LONG-TERM ATMOSPHERIC CORROSION STUDIES *VS* ISO METHODOLOGY FOR ATMOSPHERIC CORROSIVITY ASSESSMENT. A COMPARISON BETWEEN MEASURED AND EXPECTED RESULTS

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Abstract: A ten-year exposure testing program in natural atmospheres (marine, industrial, urban) was carried out at Portugal to study the atmospheric corrosion of several metals used in building components. At the same time of this study the National Atmospheric Corrosivity Map (NACM) was set based in the ISO standards testing methodology. In this paper results obtained from the ten-year study concerning the uncoated metals: aluminium, zinc and copper, are presented comprising, corrosion rates, evolution of mass losses and corrosion products characterization. These results are analyzed using the ISO parameters and a comparison between measured and expected corrosion velocities after ten years is done. Some discrepancies are found, being only some of them reasonably explained by significant changes in the atmospheric corrosivity of the exposure site during the period of study. Some of the test sites were also used for the elaboration of the NACM and a comparison of the results obtained in both studies is also done. The suitability of the ISO methodology to predict long-term corrosion data is discussed.

Keywords: Atmospheric corrosion tests, corrosivity class, aluminium, zinc, copper

1. INTRODUCTION

Atmospheric corrosion studies are usually done to evaluate the corrosion behaviour of metallic materials to several types of environments and to obtain corrosion data useful for service life prediction. To achieve this kind of information its usually necessary to extend the exposure period to, at least, ten years, which is often considered too long. The ISO standards 9223 to 9226 [1-4] describe a methodology for atmospheric corrosivity assessment, based in environmental and corrosion data measured during a shorter period (1 year), which can be used to estimate long-term corrosion rates (ten years or more) for several metals: aluminium, zinc, copper and steel.

With the purpose of studying the corrosion behaviour of the metals and inorganic coatings most used in external building components, LNEC has carried out an atmospheric corrosion study in different corrosive environments. The results obtained from this study during the first ten years of exposure have been object of several publications [5-9] and comprised corrosion rates determination by weight losses, analysis of the corrosion products formed, surface changes and the influence of climatic and pollution characteristic on corrosion mechanisms.
In this paper are gathered the results obtained in that study relative to the corrosion behaviour of the uncoated metals: aluminium, zinc and copper for all the test sites. It comprises the evolution of mass losses, corrosion products characterization, corrosion rates of after 1 year and ten years of exposure and atmospheric characterization. These results are analyzed using the ISO parameters and a comparison between measured and expected corrosion rates after ten years is done. Due to some of the test sites of LNEC's study had also been used in the elaboration of the National Atmospheric Corrosivity Map (NACM) based in the ISO standards testing methodology, a comparison of the results obtained in both studies is also done.

2. ATMOSPHERIC EXPOSURE

2.1 Materials

Aluminium, zinc and copper sheet of current fabrication were used in this study. The test specimens were cut from the metallic sheets into plates with a 120mm×200mm size having thickness ranging from 0,40 mm to 0,85 mm according to the type of metal (Table 1).

Table 1 – Characteristics of the tested metals

Material	Purity	Thickness / mm
Aluminium	Al > 99,5%	0,85
Zinc	Zn > 98,5%	0,40
Copper	Cu > 99,9%	0,85

2.2 Exposure Conditions

For this study five sites in Portugal were chosen, representing urban, marine and industrial atmospheres. They have been described in detail elsewhere [5-9]. In Table 2 are only reported the environmental parameters necessary for corrosivity classification of each test site.

Table 2 – Environmental characteristics of test sites

Test site	TOW /h.y^{-1}	SO_2 /mg.m^{-2}.d^{-1}	Chlorides /mg.m^{-2}.d^{-1}
Roca	5028	6	194
Barreiro	3388	136[a]	38
Alfanzina	1683	8	201
Lisboa	3315	14	7
Ródão	1871	21	5

[a]During the first four years of the study the average values reached 200 mg.m^{-2}.d^{-1}, but in the following three years this values decreased to an average of 50 mg. .m^{-2}.d^{-1}.

The sulphur dioxide and chlorides deposition rates were measure *in situ* by the lead dioxide and the wet candle methods, respectively. The time of wetness was estimated (TOW) from meteorological data collected at the test site or from meteorological stations nearby.

The test specimens were mounted with an exposure angle of 45º, facing south, except at Roca where they are facing west to enhance the exposure to the saline spray.

2.3 Corrosion behaviour results

The corrosion behaviour of the different metals was evaluated by weight loss, using cleaning procedures to remove corrosion products according to ISO 8407. The results obtained, averaged from triplicate specimens are given in the next Figures.

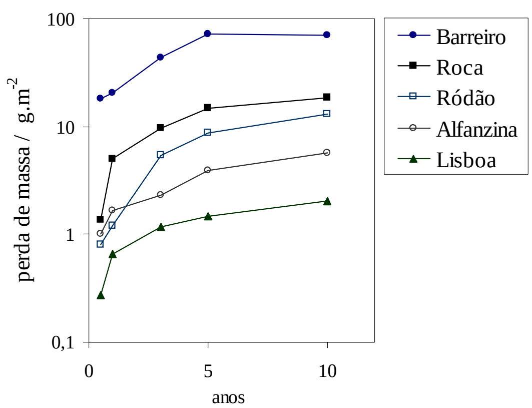

Figure 1 - Corrosion of aluminium after 6 months, 1, 3, 5 and 10 years of exposure.

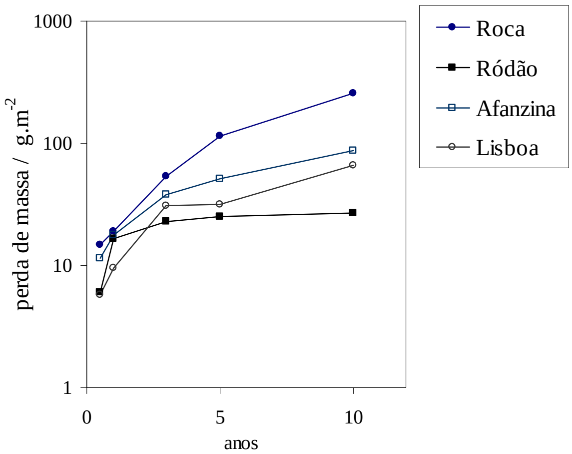

Figure 2 - Corrosion of zinc after 6 months, 1, 3, 5 and 10 years of exposure.

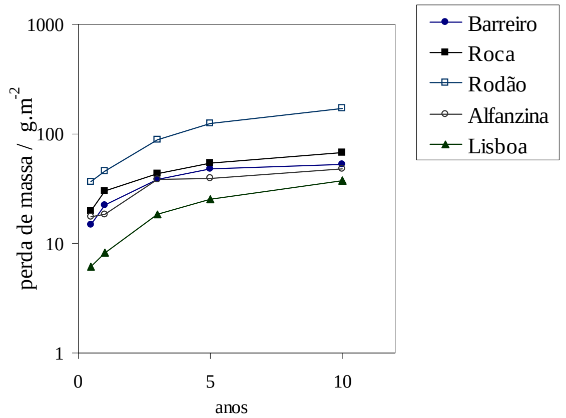

Figure 3 - Corrosion of copper after 6 months, 1, 3, 5 and 10 years of exposure.

Based on the weight loss values, the values of average corrosion rates after one and ten years of exposure were calculated for the three metals and are presented in the next tables.

Table 3 – Aluminium corrosion rates (μm/y) after 1 and 10 years of exposure

Test site	Aluminium	
	1 year	10 years
Barreiro	7,5	2,6
Roca	1,9	0,7
Ródão	0,5	0,5
Alfanzina	0,6	0,2
Lisboa	0,2	0,08

Table 4 – Zinc and copper corrosion rates (μm/y) after 1 and 10 years of exposure

Test site	Zinc		Copper	
	1 year	10 years	1 year	10 years
Barreiro	-	-	2,5	0,6
Roca	2,7	3,6	3,4	0,8
Ródão	2,3	0,4	5,1	1,9
Alfanzina	2,5	1,2	2,1	0,5
Lisboa	1,3	0,9	0,9	0,4

The composition of the corrosion products was determined by X-Ray diffraction analysis (XRD) and by scanning electron microscopy equipped with energy dispersive X-Ray spectrometry (SEM-EDS). The next tables present the main corrosion products and chemical elements found by these techniques in test specimens after ten years of exposure.

Table 5 – XRD and SEM-EDS analysis results for **copper** corrosion products

Material	**Copper**	
Test site	*XRD*	*SEM-EDS*
Lisboa	Cu_2O, $Cu_7Cl_4(OH)_{10}.H_2O$, CuCl, $Cu_4SO_4(OH)_6$	Cu, O, Cl, S
Barreiro	Cu_2O, $Cu_7Cl_4(OH)_{10}.H_2O$, CuCl	Cu, O, P, Cl, S
Roca	Cu_2O, $Cu_7Cl_4(OH)_{10}.H_2O$	Cu, O, Cl, Na
Ródão	Cu_2O	Cu, O, S, Ca

Table 6 – XRD and SEM-EDS analysis results for **zinc** and **aluminium** corrosion products

Material	**Zinc**		**Aluminium**
Test site	*DRX*	*SEM-EDS*	*SEM-EDS*
Lisboa	ZnO	Zn, O, S	Al, O, S
Barreiro	$Zn_3(PO4)_2.4H_2O$, $Zn_5(CO_3)_2(OH)_6$	Zn, O, P, Cl, S	Al, O, S, Cl, P
Roca	ZnO, $Zn_5(CO_3)_2(OH)_6$	Zn, O, S, Cl	Al, O, S
Ródão	ZnO, $Zn_5(CO_3)_2(OH)_6$	Zn, O, Ca	Al, O, S, Ca

The type of corrosion products formed is, in general, the expected according to the type of atmosphere. The only exception is for the Barreiro test site where didn't happen the formation of metallic sulphates that would be expected attending to the existing high levels of SO_2 pollution. Additionally, in this test site, it was also found on the surface of the test specimens high levels of phosphor, which inclusive, led to the formation of zinc phosphates, being the predominant corrosion product formed in this test site for zinc.

3. CORROSIVITY CLASSIFICATION

For classification of atmospheric corrosivity, the ISO 9223 defines two methods: one based on environmental parameters of time of wetness and pollution and other based on corrosion rate measurement of standard metal specimens after one year of exposure. Applying the criteria described on ISO 9223 to the results obtained in the atmospheric exposure is possible to attribute corrosivity classes to the exposure test sites (Tables 7 and 8).

Table 7 – Corrosivity classification based on **environmental parameters** according to ISO 9223

Test site	TOW class	SO_2 class	Chloride class	Corrosivity class
Roca	τ_4	P_0	S_2	C3/C4[a]
Barreiro	τ_4	P_3	S_1	C4/C5[a]
Alfanzina	τ_3	P_0	S_2	C3/C4[a]
Lisboa	τ_4	P_1	S_1	C3
Ródão	τ_3	P_1	S_1	C3

a : Depending on the metal considered

Table 8 – Corrosivity classification based on **corrosion data** according to ISO 9223

Test site	Corrosivity class		
	Aluminium	Zinc	Copper
Roca	C5	C4	C5
Barreiro	>C5	-	C4
Alfanzina	C3	C4	C4
Lisboa	C3	C3	C3
Ródão	C3	C4	C5

During the last five years of the atmospheric corrosion study presented here, three of the test sites (Barreiro, Alfanzina and Ródão) were also used for the elaboration of the National Atmospheric Corrosivity Map (NACM) based on ISO methodology. It is interesting to add here the classification attributed to these test sites under this second study for the same materials. This is done on Table 9, where the classification attributed to Lisbon is also included, because its localization and environmental characteristics are very similar to the Lisbon LNEC's test site.

Table 9 – Classification attributed by the National Atmospheric Corrosivity Map [10]

Test site	Corrosivity class based on environmental data	Corrosivity class based on corrosion data		
		Al	Zn	Cu
Barreiro	C5	C4/C5	C4	C4/C5
Alfanzina	C4	C3	C3	C4
Ródão	C3	C2/C4	C3/C4	C4/C5
Lisboa	C3	C3	C3	C4

In both studies there are some differences between corrosivity classifications attributed by environmental parameters and by corrosion data. This means that probably are present other corrosive species than those usually measured in this type of studies that could influence more or less each type of metal. In this case, the biggest difference occurred for Ródão test site, especially for copper.

4. EXPECTED CORROSION RATES

Expected average corrosion rates during the first ten years can be established for each test site atmosphere based on its corrosivity class according to the guiding values of ISO 9224 [2]. These values are presented in Table 10 and for their determination it was used the corrosivity classification attributed by corrosion data (Table 8).

Table 10 – Expected average corrosion rates (µm/y) for the first ten years according to ISO 9224

Test site	Aluminium	Zinc	Copper
Roca	n. a.	2 – 4	3 – 5
Barreiro	n. a.	-	1,5 – 3
Alfanzina	0,025 – 0,2	2 – 4	1,5 – 3
Lisboa	0,025 – 0,2	0,5 – 2	0,1 – 1,5
Ródão	0,025 – 0,2	2 – 4	3 – 5

n. a. – not applicable

A comparison between the expected corrosion rates of Table 10 with the measured corrosion rates presented in Tables 3 and 4 reveals:

- half of the cases do not agree: the measured values are inferior to the expected ones, except in the case of aluminium of Ródão test site;
- copper was the metal that presented more and higher differences;
- the values of corrosion rates for Lisbon test site coincide for all metals.

5. DISCUSSION AND CONCLUSIONS

The comparison between expected and measured corrosion rates after ten years of exposure revealed, in the case of the study carried out by LNEC, that the use of one year exposure results to estimate long-term corrosion rates would lead to overestimations of corrosion rates for zinc and copper, and to underestimation in one case for aluminium for the sites with higher corrosivity (corrosivity class >C3).

However, for the industrial atmospheres, Barreiro and Ródão, some these divergences could result from changes in atmospheric corrosivity of the test sites during the study due to external factors that, naturally, could have influenced the long-term results:

→ in Barreiro test site occurred a decrease in atmospheric pollution by sulphur gases with time due to closing of several industries. In addition to this, the presence of phosphorous products deposited on the metals surface could have exerted some inhibition of corrosion processes, namely, hindering the formation of sulphate corrosion products;

→ in Ródão test site, placed inside the industrial park of a pulp factory, during the first years of the study the exposure racks were placed near piles of wood chips. These chips, mainly of *eucalyptus*, when wetted can yield acid solutions with pH values of 2,6 or less [6], representing an additional corrosivity factor. After three years of exposure, the exposure racks were transferred to a local less subjected to the deposition of the wood chips, reducing its influence. However, aluminium must be more sensitive to wood chips presence because this change wasn't enough to reduce long-term corrosion. The acid solution yielded by these particles promotes the dissolution of the natural protective corrosion products usually formed by the aluminium in the atmosphere. In fact, it could be seen in Table 3 that corrosion rate after ten years is the same of one year of exposure. Visually the specimens of aluminium showed the biggest difference between the upper and the lower face and it was also observed that this environment caused big damages on anodized aluminium coatings [6].

The changes in atmospheric corrosivity verified in the industrial atmospheres, although significant, shouldn't be enough to justify the accentuated decrease of the corrosion rate with time presented by the copper specimens, which by the way have occurred in all atmospheres.

In relation to the marine atmospheres, Roca and Alfanzina test sites, there is no external factor that could justify the fact of corrosion rates measured after ten years were lower than the expected. In this case, one possible explanation is that the corrosion products formed were more protective than usually for this type of atmospheres, considering the values of corrosion used by the ISO 9224.

Based on the results obtained in this study it could be concluded that, in the case of the most corrosive atmospheres, the exposition of metal specimens for one year in an atmosphere (ISO methodology based on corrosion data) is not enough to estimate long-term corrosion rates in the case of metals that corrode uniformly, forming protective corrosion layers, like zinc and copper, especially this last one.

The ISO methodology based on environmental data, like has been stated before, could miss important corrosive factors present in the atmosphere of study, especially for the most polluted atmospheres which make advisably to expose test specimens, simultaneously, in this type of environments.

Comparing the results obtained by the LNEC's study and in the elaboration of the NACM relative to corrosivity classification (Tables 7, 8 and 9), it can be seen that in same cases they differ, especially those of corrosion data. These differences can not be fully justified by the changes in atmospheric corrosivity pointed for some of the test sites. It could also be attributed to the fact of the metal specimens used aren't exactly the same in both atmospheric expositions, but differences between corrosivity classes attributed based on corrosion data occur even within NACM study (Table 9). This means that the results obtained by the ISO methodology could change from year to year.

This dependence of the characteristics of only one year makes the ISO methodology highly subjected to errors when is used for long-term corrosion rates estimatives. However, it's a very useful method for corrosivity comparison between different atmospheres and the data obtained should be added to other information collected about one specific local to evaluate its real corrosivity.

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