

EVALUATION OF THE PROTECTIVE PERFORMANCE OF SEVERAL DUPLEX SYSTEMS EXPOSED TO INDUSTRIAL ATMOSPHERE

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Abstract—The atmospheric corrosion behaviour of galvanised steel sheets and steel/55%Al-Zn system with or without different paint schemes was analysed. The samples were exposed to the atmosphere in the experimental station of CIDEPINT. Periodically, all specimens were visually inspected and sampling was made to evaluate the general behaviour of the protective system. Normalised physicochemical and EIS tests were performed on each specimen. The corrosion products were characterised by SEM. The data included in the present work concern to the first step of exposure (800 days). The foreseen whole period of testing is 7 years. From the present results may be concluded that: 1) on the analysed industrial environment, the bare sheets of steel/55%Al-Zn system have suffered less damage than the bare galvanised ones, 2) chloride and sulphide are present in the corrosion products denoting the aggressiveness of environment, and 3) in general, all duplex systems have shown a fairly good protective behaviour.

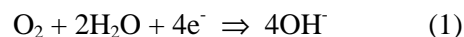
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I. INTRODUCTION

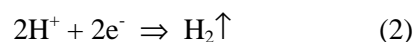
It is well-known that all materials are damaged by the atmospheric conditions, mainly by oxygen, humidity and atmospheric pollutants (SO₂, NaCl, NO_x, etc.); another important degradation source is the global radiation of the sun. From a practical point of view, at ambient temperature and in dry atmosphere, metallic corrosion could be ignored; otherwise, it is important on wet surfaces.

The corrosion mechanism is electrolytic (Feliú and Morcillo, 1982; Rozenfeld, 1972; Kucera and Mattson, 1986). The electrolyte is a very thin film of moisture (a few monolayers), or an aqueous film (a thickness of hundreds of microns) when metals show up perceptibly wet. It is proved that relative humidity (RH) plays an important role in atmospheric corrosion. Below a RH specific level, the corrosive attack is not important because the film of electrolyte on the metallic surface is almost negligible. Generally, the corrosion of iron and other metals is negligible for RH<60-80%, depending on the metal. Though humidity presence is necessary it is not enough to develop corrosion. Even in very humid environments, corrosion of uncontaminated surfaces is often relatively low in unpolluted atmospheres. Among the external factors that are determinant on the corrosion rate definition, it is possible to mention: 1) the lifetime of the electrolytic film on the metal surface, 2) the chemical composition of atmosphere (level of pollutants), and 3) the ambient temperature.

Under the electrolytic film, most of metals exposed to the atmosphere will corrode by coupling with cathodic reduction of oxygen:



although, when the level of contamination with acid products is high, the hydrogen evolution gets importance as cathodic reaction:



with independence of which reaction prevails, the pH on the cathodic region increases. From a certain level of acidity it is possible that the SO₂ of a polluted atmosphere acts as an oxidant able to impart a great acceleration to the cathodic process.

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The O₂ diffusion through the aqueous film is usually the controlling step of the metallic corrosion rate. This corrosion rate increases when the aqueous film thickness decreases, until reaching a maximum at intermediate thickness. A thick film of water hinders the oxygen arrival and, therefore, reduces the attack rate. On the other hand, a very thin film slows down the corrosion process due, not only to the high ohmic resistance, but to the obstruction of ionisation reactions and metallic dissolution.

The stability of metals or alloys in an aggressive environment will depend on the protective properties of organic or inorganic films, as well as on the layer of corrosion products. Some film characteristics, such as chemical composition, conductivity, adhesion, solubility, hygroscopicity, and morphology, determine its ability as controlling barrier to different kinds of attack and corrosion rates (Stratmann *et al.*, 1983). On the other hand, the stated characteristics depend, in turn, on chemical composition and metallurgical history of the metal, on physicochemical properties of coating, and on environmental variables such as atmospheric conditions, type and amount of pollutants, wet-dry cycles, etc. (Stratmann *et al.*, 1983; Stratmann and Streckel, 1990; Pourbaix, 1969). In this sense, a common example is galvanic protection of steel by zinc, due, not only to the preferential corrosion of zinc, but also to the barrier effect of corrosion products.

In particular, the coatings based on Zn are widely used in order to protect steel structures against atmospheric corrosion, because of the protective properties afforded by an insoluble film of basic zinc carbonate (Seré *et al.*, 1997). However, if the exposure conditions are such that there is either depletion of air but high humidity or a medium containing strongly aggressive species like chloride or sulphate ions, the Zn dissolves forming soluble, less dense and scarcely protective corrosion products, which sometimes lead to localised corrosion (Seré *et al.*, 1997; Goodwin, 1990). Studies made by SEM and EDAX on Zn samples exposed for long periods to SO₂ polluted atmospheres reveal that corrosion products are disposed in two layers of different structure; the inner one is stable, adherent, dense and its growth kinetics depends on the SO₂ concentration and the other, porous and less protective, grows continuously (Suzuky *et al.*, 1980). This condition can be reached during the storage and transportation of galvanised steel sheets or when they are exposed to marine and/or industrial

environments. Aluminium coatings have overcome these two factors. Nevertheless, as they cannot provide cathodic protection to exposed steel in most environments, early rusting occurs at coating defects and cut edges; besides, these coatings are also subjected to crevice corrosion in marine environments (ASMs Handbook, 1992).

For years, many attempts to improve the corrosion resistance of zinc and aluminium coatings through alloying were carried out. Although the protective effect by combination of these two elements was known, they were not used until the discovery that silicon inhibits the rapid alloying reaction with steel (Zoccola *et al.*, 1978). Thus, the alloy commercially known as Galvalume[®] or Cinalume[®] arose, and its composition: 55% Al, 1.6% Si, the rest Zn, was selected from a systematic study, providing an excellent combination of galvanic protection and low corrosion rate. Currently, steel sheets coated with this alloy have gained an important portion of the galvanised steel market, mainly in the building, electrodomestic and automotive industries.

In order to be used under specific conditions, the choice of the best organic or inorganic coating should be done taking into account that the longest useful life obtained at lowest cost is the paramount market parameter. Owing to the reactive nature of these coatings, the corrosion products play an important role in the protection mechanism making more difficult the selection process.

Nevertheless, taking in mind the great importance of the electrical and electrochemical properties in the degradation of the metallic substrate/coating system exposed to the atmosphere (Rosales *et al.*, 2000), kinetic and mechanistic analysis can be carried out applying electrochemical and surface analysis techniques (Ito *et al.*, 1988) together with SEM.

In the present work, the corrosion behaviour of either bare or painted steel sheets hot-dip coated with Zn or 55%Al-Zn alloy and exposed to the urban/industrial atmosphere of La Plata (Argentina) along 800 days was evaluated. The studies tending to characterise the formed corrosion products in different exposure times and to elucidate the protection mechanism in each system were carried out by SEM and EDAX complemented with adhesion (ASTM D3359-95) and electrochemical tests. Previous to the last test, the samples were immersed for 1 hour in a solution 0.5M Na₂SO₄ which was used as support electrolyte.

II. EXPERIMENTAL

The samples were made in base of commercially available steel coated sheets, they were degreased with toluene, to ensure surface uniformity, and later coated with the commercially available organic products showed in Table 1; after that, the samples were kept in a dessicator up to starting the test. The coating thickness was measured with an electromagnetic instrument, Elcometer mod. 300, using a bare sheet and patterns of known thickness as reference. The average coating thickness values are summarised in Table 1.

The average atmospheric conditions determined at the experimental station of CIDEPINT were as follows: temperature: 17°C; relative humidity: 77%; rainfall: 1248mm.y⁻¹; concentration of contaminants: SO₂: 6.92mg.m⁻².d⁻¹ and Cl⁻: insignificant.

For the electrochemical tests, the three electrode cell was formed with a Pt-Rh mesh counterelectrode oriented parallel to the working electrode (bare or painted coated metal sheet) and a saturated calomel electrode (SCE) as the reference. The samples were put in contact with the electrolyte (0.5M Na₂SO₄) one hour before the test to allow the humidifying of the organic coating. The impedance spectra, obtained as a function of exposure time, were performed in a potentiostatic mode at a corrosion potential in a frequency range $5.10^{-3} \text{ Hz} \leq f \leq 1.10^5 \text{ Hz}$. The impedance measurements were carried out using a Solartron 1255 frequency response analyser, a Solartron 1286 potentiostat and a PC. The experimental impedance spectra were interpreted in terms of equivalent electrical circuits using a suitable fitting procedure developed by Boukamp (1989).

III. RESULTS AND DISCUSSION

During atmospheric corrosion, in general, the metal is not immersed in large quantities of electrolyte but in contact with thin layers or monolayers of moisture, due to that the corrosion process develops as localised corrosion cells. In that situation, the measurement of the corrosion potential as well as of the resistive and capacitive parameters governing the electrochemical behaviour of the metal/coating interface is not always possible during the atmospheric corrosion (Kain and Baker, 1986; Zhang and Lyon, 1992).

According to Zhang and Lyon (1992), the cathodic process for metals like steel, zinc and copper coated with thin (<100µm) water films reveals a diffusional limiting current whose value depends on the water film thickness. For thinner thicknesses, like in most of the atmospheric corrosion cases, the main cathodic process is controlled by activation. In the case of zinc, due to its high electronegativity, the cathodic process is not sensitive to the water film thickness present on the surface. On the other hand, as it was mentioned earlier, the protective capacity of the corrosion products formed during the atmospheric exposure depends on a variety of properties which are also dependent on the composition and metallurgical history of the metal as well as on the atmospheric variables (Stratmann *et al.*, 1983; Stratmann and Streckel, 1990; Pourbaix, 1969).

The measured corrosion potential values (E_{corr}) point out the metal susceptibility to be corroded. In general, when a value for a given medium is more noble (positive), it will result more resistant to corrosion. As it is possible

Table 1 - Measured thicknesses (µm)

System	Metallic coating	Primer	Top coat	Total thickness
A/Z/SA	18	22	52	92
A/ZA/SA	20	22	52	94
A/Z/SE	18	4	87	109
A/ZA/SE	20	4	87	111
A/Z/SP	18	4	48	70
A/ZA/SP	20	4	48	72

A: steel; Z: zinc coating; ZA: 55%Al-Zn coating; SA: alkyd base paint system; SE: epoxy base paint system; SP: poliuretanic base paint system

to see in Fig. 1a, the corrosion potential evolution for the bare materials (Z and ZA) along the first 560 immersion days is quite different. In the case of Zn, the potentials were always active, their values remained in the range $-1.07\text{V} < E_{\text{corr}} < -1.00\text{V/SCE}$ and were related to the corrosion process (Pourbaix, 1974). These data are in accordance not only with the visual inspection but also with the results obtained by optic and electronic microscopy techniques, which put in evidence a great-developed corrosion process. The surface had big hollows and was full of corrosion products characterised as oxides, chlorides and sulphurs of zinc, these two last due to the presence of pollutant contaminants in the atmosphere. On the other hand, the 55%Al-Zn alloy had a big cathodic area where the reactions described by Eqns. (1) and (2) can take place. In this case, the surface remained

active up to 80 exposure days ($-1.04\text{V} \leq E_{\text{corr}} \leq -1.00\text{V}$) and then, due to the formation of an oxide protective or passive layer, its corrosion potential rose to more noble values. The subsequent shifting to more active potential values was attributed to the remotion of those species by rainwater and the exposition of the bare surface again. Only after 776 exposure days a few amounts of corrosion products, particularly zinc oxides, were found. This fact puts in evidence the preferential dissolution of zinc with respect to aluminium.

The impedance spectra of pure Zn (Fig. 2) may be interpreted in terms of the film structure of corrosion products that is usually formed on the surface. The first time constant (R_1C_1) may be linked with the compact inner layer of ZnO and the second one (R_2C_2) with the external and porous layer of $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$. The semicircle of high

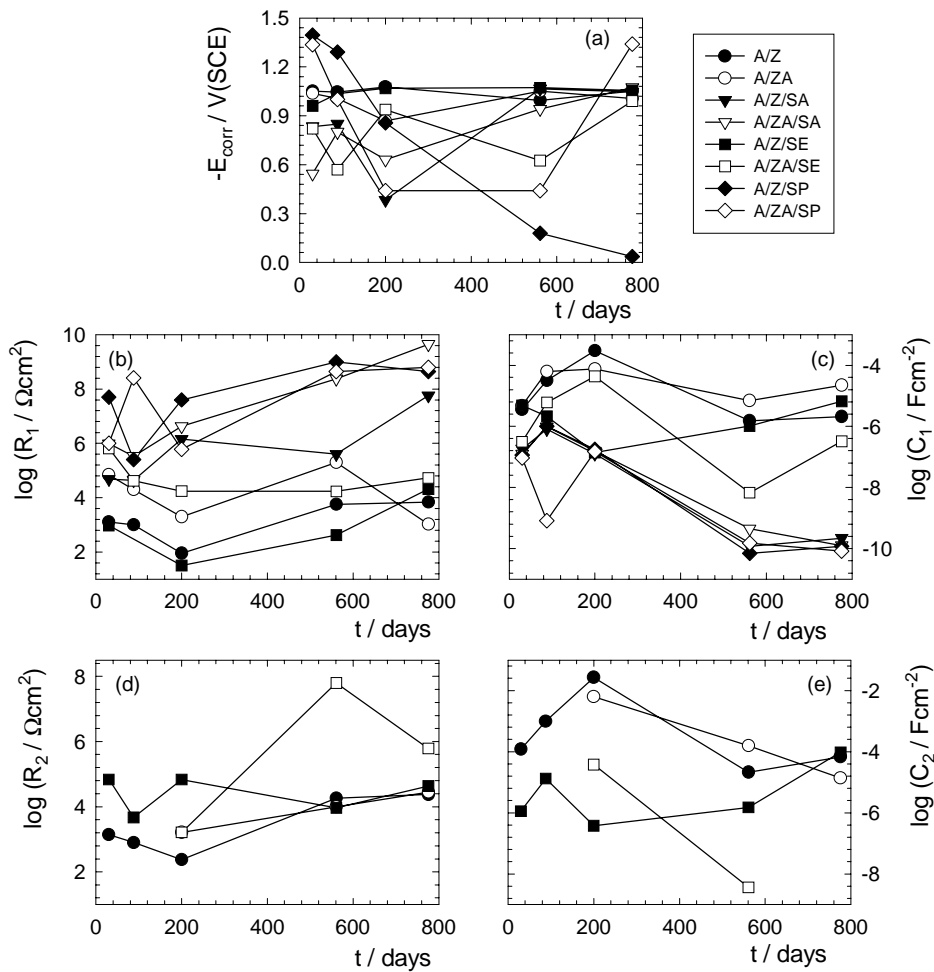


Figure 1. Evolution of the electrical and electrochemical parameters as a function of exposure time

frequencies may be associated with the contribution of the inner layer, that is to say, R_1 and C_1 are the resistance and the capacity of the passive layer of ZnO, respectively, while the second semicircle, linked to the couple R_2C_2 is related to the contribution of the external and porous layer to the impedance of the system. The fluctuations observed in the parameter values along the exposure time were attributed to the development of the complex layer of corrosion products on the surface of such material. This superficial film seems to be the inhibitor of a large dissolution of the base metal although, the atmospheric conditions like rates of rain, wind, humidity, temperature and concentration of pollutants are the determining factors of the corrosion progress due to the competition between the kinetics of film remotion and the formation reactions.

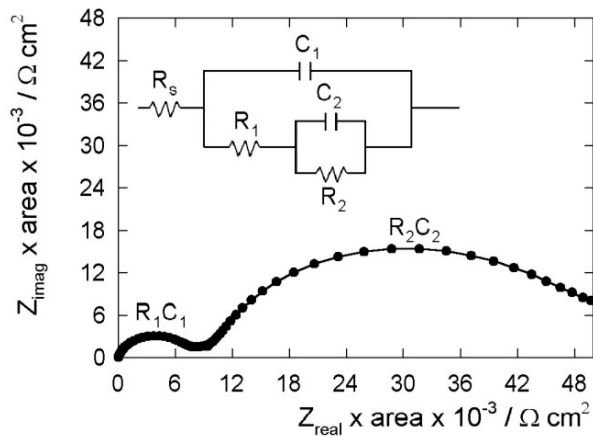


Figure 2. Electrochemical impedance spectrum of pure Zn

For similar exposure conditions, the influence of the coating composition on the formation of the corrosion products contributing to the impedance of the system was put in evidence in the transition time, 200 days, needed by the 55%Al-Zn alloy to define the couple R_2C_2 (Fig. 1d-e). This fact is in accordance with the electrochemical activation showed by the metallic surface through not only the evolution of the corrosion potential (Fig. 1a) but also by the diminishment of the resistance (R_1) afforded by the inner layer of ZnO. Such tendency is probably due to the slimming of the layer thickness (d), which can be deduced from the enlargement of the dielectric capacitance C_1 which is, by definition, inversely proportional to it.

In relation to the painted samples, it was possible to distinguish the electrochemical response of the different applied schemes. In this case, the semicircle of high frequencies was attributed to the organic coating contribution to the total impedance of the system and, particularly, R_1 and C_1 represent, its ionic resistance and the dielectric capacitance, respectively. The semicircle of low frequencies shows the existence of a metallic corrosion process in which the couple R_2C_2 allows to quantize the charge transfer resistance and the electrochemical double layer capacitance. It is important to remark that, in general, faradaic processes taking place on high active electrochemical surfaces are more complex and need more time constants to be described. Nevertheless, the assumed simplification was due to the impossibility to distinguish the different components of the complex reactions taking place on the Zn and 55%Al-Zn alloy surfaces.

When considering the painted systems, only the impedance diagrams of the system A/Z/SE showed both time constants from the beginning of the measurement at 30 exposure days (Fig 1b-e); such poor protection behaviour was confirmed by its evolution since after 560 days the parameter values were comparable to those obtained for zinc and 55%Al-Zn alloy bare coatings. On the other hand, and in accordance with the behaviour showed by the bare metallic coating, for system A/ZA/SE the corrosion process was only defined after 200 exposure days. This fact emphasised the poor protective level afforded by the SE paint system. It is very useful to observe the evolution of the R_2 resistance with time, which is related to the electrochemical active area on the metal. Figure 1d shows that along 800 exposure days, R_2 values for galvanised samples remain quite constant while those of Zn alloy increase. These facts point out that the Zn active area remained practically constant but that of the alloy diminished, probably due to a generalised or localised corrosion process underneath the organic coating for Zn and for the alloy, respectively. The dependence of C_2 on time (Fig. 1e) was explained by its inverse proportionality with such area.

From the point of view of the afforded protection level, the other paint schemes (SP and SA) played a better performance. Along 800 exposure days neither the visual inspection nor the electrochemical impedance measurements allow to detect signs of corrosion. Even with fluctuation, they show a significant increase of the barrier effect (R_1); in the same sense, the diminishment of

C_1 was indicative of an increase in the dielectric capacitance of the organic coating probably due to water expulsion from the film and its replacement by less conductive corrosion products that sealed the pores and/or holes existing inside or under the polymeric matrix. This process produces not only an increase in the resistance to the mass transport from and to the metal/organic paint interface but also the diminishment of the ionic and electronic conductivity of the whole system. Both actions lead to reduce the electrochemically active area on the base metal and, in consequence, improve the anticorrosive protection. Nevertheless, the dependence of the corrosion potential with the exposure time (Fig. 1a) showed that a slow corrosion process was taking place. Particularly for Zn in the A/Z/SP system, the galvanic protection ceases to be effective after 200 days and at this time the barrier effect (i.e. the R_1 value) increases exponentially inhibiting the steel corrosion process. The lack of definition of the second time constant R_2C_2 , corresponding to the faradaic process, is ascribed to its overlapping with R_1C_1 because not only of the paint scheme relaxation but also of the impedance afforded by the accumulation of corrosion products in and/or underneath the paint coating.

The variation with time of the organic film adhesion was evaluated according to the ASTM D 3359-95 standard. The results are shown in Fig. 3. In accordance with these data, the visual inspection showed that the alkyd systems were the most damaged ones.

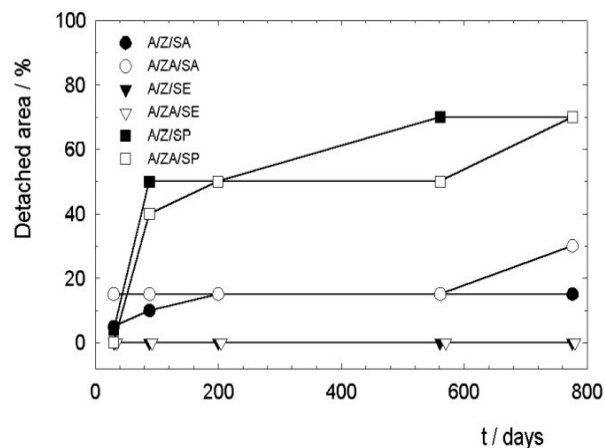


Figure 3. Evolution of the adhesion loss with exposure time

IV. CONCLUSIONS

- For the studied exposure conditions the zinc area remains active along the time while the 55%Al-Zn alloy showed a less activity from 80 exposure days due to the development of a protective oxide layer.
- In general, all the duplex systems showed a fairly good protective behaviour; the most damaged systems were those of alkyd base in which blistering was detected.
- In spite of showing the less adhesion strength, the poliuretanic base system was the one that afforded the higher barrier effect and, in consequence, the best anticorrosive behaviour.

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