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► **To cite this version:**

Maria João F. Marques, A. Benedetti, F. Castelli, M. Delucchi, M. Faimali, et al.. Influence of natural seawater variables on the corrosion behaviour of aluminium-magnesium alloy. *Bioelectrochemistry*, 2023, 149, pp.108321. <10.1016/j.bioelechem.2022.108321>. <hal-03879043>

HAL Id: hal-03879043

<https://hal.science/hal-03879043v1>

Submitted on 30 Nov 2022

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Influence of natural seawater variables on the corrosion behaviour of aluminium-magnesium alloy

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Abstract

Corrosion is an important issue for alloys in natural seawater, where microorganisms can accelerate or mitigate corrosion. Al-Mg alloys are used for marine activities and various associated technologies. Here, the behaviour of AA5083 alloy was investigated in natural seawater with marine exposure lasting up to 50 days and detailing the first 8 days in two experimental series.

Experimental work was carried out, including semi-field tests in natural seawater (biotic conditions) compared with abiotic conditions. The open circuit potential (OCP) measurements, during the immersion time, exhibited significantly different behaviours: an OCP downward displacement occurred under abiotic conditions, while, in biotic conditions OCP remained generally stable since the beginning of the immersion, revealing an inhibiting effect of the biological activity on the Al-Mg corrosion. This was accompanied by different surface modifications under biotic conditions: surface and cross-section characterization, performed by scanning electron microscopy with energy dispersive X-Ray spectroscopy, showed less corrosion developed on the surface after 8-day immersion and formation of a protective layer during 50-day immersion.

The present study shows that marine biological activity positively influences the Al alloy corrosion process, with surface modifications resulting in a protective effect counteracting the aggressiveness of chloride ions.

Keywords:

Aluminium alloy
Natural seawater
Corrosion inhibition
Protective barrier layer

Highlights

- Abiotic and biotic immersion conditions influence AA5083 surface modifications.
- NaCl solution vs artificial seawater: Influence of seawater components.
- Marine biological activity positively influences AA5083 corrosion process.
- Microbial activity promotes the formation of a protective layer on AA5083 surface.

1. Introduction

The development of marine activities and the various associated technologies (shipbuilding, offshore oil & gas extraction, ocean renewable energy, aquaculture and blue biotechnology) poses new challenges for the durability of infrastructures and facilities due to the aggressiveness of the marine environment [1]–[7].

The exposure of any material to seawater initiates a series of sequential biological and chemical events, which must be understood if we are to tackle the microbiological aspects in marine corrosion. In recent years, it has become clear that microorganisms do not only cause corrosion (Microbiologically-Influenced Corrosion - MIC), but can also inhibit it or protect against it, a process known as MIC Inhibition (MICI)[8]–[10].

At present, most of the published research on metallic corrosion induced by microbiological activity is centred on steel and stainless steel, which have been in use in marine constructions for many years. However, over recent years, Aluminium (Al) has attracted the attention of many industrial sectors linked to seawater [11]–[13]. Pure Al is relatively soft but alloying it with different elements can induce new properties, such as additional mechanical strength and corrosion resistance. The aluminium - magnesium alloys (Al - Mg) of the 5XXX series are among the most widely used in the shipbuilding industry as they have excellent properties for marine applications, such as low density, easy workability and high recyclability [14], [15].

The majority of the literature dedicated to the study of Al-Mg alloys in seawater addresses the effects of metallurgical and microstructural properties on the corrosion behaviour. The research results confirm the good resistance of these alloys to marine environments, but without attempting to understand the impact of the microbial activity on the corrosion process[16]–[20].

A previous Joint Industry Project on corrosion protection for aluminium catamarans, involving a 2-year natural exposure of AA5083 in splash and immersion zones, showed different corrosion behaviours among samples depending on the exposure zones and the presence of biofouling [21]. The formation of a compact, uniform layer on the Al alloy surface, the thickness of which was shown to increase with time, was observed in the exposed zone with presence of marine microorganisms. In contrast, the Al-Mg alloy in the absence of microorganisms showed localized corrosion [22]. Additionally, Al-Mg surface exposed in biotic conditions presented a resistance to charge transfer (measured by electrochemical impedance spectroscopy - EIS) at least 2000 times that of the surface exposed in abiotic conditions [23]. These results suggest that biochemical and microbial effects positively influence the Al alloy corrosion process [24].

The objective of the present study is to assess the influence of natural seawater with its microbial activity on the resistance of the AA5083 Al-Mg alloy during marine exposure. For this purpose, experimental work has been performed including two lines of research:

- the first, 50-day experiment, aims to follow the corrosion behaviour of a commercial alloy immersed in semi-field marine environment, representative of a real-world use. Artificial seawater was chosen as control to accurately represent natural seawater without fauna and flora and therefore without microbial activity.
- the second, 8-day experiment, aims to evaluate at a deeper detail the initial stages of the phenomena observed during the 50-day experiment. Cast Al-Mg alloy with the same composition of the commercial AA5083, and NaCl solution as control were used to focus on effects exerted by the biological component (microbial and organic & chemical linked to microbial activity) of the natural seawater.

The open circuit potential (OCP) was measured in both the 50- and 8-day experiments. After the exposure surface and cross-section of Al-Mg electrodes had been characterized by scanning electron microscopy (SEM) with energy dispersive X-Ray spectroscopy (EDX). In parallel, stainless steel was used as a reference material to monitor the presence of microbial activity on the surface as its behaviour in natural seawater is well-known [25-28]: indeed, there is a consensus that the marine biofilm catalyses the electrochemical reduction of oxygen on stainless steel surfaces and then leads to an ennoblement of

the OCP. Therefore, the time evolution of the OCP ennoblement on stainless steel has been intended as a proof of the marine microbial activity [29].

2. Materials and Methods

Experiments were performed by immersing aluminium-magnesium alloy and stainless steel electrodes in biotic and abiotic solutions for 50 days and 8 days. A commercial Al-Mg alloy was used for the 50-day experiment and a cast Al-Mg alloy for the 8-day ones.

2.1. 50-day experiment with commercial alloy

2.1.1. Electrode preparation

The elemental chemical composition of the commercial aluminium-magnesium alloy 5083-H111 (identified as Al-Mg), used in the 50-day experiments is given in Tab.1. The material was used as received in an initial rough grinding state and no additional surface preparation was performed in order to evaluate its behaviour during a real-world use. Before immersion, the electrode surfaces were carefully cleaned with water and alcohol and then dried with hot air.

For stainless steel (identified as SS), the commercial 254 SMO alloy (composition 0.01% C, 19.9% Cr, 6% Mo, 17.8% Ni, 0.5% Mn, 0.02% N) was used as a control for the microbial activity. The surfaces were cleaned for 20 min with 50–50% ethanol/acetone, then for 15 min with 2–20% fluoridric–nitric acid solution and rinsed with water.

The dimensions of both the Al-Mg and SS electrodes were 2 x 10 x 0.7 cm. A titanium rod was screwed 1 cm from the top of the electrode to allow the electrical contact.

Here Table. 1

2.1.2 Immersion test

The 50-day experiments were carried out in a natural seawater environment (semi-field biotic) at the CNR- IAS – Genoa Experimental Marine Station (GEMS, 44° 24' 25.87" N; 8° 56' 02.34" E) in the period from mid-March to mid-May. Temperature, measured once a day, was in the 15-18 °C range, the lowest temperatures occurring in March and the highest in May.

4 Al-Mg and 2 SS electrodes were partially immersed (the top 2 cm, including the electrical contact, were not immersed) using the following set-up (Fig. 1a):

- Immersion environment: 60 L tank not exposed to the natural photoperiod,
- Medium renewal: 6 L/h,
- OCP monitoring rate: 1 point day⁻¹,
- OCP acquisition device: Keithley 614 Electrometer,
- Reference electrode: Red Rod – saturated KCl (+199 mV versus SHE).

The control test (abiotic) was performed at LGC – Toulouse in artificial seawater (ASTM D1141-98, reapproved 2003) [30], the composition of which was NaCl 24.53 g/L, MgCl₂ 5.20 g/L, Na₂SO₄ 4.09 g/L, CaCl₂ 1.16 g/L, KCl 0.695 g/L, and < 0.2 g/L NaHCO₃, KBr, H₃BO₃, SrCl₂, NaF.

The set-up (Fig. 1b) was as follows:

- Immersion environment: 600 mL reactors (one reactor for 4 Al-Mg electrodes and one reactor for 2 SS electrodes),
- Medium renewal: none,
- OCP monitoring rate: 1 point day⁻¹,
- OCP acquisition device: Reference 600™ Potentiostat/Galvanostat/ZRA + ECM8™ Electrochemical Multiplexer from GAMRY Instruments using the two-electrode set-up,

- Reference electrode: Saturated Calomel Electrode - SCE (+241 mV versus SHE).

Here Fig. 1

2.2. 8-day experiment with cast alloy

2.2.1. Electrode preparation

The Al-Mg electrodes were prepared from a ternary alloy based on the composition of the commercial AA5083 alloy and basically following the thermal treatment indicated by the H111 procedure (annealing and slight strain-hardening during subsequent operations such as stretching or levelling).

The preparation was as follows. The nominal composition was Al 94.5, Mg 4.5, Mn1 (wt. %). The elements used as starting materials were Al bar of 99.999 wt. % purity (supplied by WAV-AG "Kryal"), Mg rod of 99.99 wt. % purity (supplied by Newmet Koch) and Mn flakes of 99.98 wt.% purity (supplied by Koch Chemicals). A total weight of about 10 g of the constituent metals, in stoichiometric amounts, was inserted in a tantalum tube, which was sealed by arc-melting and used as a crucible. The synthesis was performed by an induction furnace to obtain the alloy ingot; the melting, performed under a stream of pure argon, was repeated several times in order to ensure the homogeneity of the ingot. The use of sealed crucibles was necessary to prevent magnesium losses due to its high vapour pressure. After melting, the ingot was annealed in a resistance furnace for 60 hours at 600 °C. After the annealing, the ingot was hot rolled at 390 °C to obtain a 1 mm thick sheet. In order to reduce the mechanical strain, the samples were annealed at 400 °C for 72 hours.

SS electrodes were prepared from commercial 254-SMO alloy.

Al-Mg and SS electrodes were cut in 1×1 cm squares, a silver-plated copper wire was soldered, using a SnZn30 (wt.%) alloy, to make the electrical contact, then the electrodes were embedded in epoxy resin. The electrodes were finished by grinding, lapping and polishing the surfaces with diamond abrasive spray down to a grain size of 1 µm.

2.2.2. Immersion test

The 8-day experiments were carried out at the CNR-ICMATE Marine Station MARECO, in Bonassola (44° 11' 00.37" N; 9° 35' 02.73" E). Eighteen Al-Mg and eighteen SS electrodes were fully immersed in natural seawater (biotic environment), while nine Al-Mg and nine SS electrodes were immersed in NaCl solution (abiotic control). The biotic and abiotic experiments were run synchronously in the second half of October and both environments were exposed to the natural photoperiod, letting the temperature settle in the 19-22 °C range (lowest measured around dawn and the highest near noon). All the electrodes were fixed on plastic holders with the surface facing the bottom of the tanks in order to prevent direct sunlight falling on the surface.

The working parameters for the biotic environment were the following:

- Immersion environment: 200 L tank fed with natural seawater (noted tank 'B', Fig. 2),
- Medium renewal: 0.5 L min⁻¹,
- OCP monitoring rate: 1 point h⁻¹,
- OCP acquisition device: the acquisition was governed by a home-made device (Fig. 3), which was developed by integrating a Yokogawa 6551 multimeter with a lab-built relay board controlled by a PC (RaspberryPi) that stored the OCP data acquired by the multimeter. Other integrated circuits and boards like the Arduino board were used to adapt the communication standard,
- Reference electrode: SCE (+241 mV versus SHE)

The control test (abiotic) was conducted as follows:

- Immersion environment: 50 L tank filled with NaCl 35g/L solution (noted tank 'A', Fig. 2), immersed in a 200 L tank where the circulating seawater acted as a thermostatic bath.
- Medium renewal: none,
- OCP monitoring rate: 1 point h⁻¹,
- OCP acquisition device: the same as for the biotic system
- Reference electrode: SCE (+241 mV versus SHE)

Here Fig 2

Here Fig. 3

2.3. SEM/EDX characterization

2.3.1. 50-day experiment with commercial alloy

After 50 days of immersion in natural or artificial seawater, the Al-Mg electrodes were washed and dried with hot air. Then the surface and cross-section were characterized using scanning electron microscopy with associated energy dispersion spectrometry. The SEM observations were performed using a Philips FEG-SEM, mode XL30 microscope coupled with a Thermo Fisher Scientific Pathfinder energy dispersive X-Ray spectrometer (EDX) for elementary chemical analysis. The metallographic samples were prepared using a cold mounting epoxy resin. The cross-sections were then ground (SiC abrasives with several grain sizes up to 1000 grit) and polished (diamond paste up to 1 μm grain size). All prepared samples, surface and cross section, were metallized with gold (Au) prior to SEM observation to reduce charging effects.

2.3.2. 8-day experiment with cast alloy

After 8 days of immersion in natural seawater or NaCl solution, the electrodes were gently washed and SEM-EDX observations were performed on three Al-Mg electrodes chosen at random in each of the biotic and abiotic environments. The SEM observations were performed using a LEO 1450VP unit coupled with an Oxford Instruments model 7353 energy dispersive X-Ray spectrometer (EDX) for elementary chemical analysis (CNR-ICMATE - Genoa, Italy). Samples, already mounted in epoxy resin, were metallized with gold (Au) to reduce charging effects.

3. Results

3.1. Open Circuit Potential

3.1.1. 50-day experiment with commercial alloy

The OCP time evolution in the 50 day period in biotic vs. abiotic environments for SS and Al-Mg alloys is presented in Fig.4 and Fig.5 respectively.

For SS, an OCP ennoblement from ~100 mV/SCE to ~360 mV/SCE was observed in the biotic environment from day 10 (indicated by the green line in Fig. 4), while the OCP remained stable at 0 mV/SCE in the abiotic conditions.

For Al-Mg, in the biotic environment, all the electrodes exhibited stable OCP values, around -770 mV/SCE, from the beginning of immersion to day 10, as indicated by the green line on Fig. 5. Thereafter, OCP was less stable, showing variations of up to 30 mV until day 35, then all the electrodes exhibited the same OCP value (~-770 mV/ECS). Conversely, in the abiotic conditions, OCP values were slightly above -900 mV/SCE just after immersion, then rapidly jumped up to -760 mV/SCE to fall back rapidly to -900 mV/SCE. Thereafter, a roughly linear OCP decrease occurred from the fifth day, finally ending around -1000 mV/SCE.

Here Fig. 4

Here Fig. 5

3.1.2. 8-day experiment with cast alloy

The time evolution of OCP in the 8-day period for SS and Al-Mg electrodes is presented in Fig.6 and Fig.7 respectively.

For SS, OCP for most of the electrodes started to ennobles in natural seawater around the 4th day (indicated by the green line on Fig. 6), whereas this behaviour was never observed in the NaCl (abiotic) environment. For Al-Mg, OCP showed a similar behaviour in both biotic and abiotic environments in the first 4 days, exhibiting a 100-150 mV decrease from the initial immersion value, from around -660 mV/SCE to -800 mV/SCE. Beyond the fourth day, differences between biotic and abiotic conditions emerged: in NaCl solution, OCP pursued its downward shift until a mean value of about -950 mV SCE was reached, while, in the biotic environment, OCP stabilized around -800 mV SCE on average with wide oscillations that appeared in correspondence with the beginning of the SS ennoblement (green line Fig. 7b). The oscillations are detailed in Fig. 8: two maxima and two minima were observed in the 24 hour period, with an amplitude of 100-150 mV, the two maxima at dawn and in the afternoon, and two minima around noon and during the night. The frequency of oscillations seems to be related to the period of solar radiation (in full sunshine or shade), the temperature of the environment and the consequent microbiological activity.

Here Fig. 6

Here Fig. 7

Here Fig. 8

3.2. SEM/EDX characterization of Al-Mg after immersion

3.2.1. 50-day experiment with commercial alloy

After 50 days of exposure, the Al-Mg electrodes immersed in artificial seawater (abiotic condition) and natural seawater (biotic condition) presented significantly different appearances, as shown in Fig.9.

Here Fig. 9

In both exposure conditions, biotic and abiotic, the boundary between the immersed and non-immersed zones was clearly visible and, in the case of Natural Seawater exposure (biotic condition), the Al-Mg electrodes showed much more significant surface darkening. The SEM surface and cross section characterization confirmed this different behaviour.

Fig.10 summarizes the result of Al-Mg surface observations. The Al-Mg electrodes exposed in the abiotic condition (Artificial Seawater, Fig.10.a), exhibited corrosion products that were non-uniformly distributed, with the persistent presence of initial grinding lines, characteristic of the initial surface of the electrode. The elementary chemical analysis performed by EDX revealed, in addition to the presence of aluminium (Al) and magnesium (Mg), the presence of oxygen (O), chloride (Cl), sodium (Na) and traces of sulphur (S). Depending on the areas analysed, i.e., with more or less corrosion products present, the aforementioned chemical elements, such as oxygen, sodium and chloride, were detected with different intensities.

In the case of Al-Mg electrodes immersed in the biotic condition (Natural Seawater, Fig.10.b), although the grinding lines of the initial surface were still observed in some areas, the lines were significantly less visible. In addition, a more uniform and voluminous presence of corrosion products was observed, appearing as a layer with a cracked morphology. Depending on the area analysed, the EDX identified, in addition to the presence of aluminium (Al), magnesium (Mg) and oxygen (O), a minor presence of sulphur (S), calcium (Ca) and phosphorus (P). The presence of chloride was not detected in the areas analysed.

SEM cross-section characterization was performed and the results are brought together in Fig.11. The Al-Mg immersed in abiotic conditions (Artificial Seawater, Fig. 11.a) showed a thin layer of corrosion products (an average value of about 1 μm) with low-intensity localized attacks. Comparatively, the Al-Mg exposed in the biotic condition (Natural Seawater, Fig. 11b) presented a thicker corrosion product layer with an average thickness between 2 μm and 4 μm , which was relatively uniformly distributed over the Al-Mg surface and presented no localized attacks. Moreover, in the areas where the layer was not present or was unevenly formed and lacked adhesion, as was the case in the splash zone, the Al-Mg substrate presented localized attack (Fig.12).

The elemental chemical analysis performed by EDX on the corrosion product layers developed under the different immersion conditions (abiotic and biotic) identified, for both cases, the same chemical elements as those previously analysed on the Al-Mg surfaces (Fig.11).

Here Fig. 10

Here Fig. 11

Here Fig. 12

3.2.2. 8-day experiment with cast alloy

After the 8 days of immersion, the surfaces of Al-Mg electrodes randomly chosen from abiotic and biotic conditions were observed by SEM. Fig.13 shows the digital surface images of the Al-Mg electrodes at the end of immersion and the corresponding result of SEM surface observations.

At the macroscopic scale, differences were visible between the surfaces of electrodes immersed in abiotic and biotic environments (Fig.13a). The Al-Mg electrodes exposed to the abiotic condition (NaCl solution) revealed a more significant corrosion attack, expressed by the clearly observable presence of corrosion products, as well as localized corrosion. Comparatively, the Al-Mg electrodes exposed in the biotic condition (Natural Seawater), showed a surface darkening in the form of a layer/deposit covering the entire surface and presenting a random distribution of the few sites with corrosion.

The SEM observations (Fig.13b) confirm, for Al-Mg in the abiotic condition, the presence of voluminous corrosion products with poor adhesion to the substrate. Surface localized attack in the form of pitting corrosion was present too. In contrast, the Al-Mg electrodes in biotic condition revealed a smoother surface modification, with few randomly distributed diatoms and without the significant presence of corrosion products. Only a few localized attacks in the form of pitting corrosion were also observed.

Here Fig. 13

4. Discussion

Stainless steel to reveal microbial activity

Stainless steel was used here as a reference material in order to highlight the microbial activity able to settle on the surfaces of the electrodes. The evolution of OCP ennoblement on an SS electrode exhibits a typical sigmoidal curve that reflects the three main stages of microbial colonization [31-33]: 1) the latency period, with no OCP modification, is the initial stage corresponding to the time needed for the microorganisms to settle; 2) the growth stage, with an OCP increase, indicates when the microorganisms arrive and the colonies start to develop; 3) the plateau stage, when the microorganism colonies develop to an extent that is sufficient to bring the OCP to a saturation value.

It is widely accepted that, under the name of cathodic depolarization, catalysis of the O₂ reduction by the biofilm (adhered microorganisms) explains this ennoblement, which can be induced even when the microbial coverage is low [34, 35]. Consequently, OCP ennoblement on SS is a reliable indicator for the appearance and presence of microbes on the metal surface, as suggested by online techniques for detecting early biofilm formation [36, 37]. In both the 50- and 8-day immersion experiments, the OCP clearly exhibits the expected behaviour, which is observed from day 10 (Fig. 4) and day 4-5 (Fig. 6) for the 50-day and 8-day experiments, respectively. The difference in time required for the ennoblement to be observed can be explained by the impact of different factors on the microbiological activity, for instance, the season of exposure (spring versus autumn), with distinct water temperatures (15 °C versus 20 °C) and natural photoperiod exposition (inside versus outside). Initial surface preparation of the SS specimen (polished or not) can also be a differentiating factor.

Beyond these differences, as expected, the ennoblement was not observed in the control abiotic solutions.

Corrosion behaviour of Al-Mg alloy

The influence of the immersion conditions, abiotic (artificial seawater and NaCl solution) and biotic (natural seawater), on the Al-Mg surface modifications was analysed by OCP measurement during the immersion and characterized by surface and cross-section SEM/EDX after immersion.

Influence of the chemical composition of abiotic solutions

In the abiotic environments, a common behaviour was observed for both series of experiments (8 and 50 days): an OCP downward trend which can be attributed to the modification of the anodic branch towards lower potentials (from the passive to the active domain). Nevertheless, two differences occurred between the abiotic controls adopted in 50-day experiment (artificial seawater) and 8-day experiment (NaCl): 1) the -2.5 mV d^{-1} vs -35 mV d^{-1} average rates for the OCP negative shift in the 50-day and 8-day experiments respectively, and 2) the initial attempt of passivation enhancement with the $-900/-770/-900 \text{ mV/SCE}$ jump in the very first days of the 50-day experiment, not seen in the 8-day experiment.

Two reasons likely explain these differences. Firstly, the two alloys came from different sources (commercial type in the 50-day experiments versus home cast in the 8-day experiments) and their initial surface preparation was different (as received versus polished). Secondly, the presence of many chemical species in artificial seawater (not present in NaCl solution) with buffering capacity, e.g. phosphate and carbonate for instance, counteract the harmful effect of chloride ions.

To sum up, the OCP evolution, found in both abiotic media, reflected a higher level of corrosion in the environment containing only NaCl (8-day experiments), which was confirmed by the surface observations (Fig.10 and Fig.13): Voluminous corrosion products linked to severe localized corrosion were present on specimens immersed in NaCl solution, while just a very thin layer of corrosion products was observed on the specimens immersed in artificial seawater (50-day experiments).

Influence of the marine microbial activity on Al-Mg corrosion

Both NaCl and artificial seawater controls revealed the tendency of an active behaviour of the Al-Mg alloy in chlorinated solutions, as evidenced by the OCP downward shifts in the 8- and 50-day experiments. Conversely, in the biotic seawater environments OCP laid around $-750/-800 \text{ mV/SCE}$ without any electronegative shift (Fig. 5 and 7) in both the 50- and 8-day experiments. Beyond this common important feature, some OCP differences are noted. In the 8-day experiments, well defined OCP daily oscillations were visible thanks to 1 point per hour acquisition rate. These OCP variations appeared once the ennoblement phenomenon was observed on the SS electrodes, as indicated by the green vertical line, proving that OCP behaviour observed on the Al-Mg electrodes is related to the microbial activity, which is sensitive to the photoperiod. About the 50-day experiment, the immersion into a seawater environment not directly

exposed to the photoperiod and a lower OCP monitoring rate (1 point per day) resulted in random OCP variations not larger than 30 mV.

Combining the results obtained in both the 8- and 50-day experiments and looking at the evolution of the SS open circuit potential related to the different stages of the microbiological colonization, suggest the idea of a biological protection in natural seawater. This bio-protection on Al-Mg can be hypothesized to follow three main progressive steps:

1. During the latency period in the 50-day experiments (10 first days), i.e. before the green line, the protection cannot be related to interfacial processes due to microorganisms, since they were not actually present on the surface. The OCP stabilization found in the latency period of the 50-day experiment in Natural Seawater, in contrast to the OCP downward trend in the abiotic solution, may be related to the adsorption of organic molecules in sufficient quantities to act as inhibitors. This occurrence is suggested by previous, similar observations [32], and literature in the field of organic inhibition on aluminium alloys in alkaline solutions [39, 40] and also in presence of chlorides [41, 42].
2. After the latency period, i.e. after the green line, once the microorganisms had started to arrive and settle, they acted as a source of organic inhibitors directly on the surface of the material, reinforcing the adsorption phenomena [37]. Moreover, when the OCP was measured every hour (8-day experiment), large oscillations were observed (Fig.8). As suggested in [38], these probably reflected the adsorption cycles of organic mixtures responding to the light/dark phases of the natural photoperiod.
3. At a more mature stage, i.e. far beyond the green line, it can be hypothesized that, when more microorganisms had settled, these could improve the protection by active processes such as i) induction of local precipitation of minerals (i.e. CaCO_3) induced by local OH^- increase during the catalysis of O_2 reduction, as evidenced by the presence of Ca in the protective layers observed in the biotic environments (Fig. 11b), and ii) promotion of the formation of organic-inorganic complexes with the involvement of extracellular substance (EPS) that was produced.

The surfaces, which were observed after different times of biotic immersion (Fig.10-13), are in accordance with OCP behaviour described. In the first conditions (8-day experiments), the presence of microbial activity strongly decreased the corrosion, some pits were still visible, and a smooth surface modification was observed, with few randomly distributed diatoms and without the presence of voluminous corrosion products. Under the longer exposure in 50-day experiment, SEM/EDX observations (surface and cross-section) revealed the formation of a layer thicker than the abiotic one and with a uniform distribution on the Al-Mg surface (Fig.10-11).

The elemental chemical analysis performed by EDX on the corrosion products observed under abiotic and biotic conditions, did not lead to significant detection of different chemical elements for each of the immersion conditions. However, the difference in intensity observed in the spectra for the chemical elements identified in both conditions (abiotic and biotic), suggests the presence of chemical compounds of different natures, i.e. distinct chemical and physical properties, that will distinctly influence the corrosion resistance of the Al-Mg alloy [44].

The results obtained are in line with those already published in this field [38], [39], such as the study of the influence of active salt marsh microorganisms on the corrosion behaviour of Al-Mg alloy [40], which demonstrated the formation of a layer on the alloy surface with corrosion inhibition effect, after immersion in biotic conditions.

Therefore, based on OCP and surface observations, the corrosion inhibition of Al-Mg found in natural seawater is hypothesized to result from the cooperation of biological processes working at different degrees of complexity: adsorption of organic inhibitors released from planktonic or sessile microorganisms, catalysis of O_2 reduction, which increases the local pH and leads to precipitation and production of EPS. The prevalence of each phenomenon at different times expresses determined biological

stages operating during the immersion of the electrodes. Once the microbial activity takes place at the electrode surface, the cathodic depolarization of the O₂ reduction and the anodic inhibition can co-exist. This coexistence, linked to the marine biofilm development, has been previously described by some authors as apparently competitive phenomena on super austenitic stainless steel [48], leading to the statement that “the passive film reacts to the environment it is in”, evidence that satisfactorily agrees with our findings.

5. Conclusion

This study showed that, although the origin of the Al-Mg alloy, the type of surface preparation and the exposure conditions (location, season, photoperiod) were different, it was possible to observe the same phenomenon of positive influence of natural seawater on the corrosion behaviour of Al-Mg alloy. The comparison between biotic and abiotic conditions allowed demonstrating that the marine biological activity induces surface modifications on the Al-Mg alloy counteracting the corrosion aggressiveness of chloride solutions. Combining short (8 days) and longer (50 days) data, an overview concerning the bio-protection effect can be hypothesized. In the period between the immersion and the settlement of microorganisms, protection can be provided by the adsorption of inhibiting organic molecules, which are released by organisms not adhering to the metal surface. Subsequently, when microorganisms arrive and settle, they can act as an adhering source of organic inhibiting molecules. At this level, our experiments showed that the initial bio-protection resulted in the containment of corrosion. Then, as the microbial communities developed to a greater degree of maturity, their interfacial activity (especially the oxygen reduction catalysis) promoted the formation of a thicker and more complex protective layer. This process required some weeks.

Finally, in order to achieve deeper insights into the inhibition corrosion mechanisms on Al-Mg alloy mediated by the microbiological activity in natural seawater, complementary experiments (polarization techniques, microbial analysis, deeper surface analysis spectroscopy, such as XPS, ToF-SIMS, etc.) are in progress to understand i) how the bio-colonization evolves on Al-Mg in natural seawater ii) which main cathodic process is involved, and how it works, and iii) how the Al-Mg passivity is affected by the biological activity. In particular, natural seawater illuminated by sunlight has to be treated as a distinct environment featuring specific protecting biological processes.

This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

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