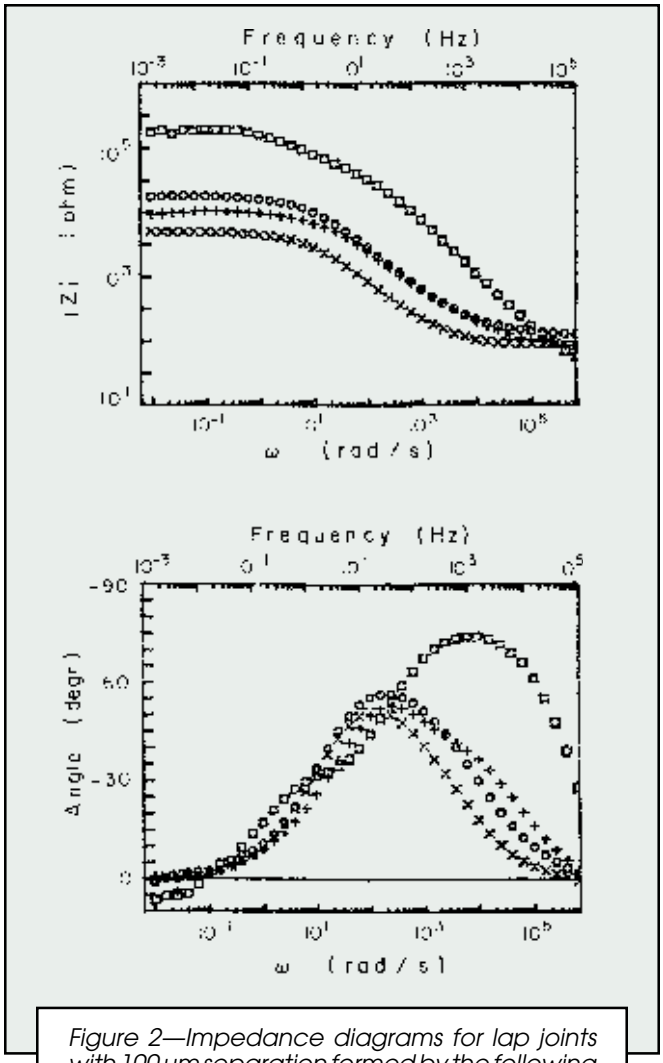

Figure 2—Impedance diagrams for lap joints with 100 µm separation formed by the following coatings: (x) electrogalvanized, (+) hot-dip galvanized, (●) galvannealed and (❑) 55% Al-Zn, after one hour of holding in an atmosphere of high RH.

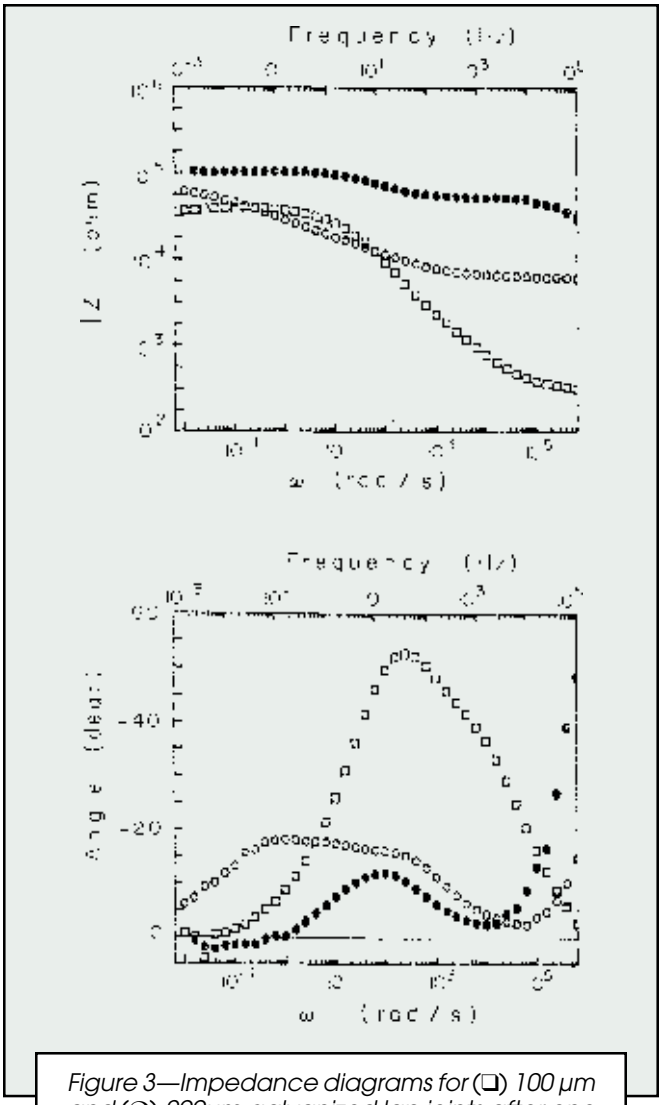

Figure 3—Impedance diagrams for (❑) 100 µm and (○) 200µm galvanized lap joints after one hour in a 95% HR atmosphere, and for (●) not-lapped galvanized steel after one hour fully immersed in distilled water (impedance data per cm² of sensor).

In submerged MS, the difference of the corrosion potential of the shielded laminae and those directly exposed to the electrolyte increased with time, as can be seen in *Figure* 9. This difference was up to 200 mV higher than the differences that can be measured between the corrosion potentials of the two blocks when none of them was lapped.

DISCUSSION

In the impedance diagrams obtained it is possible to observe several time constants, which are often superposed. The capacitive behavior of the distilled water layer trapped in the lap, C_e, and above all the resistance that this water offers to the passage of the electrical signal, R_e, is what determines the high frequency impedance. For this reason the impedance of this zone of the spectrum is greater in wide crevices than in narrow crevices (*Figures* 3 and 6). Due to the configuration of the electrochemical cell used in the sensors, with only two electrodes instead of the more typical three, the impedance measured at lower frequencies is the sum of the individual impedances of each of the two laminae (or electrodes) that comprise the cell.[15] In other words, impedance at medium and low frequencies is determined by the sum of the corrosion processes experienced by the two laminae that form the lap. The circuit in *Figure* 10a, which displays the time constant of the electrolyte (C_e and R_e) and of the protective coating degradation processes on each electrode (R_{p1}-C_{dl1} and R_{p2}-C_{dl2}), simulates the electrochemical response of this type of sensor. An example of the good fitting obtained by simulating the experimental spectra with the equivalent circuit in *Figure* 10a can be seen in *Figure* 11, though it should be noted that the small inhomogeneities existing on the surface of the sensors and in the distribution of the electrolyte layer on it mean that C_e, C_{dl1}, and C_{dl2} do not act as real electrical capacitors and that in the simulation of

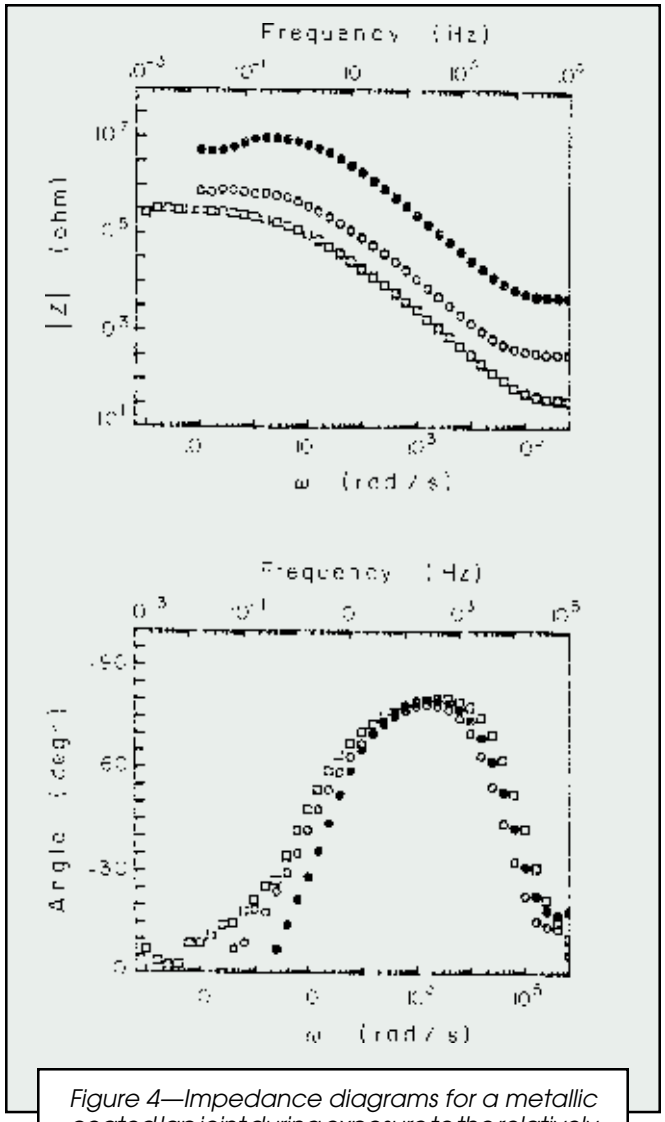

Figure 4—Impedance diagrams for a metallic coated lap joint during exposure to the relatively dry atmosphere: (❑) one hour, (❍) three hours, and (●) six hours of exposure.

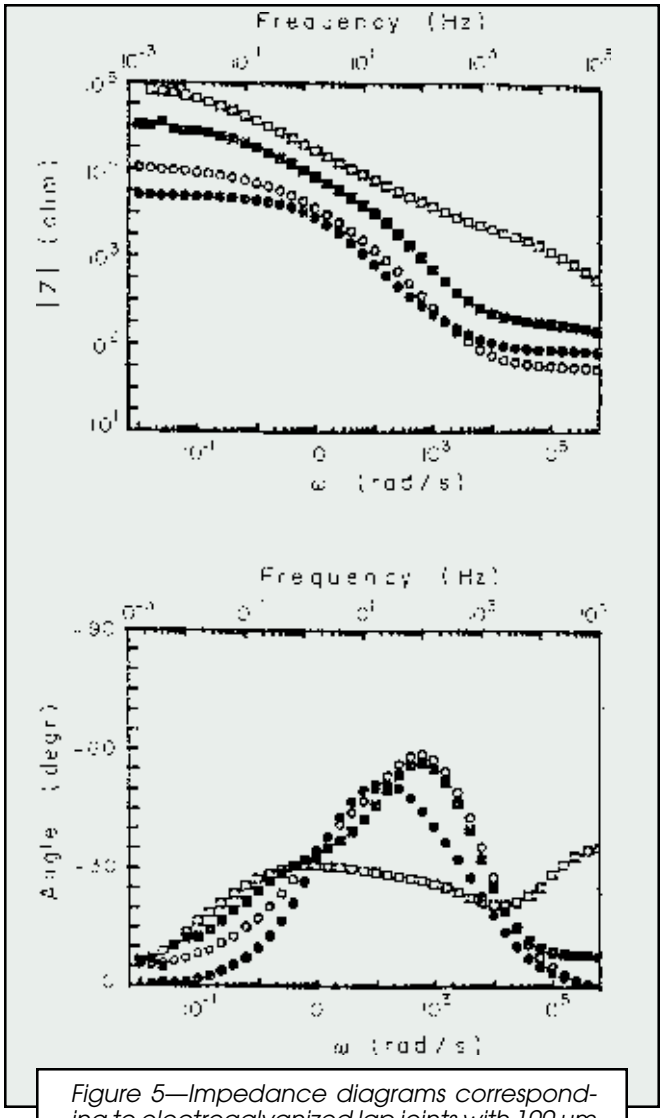

Figure 5—Impedance diagrams corresponding to electrogalvanized lap joints with 100 µm separation, for exposure times of: (●) one hour, (❍) two days, (■) seven days, and 14 days at high RH.

their response it is necessary to resort to the use of constant phase elements, CPE.[16]

The circuit in *Figure* 10a can be simplified in some cases, transforming it into a simple Randles type circuit, such as that shown in *Figure* 10b. The reason for this is that the value of C_e is often so small that it is undetectable in the frequency interval used in the measurements, and R_e is sufficient to simulate the contribution of the electrolyte layer to the impedance. Furthermore, at times the electrochemical behavior of the sensor's two laminae is so similar that it is impossible to distinguish the contribution of each electrode to the signal, even when resorting to mathematical operations. In these cases, the impedance at medium and low frequencies is determined exclusively by R_p and C_{dl}, R_p in reality being the sum of R_{p1} and R_{p2} ($R_p \approx 2\,R_{p1} \approx 2\,R_{p2}$) and $1/C_{dl}$ the sum of $1/C_{dl1}$ and $1/C_{dl2}$ ($C_{dl} \approx 0.5\,C_{dl1} \approx 0.5\,C_{dl2}$). *Figure* 12 shows an example of how in some cases the simulation of an experimental impedance spectrum with a simplified equivalent circuit can be good.

From a practical point of view, *Figure* 2, without any further mathematical analysis, shows that the 55% Al-Zn alloy offers 10 times greater corrosion resistance at the initial moments than the rest of the coatings tested, which all show quite similar behavior. Though the differences are sometimes small, the following order could be established between the different coatings, from lesser to greater corrosion resistance:

electrogalvanized < hot-dip galvanized < galvanneal << 55% Al-Zn

In fact, this classification of corrosion resistance in humid lap joints is the same as can be proposed when studying the behavior of these metallic coatings without lapping. The initial corrosion rates in lap joints are very similar to those experienced by the same materials when fully submerged (*Figure* 3), and they are obviously higher than those measured on surfaces directly exposed to the atmosphere.

The fact that iron corrosion products appear in the lap of the galvannealed sensors, but not in the galvanized

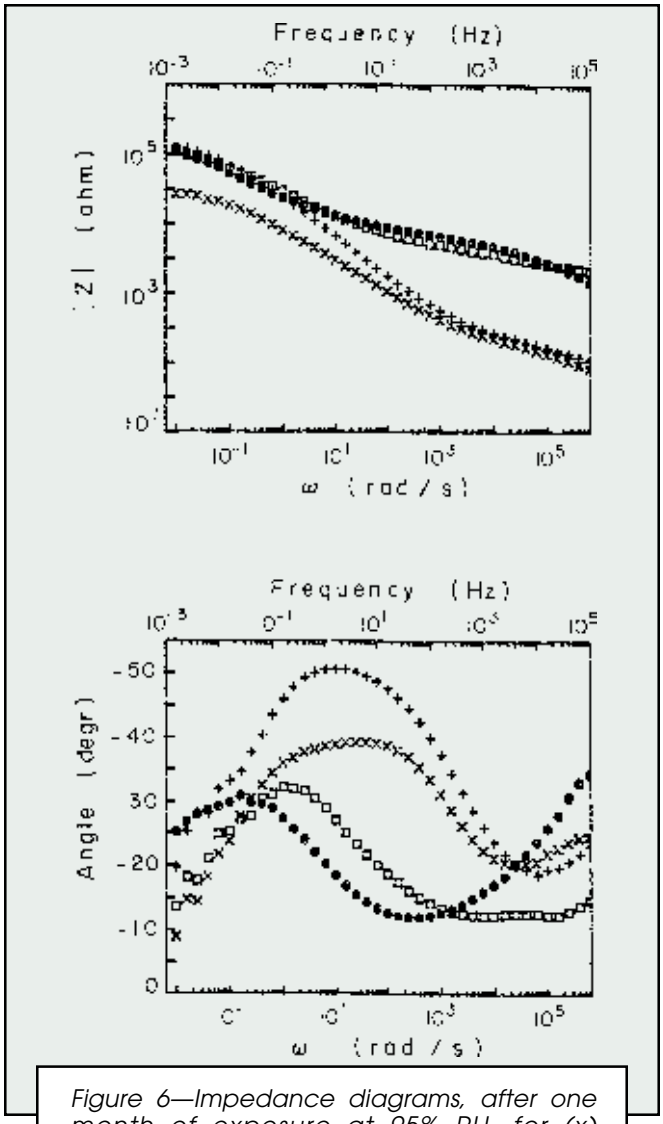

Figure 6—Impedance diagrams, after one month of exposure at 95% RH, for (x) galvannealed and (+) 55% Al-Zn lap joints with 100 µm separation, and for (●) galvannealed and (□) 55% Al-Zn with 200 µm separation.

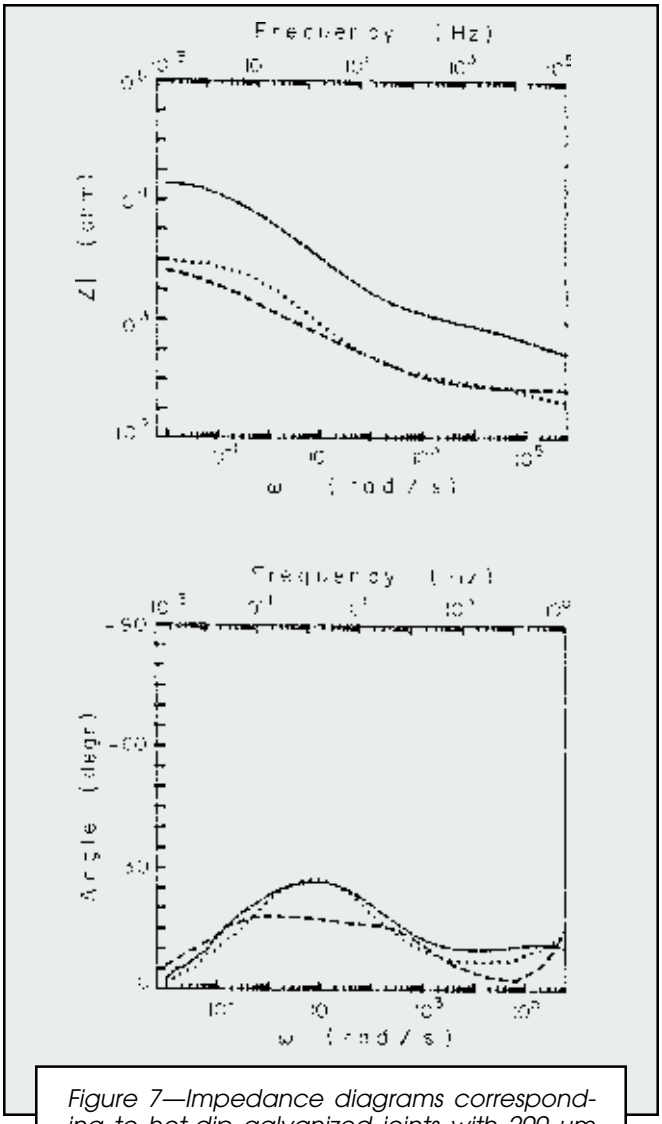

Figure 7—Impedance diagrams corresponding to hot-dip galvanized joints with 200 µm separation, for exposure times of: (---) one hour, (——) one month at high RH, and (.....) one month + immersion + one hour.

sensors, is not due to a lower corrosion rate of the galvanized material but is a result of the fact that in the latter case the protective coating has twice the thickness.

Unlike impedance, current noise alone does not permit differentiation between the different corrosion rates initially presented by the sensors of the different materials (*Figure* 8).

The progressive drying of the crevice during the exposure time in practice means a reduction in the volume of electrolyte, and thus an increase in R_e that can be seen in the high frequency impedance spectra. The decrease in the corrosion rate with exposure time can also be attributed to the progressive drying of the crevice: the low frequency impedance (*Figure* 5) increases and the current noise decreases (*Figure* 8) as the wetted area diminishes. For this reason, the changes are very fast at low RH (*Figure* 4) and slower at high RH. The great similarity of the electrochemical measurements to the initial values when the crevice is rehumidified (*Figures* 7 and 8) definitively confirms this hypothesis, especially if the small distortions that can be introduced in the spectrum by the appearance of corrosion products on the surface of the specimens during the month of exposure are accepted.

After a sufficiently long exposure time, the influence of the crevice drying rate means that the nature of the coatings ceases to be the only factor that determines the intensity of attack in the lapped zones (*Figure* 6). The effect of the crevice's width on its water retention capacity is not simple to evaluate, because though the water evaporates to a greater extent when the crevice is wider, its volume is also greater. Both factors must balance each other out, at least for crevices around 100 and 200 µm in thickness, since with the same type of material no significant differences are appreciated in corrosion rates after one month of exposure for crevices of different widths (*Figure* 8).

The fact that the attack in the lapped zone is fundamentally concentrated in the region closest to the free surface is justified, considering the activity of the differential oxygen concentration cells. The results shown in *Figure* 9

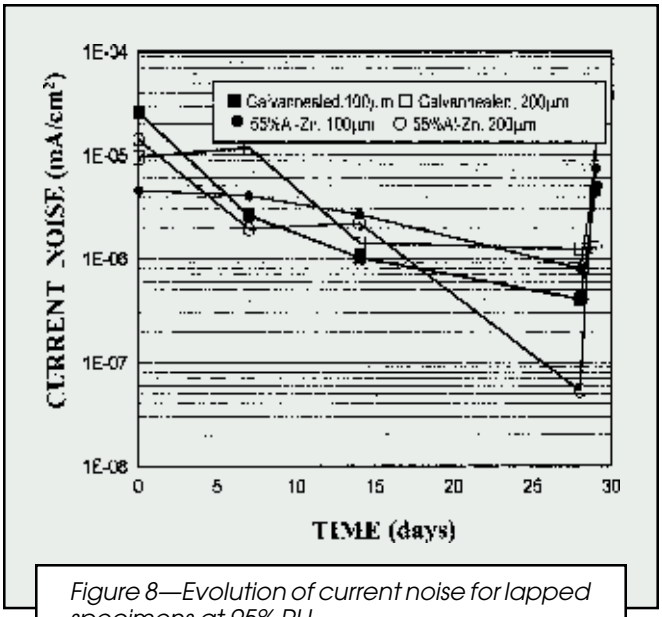

Figure 8—Evolution of current noise for lapped specimens at 95% RH.

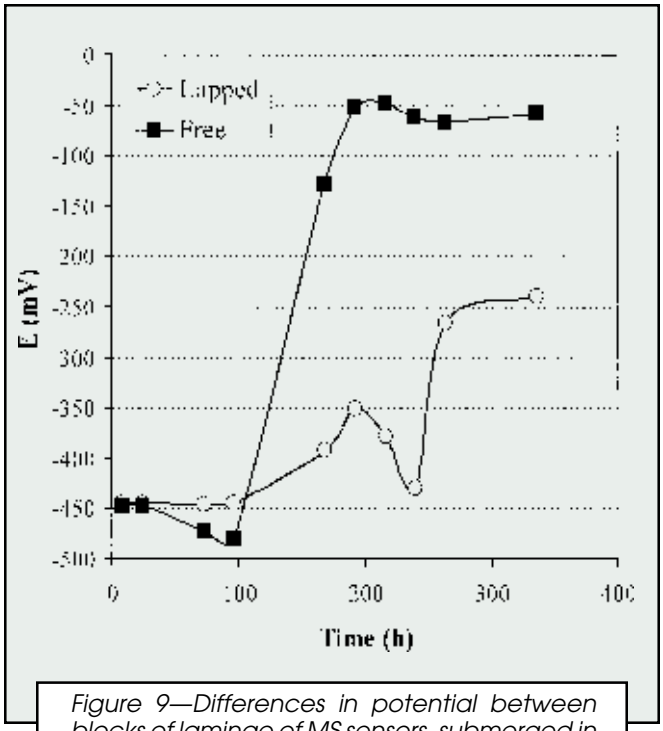

Figure 9—Differences in potential between blocks of laminae of MS sensors, submerged in distilled water.

prove that the crevices increase the driving forces of the attack. The corrosion potential of shielded laminae became with time more anodic than the corrosion potential of the ones directly exposed to distilled water. The cause of this behavior may lie in the progressive consumption of oxygen, which would be renewed with difficulties below the crevices in the case of shielded laminae. Differential aeration cells appeared near the border between lapped and free surfaces and corrosion was enhanced by Evans effect. However, in this case, and due to the design of the bilaminar sensors, the galvanic corrosion of Zn, induced by the bare steel edge of the sensor's superposed lamina, may also contribute to corrosion to a certain extent.

The initiation of corrosion at some isolated points on the base metal, as occurs with the electrogalvanized and galvannealed materials after a certain exposure time in a high RH atmosphere, is unfortunately difficult to detect by means of electrochemical techniques. Corrosion of the base steel in these cases affects a very small area of the specimen, which means it offers much greater resistance to the passage of the electrical perturbation than that presented by the surface of the coating which is being attacked, with which the electrochemical response obtained corresponds almost exclusively to the corrosion suffered by the coating.

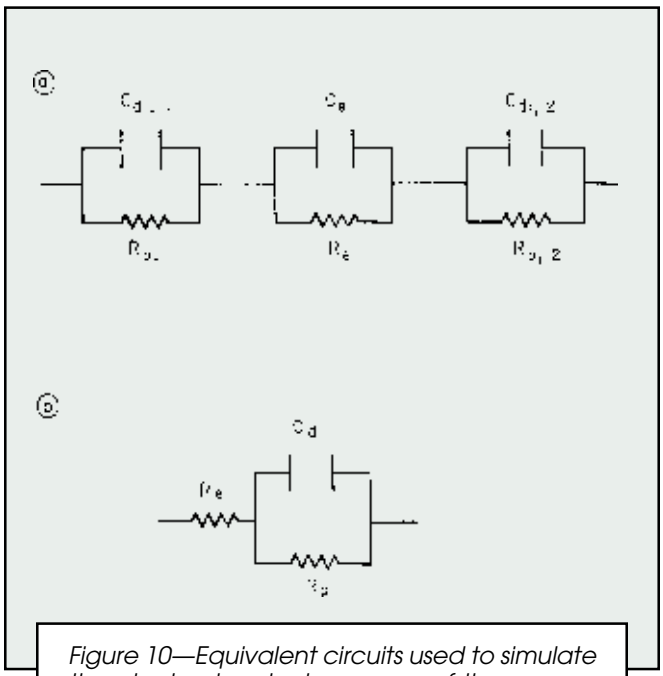

Figure 10—Equivalent circuits used to simulate the electrochemical response of the sensors. R_e: Resistance of the electrolyte between the sensor's laminae; C_e: Capacitance of the electrolyte; R_{p1} and R_{p2}: Polarization of each of the sensor's laminae; C_{dl1} and C_{dl2}: Double layer capacitance of each of the sensor's laminae; R_p and C_{dl}: Polarization resistance and double layer capacitance of the two parts of the sensor in conjunction.

CONCLUSIONS

The electrochemical sensors that have been designed, together with the use of EIS, permit the study of the degradation of metals in the lap zone. The proposed study method makes it possible to separate, by careful mathematical analysis of the data, the contributions of each element when the corrosion process presents a different intensity on each lamina.

The corrosion rate in the lap zone is fundamentally determined by the wetted area, and thus the hazardousness of the presence of crevices will depend on their water

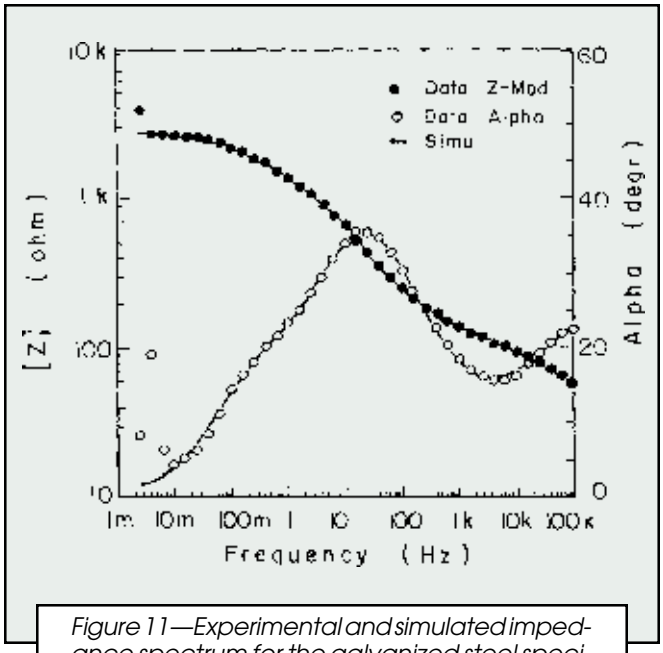

Figure 11—Experimental and simulated impedance spectrum for the galvanized steel specimen with 100 µm separation after two days of exposure at high RH, using the equivalent circuit of Figure 9a: (●) experimental impedance modulus, (○) experimental phase angle, and (—) simulated data.

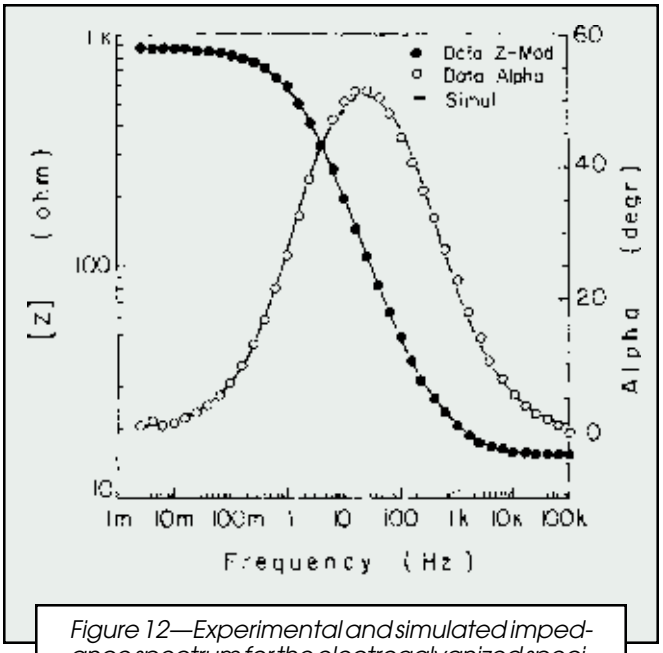

Figure 12—Experimental and simulated impedance spectrum for the electrogalvanized specimen with 100 µm separation after one hour of exposure at high RH, using the equivalent curcuit of Figure 9b: (●) experimental impedance modulus, (○) experimental phase angle, and (—) simulated data.

retention capacity, which depends on their design and orientation, and on the RH of the environment.

The corrosion rates of the different metallic coatings in the crevices, when these are totally saturated with electrolyte, are proportional to their corrosion rates in immersion conditions.

Corrosion does not occur uniformly throughout the lapped zone but takes place preferentially in the zone close to the free surface of the sensor, due to the formation of differential aeration cells.

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