



Atmospheric corrosion of reference metals in Antarctic sites[☆]

Manuel Morcillo^{a,*}, Belén Chico^a, Daniel de la Fuente^a, Elisabete Almeida^b,
Günter Joseph^c, Susana Rivero^d, Blanca Rosales^e

^aCentro Nacional de Investigaciones Metalúrgicas, Avda. Gregorio del Amo, 8. 28040-Madrid, Spain

^bInstituto Nacional de Engenharia e Tecnologia Industrial, Estrada do Paço do Lumiar, Lisbon, Portugal

^cIDIEM, Universidad de Chile, Plaza de Ercilla 883, Santiago de Chile, Chile

^dFacultad de Ingeniería, Universidad de la República, Julio Herrera y Reissig 565, Montevideo, Uruguay

^eCITEFA, Zufriategui 4380, Buenos Aires, Argentina

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Abstract

This paper presents the results obtained at three Antarctic test sites participating in the “Ibero-American Map of Atmospheric Corrosiveness” (MICAT), a project on atmospheric corrosion carried out during the period 1988–1994 at some 70 sites distributed across 12 countries of the Latin-American region, Spain and Portugal. The three Antarctic sites are located near the coastline.

The singular climatic characteristics of Antarctic regions are related with the purity of the air, the absence of rainfall and the formation of ice on the metallic surface during an important part of the exposure time. However, electrochemical activity is possible below ice layers. This situation affects the structure and morphology of corrosion product films and the resulting corrosion rates of metallic surfaces.

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1. Introduction

Data on atmospheric corrosion in very cold (polar) climates is not very abundant in the literature. An

exhaustive review about this issue has been published by Hughes et al. (1996).

These climates are special from the point of view of metallic corrosion since the metal surface is covered for most of the time by an ice layer of variable thickness. This ice layer reduces oxygen access to the metallic surface and the time of wetness of the exposed surface, limiting corrosion rates to extremely low values. Table 1 shows data obtained from the literature (Coburn et al., 1968, p. 366; Bieffer, 1981, p. 16; Hughes et al., 1996, p. 6) for metals exposed in polar

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* Corresponding author. Tel.: +34 915544506; fax: +34 915345108.

E-mail address: director@cenim.csic.es (M. Morcillo).

Table 1
Corrosion rates obtained at different stations situated in the interior of the Arctic and Antarctic zones

Exposure site	Distance from sea (km)	Steel corrosion rate ($\mu\text{m}/\text{year}$)
Arctic zone		
Norman Wells, NWT	–	1.43
(Coburn et al., 1968, p. 366; Biefer, 1981, p. 16)	Interior of the Canadian Arctic	>1
		1.14–3.08 ^a
Antarctic zone		
Vanda	80	0.87 ^b
(Hughes et al., 1996, Table 1)	Robertsollen	120
	LGB00	186
	LGB10	390
	LGB35	780
	Vostok	1200
		0.13 ^b
		0.05 ^b

^a Corrosion in these places was measured using “wire on bolt” specimens. The corrosion values that appear in the table correspond, after making the conversion, according to ISO 9226, to flat specimens.

^b Carbon steel with the addition of approximately 0.25% copper.

climate atmospheres. The lowest corrosion rate has been measured at Vostok station, in the Antarctic, where the coldest temperature on earth has been recorded ($-89.6\text{ }^{\circ}\text{C}$ in July 1983) (Hughes et al., 1996, p. 8).

However, as noted by Barton et al. (1974), in highly polluted atmospheres corrosion can continue to take place even at $-5\text{ }^{\circ}\text{C}$, due to the high saline concentration in the electrolyte film retained on the metal surface, which delays freezing (Brass, 1999, p. 29). In laboratory studies applying electrochemical techniques, different researchers have demonstrated that electrochemical corrosion activity is possible below ice layers (González, 1989, p. 297; Rosales et al., 1996, p.6).

Table 2 shows corrosion values for specimens exposed at sites close to the sea in the Antarctic region. Higher values than expected are obtained, considering the short times of wetness in this type of climate. In Antarctica salt deposition is a particular problem and in the absence of rain this salt deposits are not washed off surfaces. Thus, in many coastal locations in Antarctica it is common to see profuse marine salt deposits on the ground.

The information presented in this paper has been obtained in the framework of the Ibero-American Map

of Atmospheric Corrosivity (MICAT) project, a project on atmospheric corrosion which was carried out during the period 1988–1994 (Morcillo et al., 1999).

The MICAT project was launched in 1988, sponsored by the Ibero-American Programme “Science and Technology for Development” (CYTED). Fourteen countries were involved in the project and research was conducted both at laboratories and in a network of 75 atmospheric exposure test sites throughout the Latin-American region, considering a broad spectrum of climatological and pollution conditions and involving three test sites in the Antarctic region, in Antarctic bases corresponding to Argentina (Jubany), Chile (Marsh) and Uruguay (Artigas). These three test sites are located in Collins Bay, on King George Island, and are situated close to the shoreline.

Most of the papers contained in the literature deal with data on with metallic corrosion rates in polar climates (Biefer, 1981; Hughes et al., 1996; Morcillo et al., 1999; Chico et al., 2000; Mariaca et al., 2000), and information on the influence of environmental characteristics on corrosion product formation in this type of climate is not abundant (Morcillo et al., 1999; Marco et al., 2000; Mariaca et al., 2000; Chico et al., 2002). This paper presents a summary of the corrosion rates obtained for steel, zinc, copper and aluminium exposed at three Antarctic sites and comments on the morphology of the corrosion products formed in this singular climate of the Antarctic region.

Table 2
Corrosion rates obtained at different stations situated at a distance of less than 1 km from the sea in the antarctic zone (Hughes et al., 1996, Table 1)

Exposure site	Distance from sea (km)	Steel corrosion rate ($\mu\text{m}/\text{year}$) ^a
Antarctic zone		
Macquarie I. Isthmus	<1	222
Heard I. Spit Bay	<1	55.3
Marion I.	<1	31.9
Signy	<1	36.4
Rothera (Antarctic Pen.)	<1	27.1
Mawson	<1	3.35

^a Carbon steel with the addition of approximately 0.25% copper.

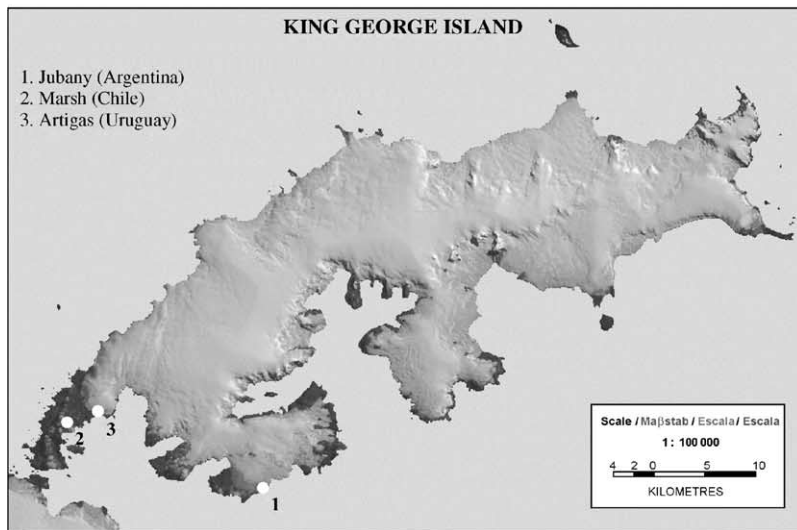
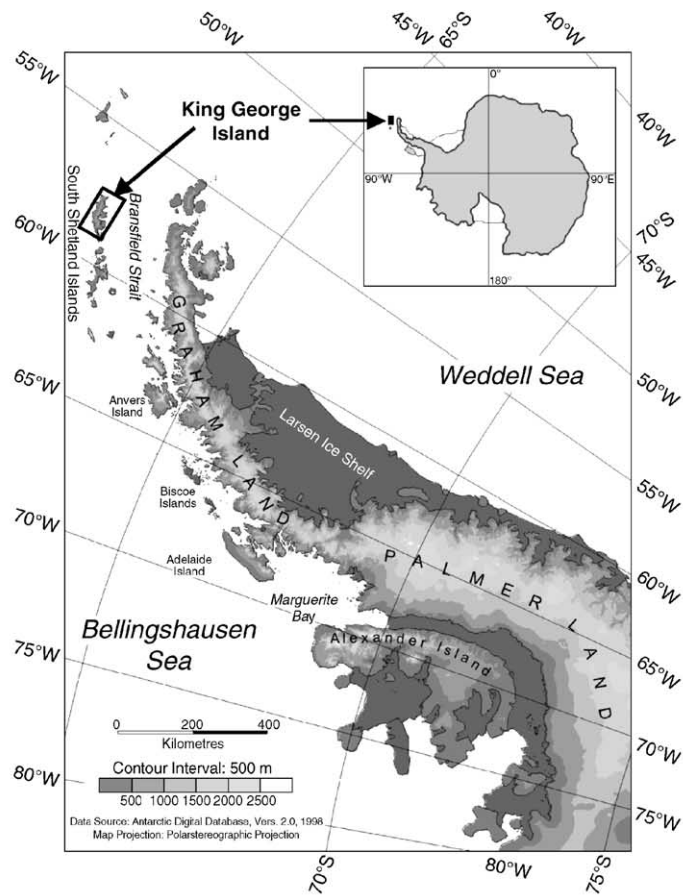


Fig. 1. Geographic location of Antarctic MICAT test sites.

2. Experimental

The organizational structure, methodology and some results have been reported elsewhere (Morcillo, 1995). Though with its own peculiarities, the MICAT project has basically followed the experimental methodology of the ISOCORRAG collaborative programme (Knotkova and Vrobel, 1990).

2.1. Test sites

This paper focuses on the results obtained in the three Antarctic MICAT test sites. Fig. 1 indicates the location of the atmospheric test sites. The names, codes and some environmental features of these sites are listed in Table 3. Due to the great difficulties involved in periodically visiting the testing stations, it has not been possible to obtain atmospheric salinity data in two of the three stations.

There follows a description of the situation and characteristics of the three Antarctic stations. Their geographic coordinates and the institutions to which they were installed are noted in Table 4 and Fig. 2 shows photographs of the three test sites.

Jubany (Argentine Antarctic) operates in the Lieutenant Jubany Scientific Base, on King George Island, in the South Shetland Islands, 1900 km from the South Pole, facing the Potter inlet. The specimen racks are situated 100 m from the coast, and accordingly the environment is marine. The effect of sea mist is very significant during the summer, but as the bay gradually freezes over the saline contribution decreases, despite the strong winds that are recorded.

Marsh (Chilean Antarctic): The station is situated at the Lieutenant Rodolfo Marsh Base, belonging to

Table 4

Geographic coordinates of the Antarctic stations and institutions to which they were installed

Test site	Geographic coordinates			Institution
	Longitude	Latitude	Altitude a.s.l. (m)	
Jubany	62°14' S	58°40' W	7.5	Dirección Nacional del Antártico. Base Científica de Jubany
Marsh	62°00' S	57°30' W	2	Fuerza Aérea de Chile
Artigas	62°10' S	58°50' W	17.2	Instituto Antártico Uruguayo

the Chilean Air Force and situated on South Shetland Island. The station is situated a distance of between 50 m (summer) and 250 m (winter) from the high tide level (according to the degree to which the bay is frozen over).

Artigas (Uruguayan Antarctic): This station is located in the proximity of the Antarctic continent, in the Subantarctic region, specifically on South Shetland Island, and furnished the most airborne salinity deposition rates of the Antarctic sites (Rivero and Krecl, 2002, p. 4).

2.2. Materials and exposure sequences

The materials investigated were reference materials, in the form of flat plate specimens, with the following characteristics: mild steel (unalloyed, low carbon), zinc (98.5% min.), copper (99.5% min), and aluminium (99.5% min).

Specimens were withdrawn from the test sites after 1 year (for three consecutive years) and after 2, 3 and 4 years of atmospheric exposure. On each occasion four specimens of each material were withdrawn, three of which were used to determine weight losses according

Table 3

Environmental characteristics of Antarctic MICAT test sites

Code (Fig. 1)	Name	Country	T (°C)	RH (%)	TOW ^a (annual fraction)	Annual precipitation (mm/year)	Deposition rate (mg/m ² day)	
							Cl ⁻	SO ₂
1	Jubany	Argentina	-2.2	84	0.314	278	–	Negligible
2	Marsh ^b	Chile	-2.3	85	0.533	114	–	6.46
3	Artigas	Uruguay	-2.1	89	0.350	486	180.1	Negligible

The data in columns 4–9 are average values for the 4 years' duration of the study.

(–) Not available.

^a Time of wetness estimated according to ISO 9223¹³ number of hours/year during which RH ≥ 80% and simultaneously T > 0 °C.

^b In this testing station the duration of the study was for 2 years.

JUBANY



ARTIGAS



MARSH



Fig. 2. Photographs of the three test sites.

to ISO 9226 (1991). The fourth specimen was used for laboratory studies.

2.3. Laboratory studies

The removal of corrosion products by chemicals to determine weight loss involves a loss of valuable information about the atmospheric corrosion process. Thus a fourth specimen of each exposure sequence, cut into 4 pieces, from which, after its withdrawal from the testing station, the corrosion product layer was not removed. These pieces were used for laboratory studies: (a) analysis of corrosion products, and (b) microscopic examination (surface and cross section) of the morphology of the corrosion product layers and base metal attack.

The corrosion products were analysed using the following experimental techniques: X-ray diffraction (XRD), Infrared spectroscopy (IRS) and Mössbauer spectroscopy, the latter only for the identification of corrosion products formed on mild steel specimens.

XRD was carried out both on the powdered corrosion products obtained by carefully scraping the weathered surface of the test specimens, and by direct radiation of the aged surface. IRS was carried out on the powdered corrosion products using the traditional technique with a KBr tablet. Mössbauer spectroscopy was carried out at room temperature using a Co source, both on the powdered corrosion products and on the aged surface using the transmission mode.

With regard to the determination of soluble salts (chlorides and sulphates) in the corrosion product layers, after light brushing to remove the non-adherent layer (only for the weathered mild steel specimens) (De la Fuente et al., 2003, p. 130) the specimens were held at boiling point for 30 min in distilled and deaerated water (Mayne, 1959), in order to leach out the soluble contents. Once the leachate was filtered, the chlorides and sulphates content was evaluated by means of a selective electrode and turbidimetric analysis (ASTM D 516, 1968), respectively.

A scanning electron microscope (SEM), equipped with energy dispersive spectrometry (EDS) was used to study the morphology of corrosion product layers and attack of the base metal. Representative specimens of $1 \times 1 \text{ cm}^2$ were cut from the aged samples using a diamond wire saw. Micrographs were obtained of the

general appearance of the specimen surfaces. Microscopic observations were also carried out on cross sections of the specimens, cut in representative zones in order to evaluate the morphology and thickness of the corrosion product layers and the profile of the attack of the base metal.

3. Results and discussion

Table 5 presents the corrosion data obtained. It should be noted that in Artigas station use was made of galvanized steel plates instead of zinc sheets, and that in Marsh station the studies had a duration of only 2 years.

Table 6 presents a summary of the different information obtained during the study, for each of the reference metals.

In view of their proximity to the coast and the chloride deposition rates detected in the atmospheres

Table 5
Corrosion rates obtained for the reference metals during the study

Test site	Test series	Mild steel ($\mu\text{m}/\text{year}$)	Zinc ^a ($\mu\text{m}/\text{year}$)	Copper ($\mu\text{m}/\text{year}$)	Aluminium ($\text{g}/\text{m}^2 \text{ year}$)
Jubany	One year	37.3	1.98	1.98	5.47
	First year				
	One year	36.0	2.48	2.10	2.89
	Second year				
	One year	41.1	1.22	2.00	3.72
	Third year				
	Two years	25.0	1.07	1.17	3.20
	Three years	16.8	0.89	0.90	0.93
	Four years	15.7	0.72	0.73	0.67
	Marsh	One year	24.1	8.00	–
First year					
Two years		15.3	5.94	1.31	1.32
Artigas	One year	55.2	2.75	2.43	2.74
	First year				
	One year	74.9	1.59	2.06	1.86
	Second year				
	One year	67.4	1.99	1.98	2.88
	Third year				
	Two years	39.5	1.37	1.42	1.64
	Three years	40.2	1.45	1.04	1.32
Four years	36.5	1.23	0.84	1.08	

(–) Not available.

^a The material used in Artigas testing station was galvanized steel instead of zinc sheet.

Table 6

Average first year corrosion rates and nature of corrosion products and their soluble salts content on reference metals exposed for 1 year at Antarctic MICAT test sites participating in the MICAT project

Test site	Mild steel				Zinc			
	Corrosion rate ($\mu\text{m}/\text{year}$)	Corrosion products	Soluble salts (mg/m^2)		Corrosion rate ($\mu\text{m}/\text{year}$)	Corrosion products	Soluble salts (mg/m^2)	
			Cl^-	SO_4^{2-}			Cl^-	SO_4^{2-}
Jubany	38.1	L	1262	417	1.89	S	591	154
Marsh	24.1	L, G	1372	892	–	S	854	664
Artigas	65.8	L, G, Mg, M	–	–	2.11	–	–	–

Test site	Copper				Aluminium			
	Corrosion rate ($\mu\text{m}/\text{year}$)	Corrosion products	Soluble salts (mg/m^2)		Corrosion rate ($\text{g}/\text{m}^2 \text{ year}$)	Corrosion products	Soluble salts (mg/m^2)	
			Cl^-	SO_4^{2-}			Cl^-	SO_4^{2-}
Jubany	2.03	Cu, At	1031	71	4.03	A	173	314
Marsh	–	–	947	373	3.65	A	N.S.	N.S.
Artigas	2.16	–	–	–	2.49	–	–	–

Corrosion data are average values for three 1-year exposures (Table 5).

(–) Not available; N.S.: not significant (Cl^- and SO_4^{2-} <50 mg/m^2); L: lepidocrocite ($\gamma\text{-FeOOH}$); G: goethite ($\alpha\text{-FeOOH}$); Mg: maghemite ($\gamma\text{-Fe}_2\text{O}_3$); M: magnetite (Fe_3O_4); S: simonkolleite ($\text{Zn}_5\text{Cl}_2(\text{OH})_8 \cdot \text{H}_2\text{O}$); Cu: cuprite (Cu_2O); At: atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$); A: alumina ($\delta\text{-Al}_2\text{O}_3$).

surrounding the three MICAT corrosion testing stations operating in the Antarctic region, these sites can be classified as pure marine, since atmospheric pollution by SO_2 of anthropic origin can be considered negligible. Nevertheless, among the corrosion products formed on the weathered metals it is possible to find appreciable quantities of sulphates, whose origin may be attributed to the marine aerosol.

Thus, on the basis of these atmospheres' chloride contents, they may be classified according to ISO 9223 (1991) under the denomination S_2P_0 , with chloride deposition rates of between 60 and 300 $\text{mg Cl}^-/\text{m}^2 \cdot \text{day}$ and SO_2 deposition rates of less than 10 $\text{mg SO}_2/\text{m}^2 \cdot \text{day}$.

It is interesting to analyse the corrosion processes that take place in these marine atmospheres, with their singular climatic conditions, and compare them with the processes found in marine atmospheres of a similar atmospheric salinity but corresponding to temperate climates (Mariaca et al., 2000). This is the aim pursued in the following discussion, which is structured under four subheadings dedicated respectively to the four reference metals tested.

3.1. Mild steel

The corrosion rates found in the Antarctic region were, in general, lower than those corresponding to

temperate climates atmospheres of a similar salinity. This may be due to the decrease in electrochemical activity at the metal/rust interface during long time periods as a result of the low temperatures, the low times of wetness of the metal surface and the reduction of oxygen access to the metallic surface due to the formation of ice layers during a significant part of the exposure time.

However, taking into account the presence of ice particles on the metallic surface during such long periods of time, the relatively high corrosion rates that are found may be considered surprising. Laboratory studies carried out in Spain and Argentina, applying electrochemical techniques, showed that as low as -8°C it is possible to measure electrical activity at the ice/metallic surface interface (González, 1989, p. 297; Rosales et al., 1996, p. 6). These currents may indicate the existence of a liquid electrolyte film at this "interface". This observation lends weight to the hypothesis that the electrolyte film may be capable of solubilizing the chloride ions present in the corrosion product films formed in the Antarctic atmospheres, giving rise to concentrated chloride solutions.

As in the case of marine atmospheres in temperate climates, the corrosion products found after the first year of exposure are usually comprised fundamentally by lepidocrocite ($\gamma\text{-FeOOH}$), goethite ($\alpha\text{-FeOOH}$),

Table 7

Relative proportions of corrosion products in MICAT atmospheres in Uruguay Antarctic site (%) (Quagliata et al., 1994)

Product	Artigas (Antarctic)	
	1 year	2 years
Lepidocrocite	69.0	78.7
Goethite	23.4	19.3
Maghemite	7.6	2.0

maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4), the last two in lower proportions. Studies carried out in Uruguay using Mössbauer spectroscopy (Quagliata et al., 1994) show that, in contrast with what is normally seen in the atmosphere, at Artigas (Antarctic) there was an increase in lepidocrocite and a decrease in goethite during the second year of exposure, as can be seen in Table 7.

The particular exposure conditions in these special atmospheres could be the reason behind the impeding of the natural reaction of the transformation of lepidocrocite into goethite with increasing exposure time. The eventual transformation of goethite into

maghemite, after longer exposure times, also seems to be inhibited here.

The surface micrographs (Fig. 3A,B) show flattened structures which are explained by their formation under ice, while the cross sections (Fig. 3C,D) show the effect of the accumulation of soluble salts (from the marine salts) at the metal/corrosion products interface. Dissolved in extremely thin films of water which infiltrate the rust, these salts must have provided the highly aggressive electrolyte (Rosales, 1997, p. 218), responsible for the serrated profiles of the steel/rust interface, resulting from the deep localized attack of the base metal which is observed. The surface micrographs (Fig. 3A,B) show typical fractures associated with changes in the state of the electrolyte. The decrease in the density of the electrolyte when it freezes must cause the fracturing of the rust layer, facilitating the access of corrosive agents from the environment in the following periods of free exposure to the environment when the ice melts.

The surface morphology of the corrosion product layers that are formed corresponds to more or less

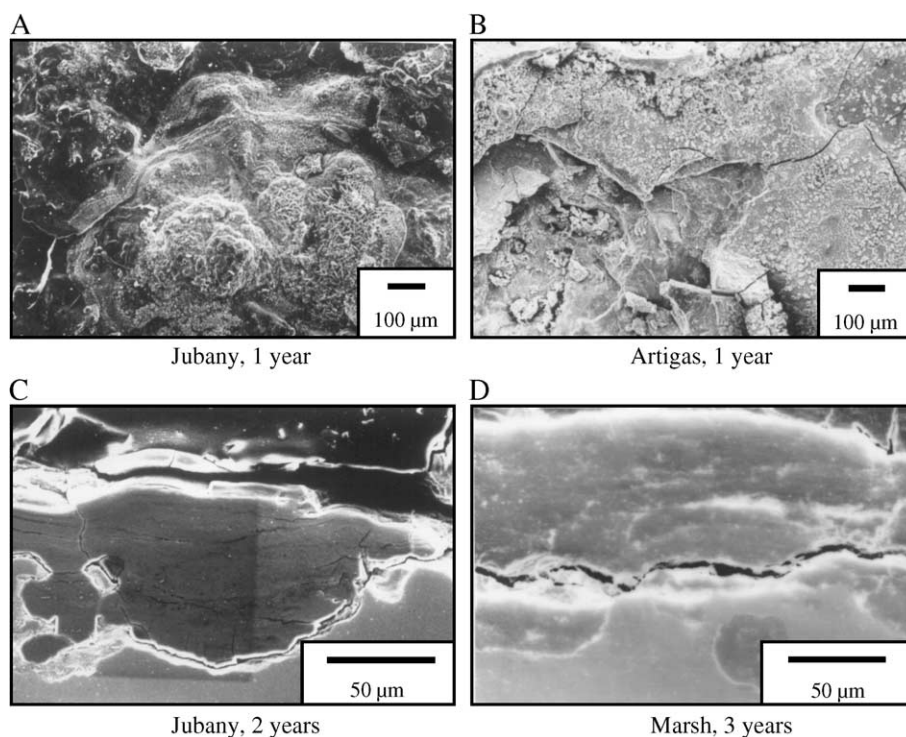


Fig. 3. SEM micrographs, surface (A and B) and cross section (C and D) of steel weathered in marine Antarctic atmospheres.

generalized honeycomb structures (Fig. 3A,B), composed mainly of lepidocrocite and goethite. In cross section, these layers showed an inner phase, which is inlaid between the crests of the steel profile and composed mainly of magnetite. Another outer phase, which is fairly compact but cracked in parallel direction to the steel surface, presents cleavage planes by which flaking easily occurs (Fig. 3C,D). The relatively high density of the corrosion product layers formed also contributes to reducing the steel corrosion rates.

3.2. Zinc

As in the case of mild steel, the corrosion rates found for zinc in the Antarctic stations of Jubany and Artigas (Table 5) ($\sim 2 \mu\text{m}/\text{year}$) are lower than those found in marine atmospheres of a similar salinity belonging to other temperate or tropical climatic regions (Mariaca et al., 2000, p. 8).

The corrosion products formed during the first year of exposure included simonkolleite (Table 6), a basic zinc chloride ($\text{Zn}_5\text{Cl}_2(\text{OH})_8 \cdot \text{H}_2\text{O}$) that is commonly

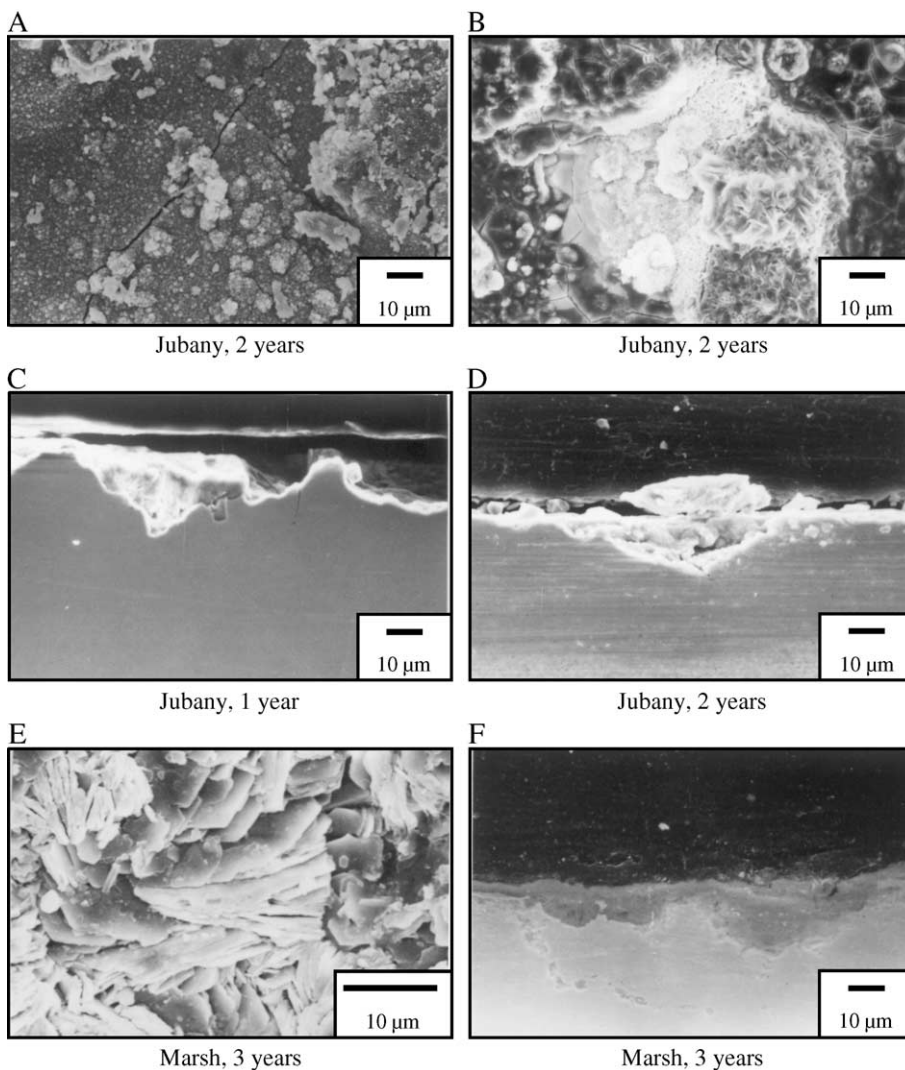


Fig. 4. SEM micrographs, surface (A, B and E) and cross section (C, D and F), of zinc weathered in marine Antarctic atmospheres.

found on zinc surfaces exposed to atmospheres with a high saline content. The SEM micrograph in Fig. 4B shows the presence of small simonkolleite crystals on the zinc surface exposed for 2 years in the Antarctic atmosphere of Jubany, while Fig. 4E shows a larger degree of simonkolleite crystallization on a zinc surface exposed for 3 years in the Marsh atmosphere.

Fig. 4C, D and F show cross sections of zinc specimens exposed for 1, 2 and 3 years in different Antarctic test sites, where it is possible to observe severe localized corrosive attack.

As has already been mentioned in the case of mild steel, the zinc surfaces exposed in Antarctic conditions remained under a relatively thick ice block for long periods. During these periods, temperature changes could lead to the formation of a thin liquid water layer at the metal/corrosion product layer interface. This water dissolves the occluded chlorides in these layers, forming high concentration chloride solutions, at least every time the sun's radiation promotes temperature increases of the metal surface, leading to the melting of the adjacent ice layer. The concentrated chloride solution formed seems to be responsible for the pitting corrosion phenomenon and for simonkolleite crystallization during drying periods.

These results suggest that the controlling parameters for simonkolleite crystallization seem to be the chloride and water contents of the corrosion product layers but not the temperature, as has previously been proposed (Almeida et al., 1989). The MICAT project proved that crystallized simonkolleite, consisting of large and almost perfect pseudo-hexagonal crystals, can be formed from tropical to Antarctic conditions (Morcillo et al., 1999, p. 529).

The SEM micrograph of the zinc surface aged in these atmospheres (Fig. 4A) shows a scarce formation of corrosion products, since these are continuously dissolved during their formation by the leaching effect of water films at the interface between the corroded zinc and the ice layer that covers it for most of the year.

However, these results are not inconsistent with the high pitting rates of zinc in these atmospheres, which are due to the existence of an aqueous solution with a high chloride content at the zinc/ice interface. These saline solutions can continue to remain in liquid state at air temperatures of the order of -3 °C.

3.3. Copper

In principle it seems surprising to find a relatively low copper corrosion rate in these atmospheres (≈ 2 $\mu\text{m}/\text{year}$), compared with other atmospheres of a similar atmospheric salinity (Table 5). However, considering that electrochemical activity on the copper surface is impeded (or at least reduced) by the formation of ice during a considerable part of the exposure time, the lower corrosivity of these atmospheres for copper could be justified.

Atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$) is the corrosion product most commonly found in marine atmospheres. In some cases paratacamite, an isomorphic compound of atacamite, is also found. It is also common to find brochantite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6$) and posnjakite ($\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) in marine atmospheres, even when the atmosphere presents low SO_2 deposition rates, due to the easy retention of background atmospheric pollution in copper corrosion product layers (Morcillo et al., 2001, pp. 971–972). The mixture of basic copper chlorides and sulphates presents a blue-greenish colouring, which is characteristic of the copper patinas found in marine atmospheres contaminated with SO_2 .

As has already been mentioned, Antarctic atmospheres present singular characteristics that distinguish them from marine atmospheres corresponding to temperate or tropical climates. These singular characteristics are related with the purity of the air, the absence of rainfall in these frozen climatic conditions, and the formation of ice on the metallic surface during a large part of the exposure time.

With regard to air purity, the atmospheres of Artigas, Jubany and Marsh register a practically complete absence of SO_2 . Only basic copper chlorides are formed (basically atacamite), without the coexistence of basic copper sulphates (brochantite and posnjakite), and the corrosion products present an attractive blue-turquoise colouring.

On the other hand, the absence of rainfall, and its effect of washing off the salts from the marine aerosol deposited on the metallic surface, favours the rapid precipitation of basic chlorides and the surface soon becomes coated with corrosion products. As a result, a large percentage of the copper surface becomes covered with atacamite even during the first year of exposure, thus reducing the corrosion rate of copper.

Fig. 5 displays SEM micrographs of the surface and cross section of copper exposed in the Antarctic test sites of Jubany and Marsh.

The morphology of atacamite spheres spread across the metallic surface, commonly observed in marine atmospheres, is seen in the Antarctic atmospheres to be flattened by the effect of the ice block which keeps the surface covered for most of the time. The corrosion product layer is cracked and flaked in relatively large areas (Fig. 5A, B and E). The existence of an aqueous layer with a high salt concentration at the copper/ice interface, in

addition to promoting a certain generalized attack of all the exposed surface, could perhaps favour the formation of gel type hydrated basic chlorides, which would subsequently crack during drying cycles when losing their hydration water. The expansion of the water upon freezing would also favour this cracking. In spite of this, the corrosion rates were seen to decrease with exposure time, indicating the presence of films of a certain protective power.

The cross sections of the patinas formed in these atmospheres (Fig. 5C, D and F) show an irregular

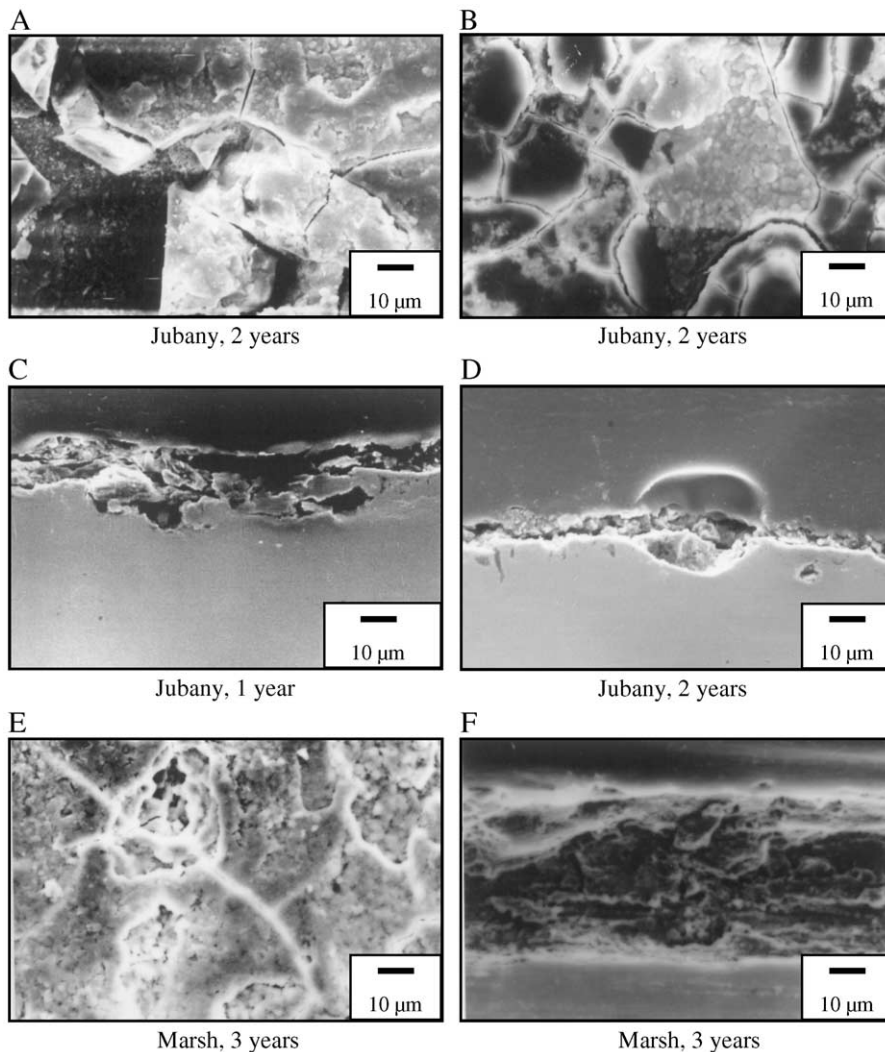


Fig. 5. SEM micrographs, surface (A, B and E) and cross section (C, D and F) of copper weathered in marine Antarctic atmospheres.

morphology with numerous imperfections and pitting of the base metal, as occurs in typically marine atmospheres in temperate or tropical climates.

3.4. Aluminium

The corrosion rates found for aluminium in the Antarctic stations were considerably greater than those found in other equivalent marine atmospheres corresponding to temperate or tropical climates (Mariaca et al., 2000, p. 8). Aluminium attack in Antarctic atmospheres varies from one test site to another probably as a function of the salt deposited on the metal surface. Salinity data is available only for the Artigas atmosphere (Table 3), which seems to be rather less aggressive to aluminium than the other two atmospheres (Table 5). Pitting observed in Jubany atmosphere is considerably more pronounced than the corresponding exposures at Artigas (Fig. 6).

Corrosion rates variation with the exposure time reveal a better protective power of the layers formed in this environment, compared with those found in other climatic conditions. The attack decay ratio (R)

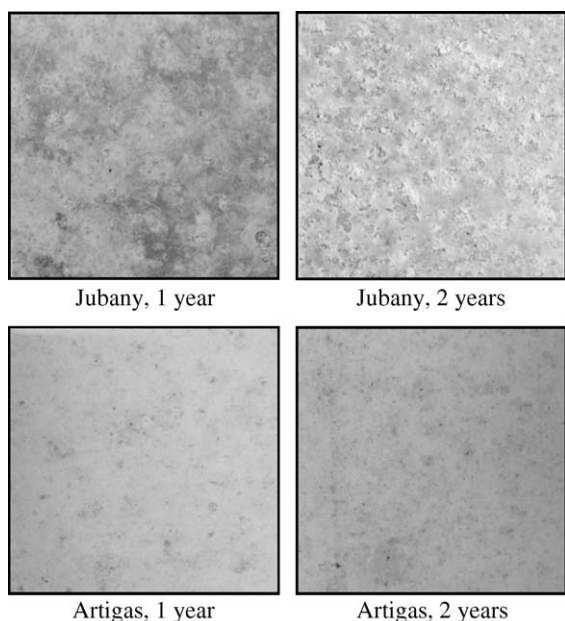


Fig. 6. Aspect of aluminium surface weathered in marine Antarctic atmospheres.

Table 8

Corrosion rates (C , g/m^2 year) and corrosion decay ratios (R) of aluminium exposed in two Antarctic atmospheres

Test site	1st year		2nd year		3 years		4 years	
	C	R	C	R	C	R	C	R
Jubany	4.03		3.20	0.79	0.93	0.23	0.67	0.17
Artigas	2.49		1.64	0.66	1.32	0.53	1.08	0.43

for aluminium in this type of atmospheres decreases very quickly with exposure time (Table 8), in agreement with the thick and continuous corrosion product layers that form on the aluminium surface after only 2 years of exposure (R is defined as the relationship between the corrosion rate after two or more years and after 1 year of atmospheric corrosion).

The formation of alumina on these surfaces is so abundant that it is easily detected by XRD after the first year of exposure (Fig. 7A,B). After 4 years of exposure most of the surface has been attacked, showing the abundant formation of alumina.

The climatological conditions prevailing in the Antarctic promote a singular attack of aluminium surfaces, not seen in any of the other MICAT atmospheres. Aluminium corrosion in this type of atmosphere is practically generalized (Fig. 7A,B) and reaches the highest levels of all the pure marine atmospheres, despite the fact that the surface of the metal is covered by ice during a large part of the exposure time. The indications seem to be that saline particles from the sea are initially deposited on the aluminium surface where they accumulate due to the absence of rain. The deposition of snow and the formation of ice on the aluminium surface is not an obstacle, in cryoscopic terms, for there to be a highly concentrated chloride solution at the metal/ice interface, which promotes a practically generalized attack of the aluminium surface. This concentrated saline solution already promotes a strong attack of the aluminium in the first year of exposure, degrading all of the surface in an almost uniform way (Fig. 7D). Pitting is also observed (Fig. 7C) as commented before.

SEM observation of the surface shows a morphology similar to that of a honeycomb, in which all of the surface is attacked and covered with alumina. Dehydration of the alumina coating causes local

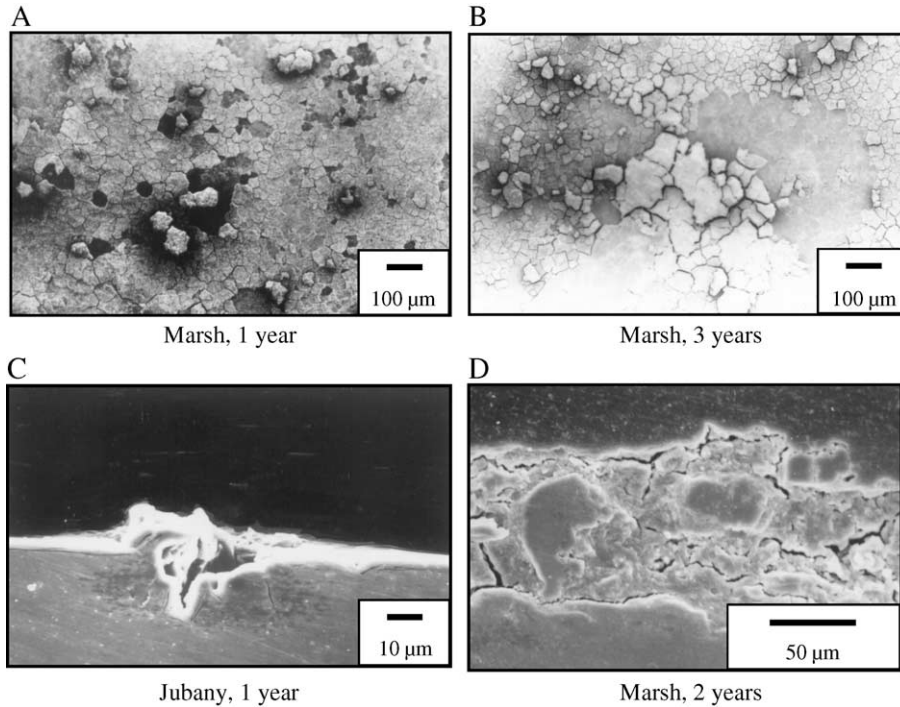


Fig. 7. SEM micrographs, surface (A and B) and cross section (C and D) of aluminium weathered in marine Antarctic atmospheres.

cracking and flaking, offering an attractive and singular mosaic-like appearance (Fig. 7A,B).

4. Conclusions

The singular climatic conditions presented by the Antarctic region, with its great air purity, very low temperatures, strong winds and low rainfall, mean that for a large part of the year metallic surfaces are covered by an ice layer which makes it extraordinarily difficult for metallic corrosion processes to develop.

Nevertheless, as different researchers have shown, below this ice layer there can be a water layer that permits a certain degree of electrochemical activity on the metallic surface.

The three Antarctic stations where this study has been carried out were situated close to the shoreline and the atmospheres did not include significant sulphur dioxide concentrations. In this case, the underlying electrolyte layer can include a high saline concentration, which extraordinarily delays the freez-

ing process and leads to unexpected metallic corrosion rates.

The corrosion rates found for mild steel, zinc and copper were higher than expected but below those found in equivalent atmospheres belonging to temperate or tropical climates. In the case of aluminium, on the other hand, the corrosion rates were notably higher.

The morphology of the attack in the case of the mild steel, zinc and copper was not different to that found in temperate or tropical climates: a generalized attack over all the surface with the presence of localized focal points (pitting) due to the existence of the chloride ion at the metal/corrosion products interface.

In the case of aluminium, the attack is also generalized, similar to that experienced by aluminium in conditions of immersion in seawater, and unlike the localized attack presented by aluminium in marine atmospheres corresponding to other climatic zones. This generalized attack of aluminium reinforces the hypothesis of the existence of a water layer with a high saline concentration between the metal and the ice layer.

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