

CORROSION OF ALUMINIUM AND ITS ANODIC COATINGS. TEN YEARS OF NATURAL EXPOSURE

R. Fontinha, M. Salta

Laboratório Nacional de Engenharia Civil, Av. Brasil, 101, Lisbon, Portugal

Abstract

Non-ferrous metals like aluminium, copper and zinc have been widely employed in a large number of building components. These metals, especially aluminium, are more or less vulnerable to deterioration by corrosion in atmospheric exposure. The aluminium atmospheric corrosion resistance however, can be improved by the use of anodic oxidation coatings, which must be used especially in aggressive conditions.

An extensive testing programme involving natural exposure in marine, industrial and urban environments has been carried out by LNEC since 1985 for studying the corrosion of aluminium, copper and zinc and the protection of steel by metallic zinc coatings and of aluminium by anodic coatings. The weight loss, number and depth of pits and analysis of corrosion products composition by XRD and SEM-EDS were made after 6 months, one, three, five and ten years of exposure of the different metals. In this paper are presented the results concerning the aluminium and its anodic coatings with different thickness.

Introduction

The choice of materials for usage in permanent external architectural applications must comply with technical and aesthetics requirements in addition to economics, the latter, frequently, the most conditioning one. From this point of view, it is necessary to account for not only the initial cost of the material, but also its expected durability and maintenance costs. The atmospheric corrosion resistance of these materials is nonetheless an important component in the final choice since it will affect both economics and mechanical properties over the lifetime of the product or structure.[1,2]

With the purpose of studying the corrosion behaviour of the metals and inorganic coatings most used in external building architectural applications in Portugal, a long-term atmospheric corrosion study in different aggressive environments was initiated in 1985 by Cravo[1,3,4]. The results obtained from this study during 10 years of exposure concerning the aluminium and its anodic coatings, are presented in this paper. It comprised corrosion rates, types of corrosion products formed, surface changes and the influence of the atmospheric conditions (climatic and pollution characteristics) on the corrosion mechanisms.

Materials

Two aluminium alloys of current fabrication in sheet form, one corrugated, were chosen for this study. The chemical composition of these alloys is given in Table 1. The anodic oxidation coating studied was produced by the sulphuric acid process and steam sealed. The thickness values of this coating chosen for this study correspond to the classes recommended by the EURAS/EWAA (European Anodisers Association/European Wrought Aluminium Association) for environments of different aggressiveness[5]. The thickness ranges of the coating are presented in Table 2.

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

Alloy	Elements concentration				
	>98,5%	<1%	<0,3%	<0,1%	Traces
Aluminium I (plain sheet)	Aluminium	Iron, Manganese	Silicon, Copper	Titanium	Lead, Magnesium, Nickel, Vanadium
Aluminium II (corrugated sheet)	Aluminium	-	Silicon, Iron	Titanium	Copper, Manganese, Nickel, Lead, Magnesium

Table 2 – Anodic oxidation coating thickness ranges [1] and type of atmosphere for which are recommended[5]

Thickness / μm		Atmosphere
Class 30	30 – 34	Severe marine and industrial atmospheres
Class 20	20 – 24	Marine or industrial atmospheres, highly polluted urban atmospheres
Class 15	15 – 19	Atmospheres without industrial pollution, moderated polluted urban atmospheres

The test specimens were cut from the metallic sheets into plates with a 120mm×200mm size, having a thickness ranging from 0,85 mm to 1,45 mm. The identification of the specimens was done through a set of perforations in the plates, at 3 mm from the edges, representing the number of specimen, type of material and test site. Prior to exposure, all the specimens were degreased with an organic solvent and weighed to the nearest 0,1 mg.

Exposure conditions

For this study four sites in Portugal were chosen, representing urban, marine and industrial-marine atmospheres:

Roca, marine atmosphere, a promontory in the West Coast, 50 km far from Lisbon. Altitude 140 m, 10 m from the ocean. Frequently under dense fogs during all seasons of the year.

Barreiro, industrial-marine atmosphere, inside the industrial park on the roof of a one-storey building, surrounded by chemical plants (sulphuric acid, fertilisers, etc.), close to a fuel burning power generation factory, near Lisbon, on the south banks of the river Tagus. This site has undergone a substantial change in its corrosivity during the study, as the SO₂ content in the air has decreased, due to the closing of several factories (see Table 3).

Lisbon, urban atmosphere, on LNEC's roof, near the airport and roads of intense traffic.

Alfanzina, marine atmosphere, a promontory in the South Coast (Algarve). Altitude 37 m, 10 m from the ocean.

During the first 7-8 years of exposure, *in situ* regular analysis of chloride and sulphur dioxide contents in the air were made by the wet candle and the lead dioxide methods, respectively. The results obtained are given in Table 3. The climatic characteristics for the different localisation of the test sites were taken from data reported by the Meteorological Institute for the test site areas, during the period from 1985 to 1988. This meteorological data is given in Table 4, in which the time of wetness (TOW) presented was estimated from the temperature and relative humidity (RH) values, considering the number of hours with RH higher than 80% and temperature above 0°C.

Table 3 – Average Chloride and Sulphur dioxide deposition rates measured in the test sites during the period from 1985 to 1993

	Roca	Barreiro	Lisbon	Alfanzina
SO ₂ deposition rate/ mg.m ⁻² .d ⁻¹	6	136 ^b	14	8
Chloride deposition rate/ mg.m ⁻² .d ⁻¹	194	38	7	201

^bDuring the first four years of study (1985-1989) the average values reached 200 mg.m⁻².d⁻¹, but in the following three years (1990-1993) this value decreased to an average of 50 mg.m⁻².d⁻¹

Table 4 – Yearly average values for meteorological characteristics for test sites areas during the period from 1985 to 1988

Meteorological station (Test site)		Roca (Roca)	Lavradio/Montijo (Barreiro)	Lisbon (LNEC)	P. Rocha (Alfanzina)
Temperature / °C (Min. - Max.)		15,4 (9,1 - 23,1)	14,8 (5,9 - 29,4)	16,6 (6,7 - 29,1)	14,5 (8,3 - 28,2)
Sun hours	Totals / h.y ⁻¹	2130 ^c	2776	2591	2847
	% of the maximum possible	48%	64%	60%	64%
TOW / h.y ⁻¹		5028	3388	3315	1683
% of the year		58%	39%	38%	21%
Precipitation / mm.y ⁻¹		491	620 ^d	723	518
Wind	speed/ km.h ⁻¹	18	11	13	13
	Most frequent direction	North, West	North, West	North, West	variable

^cfrom Cabo Carvoeiro; ^d1985/87;

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 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.

The atmospheric exposure started in 1985, in the summer for Lisbon and in autumn for the other test sites. 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.

Evaluation of results

Evaluation of results of the first periods of exposition was done some time after its collection from the test sites. During this time, the test specimens were kept stored in closed plastic bags away from light, in a dry place.

Visual appearance

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 5.

Corrosion of aluminium

Corrosion behaviour of the uncoated aluminium alloys was evaluated by weight loss. The following cleaning procedure for removal of corrosion products, according with ISO 8407, was used: immersion in a solution of phosphoric acid (50 ml) and chromium trioxide (20 g) in distilled water to make 1000 ml, at 80°C to 85°C, for 5 to 15 minutes. Rinse in distilled water.

The cleaning procedure was repeated in equal cycles whenever it was necessary until the samples were all free of corrosion products. After cleaning, test specimens were reweighed to the nearest 0,1 mg. The results, averaged from triplicate specimens (except those from 6 months and 1 year that correspond to one specimen only), are given in the Fig.1.

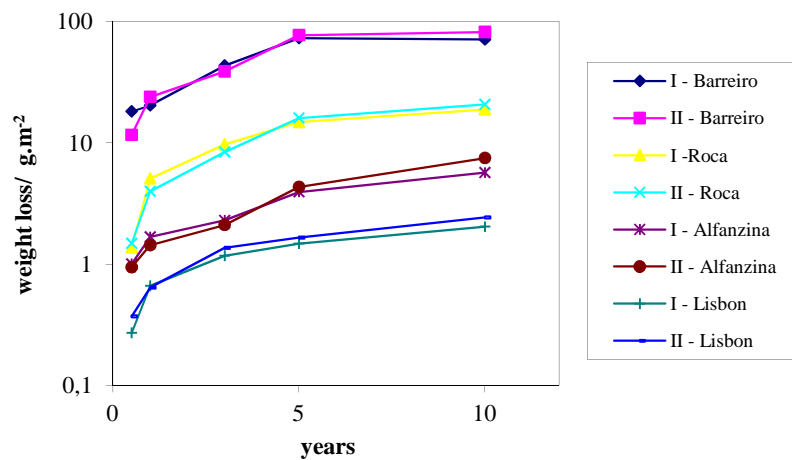


Fig. 1 – Corrosion of aluminium (alloys I and II) after 6 months, 1, 3, 5 and 10 years' exposure.

Aluminium corrosion was also evaluated by pit depth, for the marine atmosphere sites (Roca and Alfanzina). The results are given in the Fig.2 and a comparison is established with those obtained by the weight losses.

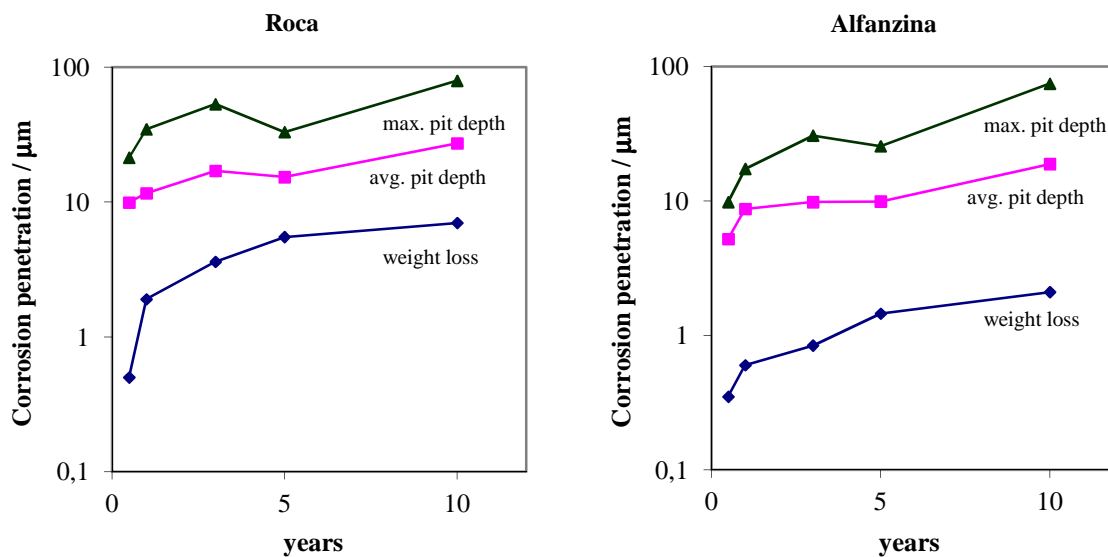


Fig.2 – Aluminium corrosion penetration measured by weight loss and pit depth

Pit depths were measured by a method similar to ISO 1463 using a metallographic section microscope. Both average and maximum depth of attack were determined.

Corrosion of anodised aluminium

The behaviour of anodised aluminium was compared with aluminium alloys concerning the time necessary to develop pitting corrosion, the extent of pitting corrosion developed and surface condition (Tables 5 and 6).

Table 5 – Comparison between aluminium and anodised aluminium surface condition after 10 years' exposure

	Barreiro		Roca		Alfanzina		Lisbon	
	aluminium	anodised aluminium	aluminium	anodised aluminium	Aluminium	anodised aluminium	aluminium	anodised aluminium
Type of corrosion ⁽¹⁾	G	P/G ^(a)	P	None	P	None	G	None
Corrosion degree ⁽²⁾	S	S/L ^(a)	S	-	S	-	L	-
White stains ⁽³⁾	0	4	5	2	4	1	3	1
Gloss loss ⁽⁴⁾	3	2	2	1	1	1	1	1
Surface appearance	reddish dark grey, severe etched, rough	reddish light grey, deep pits mostly in the edges, rough	light grey, frosty white spots, numerous pits, rough	glossy light grey	Light grey, frosty white spots, numerous pits, rough	glossy light grey	metallic light grey, white stains, smooth	glossy light grey

^(a) severe localised pitting and light generalised corrosion

⁽¹⁾ G – generalised corrosion; P – pitting corrosion ⁽²⁾ S – severe; L – light

⁽³⁾ 0 – without stains; 1 – rare stains to 5 – high density of stains

⁽⁴⁾ 1 – slight reduction; 2 - great reduction; 3 – completely lost

Table 6 – Comparison between aluminium and anodised aluminium pitting corrosion behaviour during the 10 years' exposure

	Barreiro		Roca		Alfanzina		Lisbon	
	aluminium	anodised aluminium	aluminium	anodised aluminium	aluminium	anodised aluminium	aluminium	anodised aluminium
Pitting distribution								
6 months ⁽¹⁾	5	0	2	0	1	0	0	0
1 year	5	1	3	0	1	0	1	0
3 years	5	2	4	0	2	0	2	0
5 years	5	2	5	0	3	0	2	0
10 years	5	3	5	0	4	0	3	0

⁽¹⁾ 0 – without pitting; 1 – rare pitting to 5 – high density of pitting

Composition of corrosion products

The surfaces of the uncoated test specimens were observed with a scanning electron microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS) to determine the elemental composition of the corrosion products layer. The results obtained for 10 years, 5 years and 6 months of exposure are presented in the figures 3 and 4.

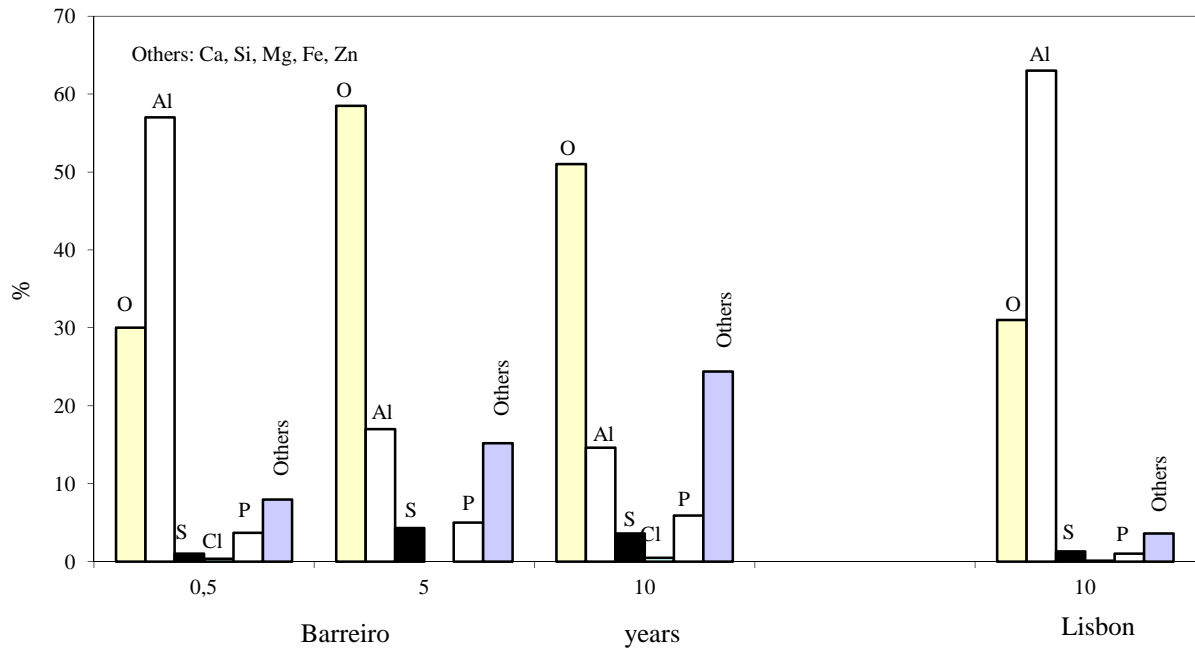


Fig. 3 – SEM-EDS elemental semi-quantitative analysis of corrosion products layer for aluminium test specimens of Barreiro (*marine-industrial*) and Lisbon (*urban*) test sites.

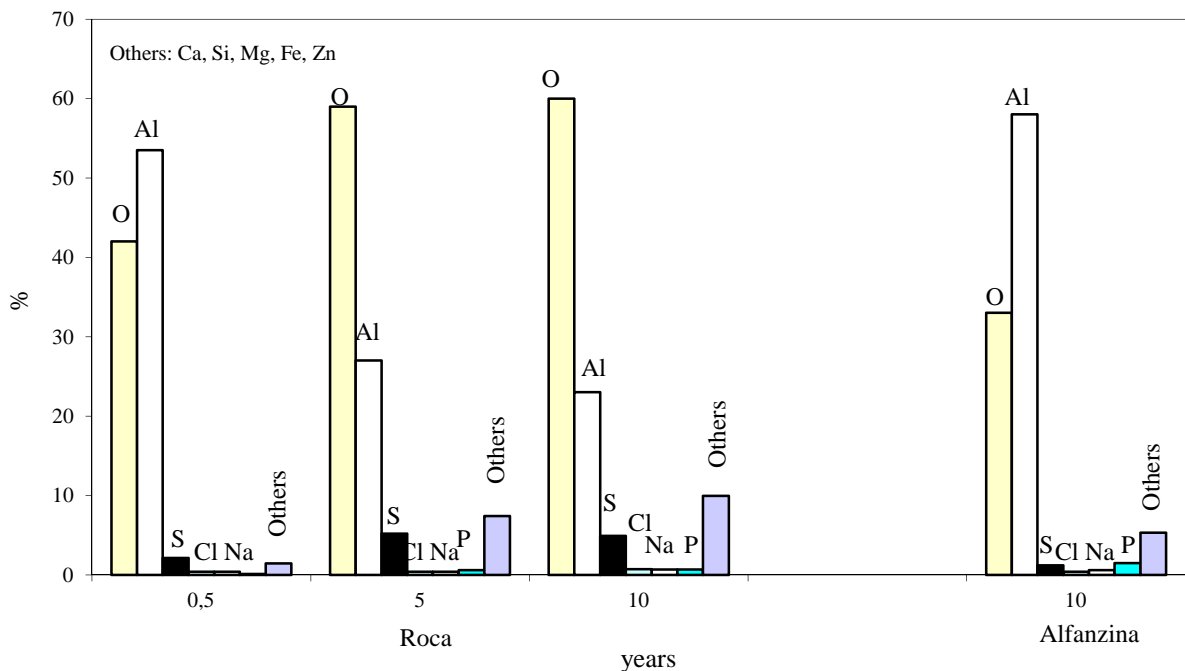


Fig. 4 - SEM-EDS elemental semi-quantitative analysis of corrosion products layer for aluminium test specimens of Roca (*marine*) and Alfanzina (*marine*) test sites.

In addition to the SEM-EDS analysis, the mineralogical composition analysis of corrosion products samples, scrapped from the topside of the uncoated test specimens, was done by X-

Ray diffraction techniques (XRD). No crystalline corrosion products with aluminium were identified in the analysis, only products resulting from deposition of atmospheric dust: Fe₂O₃, SiO₂ at Barreiro and SiO₂, CaSO₄.2H₂O at Roca.

Corrosion behaviour as function of time

In general the weight loss values show a tendency to be proportional to the time of exposure or to exhibit slower increases with time. This behaviour is often represented by an expression of the following type [6,7]:

$$M = Kt^n \quad (1)$$

in which:

M is the total weight loss caused by corrosion per unit of exposed area, g.m⁻²

K is a proportionality constant, expresses the mass loss occurring in the first year

n is the mass loss exponent

t is the exposure time, years

Values of n smaller than 1 indicate reduction of the corrosion rates with time, characteristic of a system with a uniform protective corrosion product layer. Aluminium alloys usually follow the kinetics equation (1) with n values generally between 0,5 and 1 [7,8].

In order to calculate the constants K and n in Eq.1 from the weight loss data (Fig. 1), a linearization by logarithmic conversion was made in order to use the simple least square regression analysis. The calculated values of K , n and r (regression coefficient) are given in Table 7.

Table 7 - Results of regression analysis of weight loss with exposure time

Material	Barreiro			Roca			Alfanzina			Lisbon		
	n	K	r	n	K	R	n	K	r	n	K	r
Aluminium I	0,53	24	0,97	0,83	3,5	0,96	0,56	1,5	0,99	0,64	0,52	0,97
Aluminium II	0,66	20	0,98	0,88	3,3	0,99	0,67	1,4	0,98	0,62	0,61	0,99

Influence of Sulphur Dioxide and of Chlorides atmospheric contamination

Chlorides and nowadays, sulphur compounds, especially sulphur dioxide (SO₂), are the most important aggressive agents in atmospheric corrosion [9]. In order to evaluate the correlation between the corrosion rate of the uncoated aluminium alloys at each test site and the content of sulphur dioxide and chlorides in the atmosphere, a multilinear regression analysis was performed by the least squares method based on the following equation:

$$CR = aSO_2 + bCl + c \quad (2)$$

in which:

CR is the corrosion rate, in $\mu\text{m.y}^{-1}$, for a given time of exposure

SO_2 and Cl are the correspondent average deposition rates, in $\text{mg.m}^{-2}.\text{y}^{-1}$, for the same time of exposure

Eq.2 was applied to data from one year and ten years of exposure, considering that SO₂ and chloride deposition rates average values do not change from the eight years to the ten years of exposure. The results for the two aluminium alloys were considered. Tables 8 and 9 show the

corrosion rates and pollution data for 1 and 10 years of exposure as well as the results of the regression analysis for the application of equation (2).

Table 8 - Corrosion rates after 1 and 10 years' exposure and corresponding SO₂ and Chlorides average deposition rates

Site	Corrosion rates / $\mu\text{m}\cdot\text{y}^{-1}$				Deposition rate / $\text{mg}\cdot\text{m}^{-2}\cdot\text{y}^{-1}$			
	Aluminium I		Aluminium II		SO ₂		Cl	
	1 y	10 y	1 y	10 y	1 y	10 y	1 y	10 y
Barreiro	7,5	2,6	8,9	3,0	220	136	41	38
Roca	1,9	0,7	1,5	0,8	5	6	132	194
Alfanzina	0,6	0,2	0,5	0,3	5	8	56	201
Lisbon	0,2	0,08	0,2	0,1	14	14	2	7

Table 9 - Least squares coefficients for Eq.(2)

Material	1 year				10 years			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>r</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>r</i>
Aluminium I	0,0327	0,015	-0,31	1,00	0,020	0,003	-0,2	0,98
Aluminium II	0,0398	0,013	-0,36	1,00	0,023	0,003	-0,2	0,98

Conclusions

- The mass losses caused by corrosion on the aluminium alloys exposed show a clear trend with respect to the relative severity of the test sites, being Barreiro (*industrial-marine*) and Roca (*marine very wet*) the most severe to aluminium. Alfanzina (*marine*) in spite of having similar levels for sulphur and chloride atmospheric contamination as Roca, has a more dry climate thus lower TOW and consequently lower corrosion rate.
- For aluminium alloys the extent of localised corrosion at marine sites is misled by the mass loss determinations (Fig.4). Corrosion rates determined by pit depth are, in general, 4,5 times higher at Roca and 12 times higher at Alfanzina than those determined by mass losses. These results show that weight loss data should not be used indiscriminately to calculate corrosion rates when localised corrosion is the primary form of corrosion.
- Test specimens removed from Barreiro showed an unnatural reddish colour that is assumed to result from the deposition of airborne particles of iron compounds coming from air open deposits of pyrites or from the emissions of the siderurgy nearby. The significant values of phosphorous found in these specimens by SEM-EDS analysis, may result from deposition of airborne phosphate particles from the fertiliser production plant near. The presence of these two types of deposits, conjugated with higher values of SO₂ pollution, could justify the relative high corrosion rates, when compared with other studies[6,10], that were observed for this site.
- The anodisation of aluminium improved significantly the corrosion resistance of aluminium at marine sites; no visible pitting was evident after 10 years of exposure. However, at Barreiro the protective action of the anodised coating was not as effective as the former; the test specimens from this site present uniform weariness of the coating and pitting extending beyond the coating depth. No significant differences in corrosion behaviour were found within the three anodic coating thickness classes studied: 15 μm , 20 μm and 30 μm . This

confirms the general observations from the literature that optimum protection against atmospheric corrosion is achieved in the coating thickness range of 18 μm to 30 μm and that thicker coating provides little additional protection[10].

- Aluminium showed a strong linear relation between SO_2 and chloride contents in the atmosphere and its corrosion rates after 1 year and 10 years of exposure.
- Corrosion rates for both aluminium alloys agreed well with the kinetic law $M=Kt^n$. The mass loss exponent values were similar to those found in literature[6] and indicate the formation of protective corrosion layers.

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