Protection of steel and aluminium by inorganic coatings. Results from natural exposure tests.

R. Fontinha, M. Salta

Keywords: atmospheric corrosion, zinc coatings, aluminium, anodised aluminium, pitting

Working Party 14: Coatings

Abstract

An extensive testing program involving natural exposure in marine, industrial and urban environments has been carried out by LNEC for studying the corrosion of aluminium, zinc and the protection of steel by metallic zinc coatings and of aluminium by its anodic coatings. The weight losses were followed during ten years of exposition for all the materials. Analysis of corrosion products composition by X-ray diffraction and electron microscopy with EDS was done on the uncoated metals. The protective action of the coatings was mainly evaluated by the quantification of the corroded area and measurements of pit depth.

R. Fontinha is a research assistant at the Building Materials Department of Laboratório National de Engenharia Civil – LNEC. E-mail: rfontinha Adress: LNEC. Av. do Brasil, 101, 1700 LISBOA, Portugal Fax:+351.1.8473809

Introduction

Zinc coatings and anodic oxidation coatings are often solutions chosen for the protection of steel and aluminium. With the purpose of studying the corrosion behaviour of these inorganic coatings, in 1985, a long-term atmospheric exposition test in different aggressive environments was initiated [1,2]. This paper presents the results obtained from this study during 10 years of exposure concerning zinc, zinc coatings, aluminium and its anodic oxidation coatings with different coating thickness

Materials

The aluminium and zinc alloys chosen for this study, whose composition is given in Table 1, were of current fabrication in sheet form. The zinc coatings studied included: hot dip galvanised, electroplated and metal-sprayed coatings. These were applied on steel sheet by industrial processes in different thickness classes. The anodic oxidation coatings were produced by the sulphuric acid process and steam sealed. Different thickness values of the anodic coating were chosen, corresponding to the classes recommended by the EURAS/EWAA (European Anodisers Association/European Wrought Aluminium Association) for environments of different aggressiveness. The thickness ranges of the coatings are presented in Table 2.

Table 1 – Alloys chemical composition by spectrographic analysis[2]

Alloy	Elements concentration				
	>98,5%	<1%	<0,3%	<0,1%	Traces
Aluminium	Aluminium	Iron, Manganese	Silicon, Copper	Titanium	Lead, Magnesium, Nickel, Vanadium
Zinc	Zinc	Lead	-	Silicon	Iron, Copper, Aluminium, Cadmium

Table 2 – Coatings thickness ranges [2]

Coatings	Galvanised I	Galvanised II	Electroplated I	Electroplated II	Metal Sprayed	Anodised Aluminium
Thickness / μm	29 – 36	15 – 25	14 – 29	6 – 15	130 - 320	15 – 24 30 - 34

The test specimens were cut from the metallic sheets into plates with a 120mm×200mm size, the thickness of the plates ranged from 0,40 mm to 1,45 mm. The zinc coatings were applied to the plates after cutting. Prior to exposure, all the specimens were weighed to the nearest 0,1 mg.

Exposure conditions

For this study five sites in Portugal were chosen, representing urban, marine, industrial and marine-industrial atmospheres. During the first 7-8 years of exposure, *in situ* regular analyses of chloride and sulphur dioxide contents in the air were done, respectively, by the wet candle and the lead dioxide methods[2]. Table 3 shows the results obtained. The time of wetness (TOW) presented was estimated from the temperature and relative humidity (RH) values reported by the Meteorological Institute for the test site areas, from 1985 to1988, considering the number of hours with RH higher than 80% and temperature above 0°C.

Table 3 - Test sites locations and yearly average chloride and sulphur dioxide deposition rates (1985-1993) and estimated TOW values (1985-1988)

Test site	location	Chloride / $mg.m^{-2}.d^{-1}$	SO_2 / $mg.m^{-2}.d^{-1}$	TOW / $h.y^{-1}$
Roca *Marine*	West coast, altitude 140 m, 10 m from the ocean. Frequently under dense fogs during all seasons of the year.	194	6	5028
Barreiro[1] *Industrial - -marine*	near chemical plants (sulfuric acid, fertilizers, etc.) and a fuel burning power generation factory, near Lisbon, on the south banks of river Tagus.	38	136[1]	3388
Lisbon *Urban*	on LNEC's roof, near the airport and roadways of heavy traffic.	7	14	3315
Alfanzina *Marine*	South coast (Algarve), altitude 37 m, 10 m from the ocean.	201	8	1683
Rodão *Industrial*	inside the industrial park of a pulp factory, close to wood chip deposits	5	21	1871

[1]This site has undergone substantial change in its corrosivity during the study, as the SO_2 content in the air has decreased, due to the closing of several factories. During the1985-1989 period, the average values reached 200 $mg.m^{-2}.d^{-1}$, but in the following three years, 1990-1993, this value has decreased to 50 $mg.m^{-2}.d^{-1}$.

The test specimens were mounted to porcelain insulators on racks of painted galvanised steel positioned at 45° to the horizontal, facing south, except in Roca site where they are facing west to enhance the exposure to the saline spray. The lower row of test specimens is 0,75 m above ground. During the 10 years of exposure, several visual inspections have been made, especially in the first years. Triplicate specimens for corrosion evaluation plus one for reference were taken after 6 months, 1 year, 3 years, 5 years and 10 years of exposure. Some of the zinc-coated specimens were taken outside these periods as they became significantly rusted.

Evaluation of results

All the specimens were subjected to visual inspection for assessment of surface condition after each period of exposure. The aspects observed after 10 years of exposure are reported in Table 4.

Table 4 – Surface appearance of test specimens after 10 years of exposure

	Zinc
Roca	Yellowish grey with voluminous yellow-white spots, numerous pits, rough. Dented in contact with the insulators, cracks departing from the dented zones
Barreiro	Purple brown, white spots, worn, severe etched, rough
Lisboa	Light grey, sparse white spots, smooth
Alfanzina, Rodão	Light grey, sparse white spots, askewed
	Zinc coatings
Roca	*Metal sprayed* – Yellowish grey with protubing yellow-white spots, numerous pits, without rust *Others* – rusted
Barreiro	*Metal sprayed* – Purple brown, white spots, without rust. *Others* – rusted
Lisboa, Alfanzina	*Metal sprayed, Galvanised I, II* - Light grey, white stains *Electroplated I* – Dark grey, white spots. *Electroplated II* – rusted
Rodão	*Metal sprayed, Galvanised I, II* - Light grey *Electroplated I* – Dark grey *Electroplated II* – Dark grey, some rusted
	Aluminium
Roca	Light yellowish grey, frosty white spots, numerous deep pits, rough
Barreiro	Purple dark grey, severe etched, rough
Lisboa	Metallic light grey, white stains, smooth
Alfanzina	Light grey, frosty white spots, numerous pits, rough
Rodão	Yellowish grey
	Anodised Aluminium
Roca , Lisboa, Alfanzina	Glossy light grey (retained almost the original aspect)
Barreiro	Reddish light grey, deep pits mostly in the edges, lightly rough
Rodão	Light yellow, extremely worn and rough

Corrosion evaluation by weight loss

Evaluation of corrosion behaviour by weight loss was done on the uncoated metals, on the anodised aluminium and on the zinc coated specimens before rust formation (Fig.s 1, 2). The following cleaning solutions for removal of corrosion products, based on ISO 8407, were used:

- Aluminium: solution of phosphoric acid and chromium trioxide, at 80°C to 85°C.
- Anodised aluminium: nitric acid (65%) at room temperature. (The solution was previously tested in unexposed specimens to assess the degree of dissolution of the coating).
- Zinc and zinc coatings: solution of ammonia hydroxide, at ambient temperature, and a solution of chromium trioxide and silver nitrate at boiling temperature.

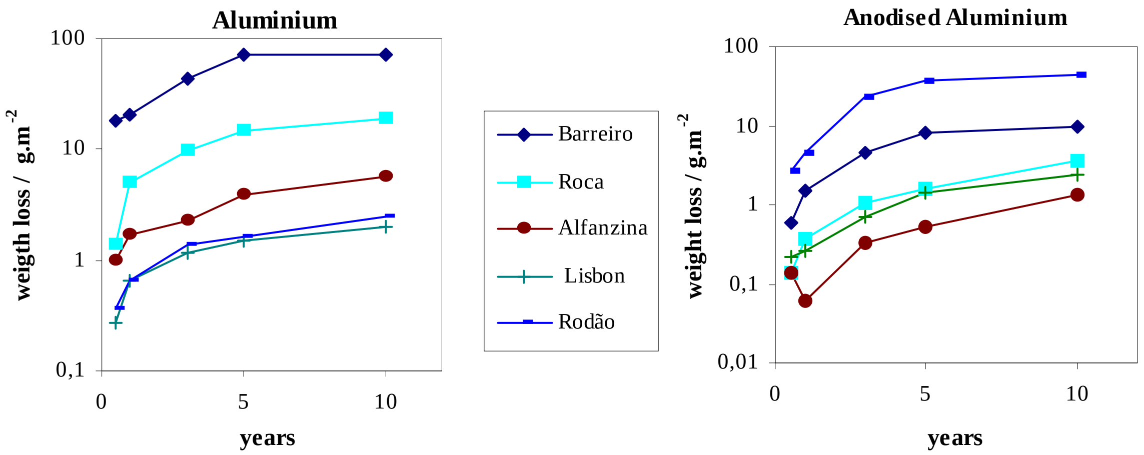

Fig. 1 – Corrosion of aluminium[1] and anodised aluminium after 6 months, 1, 3, 5 and 10 years of exposure.

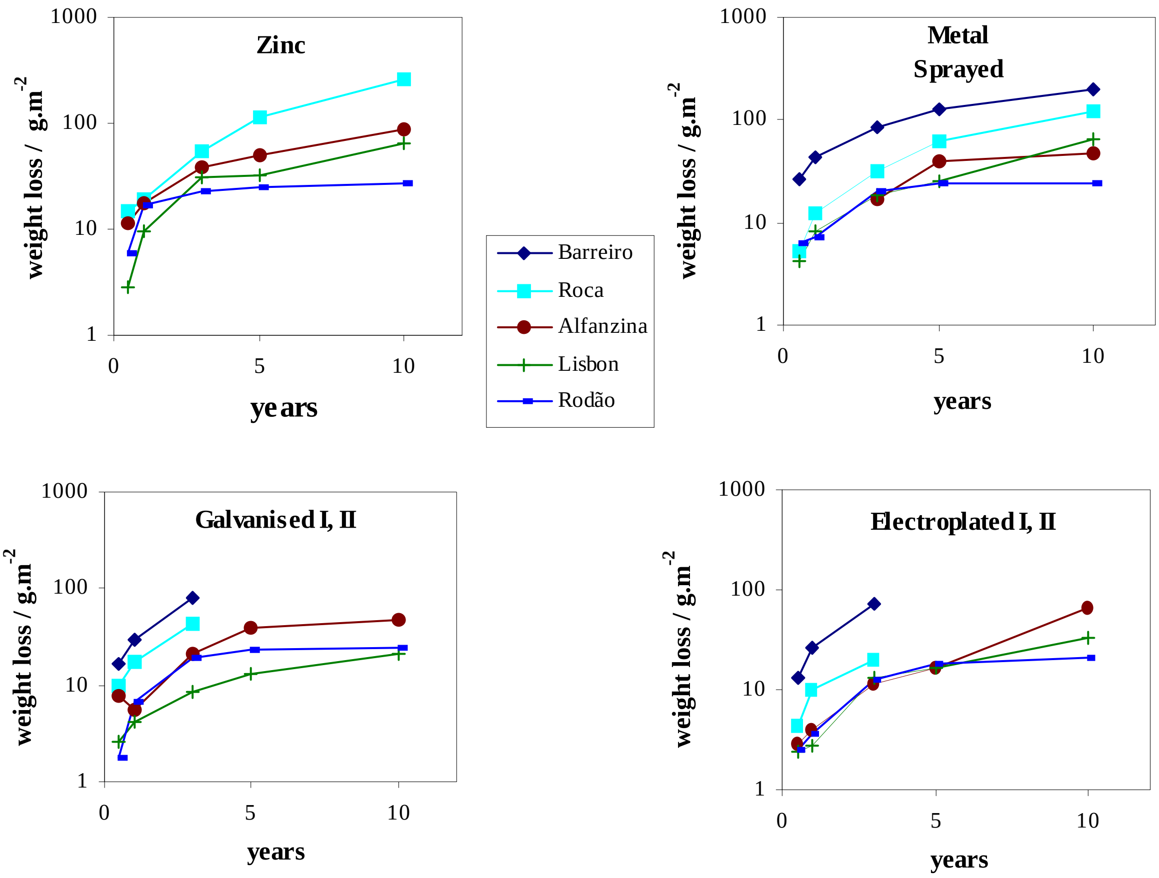

Fig. 2 – Corrosion of zinc and zinc coatings after 6 months, 1, 3, 5 and 10 years of exposure.

Rust development on zinc coatings

In addition to the weight loss, the zinc coatings corrosion behaviour were evaluated by the years necessary to the appearance of the first rust signals (Fig.3) and the percentage of rust area after ten years of exposure (Table 5). The metal-sprayed coating did not show any signs of rust during the time of exposure at all sites. The electroplated coatings, however, have early developed extensive areas covered with rust at the most aggressive sites and were withdrawn before the ten years. The percentage of rusted area was assessed merely by visual observation.

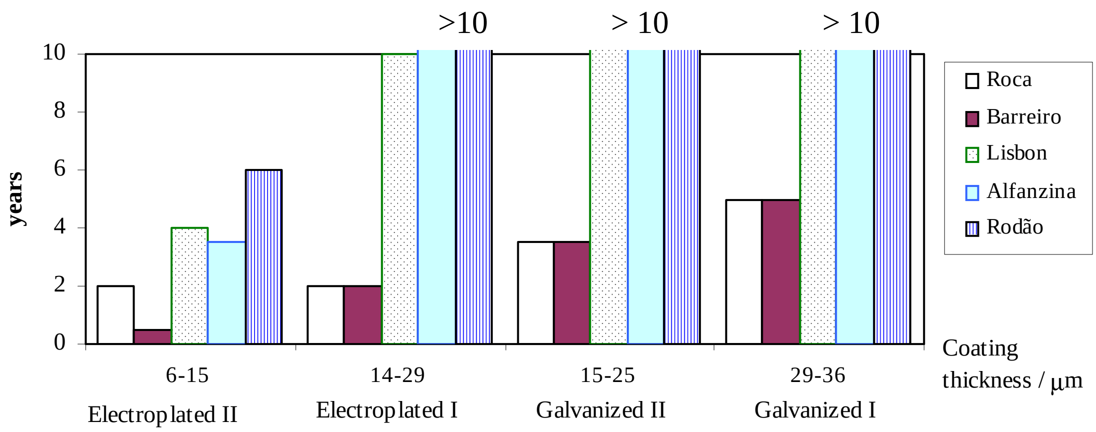

Fig.3 – Time to rust versus coating thickness for galvanised and electroplated zinc coatings.

Table 5 – Rusted area (%) on zinc coatings specimens after 10 years of exposure

Test site	Galvanised I	Galvanised II	Electroplated I	Electroplated II
Barreiro	10% - 40%	95% - 100%	10 – 70%(1)	25% - 100%(2)
Roca	10% - 40%	15% - 60%	30% - 80%(1)	25% - 75%(3)
Alfanzina	0%	0%	0%	10% - 95%
Lisbon	0%	0%	0%-10%	60% - 90%
Rodão	0%	0%	0%	0% - 80%

(1), (2) and (3) – values after 5, 2 and 3 years' exposure, respectively, when all the test specimens were withdrawn

Development of pitting corrosion on aluminium and anodised aluminium

Pitting corrosion occurred in the uncoated aluminium exposed in all the sites, being more severe at the marine sites (Table 3). At Rodão, mainly uniform corrosion was observed. Only the anodised specimens with coating thickness less than 30 μm exposed at Barreiro showed pitting (Fig. 6). At Rodão a generalised attack of the coating occurred. The evaluation of pitting extension was carried out using images-type from the ISO/DIS 10289. Measurement of pit depth for the most severe situations was also done by a method similar to ISO 1463, using a metallographic microscope.

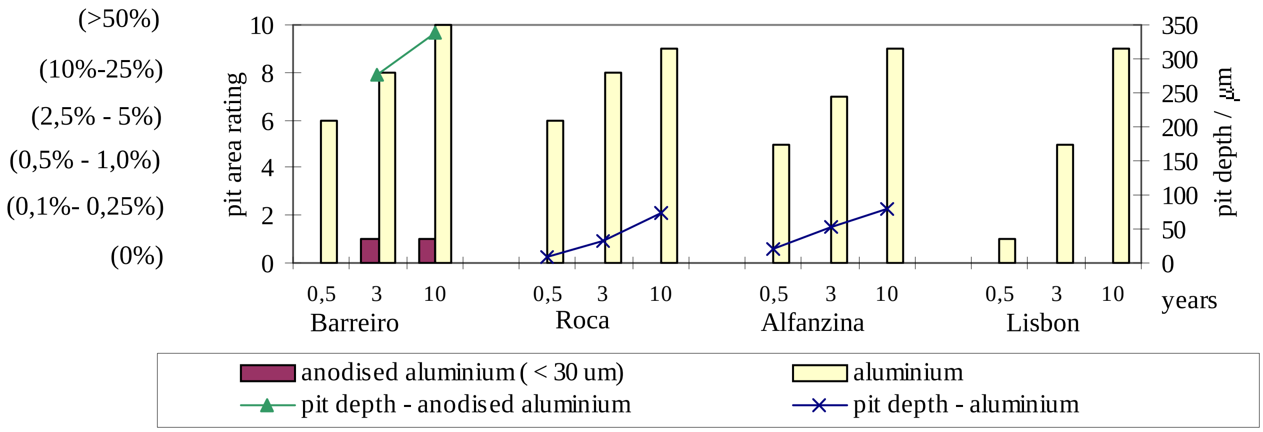

Fig. 6 - Rating of area occupied by pitting corrosion and maximum pit depth on aluminium and anodised aluminium for different exposure times and sites.

Composition of corrosion products

The mineralogical composition of the corrosion products for zinc and aluminium after 10, 5, 3 years of exposure was determined by X-Ray diffraction analysis (XRD) on the uncoated test specimens and for some test sites (Table 6). No crystalline corrosion products with aluminium were identified in the aluminium test specimens.

Table 6 – XRD analysis of corrosion layers on zinc

Exposure time	Barreiro	Roca	Lisbon	Rodão
10 years	$Zn_3(PO_4)_2.4H_2O$	ZnO, $Zn_5Cl_2(OH)_8$ $Zn_5(CO_3)_2(OH)_6$	ZnO	ZnO $Zn_5(CO_3)_2(OH)_6$
5 years	$Zn_3(PO_4)_2.4H_2O$, ZnO, $Zn_4SO_4(OH)_6.4H_2O$	n.a.	n.a.	n.a.
3 years	$Zn_3(PO_4)_2.4H_2O$, ZnO, $Zn_5(CO_3)_2(OH)_6$	n.a.	n.a.	n.a.

n.a. - not analysed

The surfaces of uncoated test specimens were also observed by scanning electron microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS) to determine the elemental composition of the corrosion products layer. This analysis revealed relatively high phosphorous contents in all the samples from Barreiro, what is in accordance with the results from XRD for zinc. For aluminium it has revealed predominantly high levels of oxygen for all the test sites (especially on those from the last years), besides aluminium and small amounts of sulphur and chloride. The significant values of phosphorous found in all specimens from Barreiro by SEM-EDS analysis, which have led to the formation of zinc phosphates, may result from the deposition of airborne phosphate particles from the fertiliser production plant in the vicinity.

Conclusions

• The weight losses show a clear trend with the severity of the test sites, being Barreiro (*industrial-marine*) and Roca *(marine very wet*) the two most severe to aluminium and zinc. Alfanzina (*marine*) with the same atmospheric contamination as Roca, has a more dry climate thus lower TOW and consequently lower corrosion rates. The exceptionally bad performance of anodised aluminium at Rodão may be explained by the additional attack of the coating by wood chips deposited on its surface during the first years of exposure. These chips, mainly of *eucalyptus*, during the wetting periods can yield acid solutions with pH values of 2,6 or less [3].

• The anodisation of aluminium improved significantly its corrosion resistance at marine sites; no visible pitting was evident after 10 years of exposure even on the thinner coatings. However, at Barreiro, the test specimens showed uniform weariness of the coating and those with coating thickness less than 30 μm present pitting extending beyond the coating depth.

• The results obtained for zinc coatings show that between coatings with similar thickness, galvanised coatings seem to have a better performance than electroplated ones. However, in the most aggressive conditions (Barreiro and Roca), galvanised and electroplated coatings, even those with the higher thickness, have not given enough corrosion protection to steel. For the other sites, galvanised coatings have had a good performance during the ten years of exposure. The metal-sprayed coating, due to its greater thickness, has presented a good performance in all test sites.

References

1. Fontinha, I. R; Salta, M., "Corrosion of aluminium and its anodic coatings. Ten years of natural exposure", EUROMAT'98, 22-24 July, Lisbon, 1998.
2. Cravo, M. R., "Estudo da corrosão atmosférica the metais e revestimentos inorgânicos utilizáveis em cobertu ras e caixilharias – 2º Relatório-Caracterização de materiais e detecção de poluentes atmosféricos agressivos", LNEC Report, Lisbon, 1980.
3. Hillis, W.E.; Gardner, J. A. F., "Wood extractives", Academic Press, New York, 1962.