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ABSTRACT

Several oil and gas offshore platforms are approaching the end of their production life, thus requiring sounding sustainable management solutions. This study aimed to improve the current knowledge on the low voltage mineral deposition technology as an eco-friendly strategy to protect offshore platforms from corrosion and to create suitable substrates for the colonization and growth of sessile marine organisms, thus minimizing environmental impact due to metal release, supporting biodiversity and increasing ecological sustainability. To do so, experimental prototype structures were installed in the Ligurian Sea (NW Mediterranean Sea) with the aim to simulate the sub-merged parts of offshore platforms and to analyze over time (up to ca. 6 months), elemental and chemical composition, growth rates and corrosion protection ability of the minerals deposited on steel substrates, through the alkalization induced by cathodic polarization of the metal. The influence of operational (applied current density) and natural environmental parameters on the deposition process was investigated. Results of this experiment revealed that in general the mineral deposits were mainly composed by aragonite ($CaCO_3$) and brucite ($Mg(OH)_2$) and, more specifically, the amount of the latter prevails a little bit on the amount of the former. This result is most likely related to high cathodic polarization current densities reached during the experimentation. Despite brucite is expected to worsen the physical–mechanical characteristics of the mineral deposits, the overall deposits were able to protect to a certain extent the electrified steel material from corrosion. After about 6 months of induced mineral deposition, the layer over the steel reached the maximum thickness of about 2.4 mm, following a non-linear trend as a function of time, whereas the deposition rates ranged from 20.0 to 50.3 μm d^{-1}, in relation with the applied current densities. At the same time, a positive relationship of the deposit grow rates with seawater temperature has been observed. Overall, the outcomes reported in this study provide new elements for the application of low voltage mineral deposition technology in temperate seas and pave the way for

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1. Introduction

The rising of energy demand along with the need to reduce greenhouse gas emissions for contrasting global climate changes is leading the energy sector in moving from fossil fuel to renewable energies. The transition may consist in the replacement of production facilities, or in their conversion or repowering, maximizing the efficiency and minimizing the environmental impact. Oil and gas extraction infrastructures include more than 7500 offshore platforms, half of which located in the Gulf of Mexico and in the North Sea (Leporini et al., 2019; Sommer et al., 2019). Several of such installations, located also in the Mediterranean Sea (ca. 200 offshore platforms, half of which located in the Northern and Central Adriatic Sea; Ministero dello Sviluppo Economico DGS-UNMIG, 2020) will reach the end of their life cycle in the next decade and will require large economic investments for their dismantling (Leporini et al., 2019). The management of oil and gas offshore platforms during this phase is a complex issue for technological, socio-economic, ecological and safety reasons. Various decommissioning options (Fig. 1), such as complete removal, in situ reefing, ex situ reefing and alternative uses also differ greatly for their effects on marine biodiversity, particularly between partial and complete removal options, the latter of which will result in an almost complete loss of the associated biological components (Sommer et al., 2019; Claisse et al., 2015; Pondella et al., 2015).

Policies of complete removal assume that "leaving the seabed as found" represents the most environmentally-sound decommissioning option. However, offshore platforms can support abundant and diverse marine communities during their service lives, with some structures supporting communities of regional significance. Examples include oil platforms in the northern Gulf of Mexico, supporting a commercially and recreationally important red snapper fishery, and platforms off southern California, supporting substantial juvenile populations of declining rockfish species (Snodgrass et al., 2020). In other cases, offshore platforms may provide important refuges for species (including overexploited and endangered species) and habitats to ensure connectivity of populations, as for the cold-water corals in the North Atlantic Ocean (Macreadie et al., 2011). Removal of such structures is unlikely to represent the best sustainable solution also on the light of the increasing interest for marine space of the blue economy sector. To this regard, there is an increased awareness, documented by different research projects, that obsolete oil and gas platforms can represent multi-use hubs for the development of economic sectors, such as wind and wave energy production and aquaculture in line with the principles of the sustainable use of marine space and its resources.

Cathodic protection performed by sacrificial anodes is quite commonly used method to protect the submerged part of oil and gas platforms (i.e., jacket) from corrosion, thus increasing their durability and avoiding structural failures; the anodes need periodic substitutions due to their consumption during service life and their progressive consumption, leading to metal release, can determine impacts on marine life (Kirchgeorg et al., 2018 and references therein). Alternatively, when there are the suitable operative conditions of power supplying, cathodic protection is carried out using inert anodes by applying impressed currents. In both cases, mineral precipitation occurs on the steel structure surface, working as the cathode of the protection system (Yang et al., 2015). In particular, the formation of the mineral deposit, mainly represented by compounds of calcium and magnesium, present in natural seawater, is induced by the application of an electrical current, which determines the alkalinization of steel substrate as a consequence of the electrochemical processes involved, such as the reduction of dissolved oxygen in seawater and/or reduction of water, which determines hydrogen evolution. Different experimental laboratory studies have been carried out for the understanding of the mechanisms involved in the formation of mineral deposits and to set the most appropriate conditions for cathodic protection (Wolfson and Hartt, 1981; Barchiche et al., 2003, 2009; Zakowski et al., 2013; C. et al., 1998). This technology has been also investigated for using the mineral deposits as construction material (Hilbertz, 1979, 1992), for creating nature-like substrates suitable for the colonization of a variety of sessile marine organisms (Schuhmacher and Schillak, 1994), thus supporting biodiversity, or for its application to restore degraded marine habitats by enhancing the growth rates of calcifying organisms (Sabater and Yap, 2002; Strömberg et al., 2010; Goreau, 2014; Goreau and Prong, 2017). This latter use has been widely applied in different tropical systems, where the rather constant environmental conditions (e.g., temperature) appear to be suitable for maximizing the efficiency of the electrochemical processes inducing mineral deposition and thus promoting the growth rates of corals (e.g., Sabater and Yap, 2002; Goreau and Sarkisian, 2010; Wells et al., 2010; Jompa et al., 2012; Zamani et al., 2012; Goreau and Hilbertz, 2013).

The growth rates and composition of the mineral deposits depend on the voltages and currents used (Goreau, 2012), which are reciprocally related, as well as from different natural environmental conditions such as marine current regimes, water temperature, pH, salinity and dissolved oxygen concentrations, which altogether needs to be taken into account. From an electrochemical point of view, the technology devoted to mineral deposit accretion determines the reduction of dissolved oxygen and/or water at the cathode resulting in an increase of pH (alkalinization) at the metal/water interface.
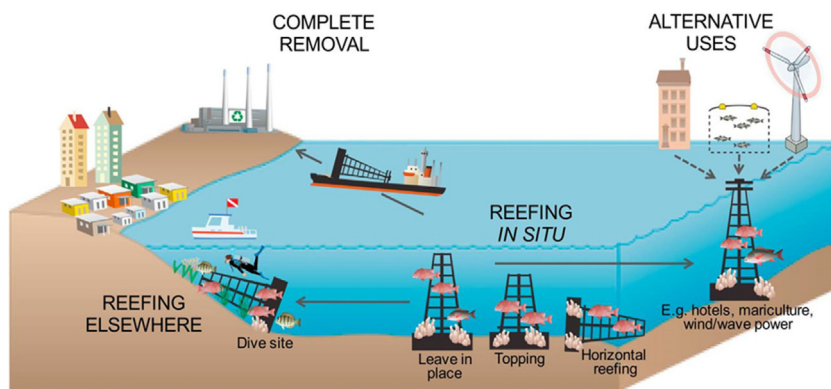
Fig. 1. Conceptual scheme of decommissioning options after Sommer et al. (2019).

The increase of pH influences the bicarbonate-carbonate chemical equilibrium according to the following equations (Stumm and Morgan, 1996; Yang et al., 2015):

$$H_2CO_3 + OH^- \leftrightarrows HCO_3^- + H_2O \tag{1}$$

with $pK_{a1} = 6.1$ a 25 °C in seawater

$$HCO_3^- + OH^- \leftrightarrows CO_3^{2-} + H_2O \tag{2}$$

with $pK_{a2} = 9.3$ a 25 °C in seawater The concentration of CO_3^{2-} increases at the interface and by the combination with calcium ions, present in seawater, the precipitation of calcium carbonate is induced:

$$CO_3^{2-} + Ca^{2+} \leftrightarrows CaCO_3 \tag{3}$$

$CaCO_3$ can form two different polymorphs depending on environmental conditions such as temperature and ion concentration: aragonite and calcite. Moreover, in seawater being the Mg:Ca ratio about 5:1, aragonite is the main form as Mg^{2+} ions inhibit the formation of calcite and favor the formation of aragonite (Lin and Dexter, 1988).

When the pH of the electrode surface exceeds 9.2 (Deslouis et al., 2000; Carré et al., 2020) precipitation of magnesium hydroxide (reaction 4) also takes place bringing to the formation of brucite (Sung-Tsuen and Nancollas, 1973).

$$Mg^{2+} + 2OH^- \leftrightarrows Mg(OH)_2 \tag{4}$$

Considering the solubility product of $CaCO_3$, other authors (Lazzari and Pedeferri, 1981; Yang et al., 2015) reported that the precipitation (Eq. (3)) can occur at pH 8–8.7, but taking into account ionic strength of seawater this value moves to values above 10 due to oversaturation phenomenon. At pH over 10–11 starts also the deposition of $Mg(OH)_2$ (Eq. (4)), giving in this way an induced mineral co-deposition phenomenon of both compounds, due to a strong alkalinization of the steel substrate. Such condition is promoted by high cathodic current densities bringing the steel in cathodic overprotection conditions, where the reduction of water to gaseous hydrogen is the half-reaction that mainly occurs and gives the high alkalinization of metal-water interface.

Preliminary studies carried out both in laboratory and *in situ* at the Hanstholm harbor in the North Sea (Margheritini et al., 2020) provided some insights on mineral accretion processes at low temperature regimes that, by the way, do not allow to drawn general conclusions how changes of environmental conditions (e.g. temperature, salinity, dissolved oxygen concentrations) occurring in temperate ecosystems, such as the Mediterranean Sea, can influence such processes.

At the same time, although chemical reactions on the cathode surface of the mineral deposition technology have been clarified, the growth rates of the mineral deposits and their chemical composition under *in situ* conditions needs to be further investigated.

In this study, the performance of the mineral deposition technology based on low voltage (i.e. constant value of 2.5 V) was investigated in the Mediterranean Sea by the installation of experimental prototype structures, which mimic the jacket of offshore platforms. Such experimental prototype structures and operational conditions are different to those previously used in the Mediterranean Sea, based on steel mesh deployments (as cathode) and higher voltage supply (from 8 to 12 V; Schuhmacher and Schillak, 1994; Vaccarella and Goreau, 2013). The aim of the present study is to provide new knowledge on the growth rates and composition of mineral deposits and their effectiveness for the protection of the steel material from corrosion in relation with operational parameters and the natural variability of environmental conditions. Besides steel protection, results of this study provide new insights for the creation of a nature-based substrate, which can be suitable for the colonization and growth of marine organisms, thus contributing to sustain biodiversity.
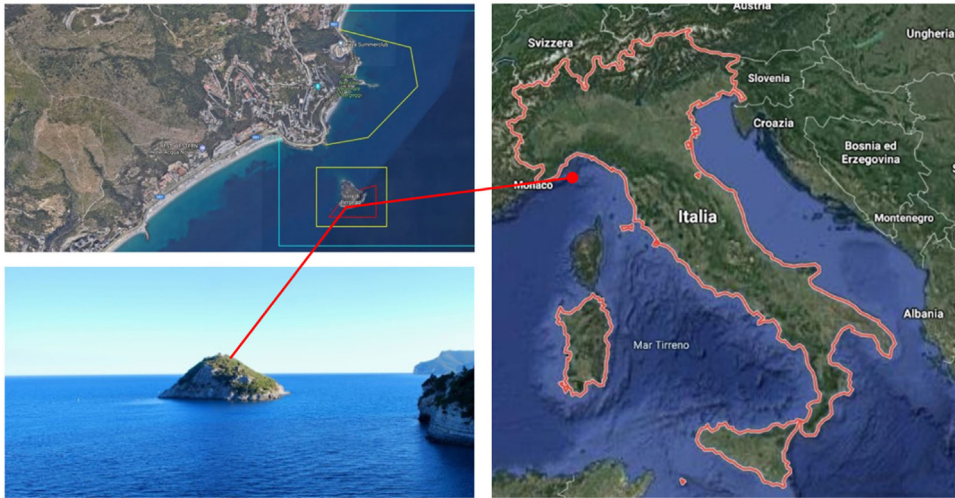
Fig. 2. Location of the Marine Protected Area of the Island of Bergeggi where field experiments were carried out.

2. Experimental setup

2.1. Study site

Field experiments were carried out in the Marine Protected Area of the Island of Bergeggi (Ligurian Sea, NW Mediterranean Sea; Fig. 2), established by the Ministry of the Environment and Land and Sea with Ministerial Decree in May 2007. The Island of Bergeggi is located about 250 m far from the coastline, and it is separated from the mainland by a channel with a maximum depth of about 70 m. The seafloor is generally sandy and is also characterized by the presence of numerous rocky outcrops which host a rich biodiversity. This installation site was selected as the best compromise to minimize potential interference with benthic assemblages and logistical needs, respecting the Italian regulations governing the activities permitted in Marine Protected Areas (Article 19, paragraph 5, of the Italian law no. 394 of 1991).

2.2. Experimental system setup for mineral deposition investigations

The experimental system setup for mineral deposition investigations consisted of two tween structures (Fig. 3), that were installed on coarse seafloor at ca. 20 m depth and at a distance of about 10 m far each other.

Each structure had 8 cylindrical steel tubes, working as cathodes in one of the two structures, each of which with a diameter of 33.4 mm and a length of 90 cm. An API 5L standard profile (EN10210-2 standard) of class STD was chosen to manufacture the steel tubes, in order to use, as much as possible, the same material destined to the construction of the sub-merged part of offshore platforms. Each tube was made up of two elements of equal length (45 cm) butt-welded, according to the UNI EN ISO 4063: 200 standards. Each tube was mounted on a circular frame by means of a quick release system to facilitate removal during the various monitoring phases of the experiment. At the center of one structure has been installed a cylindrical PVC tube (15 cm diameter and 90 cm length), on which was externally wrapped a thin activated titanium mesh (type ASTM B 265 Gr 1), working as anode for supplying the impressed currents, able to make cathodic polarization of the surrounding steel tubes, working in this case as effective cathodes. The cylindrical PVC tube was suitably filled and sealed with epoxy resin for marine applications. The final geometry of the electrochemical cell was realized to ensure an equal distance of each cathode from the central anode.

The second structure had not a central anode and then the steel tubes were left in free corrosion conditions. They were used as term of comparison with respect to the cathodes, where the mineral deposition takes place. In this way, it is possible to study the influence of physical–chemical variables on the steel tubes working in two completely different conditions.

To assess the potential influence of the main physical–chemical variables (temperature, salinity, dissolved oxygen concentrations) of seawater on the deposition processes occurring on the cathode surface, a multiparametric probe (MicroCatalog Conductivity, Temperature, Pression-Optical Dissolved Oxygen Recorder) was installed in between the two tween structures. The multiparametric probe has been set with an acquisition time of 5 min and it has been periodically removed from its position to collect and process the recorded environmental data and re-deployed in its original position.
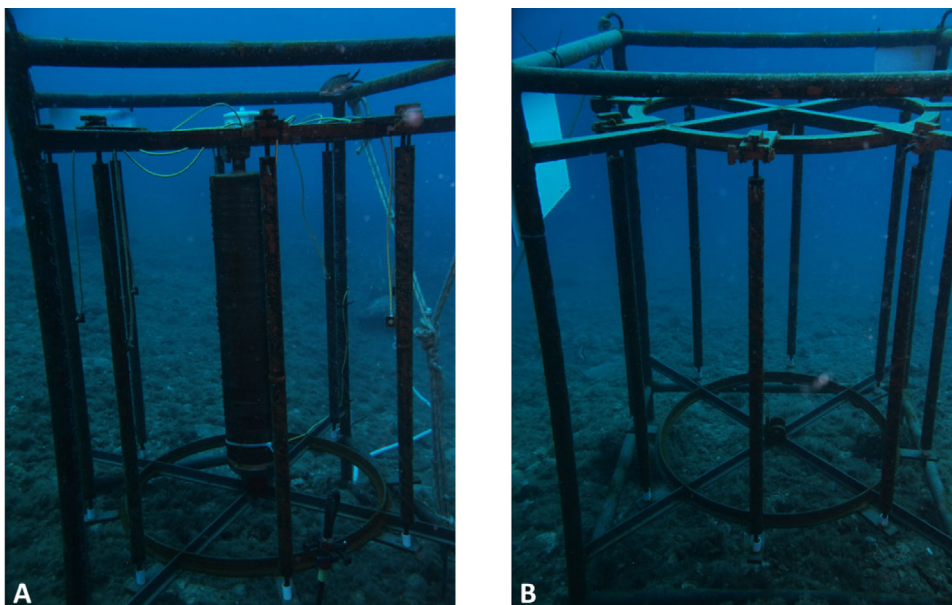
Fig. 3. Images of the structure used for the mineral deposition experiment with a central anode and 8 external cathodes (A), twin structure without the central anode (B), used as control.

2.3. Design and installation of the power supply system of the electrified structure

The structures with the titanium anode have been powered by a low DC voltage at 2.5 V, which has been selected based on previous experiment carried out in the North Sea (Margheritini et al., 2020). To this aim, the electrified structure has been connected to the power supplier through a bipolar cable (length 300 m) partly laid on the cliff of the Bergeggi Island and partly submerged.

The power supply system consists of four polycrystalline solar panels with charge regulators and six 200 Ah buffer batteries with 12 V DC output. An inverter transforms 12 V DC in 220 V AC and makes the function of a current stabilizer, thus preventing batteries under-charging and breaking. Through a transformer, the impressed DC current was applied to the electrified structure and measured by an ACS712ELC chip. The resulting current was recorded on a SD card sending the output of this device to a microcontroller (Arduino Mega), which recorded the data by Datalogger Shield each 60 s, as acquisition time. The overall experimental setup is illustrated in Fig. 4.

2.4. Sampling and monitoring activities

The sampling/monitoring activities included:
1. video inspections by means of scuba divers of the installations and check of their structural and functional integrity;
2. sampling of the steel tubes from the electrified (E) and non-electrified (NE) structures;
3. data acquisition from the multiparametric probe among the different time intervals, when steel bars have been collected.

Once detached from the structures, each steel tube was placed in a PVC tube. On land, the tubes were gently washed with fresh water and then sectioned in three different parts of about 30 cm each. One section was subjected to manual scraping by means of sterile scalpel to remove the material present on the surface to be used for physical–chemical analysis; a second and third section was maintained at room temperature for the determination of the thickness of the material deposited on the bar surface and to make the electrochemical analyses.

The cathodes have been collected at four-time intervals after their installations, which occurred on July 17th, 2020 (Table 1). The first sampling of the steel tubes has been carried out 15 days after the installation for the purpose of a short-term assessment of processes occurring on E and NE steel substrate. Subsequently, the sampling of the cathode and of the control steel tubes (coming from NE structure) took place 51, 100 and 185 days after the installation.

2.5. Laboratory analyses

Analyses were performed on material deposited on the surface of steel substrate after its grinding to fine powder. In particular, the elemental composition of the deposits collected from E and NE structures was analyzed by X-ray
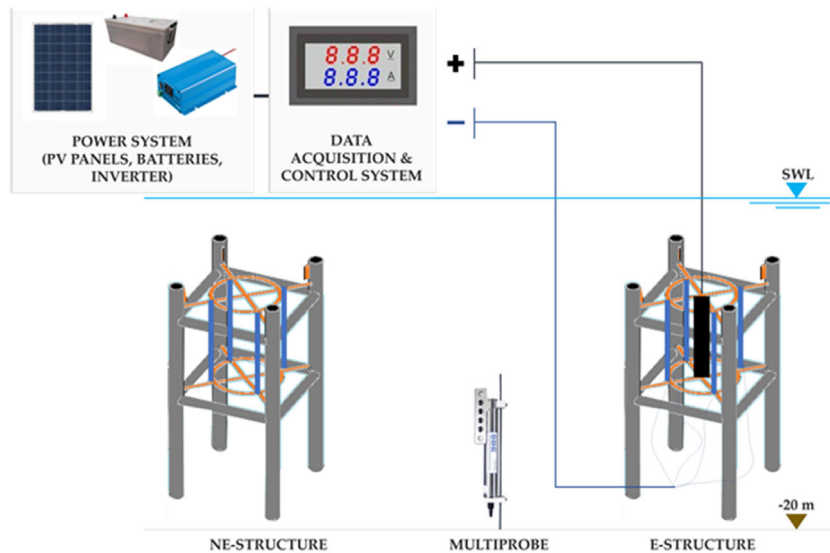
Fig. 4. Schematic overview of the experimental setup used for investigating the performance of the mineral deposition technology.

Table 1
Dates of the four-sampling periods of the E and NE steel tubes, with the explicit indications of the real time of sampling from the beginning of the experiment and those corresponding to the real duration of cathodic polarization, only for E tubes.

Name of sampling	Date of sampling	Real duration of the sampling (days)	Real duration of cathodic polarization only for E tubes (*) (days)
Time 1	31 July 2020	15	11
Time 2	5 September 2020	51	25
Time 3	24 October 2020	100	46
Time 4	16 January 2021	185	120

*For each sampling Time i (with $i = 1, 2, 3, 4$), the E steels tubes were not always under cathodic polarization for the reasons given in Section 3.

fluorescence (XRF) using a Rigaku-Supermini200 spectrometer. For XRD analysis of the compounds present on the mineral deposit, a PANalytical AERIS XRD instrument was used. The diffractometer used a Cu Kα radiation (40 kV and 15 mA; $\lambda = 1.54$ Å) and 2θ angle scan from 15 to 90° with the time constant set to 12 min. The fractions of minerals in the samples were calculated using Rietveld refinement (PANalytical HighScore Plus).

Electrochemical tests were carried out on samples of E and NE steel tubes collected on July 31 (Time 1) and on October 24 (Time 3) 2020 by means of electrochemical impedance spectroscopy (EIS) analysis. For such analysis, the steel tubes were suitably shielded with epoxy resin to obtain a surface as much as possible homogeneous and geometrically defined. The same analysis on the samples collected at Time 2 and Time 4 were not performed due to difficulties encountered in the preparation of the sample, which led to deposit damaging and, consequently, to non-reproducible results.

A typical three-electrode configuration electrochemical cell was used, where the samples represented the working electrode, whereas, as reference, a saturated calomel electrode (SCE, +0.241 V vs SHE) and, as counter, an activated titanium wire were used, respectively. The electrolytic medium was a 3.5 wt% NaCl solution. The measurements were done by means of a Gamry Reference 600 potentiostat in 100 kHz–0.01 Hz frequency range, with a potential amplitude of 10 mV. From these measurements, the value of the impedance modulus at lowest frequency has been taken to express surface impedance of the examined samples in order to quantify the "relative degree of protection" offered by the mineral deposit or rust layers for E and NE samples, respectively.

The surface of each sample exposed to the electrolyte solution is reported in Table 2.

To assess the potential relationships between values of surface impedance and the thickness of mineral deposits, measurements of the thickness of the mineral deposit from E samples and of the rust layer for NE samples were carried out by means of the magnetic probe Fisher DELTASCOPE MP2. The measurements were made on 20 different points of the entire tested samples and the average thickness and standard deviation were calculated.

Finally, to assess the growth rate of the mineral deposits on the surface of the E cathodes, the increment of the diameter of the steel bars collected in the four-sampling period was determined. To do so, by using a digital thickness gauge

Table 2
Area of the various samples exposed to the electrolyte solution (3.5 wt% NaCl solution) for the EIS measurements.

Sample	Area (cm^2)
E collected at Time 1	163
NE collected at Time 1	152
E collected at Time 3	121
NE collected at Time 3	91
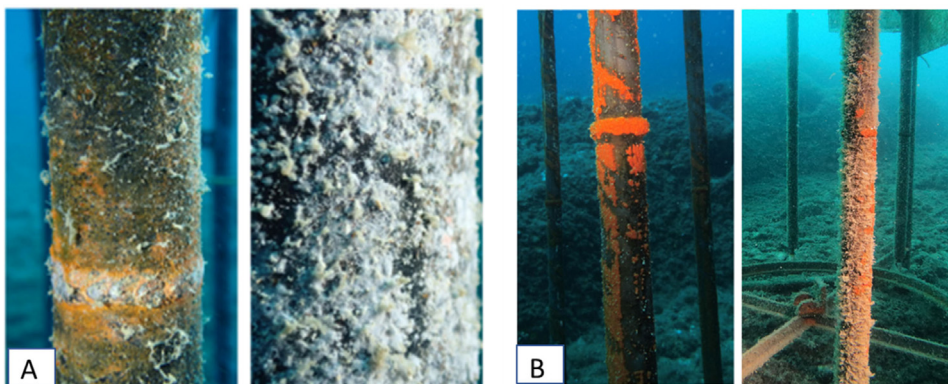
Fig. 5. Images of the evolution of the E (A) and NE (B) steel tubes over time.

(accuracy 10 µm), 50 measurements, randomly distributed on the entire bar profile, were done and collected in each of the four-sampling periods. The average values and standard deviations of the thickness of the deposits, as a function of deposition time, were then calculated considering the diameter of the steel tubes before the beginning of the experiment.

3. Results and discussion

Clear macroscopic differences between E and NE steel tubes were highlighted by underwater visual observations (Fig. 5). Indeed, E cathodes were characterized by the presence of white material (Fig. 5A), whereas NE steel tubes (Fig. 5B) were characterized by the presence of rust on the surface and a biofouling coating.

The macroscopic differences of E and NE tubes were further confirmed by XRF analysis carried out on the material deposited/formed (Fig. 6).

Iron was the dominant element present on NE steel tubes (Fig. 6A), with a quantitative relevance ranging from 74.2 to 92.0 wt% of the overall elemental composition. The massive presence of Fe is due to the free corrosion phenomenon of steel caused by the contact with seawater in absence of any protection method. Over time, the iron content on the surface of the NE steel tubes decreased with a concomitant slight increase of Ca and Mg, likely due to their precipitation favored by biofouling and/or the presence of such elements into the colonizing biomass (Bathurst, 1972; Abdel-Aal and Hussein, 1993).

The E cathodes were characterized by the dominance of Ca and Mg (on average for the four tubes collected at the different time intervals 43.7% and 37.0%, respectively; Fig. 6B). Calcium accounted for ca. 53% in the deposit of the first collected tube and then decreased at a constant value of ca. 40% in the deposits of the other steel tubes collected in the other sampling times (Table 1). Mg contribution was very low in the mineral deposit of the first sampling period and then increased at constant values of ca. 50%. Such findings highlight that the Ca/Mg ratio can vary over time within the deposit due to dissolution/precipitation phenomena (Goreau, 2012), which mainly depend on pH values, regulated by the electrochemical reactions that take place on the surface of the metal (Dexter and Lin, 1992; Katona et al., 2020).

The almost constant value of the Ca/Mg ratio, after the first sampling time, suggests that the electrochemical reactions (dissolved oxygen and/or water reduction) occurring in the E structure can promote similar deposition rates of compounds containing these two elements. More specifically, these electrochemical reactions are strongly related with the applied cathodic polarization current densities (Lazzari and Pedeferri, 1981): Ca/Mg decreases with the increase of cathodic current density, indicating that the E structure was most likely under cathodic overprotection conditions after Time 1, when the content of Mg became comparable with that of Ca (Fig. 6B). Beside Ca and Mg, the deposits analyzed in the present study contained also other elements such as Al, Si, S, Cl, K, Mn, As, Sr, P, Cu, V, Ag, Co, which in general accounted for a very low mass fraction (< 5%). The presence of such elements in the deposits can be due to their co-precipitation with Ca and Mg from the seawater and to the dissolution of elements present in the steel substrate (e.g., P and Mn).
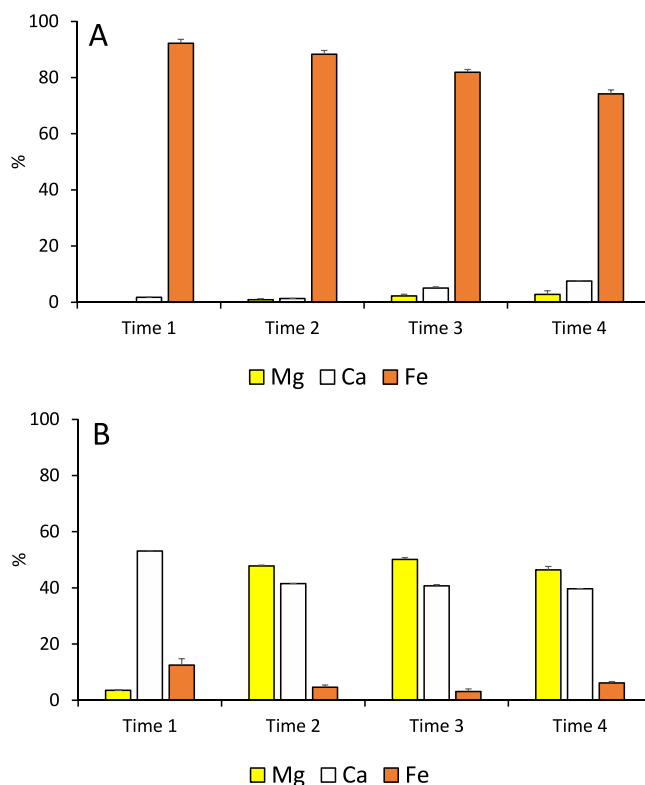
Fig. 6. Chemical composition of the deposits present in NE (A) and E (B) tubes collected in the four-sampling times.

XRD analysis provided further evidence of the differences between the mineral composition of the deposits present on the surface of E and NE steel tubes. Lepidocrocite (γ-FeO(OH)) and Maghemite (γ-Fe$_2$O$_3$) accounted together for ca. 90% of the material present on the surface of NE steel tubes with a different contribution occurring over time (Fig. 7A).

Conversely, the E cathodes were dominated by an electrochemically induced co-deposition of aragonite and brucite (Eqs. (3) and (4)), whose relative contribution was rather similar over time, except for sample collected after 15 days (Time 1), characterized by an aragonite content > 95% (Fig. 7B).

A previous study carried out in the North Sea (Hanstholm harbor), using the same voltage of the present study (i.e., constant value of 2.5 V), reported an aragonite content of mineral deposits obtained after 3 months of experiment higher (75.8%) than that shown in Fig. 7B (Margheritini et al., 2020). Aragonite and brucite have different mechanical properties, with the former harder and with a high compressive strength (80 MPa; Goreau, 2012). A high aragonite content of the mineral coating on the cathode surface can progressively lead to a deposit more compact and characterized by a high mechanical strength with a potential higher protection capacity against corrosion of the metal substrate. At the same time, the calcium carbonate coating of the cathode surface (by mimicking natural calcareous rocks) can represent a suitable substrate for the colonization and growth of a wide variety of marine organisms, in particular, as previously reported, once the electric supply is switched off (Schuhmacher and Schillak, 1994). As such, the formed deposits on the cathode surface could be beneficial not only for protecting metals from corrosion, but also for sustaining biodiversity and improving ecosystem services (e.g. C sequestration).

In this study the electrochemical characteristics of the mineral deposits in terms of "relative degree of protection" against corrosion has been investigated by EIS measurements. This technique is quite commonly used to study the corrosion resistance of bare, coated and differently treated metallic materials to evaluate their durability under different exposure conditions (Orazem and Tribollet, 2008). Values of the surface impedance of E and NE samples collected at Time 1 and Time 3 in relation to the thickness of the relative deposit/rust layers (measured by the magnetic probe) are reported in Fig. 8.

E and NE samples collected at Time 1 were characterized by very similar values of the surface impedance. Thus, in the short term (after 15 days), the low amount of mineral deposit present on E sample was insufficient to increase surface impedance above values that can be due to the rust layer formed on NE sample. The values of the surface impedance determined on E and NE steel samples collected at Time 3 were much higher than those of the samples collected a Time 1.

This result agrees with the fact that, in particular, the E sample collected at Time 3 was characterized by a mineral deposit more compact, homogeneously distributed and thicker than that present on the cathode collected at Time 1 (Fig.
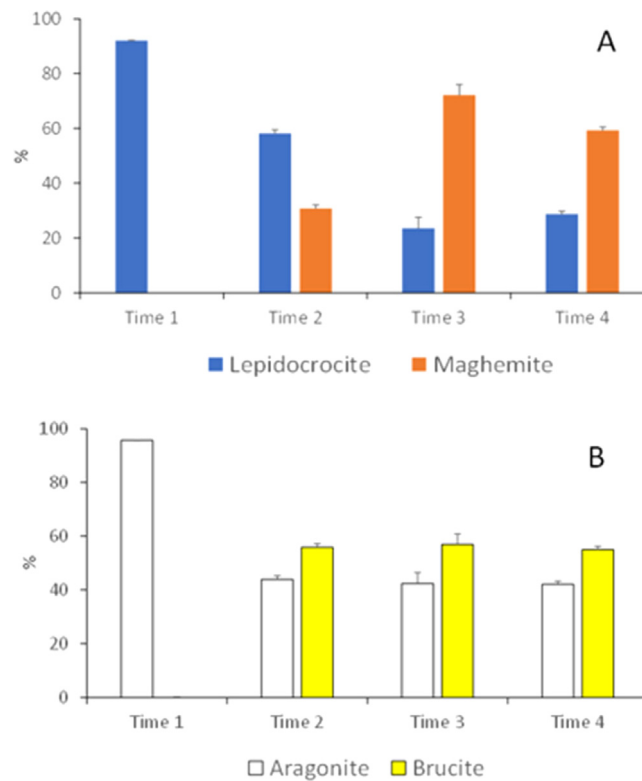
Fig. 7. Chemical compounds present on NE (A) and E (B) steel tubes collected in the four-sampling periods (Time 1, 2, 3 and 4).
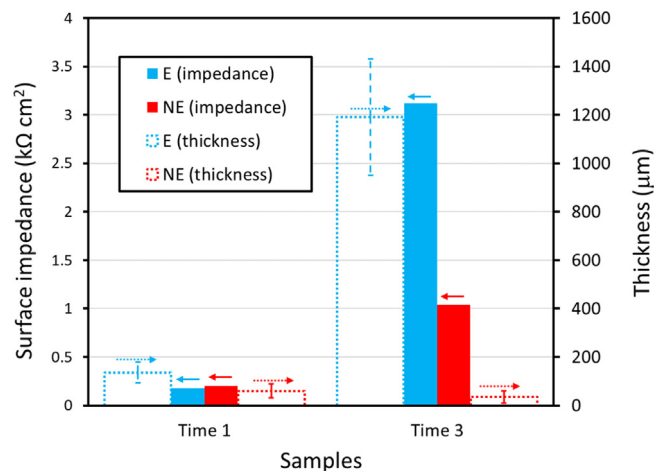

Fig. 8. Values of surface impedance, determined after 1 h of immersion in 3.5% NaCl solution of the E and NE samples collected on 31 July (Time 1) and 24 October 2020 (Time 3), and their relationships with the thicknesses of the relative mineral/rust deposits (dashed bars)

S1, in Supplementary Materials), thus more protective against corrosion. The higher surface impedance of the NE sample collected at Time 3, compared to sample collected at Time 1, is likely to be due to the changes occurring on the material present on the steel including that associated to biofouling components. Nevertheless, E cathodes collected at Time 3 displayed a surface impedance of 2 order of magnitude higher than that measured on NE samples, indicating that the mineral deposit is much more protective than the layer of corrosion products that forms on the steel left in seawater without applying any protection method.

Although the observed relationship between values of the surface impedance and the thickness of the material present on the steel tubes cannot be generalized, being the impedance dependent also by the porosity and/or tortuosity of the pores present on the deposit, the obtained results suggest that the mineral deposits formation, induced by the impressed
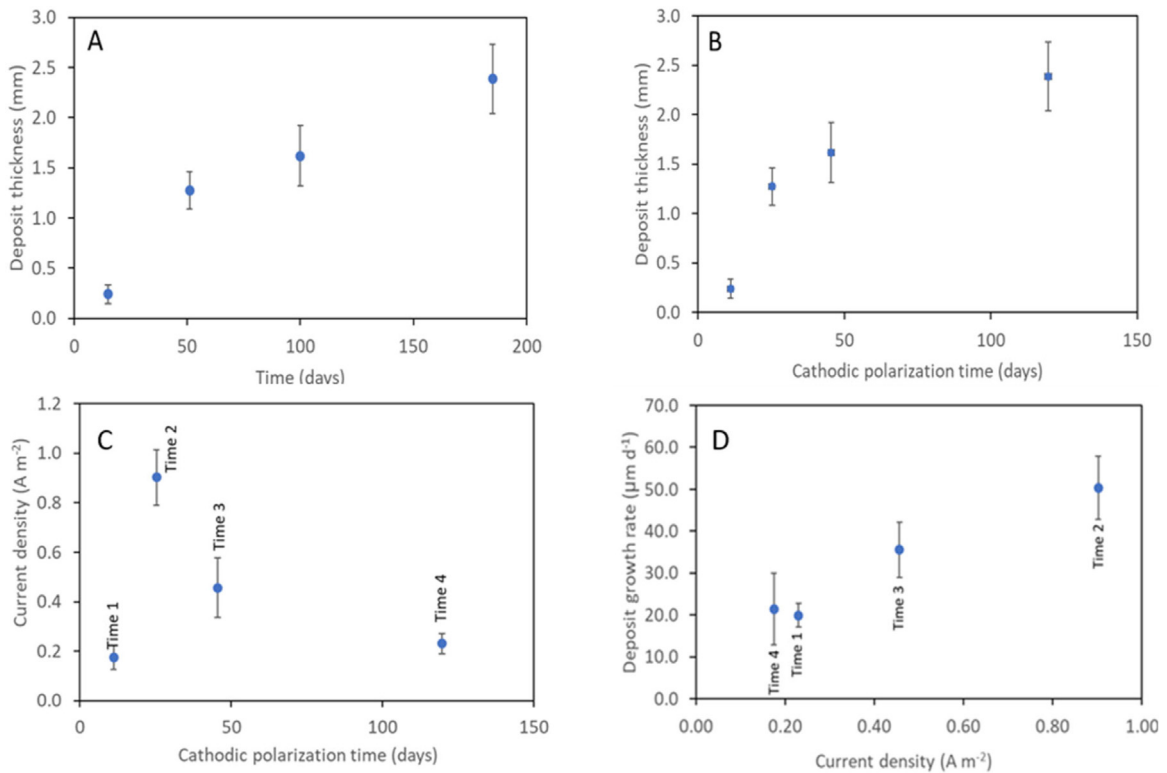
Fig. 9. Changes of the deposit thickness (as mean value and standard deviation) determined on the E steel tubes collected at each time interval in relation with the whole duration of the in-situ experiments (A) and in relation with the actual time of the effective cathodic polarization occurring at each sampling interval (B); current density (as mean value and standard deviation) as a function of cathodic polarization time estimated for the four-sampling period (C); deposit growth rates (as mean values and standard deviations) estimated for the four-sampling period in relation with the current density measured at each sampling interval (D).

cathodic current, can progressively protect to a certain extent the metal substrate against corrosion, independently from its relatively high brucite content (Fig. 7B).

In this work, quantitative information on the efficiency of mineral deposition induced by low voltage technology in temperate seas (i.e., the Mediterranean Sea) has been also provided. The thickness of the mineral deposit on the cathode surface increased progressively, but not linearly over time, reaching after ca. 6 months from the beginning of the experiment a value of 2.39 ± 0.35 mm (Fig. 9A).

Considering that the power supply system worked at a constant potential difference (2.5 V) during the whole experimentation, the polarization of steel was most likely not always going towards an effective cathodic polarization, namely that necessary for the induced mineral deposition. This phenomenon is related to the concentration of dissolved oxygen and, in particular, to its diffusion in seawater towards the steel surface, which, in turn, depends on uncontrollable marine currents. In conclusion, the power system was probably not able in certain periods of time to supply the necessary impressed current for an effective cathodic polarization of the steel tubes. Therefore, the actual period of effective cathodic polarization, determining the mineral deposition, was as a whole 120 days from the beginning to end of the time-course experiments (i.e., 15 July 2020–16 January 2021), while in correspondence of the intermediate sampling periods Time i ($i = 1, 2, 3, 4$), it is given in the 4th column of Table 1. Despite the temporal discontinuity of the cathodic polarization and taking into account the only cathodic polarization periods of the E structure, a non-linear increase of the thickness of the mineral deposit has been observed, as well (Fig. 9B).

The kinetics of the electrochemical reactions occurring on metal surface are dependent upon the impressed current, which in turn influences the growth of the calcium/magnesium deposits over time.

Based on the current intensity data measured by the installed device and the surface and number of cathodes, the current density (i, A/m^2) has been calculated over time as follow:

$$i = \frac{I}{S_{cat} n_{cat}} \qquad (5)$$

where:

I is the current;

S_{cat} is the single cathode surface (0.094 m^2);

n_{cat} is the number of cathodes (8, 7, 6 and 5 at the first, second, third and fourth sampling Time).

Values of current density displayed a wide temporal change during the first and second sampling period as showed in Fig. 9C.

Taking into account that during the early phase of the experiment (Time 1), when the steel tubes are almost bare and without any significant amount of deposit (Fig. S1A, tube E), the current densities of the system are more controlled by marine currents, which could determine a non-effective cathodic polarization and, as a consequence, the observed low average value of current density at this sampling time (0.175 A m^{-2}, Fig. 9C). At Time 2, the current density increased up to about 0.902 A m^{-2}, which is a value that enhances the growth rate of the mineral deposit (Lazzari and Pedeferri, 1981). Going on with cathodic polarization time, the current density decreased due to the further growth of the deposit on the steel tubes (see Fig. S1B, corresponding to Time 3), which in turn agrees to the surface impedance increase (Fig. 8). At this stage of the experiment, it is expected that the current density progressively decreases (Fig. 9C, going towards Time 4); moreover, it could be less controlled by the marine currents due to the presence of a thicker mineral deposit, which could become the main factor limiting the flow of electrolytic current towards the steel substrate (Lazzari and Pedeferri, 1981), even if it is not completely homogeneous.

On the basis of the mineral deposit thickness vs. effective cathodic polarization time (Fig. 9B), the daily growth rates of the mineral deposit following the application of low voltage technology were estimated. Changes in the applied current density were associated with changes in the daily growth rates of the mineral deposit (Fig. 9D), indicating that the applied current density can have a major role in the promotion and evolution of induced mineral deposition under cathodic polarization of the steel.

The daily growth rates were variable, being characterized by the highest value at Time 2 and the lowest one at Time 4 of effective cathodic polarization conditions (i.e., 50.3 ±7.5 µm d^{-1} and 20.0 ±2.9 µm d^{-1}, respectively). Such values are difficult to compare to those available in the literature since the growth rates induced by the use of the low voltage technology have been mainly assessed for restoration purposes of calcifying organisms (e.g., tropical corals, cold water corals, oysters) rather than for evaluating the performance of the mineral deposition process on a cathode surface occurring over time (Akamine and Kashiki, 2003).

Furthermore, the measured cathodic current density over time (Fig. 9C) explains the results obtained with the analysis of deposit composition: at Time 1, when the current density assumed the lowest value, the content of Ca prevailed on that of Mg (Fig. 6B) and the deposit was almost composed by aragonite (Fig. 7B); high current densities values, observed after Time 1, are in agreement with the increase of Mg and of brucite in the deposit (making reference to the same mentioned figures). These results are consistent with the previously cited literature, giving further confidence to the dataset. In addition, higher impressed currents, and consequently higher deposition rates, favoring deposition of brucite over aragonite, determines a worsening of the mechanical properties of the formed deposit (Pokrovsky and Schott, 2004).

Changes in physical–chemical characteristics of the water masses can also influence the performance of the mineral accretion as well as its composition (Carré et al., 2020). Temperature, indeed, influences the solubility of the calcium/magnesium compounds with a decrease of the solubility of calcium carbonate, unlike brucite (Karoui et al., 2013). This implies that the Ca/Mg ratio increases (Lazzari and Pedeferri, 1981) with temperature and that the calcium rich mineral deposit is more favored in warm waters rather than in cold waters. At the same time, since dissolved oxygen is reduced on the electrode surface, its concentration can influence the interfacial pH and consequently the composition of the mineral deposit. With a high concentration of oxygen, the interfacial pH is more alkaline so that the formation of Mg(OH)$_2$ could be favored.

In the present study, clear temporal variations of thermohaline conditions, typical of the North-Western Mediterranean Sea, were observed, with higher temperature and salinity values in summer than in the autumn–winter period (Fig. S2A–B). Also dissolved oxygen concentrations displayed a wide temporal variability (Fig. S2C), with values generally inversely related to the temperature regime.

Such changes in environmental conditions were apparently associated with changes in the growth rate and composition of the mineral deposit formed on the cathode surface. In this regard, higher temperature (in correspondence of Time 2, Fig. S2A) and salinity regimes (from Time 1 to Time 2, Fig. S2B) favor the formation of the deposit (Lazzari and Pedeferri, 1981) and, in details, a linear relationship between the increasing daily growth rate of the mineral deposits as a function of the temperature can be observed (Fig. 10).

The current density has a major effect on the composition of the mineral deposited on the cathode surface, as more brucite is formed at higher levels of current density and *vice versa* for aragonite, as discussed above. Therefore, brucite forms in a competitive reaction to the deposition of aragonite, according to the expectations of an increase of the concentration of hydroxide ions (OH$^-$) with increasing current densities, when the reduction of water can take place, as most likely occurred in the present experimentation. As such, the applied current of the present study, although effective for promoting mineral deposition as previously reported (Margheritini et al., 2020), was probably too high to favor the precipitation of calcium carbonate (as aragonite) on the cathode surface over magnesium hydroxide (i.e., brucite), obtaining in this way what is expected under cathodic overprotection (Lazzari and Pedeferri, 1981).

To provide further insights on the effect of the operational conditions (current density) and environmental variables (temperature, salinity and oxygen concentrations) on the chemical composition of the mineral deposits obtained in the
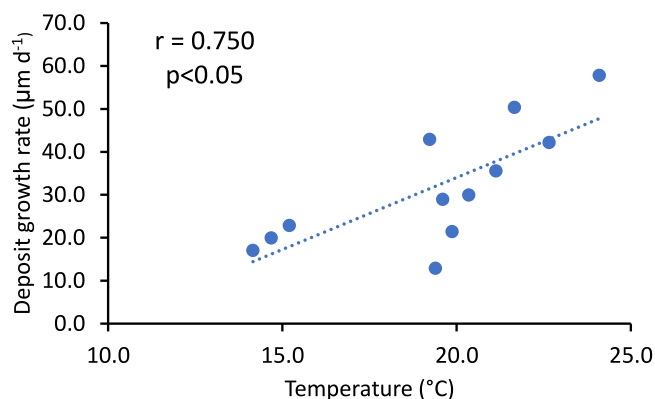
Fig. 10. Relationship between the deposit growth rate estimated for the four-sampling periods and temperature values recorded at each sampling interval. The significance of the fitting line is reported.

present study, a multivariate multiple regression analysis was carried out using a routine distance-based multivariate analysis for a linear model (DISTLM) forward (Anderson, 2004). This analysis revealed that current density and environmental variables explained all together 70% of the observed variation in chemical composition of the mineral deposits, with current density significantly explaining 39% of the total variance.

These results suggest that an interplay of factors takes place and this should be considered for a better comprehension of the mechanisms involved in mineral deposition and for the assessment of the timescale for achieving a mineral coverage suitable for protecting steel from corrosion and for promoting the settlement and growth of sessile marine organisms, thus minimizing environmental impact due to metal release, supporting biodiversity and increasing ecological sustainability.

4. Conclusions

The management of oil and gas offshore platforms at the end of their service life is a complex issue for socio-economic, environmental and safety reasons. The "green" policies of complete removal are based on the assumption that the sea bottom should be left as it has been found, but there is a scientific debate whether such strategy represents the most environmentally-sound decommissioning option.

The time-course *in situ* experiment carried out in this work allows improving knowledge on the application of the low voltage mineral deposition technology as an eco-friendly strategy to protect offshore platforms from corrosion, thus extending their potential life for alternative uses. The physical–chemical analyses analysis showed that mineral deposits are mainly composed by aragonite ($CaCO_3$) and brucite ($Mg(OH)_2$): a little bit higher content of the latter has been observed with respect to the former in all samples collected after ca. 50 days of the experiment, with the exception of the sample collected after 15 days, whose deposit was almost completely represented by aragonite. The preferential precipitation of brucite was favored by a combination of environmental (lower temperature) and especially operational (high cathodic current densities, most likely going towards cathodic overprotection conditions) factors, which changed over time. Despite the relatively high brucite content, which could worsen the physical–mechanical characteristics of the obtained mineral deposit, the thickness of the mineral deposit reached about 2.4 mm after 6 months from the beginning of the experiment. In addition, the deposit was found to protect to a certain extent the steel from corrosion, because it can work as a porous "coating", showing a surface impedance that increases few orders of magnitude as a function of time.

Daily mineral deposition rate increased not linearly with time, from 20.0 to 50.3 μm d^{-1}, in strict relation to the applied current density (higher is the latter, higher is the former), as well as changes in environmental conditions, with particular reference to an almost linear relationship with temperature. Results of the present study suggest that the modulation of the current density in relation with the natural environmental variability represents a crucial aspect for promoting in the field the suitable induced deposition of minerals, characterized by a high mechanical strength (i.e. aragonite-rich material) and a high protection capacity against corrosion of the metal substrate in seawater.

Overall, the outcomes reported in this study provide new elements for the application of low voltage mineral accretion technology in temperate seas and pave the way for defining the best operating conditions to protect steel structures from corrosion and support biodiversity, thus contributing to the sustainability of the natural capital.

CRediT authorship contribution statement

Giuseppina Colaleo: Investigation, Methodology, Formal analysis, Writing – review & editing. **Pasquale Contestabile:** Conceptualization, Methodology, Writing – original draft. **Tiziano Bellezze:** Methodology, Formal analysis, Writing –

original draft. **Lucia Margheritini:** Methodology, Formal analysis, Writing – original draft. **Antonio Dell'Anno:** Formal analysis, Writing – review & editing. **Diego Vicinanza:** Conceptualization, Supervision, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2022.102412.

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