



Influence of soil chemical characteristics on corrosion behaviour of galvanized steel

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ABSTRACT

Hot-dip galvanized steel is widely used for the construction of underground structures, thanks to the presence of a zinc coating that is able to protect the carbon steel substrate through the formation of a corrosion products layer. Soil corrosion is a very complex process and hence it is difficult to predict the corrosion resistance of a specific component because many factors can directly influence the behavior of material immersed in soil. This work focused on the effect of chlorides and sulphates concentrations on the corrosion of hot-dip galvanized steel wires buried in soil. In particular, the wires were monitored by means of electrochemical techniques, as open circuit potential, electrochemical impedance spectroscopy and potentiodynamic polarization. Moreover, at the end of the exposure, the samples were extracted and observed by optical and electron microscopy, to examine the corroded surface and the corrosion morphology. The analysis evidenced that the effect of chlorides and sulphates is very severe, producing a great degradation of the zinc coating. In particular, the synergistic effect performed by the combined action of these elements caused, in the most critical situation, the protection loss of the external layer, putting steel substrate in direct contact with soil, and therefore obtaining a substantial reduction in material corrosion resistance.

1. Introduction

The corrosion behaviour of galvanized steel in atmospheric environment has been deeply studied over the years [1–4], due to the high efficiency of zinc coating in improving the corrosion resistance of steel products in aggressive environments [5–8]. Thus, the galvanized steel is often employed in architectural, infrastructural and automotive applications. The hot-dip galvanizing (HDG) process in certain situations is even more convenient than, for example, the typical painting, as it requires low cost, while it is pretty fast, ensuring high productivity [9]. Moreover, the HDG deposition is ecological, and zinc is a natural no-toxic element present in water and in the soil, as a consequence of natural processes. On the contrary, the diffusion of paints produces a severe environmental impact and the disposal of the many tons of paint, that are removed at each maintenance phase, requires a high cost [10].

The Zn coating corrosion protection is conferred to steel in two ways: as a continuous barrier layer that can separate the steel from the corrosive environment and by means of the galvanic protection. Indeed, zinc acts as a sacrificial material to protect the underlying steel at defects, scratches and cut edges of the coating, by the formation of a patina consisting in Zn oxides and hydroxides able to significantly reduce the rate of corrosion reactions [11,12]. By adding aluminum, the coatings offer higher corrosion resistance than conventionally galvanized steel, because the presence of Al introduces a long-lasting physical barrier thanks to the formation of

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aluminum oxide in the most natural environments. Hence, the improved behavior against corrosion can be attributed to the presence of these oxidized products, in particular aluminum oxides and layered double zinc–aluminum hydroxides (ZnAl–LDH). The used Zn–Al coatings has become a common practice in the conventional galvanizing process and the most employed alloys are Galfan (Zn + 5 wt% Al) and Galvalume (Zn + 55 wt%Al + 1.6 wt% Si). The coating is obtained by immersion in molten metal and is formed by high temperature diffusion processes. It is therefore made up of layers of zinc-aluminum/iron alloys richer in iron near the substrate and increasingly richer in zinc-aluminum towards the outside [10].

Numerous studies of zinc in atmospheric environments have resulted in the ISO classification system [13], which is used for practical purposes in order to predict the corrosion rates of zinc in different corrosivity classes. Zinc has also been extensively studied for a better fundamental understanding and it is today probably the most investigated metal from an atmospheric corrosion perspective [14].

Besides estimating the useful life of the component, today the corrosion products of zinc are also analysed to get useful information on the corrosion mechanisms and on the impact of aggressive species in the environment, such as chlorides and sulphates [15]. In fact, the presence of these compounds is very critical when galvanized steel is used in applications in the soil, to form gabions for MSE (mechanically stabilized earth) walls and steep slopes, or rockfall barrier [16].

The MSE system consists of three major structural components: the vertical facing element, the level pad, and the soil reinforcements. The soil mass behind the pre-cast concrete wall is generally composed by selected granular backfill material reinforced by metal strips or grids. These soil reinforcing elements have tensile strains generally smaller than those of the surrounding soil under the same stress condition, and hence they are usually assumed to be inextensible in practice [17,18]. The use of MSE reinforced systems has increased in the last decades worldwide, with the construction of thousands of walls and slopes. The tensile elements consist of metal and polymer strips and grids. The walls are designed to transfer the loads to the tensile elements, attached to the wall face [18]. The most used soil-reinforcement elements for retaining walls on transportation projects include galvanized steel.

Despite the widespread use of galvanized steel in underground applications, such as the MSE systems, the phenomena of soil corrosion have not yet been studied in depth. Indeed, many aspects of underground corrosion are still unclear, due to complex composition, porosity and discontinuity of the soil, which can influence the corrosion process [19], as the presence of inorganic and organic solid phases, a water-based liquid phase, air and other gas phases. The chemical soil composition is typically defined by the compounds that are present in the water. These constituents can have a basic nature as in case of sodium, potassium, calcium and magnesium, or an acidic nature, such as chlorides, sulphates and carbonates. The nature and concentration of soluble salts, together with the moisture content, mainly determine the ability of the soil to conduct electric current, which is very important in relation to corrosion processes [20].

The soil properties are even affected by organic matter and organisms. For example, sulphate reducing bacteria (SRB) cause the so called microbiologically-influenced corrosion. These bacteria are very aggressive, favouring the formation of sulphates on the steel surface that consequently promote the origin of soluble products, inducing a reduction in the corrosion resistance of the structure [21]. The oxygen content that is able to penetrate in the soil play an essential role in the behavior of galvanized steel, because the predominant cathodic reaction is the oxygen reduction. Thus, the amount of oxygen is fundamental to define the cathodic reaction rate and hence the rate of the whole corrosion process. The formation of corrosion macrocells produces an increase of corrosion rate in the clay soil, due to concentration of the anodic reaction, while the cathodic one occurs mainly in the sand soil, as the presence of oxygen is much higher [22]. Regarding the pH influence, the corrosion resistance of galvanized steel is very high in neutral conditions, while the corrosion rate increases for high acid or alkaline environments, due to loss of stability of the corrosion products [23]. The resistivity is a measure of the ability of a soil to act as an electrolyte and is correlated with the soil compaction, temperature, moisture and salt content. In general, the corrosion rate increases as the resistivity decreases: therefore, resistivity parameter can be used to predict water content and degree of saturation of the soil [24].

Finally, the chlorides and sulphates concentrations are in general the most critical parameter for the corrosion behavior of buried steel. Indeed, these elements are very detrimental for the corrosion resistance because the obtained corrosion products are not stable and well adherent to the substrate. Moreover, chlorides promote the pitting corrosion, localized attack that occurs in correspondence of coating defects, where pit forms due to concentration of the anodic reaction inside the pit, while the cathodic reaction develops mainly in the region around the pit. Pitting corrosion is very important for the corrosion behavior of galvanized steel, because it leads to the complete penetration of the zinc coating and the consequent direct contact between aggressive environment and steel substrate [25]. A soil is considered corrosive if it contains even a low concentration of these elements, in particular a concentration of chlorides greater than 500 ppm and a concentration of sulphates greater than 1000 ppm [26]. The content of these compounds inside the soil depends even on the external atmospheric environment. For example, chlorides ions are present mostly in marine environments, while both have a critical high concentration in case of polluted atmospheres due to human activity [26].

MSE walls are expected to remain stable for many decades: for that reason, the corrosion study of the tensile elements is fundamental in order to obtain useful data and information about the lifetime of these systems, since a rapid deterioration can provide instability on the structure, eventually leading to its failure. Long-term durability of reinforcing materials is a major concern for MSE systems, due to suspected corrosion of the tensile elements as a consequence of the chemical aggressiveness of the soil-water environment [27].

The aim of this work is to analyse the behavior of the galvanized steel wires against soil corrosion, trying to deduce the influence of the chemical characteristics of the soil, with a particular focus on the effect of chloride and sulphate compounds. The study was performed by monitoring the samples behaviour with electrochemical measurements over time so as to have information on corrosion process characteristics. Then, the samples were extracted from the soil and analysed by optical microscopy and scanning electron microscopy SEM, with the aim to evaluate the intensity and the morphology of the corrosion process, studying the corroded surface.

2. Experimental

2.1. Materials

The hot-dip galvanized steel wires (6 mm in diameter) covered by Galfan were produced and provided by Metallurgica Ledrense (Tiaro di Sopra, TN, Italy). The thickness of the metallic coating is about 70 μm , in agreement with the CE marking. The soil employed in the study was picked up in Ville d'Anania (Val di Non, TN, Italy). Sodium sulphate, sodium chloride, citric acid, silver nitrate, barium chloride and hydrochloric acid were purchased by Sigma Aldrich and used as received.

2.2. Samples arrangements

With the purpose to study the influence of chlorides and sulphates presence, several testing environments were prepared with different concentration of these compounds. In particular, two sets of environments were performed, each consisting of four different soil conditions:

- The first set of environments contained only sulphate with different concentrations, while the chloride content was totally absent;
- The second set was composed by both sulphates and chlorides, in order to evaluate the synergistic effect given by the presence of both elements. Specifically, the sulphates content was maintained unchanged, while the chlorides amount was progressively increased.

The first and the second set of samples are summarized in [Table 1](#) and [Table 2](#), respectively.

The specific values of concentration for chlorides and sulphates were chosen by reference to the lower corrosivity limit defined for structural elements buried in soil (chloride concentration higher than 500 ppm and sulphate concentration higher than 1000 ppm [26]). The selected values are much higher than the reference ones in order to simulate highly corrosive environment that can be found in the most critical situations. The value of pH, since it is not a parameter of interest, was maintained around 7, because in neutral region the effect of pH on the corrosion behavior of galvanized steel is very low. Instead, for high acidic or alkaline environments, the effect of pH becomes fundamental, due to the loss of stability of the corrosion products.

In addition to the galvanized steel, a second sample formed by bare steel was immersed in the same soil. The sample was obtained through the removal of the zinc coating from the same used galvanized steel. The aim of this sample was the comparison between the corrosion behavior of bare steels and Zn-coated steels. The zinc removal was carried out by immersing the wires in a dilute solution of hydrochloric acid at 10 wt%.

2.3. Testing environments setup and preparation

Sulphates and chlorides were added to the soil through specific aqueous solutions by using respectively sodium sulphate and sodium chloride, that have been dissolved in demineralized water. All solutions were neutral and hence they were not able to change the pH of the system.

The sample setup was composed by a tubular container set on a perforated plate. The system was placed in a vessel with low edges. 300 g of soil were introduced in the tubular container with the addition of 110 ml of solution, in order to have a wet soil that allows the execution of electrochemical tests. Moreover, the flowerpot saucer was fulfilled with solution with the aim to maintain as much as possible constant the moisture content, since the solution was able to reach the soil through the small holes of the plate due to capillarity. Both soil and saucer were covered to avoid excessive evaporation of the solution and water. The scheme of sample setup is illustrated in [Fig. 1](#).

In each tubular container were placed a galvanized steel and a bare steel wires, immersed with same depth in order to keep the same area of contact with the corrosive environment. In particular, the wires were immersed for 8 cm and, since wires had a diameter of 0.6 cm, the buried lateral area was equal to 15.1 cm^2 . The buried edges of the wires were not coated by zinc and therefore, to avoid the direct contact between the soil and the steel substrate with the consequent galvanic coupling, they were covered by silicon.

The initial pH of the soil, measured with a pH meter by means a specific procedure [28], exhibited a value around 8. For this reason, in order to shift the pH until 7, a dilute solution of citric acid was added to the soil of the samples. After a week, monitoring the pH value, a slightly increase was observed, until a maximum value of 7.4. Thus, in any case it remained in neutral conditions.

Firstly, chlorides and sulphates concentrations were measured, obtaining a filtered transparent soil solution [29]. For chloride analysis, silver nitrate was added in order to react with chloride ions to promote the precipitation of white silver chloride. While for the sulphates, the addition of barium chloride was performed in order to form, as in case of chlorides, white precipitates in a transparent soil solution. In both cases, no changes were observed, thus the content of chlorides and sulphates inside the initial soil was considered

Table 1
first set of testing environments with different concentration of sulphates.

Sulphates concentration [ppm]	5000	7000	9000	11000
Chlorides concentration [ppm]	Not present			

Table 2
second set of testing environments with different concentration of chlorides.

Sulphates concentration [ppm]	7000			
Chlorides concentration [ppm]	1000	3000	5000	7000

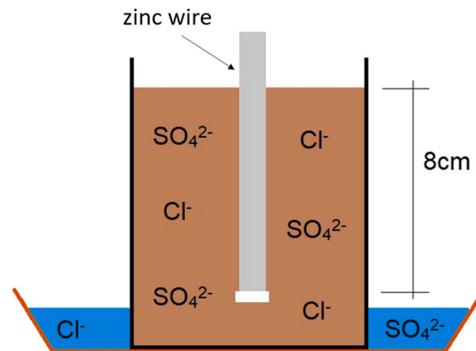


Fig. 1. testing setup scheme.

as lower than 20–30 ppm and consequently negligible respect to the amount added in the sample solutions.

2.4. Characterization

Potentiodynamic analysis were carried out with Ametek Model 273 A potentiostat with a scan rate equal to 0.166 mV/s and step potential equal to 1 mV, to acquire information about the corrosion rate of the samples [30]. The tests were performed in the soil but also immersing the samples directly in the different solutions of chlorides and sulphates, with the aim to compare the two different results and to deduce the influence of the soil in the corrosion process rate.

Open circuit potential (OCP) measurement and electrochemical impedance spectroscopy (EIS) test were carried out two times a week and conducted to monitor the corrosion process over time. The measurements were exploited using a Ametek Model 273 A potentiostat equipped with the PowerSuit ZSimpWin software. The EIS were carried out applying a signal of about 10 mV (peak-to-peak) amplitude in the 10^5 - 10^{-2} Hz frequency range. The cell setup for the three different analyses was composed of an Ag/AgCl reference electrode (+207 mV SHE) and a platinum counter electrode, immersed in the soil of the tubular containers. The platinum counter electrode is represented by a standard laboratory counter electrode consisting of a ring with a diameter of 0.4 cm and an area equal to 1.0 cm².

The wires were immersed in the soil (test setup) and monitored for 4 months; thus, the samples were extracted and cleaned, in order to be analyzed with the optical microscope Nikon SMZ25, to study the corroded surface of the samples with and without corrosion products. Finally, the samples were observed with SEM JEOL IT 300 to assess the corrosion morphology and to examine the elements present on the surface after the corrosion process.

3. Results and discussion

3.1. Soil composition

The soil was subjected to elemental analysis through SEM-EDXS observations. Carbon element was not considered in the analysis,

Table 3
Elemental analysis of soil used in the study.

Element	Mass Norm. [%]
Oxygen	53.46
Sodium	1.03
Magnesium	1.51
Aluminum	8.00
Silicon	21.19
Potassium	2.26
Calcium	7.39
Titanium	0.50
Iron	4.52
Phosphorous	0.15

so as not to falsify the results. The results illustrated in the Table 3 show high concentration of oxygen, silicon, aluminum, calcium and iron. The results suggest a brown calcareous or forest rendzina nature of the soil. These two types of soils are very similar, as they arise from the same parental materials, such as limestone, marly limestone and dolomite [31]. The composition of these two typical soils is a mixture formed mainly by sand and silt, with a low content of clay (around 12%) and in general it is characterized by slightly alkaline pH (a value around 8). Total carbonates are particularly abundant in calcareous soils and, about heavy metals, since developed from carbonate rocks, they present the largest median values for zinc and lead. Moreover, they contain even chromium, copper, nickel and iron with a lower concentration. The most major and trace elements are slightly mobile and accumulate at surface, while their concentration decreasing regularly with the soil depth [32].

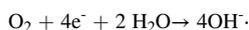
This analysis of the soil can be very useful in the study of the composition of the corrosion products formed on the surface, because some elements that can be present in the corrosion products or attached on the surface could come from the soil. As a matter of fact, the corrosion reactions develop on steel surface and therefore an interaction occurs between the sample and the surrounding environment during the corrosion process.

3.2. Potentiodynamic polarization

The first potentiodynamic analysis was performed by immersing the samples directly in the different aqueous solutions. The goal of this preliminary test was to compare these results with ones obtained by immersing the samples in the ground, in such a way to establish the influence of the soil on the corrosion rate.

Fig. 2 shows the anodic and cathodic branches of the wires in different sulphate solutions. The anodic curves evidence that at higher polarizations there is an increase in the current density from 9000 ppm onwards. Differently, the cathodic curves are approximately superimposed, as the reduction reactions should be in diffusion control of oxygen and, since the test was carried out directly in the sulphate solutions, the oxygen availability is practically the maximum possible [25]. The free corrosion potential is around -1050 mV vs Ag/AgCl that is equal to the values observed by pure zinc, following the Galvanic Series in seawater [33].

At these potentials there is the reduction of the oxygen present in the electrolyte, typical of a neutral oxygenated environment, represented by the following reaction:



The process is under oxygen diffusion control, as is evident from the trend of the cathode curves shown in Fig. 2, where the current density is not affected by the potential values. This trend is observed for the whole cathode branch shown in the figure up to potentials equal to -1200 mV vs Ag/AgCl.

The curves were analysed in order to extract the Tafel lines of each sample and then the correspondence corrosion currents (expressed as current density). The results are reported in Table 4. Assuming that the type of corrosion remains the same, the corrosion current is proportional to the corrosion rate, therefore higher current means higher rate. The currents in Table 4 do not arise following the increase in sulphate concentration: only the sample with 11000 ppm exhibits an appreciable increase in current density.

Thus, the analysis was performed in the soil in order to understand if the increase in sulphates concentration leads to a consequent arise of the corrosion rate. The potentiodynamic curves collected from the test are illustrated in Fig. 3. From the anodic plot, no active-passive transition can be observed; hence the activation continues on the anodic branch. On the other hand, the cathodic branch of the potentiodynamic polarization curve indicates diffusion-controlled behavior, implying that the reduction reaction is mainly related with oxygen content [34]. This phenomenon is due to the greater difficulty of oxygen to diffuse into the ground, as can be seen by comparing the cathode current density of Fig. 3 with Fig. 2. The current density decreased with the concentration of sulphate, as the

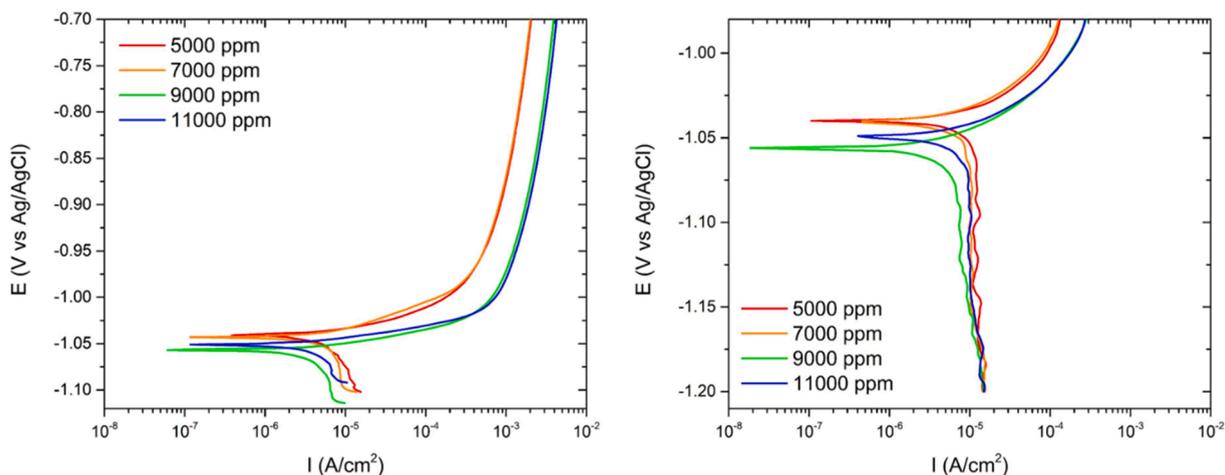


Fig. 2. anodic (on the left) and cathodic (on the right) curves of the samples immersed in solutions with different sulphate concentration.

Table 4
corrosion current of the samples immersed in the different sulphate solutions.

Sulphate concentration [ppm]	I_{corr} [mA/cm ²]
5000	64.17
7000	59.05
9000	61.58
11000	78.19

increase of the concentration of salts results in a consequent reduction in oxygen, which leads to a decrease in the current density. However, the differences are not that significant.

The obtained values of I_{corr} , calculated on 5 measurements for each testing environments, are summarized in Table 5. The results perfectly show the influence of different concentration in the soil: a gradual increase of corrosion current can be observed due to the consequent rise in the sulphates content. However, comparing the minimum value for 5000 ppm sample and the maximum one of 11000 ppm sample, current density approximately doubles, hence an important growth occurs, considering that even the concentration is doubled from the first to the fourth environment. Moreover, by comparing these results with ones in Table 4, it is possible to note a significant reduction in the corrosion current, due to higher oxygen availability and sulphates mobility in the solution respect to the soil. Therefore, cathodic reaction can occur readily in the first case producing an increase in the velocity of whole corrosion process.

As for the first set of testing environments, potentiodynamic test was performed also with different chloride content, immersing the galvanized steel wires directly in the different solutions and then in the soil. The two branches of potentiodynamic curves obtained for samples immersed in the solutions with different chloride concentrations are reported in Fig. 4. The free corrosion potential is constant for all the four samples, and it is equal to -1050 mV vs Ag/AgCl, value, similarly to the corrosion potential of zinc. The anodic curves shift slightly to the right due the increment of chloride content in particular at high level of anodic polarisation, while the cathodic ones are more or less superimposed and seems to be in diffusion control.

Table 6 summarizes the corrosion current densities obtained by extrapolating the Tafel lines from the potentiodynamic curves. The I_{corr} do not show a progressively increasing according to the increment of chloride content. However, the difference between the values is quite small, therefore the corrosion rate is approximately the same regardless to the aggressiveness of the environment.

Subsequently, the analysis was performed in the soil and the obtained potentiodynamic curves are illustrated in Fig. 5. By observing the anodic branch, no passivation phenomena can be appreciated, as the zinc remains in the active state. Moreover, even in this case the curves shift rightwards with the increase of chloride concentration. The difference between cathodic curves is practically insignificant except for the 7000 ppm sample. A possible explanation for this phenomenon lies in the activation of the cathodic reaction on the surface, due to the presence of a high amount of chlorides. However, all the curves exhibit a diffusion control situation governed by reduction of oxygen.

The current densities of samples were derived and reported in Table 7. The values of current density relative to 1000 ppm and 3000 ppm samples is approximately the same, while then progressively increase due the increment of chloride concentration, in agreement with the greater aggressiveness of the environment. However, despite the large difference in content of chlorides between the 1000 ppm of the first soil and the 7000 ppm of the last one, I_{corr} evidence a residual increase. This result suggests that the influence of chlorides on corrosion current is quite low in comparison of the effect of the sulphate presence. As expected, the values of current are much lower than the ones obtained by performing the analysis immersing the galvanized steel wires directly in the solutions (Table 6).

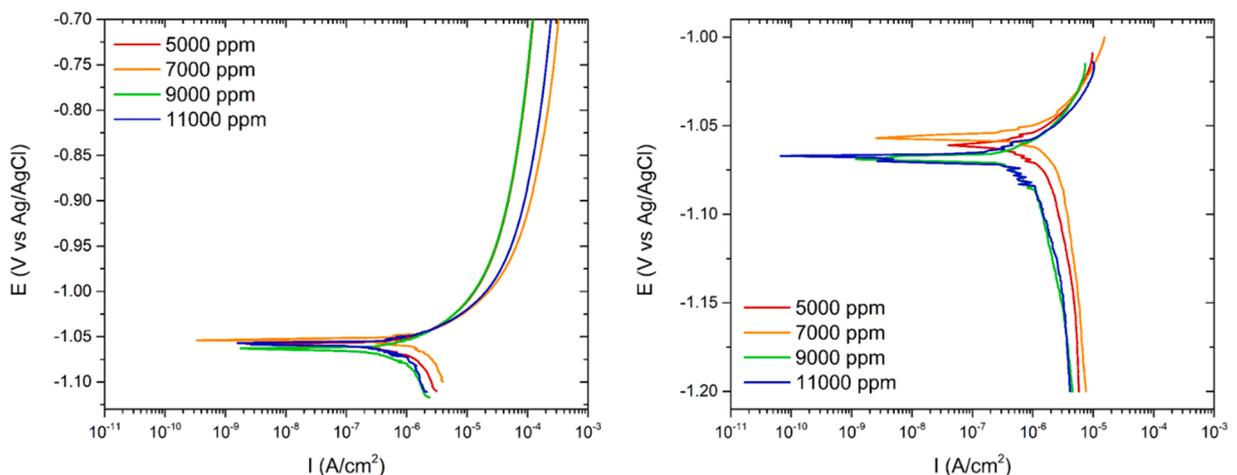


Fig. 3. anodic (on the left) and cathodic (on the right) curves of the samples immersed in soils with different sulphate concentration.

Table 5
corrosion current of the different samples immersed in soil.

Sulphate concentration [ppm]	I_{corr} range [mA/cm ²]	
	min	max
5000	8.26	9.43
7000	10.11	12.58
9000	12.17	13.69
11000	15.84	16.38

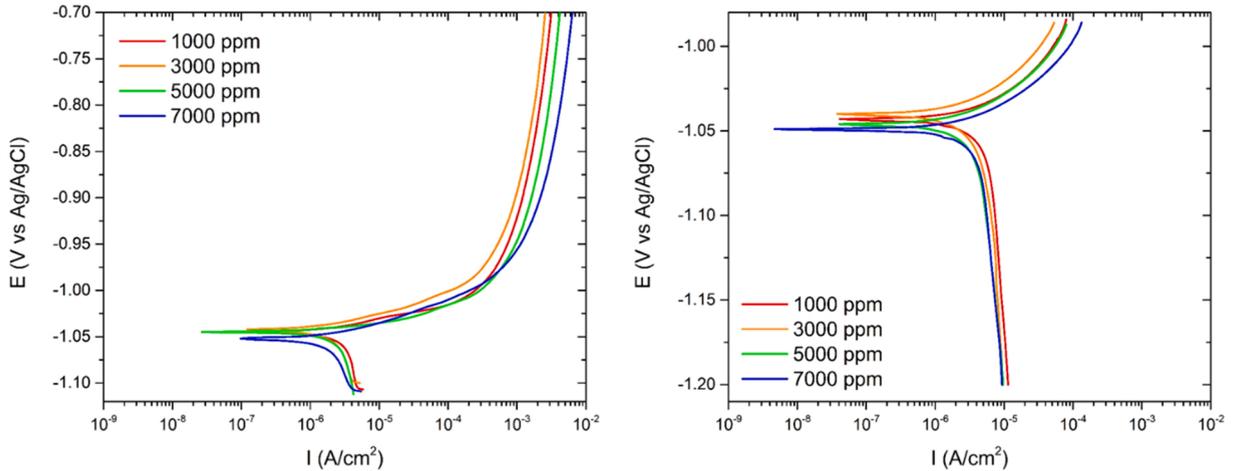


Fig. 4. anodic (on the left) and cathodic (on the right) curves of the samples immersed in solutions with different chloride concentration.

Table 6
corrosion current density of samples immersed in solution containing chloride ions.

Chloride concentration [ppm]	I_{corr} [mA/cm ²]
1000	34.15
3000	39.69
5000	36.61
7000	38.78

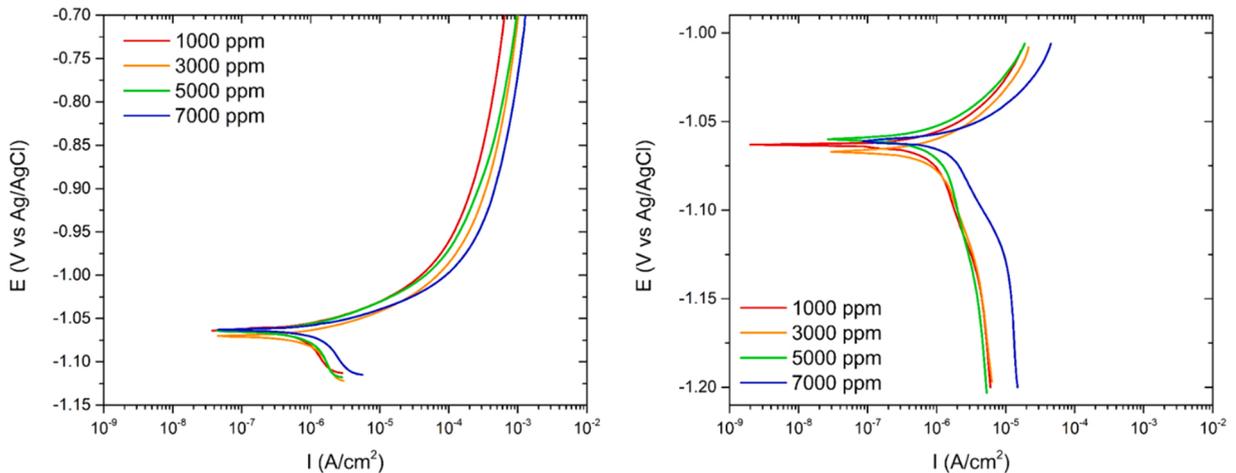


Fig. 5. anodic (on the left) and cathodic (on the right) curves of the samples immersed in soils with different chloride concentration.

Table 7
corrosion current of the different samples immersed in soil.

Chloride concentration [ppm]	I_{corr} range [mA/cm ²]	
	min	max
1000	10.96	11.66
3000	10.97	11.02
5000	14.95	15.49
7000	15.68	16.11

This could be explained with the lower diffusion and oxygen availability that is present in the soil. Therefore, cathodic reactions are hindered respect to the case of aqueous solution.

3.3. OCP measurements

The open circuit potential was monitored twice a week over all the immersion time to get useful information on the corrosion process. Considering the trend of potential, it is possible to highlight the tendency of the metal to passivate, the eventual formation of corrosion products and it possible to acquire information about the type of metal in corrosion state. Fig. 6 exhibits the OCP curves of the two series of environments. Regarding the soil with sulphate presence, the OCP starts from a value approximately equal to the potential of zinc. The curves initially show a rapid increase and thereafter tend progressively to a plateau. The maximum value considering all samples is -940 mV vs Ag/AgCl, therefore it is possible to assert that whole corrosion process is remained in the zinc predominant region, meaning that probably the consumption of the external layer was not sufficient to reach the steel substrate. This trend of potential variation was exhibited from all samples, as the potential difference between the samples is very small. Thus, the corrosion behavior was roughly the same regardless of sulphate concentration. Moreover, the soil pH of all the samples was maintained in neutral region, with a value more or less equal to 7. Therefore, considering the values of OCP and the Pourbaix diagram of zinc, it is possible to deduce that the corrosion process occurred in the corrosion zone. Hence, zinc oxidation should be induced with the progressive formation of Zn^{2+} . Definitely, no passivation of zinc was expected to occur on the surface, but the formation of corrosion products, as zinc oxides and hydroxides connected with the zinc ions.

Similarly, all the samples immersed in soils with different chloride concentration (on the right of Fig. 6) behave approximately in the same way: the OCP initially increased from -1050 mV vs Ag/AgCl and subsequent gradually tended to a constant value. The difference between all steel wires in the corrosion potential values at the end of immersion time was negligible. During the entire immersion in the soils, the potential has been maintained in the zone governed by zinc corrosion: hence, only zinc was involved in the corrosion process, while the underlying iron did not undergo corrosion phenomena.

3.4. EIS analysis and microscope observation of the corroded surfaces

This analysis was employed, as for OCP, to monitor the corrosion process over time. The measurements were carried out two times a week, together with the analysis of free corrosion potential. Then, the collected data were analyzed by introducing an equivalent (electrical) circuit composed of a number of elements such as resistances (R), capacitances (C), and inductances (L), that is able to represent the actual state of electrochemical interface during the corrosion process [35].

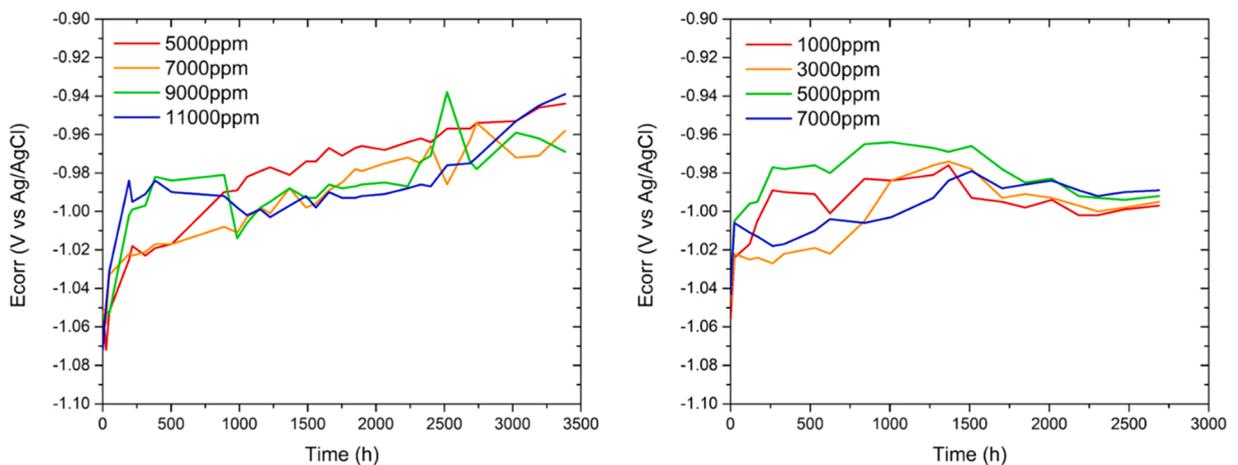


Fig. 6. evolution of the OCP of the sample immersed in soils with different sulphate and chloride concentrations, on the left and on the right, respectively.

In particular, two different equivalent circuits have been employed for the analysis of the galvanized steel samples, as shown in Fig. 7. For the first period of immersion of the sample (the black curve with square points in Fig. 7), the used circuit for the fitting was composed by electrical circuit solution resistance (R_s), charge transfer resistance (R_{ct}) and double electrical layer capacity (Q_{dl}) [36]. This circuit was suitable for the data analysis for the initial period because of the absence of corrosion products. Subsequently, when the corrosion process is developed enough and a well-defined layer of corrosion products is formed on the surface (the red curve with dot points in Fig. 7), a different equivalent circuit was introduced, as it is commonly used to model porous corrosion product layers. It was composed by R_s accounting for the solution resistance, Q_c and R_p for the film capacitance and resistance of the porous layer, respectively, Q_{dl} and R_{ct} accounting for the capacitance and transfer resistance/diffusion through the pores, respectively [37].

Indeed, in case of galvanized steel corrosion, during the first phase of corrosion, a semi-compact layer of precipitates, mainly Zn and ZnO with small amounts of $Zn(OH)_2$, is present on the surface of the wires. However, as immersion time increases, the layer grows, depleting the zinc coating and forming a thick, porous layer consisting mainly of a non-protective and soluble layer of $Zn(OH)_2$ [38]. Thus, after the 4 months' immersion in the different soils, the samples were analysed at the optical an electron microscope, to deeply study the corrosion morphology of the wire surfaces.

3.4.1. Soils with different sulphate concentration

The EIS diagrams of the samples immersed in soils with different sulphate concentration initially exhibited only one-time constant, while after a certain period of immersion, the development of the corrosion products led to the evolution of a second time constant, as described in Fig. 7. For this reason, at the beginning the impedance spectra were fit with a R(QR) model circuit. Subsequently, approximately after 38 days of immersion, the R(Q(R(QR))) model were used to account even the effect of corrosion products layer on the surface.

Initially all the samples exhibited an increase of the impedance modulus measured at the low frequency, probably because of the increment of double electrical layer and oxide layer. However, at a specific point the impedance modulus decreases for 7000 ppm, 9000 ppm and 11000 ppm environments, while the modulus of 5000 ppm sample revealed a constant raise. In fact, in the less aggressive environment the corrosion products are partially protective, consequently increasing the total impedance. Otherwise, in more aggressive environments there is a tendentially constant corrosion rate. All the impedance spectra were analyzed with equivalent electrical circuits in order to get information on the resistances related with corrosion products (R_p) and with charge transfer phenomena (R_{ct}). Their variations of these two parameters as a function of the time are reported in Fig. 8. The solution resistance (R_s) was considered fixed for whole immersion period.

The R_{ct} values of 11000 ppm sample were significantly lower respect to the other wires. Consequently, the corrosion products provided a weaker protective effect. Differently, the other three curves initially exhibited an increase of R_{ct} with increasing the exposure time, thus indicating that the corrosion products layer hindered the corrosion progress. Nevertheless, only the 5000 ppm curve had a constant increment, while the 7000 ppm and 9000 ppm environments evinced a change of trend and R_{ct} values start to decrease, due to the possible damage of the porous layer, leading to a consequent increase of the corrosion rate [39].

Similarly, the increment of R_p can be related to the formation of corrosion products, when a subsequently decrease of the resistance polarization can indicate the deterioration of the zinc oxide layer on top of the underlying steel, brought forward by the dissolution of the zinc layer [40].

The trends of the curves are not linear due to the development of corrosion products that are not totally uniform, due to the local non-homogeneity of the electrolyte. Therefore, the presence of water and the absorption of oxygen can vary from area to area on the sample surface.

After approximately 4 months, the samples were extracted from the soil and cleaned as much as possible by means of a dilute

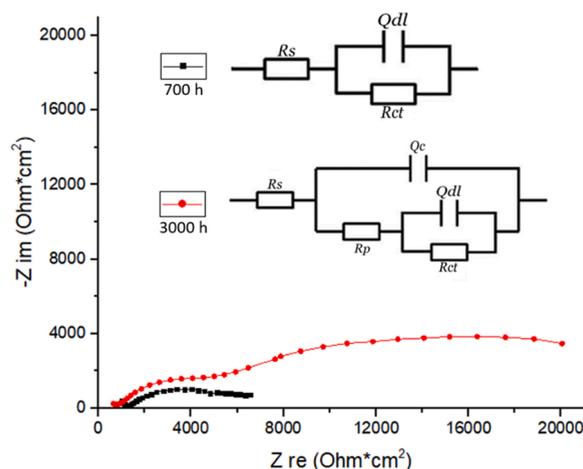


Fig. 7. evolution of the Nyquist diagram of the sample with sulphates concentration equal to 5000 ppm over time. Representation of the two equivalent circuits used for the fitting of the experimental data.

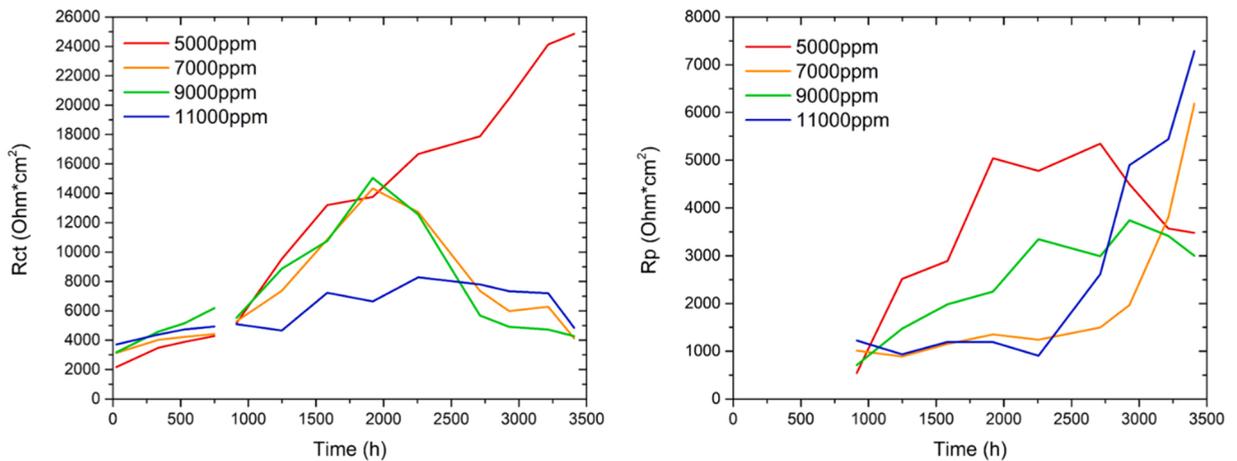


Fig. 8. variation of Rct and Rp, on the left and on the right, respectively, as a function of the immersion time for samples in soil with different sulphate concentration.

solution of citric acid (40 ml/L) and ultra-sonic bath, with the aim to get information on the morphology of the corrosion processes. As can be seen in Fig. 9, no significant differences can be identified between the surfaces of the wire immersed in different four soils and even no sign of possible localized corrosion seems to be present. Therefore, the corrosion process induced by sulphates was a generalized corrosion that was approximately uniform on whole surface. However, observing the sections of the wires, it was possible to notice a decrease in the thickness of the galvanized layer as a function of the concentration of sulphates in the soil. Starting from a thickness of about 75 μm , the exposure to soils caused a decrease to about 55 μm , 43 μm , 35 μm and 32 μm in the presence of 5000 ppm, 7000 ppm, 9000 ppm, 11000 ppm of sulphates, respectively. With so thin zinc layers it is possible that certain points of the intermetallic layer came in direct contact with the soil, explaining the presence of red rust.

Initially when it is flawless, the zinc-aluminum coating protects the steel due to the barrier effect. However, being electrochemically active, zinc also exhibits degradation phenomena. During exposure in the ground, the corrosive phenomena that can be different from area to area, as can be seen in Fig. 9, lead to a non-uniform degradation of the coating. When the electrolyte, due to the zinc degradation, comes into contact with the steel substrate, a galvanic coupling is formed where the electrochemically less noble material will increase its corrosion rate, while the more noble material (steel) will be protected, as it is the seat of oxygen reduction reactions.

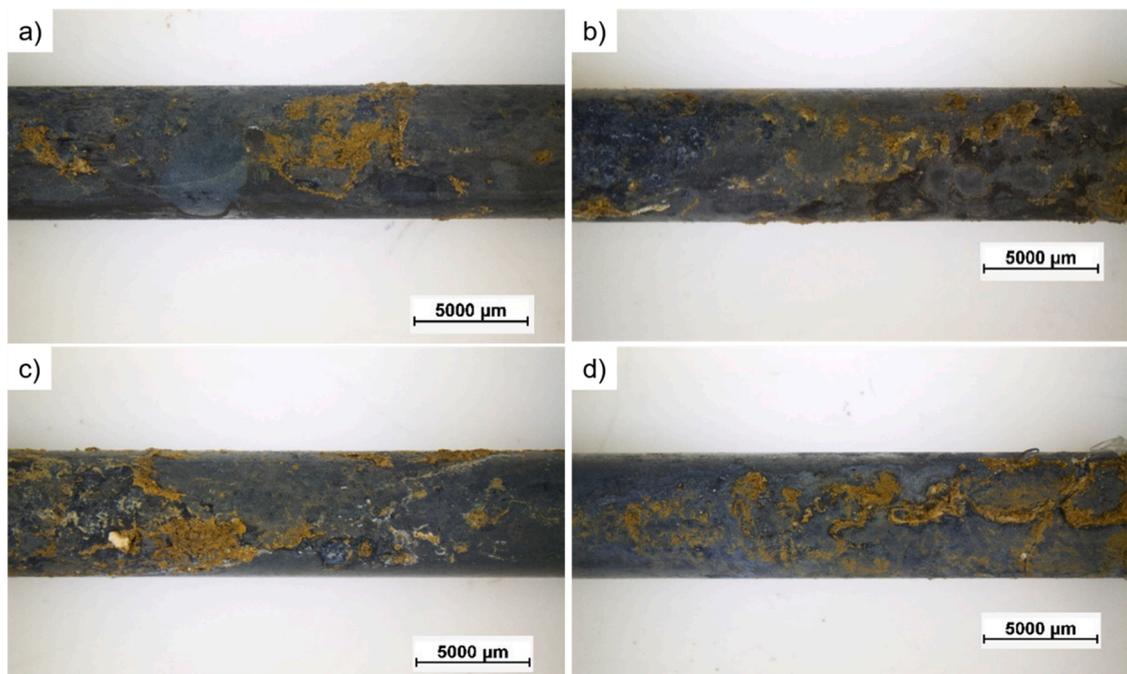


Fig. 9. optical images of the galvanized steel wires without corrosion products. a) 5000 ppm, b) 7000 ppm, c) 9000 ppm and d) 11000 ppm.

The intensity of the galvanic coupling will depend on the conductivity of the electrolyte. For this reason, the zinc, when the area of steel uncovered or the resistivity of the electrolyte will be high, will no longer be able to protect the substrate steel which will begin to corrode.

Thus, the samples were observed at SEM, performing qualitative and semi-quantitative elemental analysis by means of EDXS and mapping in order to study the corrosion morphology that took place and the elements that participated in the corrosion process, considering even the elements coming from the soil and the added sulphate solution. The analyses carried out with SEM on all samples show similar results both in elemental analysis and in mapping. Table 8 summarizes the results of the analysis performed on 11000 ppm soil, as example for the wires immersed in four environments. As expected, the external layer is almost totally composed by zinc, aluminum and oxygen (together include roughly the 86% of the elements). Therefore, the external surface is mainly formed by zinc and aluminum oxides, hydroxides or more complex compounds produced by the corrosion reactions. At the same time, the absence of strong iron signal suggests that the outer part of the coating is made of the zinc porous layer, while the Zn-Fe intermetallic layer is still covered.

Thus, the area analysed with the EDXS was mapped in order to obtain the distribution of the different elements present on the surface. The maps of the elements connected with the corrosion process are reported in Fig. 10. Oxygen and aluminum content are concentrated in the darker regions, while zinc is present mostly in the rest of the surface. Thus, the passivation of aluminum occurred principally in these three areas and zinc oxides form mainly on the other part of the surface. However, only a small trace of iron can be observed, and it is even present in the soil composition as shown the soil analysis in Table 3. Definitely, this analysis demonstrates that the outer layer is formed by Zn-Al oxides and hydroxides, while Zn-Fe layer is totally covered.

In general, it is possible to affirm that the surface of these four samples is composed for the greater part by large amount of zinc corrosion products and in minor way by aluminum compounds. Therefore, zinc is involved in the predominant corrosion process, while the passivation of aluminum becomes important only in few spots. Moreover, the presence of sodium, sulphur and carbon can be explained with the development of more complex products than oxides and hydroxides, such as specific compounds as hydrozincite ($Zn_5(CO_3)_2(OH)_6$), hydrotalcite ($Zn_6Al_2(OH)_{16}CO_3 \cdot 4 H_2O$) and ($Na_4Zn_4SO_4(OH)_6Cl_2 \cdot 6 H_2O$), that are typical corrosion products of Galfan alloy [41].

3.4.2. Soils with different chloride concentration

As for the first series of soils, The EIS diagrams initially exhibited only one-time constant, while after a certain period of immersion, the development of the corrosion products led to the evolution of a second time constant. Again, the impedance modulus of all the four wires shows the same behavior: an initial increasing and a subsequent decreasing approximately after a certain time of burial. This phenomenon is explained with the initial formation of double electrical layer and the development of corrosion products, while the following reduction can be caused by gradual damaging or completely failure of the galvanized coating in specific surface points.

As previously described, all impedance spectra were fitted in order to obtain the variation of R_p and R_{ct} and the results are illustrated in Fig. 11. The samples exhibited similar R_{ct} variation curves, except for the 7000 ppm sample, which revealed lower R_{ct} values. Moreover, all curves exhibit the same trend: a first increase, symptom of formation of a protective layer, and a subsequent reduction after a certain exposure time, indicating either a breakdown of that layer or that the formed film is porous and fails to fully protect the surface over time [42]. Similarly, R_p value initially increased, due to the development of corrosion products generated and absorbed on the electrode surface. However, the R_p value decreased gradually with the increment of exposure time, and it decreased even as the Cl^- concentration increased. This phenomenon suggests that corrosion products film absorbed on the electrode surface progressively damaged under the effect of chlorides ions [43].

Fig. 11 reveals the appearance of the surfaces of the four wires, after the removal of the corrosion products. The corrosion on 1000 ppm Cl^- soils (Fig. 11a) is roughly generalized on whole the surface, due to the effect of sulphate concentration of 7000 ppm present in the soil. Differently, increasing the chloride content, the corrosion tends to localize in specific spots of the surface. These phenomena are correlated to strong formation of white rust composed by zinc oxides, hydroxides, or more complex compounds, due to the greater dissolution of zinc. This behavior is typical of localized corrosion produced by chloride ions [44].

The profile of the zinc coating of 1000 ppm soil is uniform along the surface. Therefore, the chlorides were not able to attack the external layer to form a pit and the generalized corrosion was mainly due to the presence of sulphates. The average thickness of the galvanized coating of the other three wires is similar to that of the 1000 ppm wire. Nevertheless, in specific regions of the surface, the thickness is subjected to a strong reduction. As a matter of fact, the increased chlorides concentration favours the development of localized corrosion morphology, leading to a minimum thicknesses of the zinc film even lower than 20 μm , more or less one fourth of the initial layer depth. Therefore, in certain localized spots the corrosion process probably reached the underlying intermetallic layer, putting it in direct contact with the aggressive environment or even the steel substrate in the worst situation (Fig. 12).

The profile of zinc coating immersed in 1000 ppm soils is uniform along the surface, therefore the chlorides were not able to attack the external layer to form a pit and the corrosion is generalized mainly due to the presence of sulphates. By observing the other wires, it is possible to note that on average the thickness of galvanized coating is similar to 1000 ppm one, but in specific regions of the surface, thickness is subjected to a strong reduction. The meaning is related with the increased chloride effect that favors localized corrosion morphology, leading to a minimum thicknesses even lower than 20 μm in these points, that is more or less one fourth of the initial layer depth. Therefore, it is probable that corrosion process reached underlying intermetallic layer in certain points, putting it in direct contact with the aggressive environment or even the steel substrate in the worst situation.

Table 9 summarizes the results of the EDXS analysis performed on the four wires, highlighting the difference evidenced between the 1000 ppm wire (representative also of the 3000 ppm and 5000 ppm samples) and the 7000 ppm wire. The elemental analysis evidenced that the greater part of the surface of 1000 ppm sample is covered by oxygen (27.78%), zinc (52.15%) and aluminum

Table 8
elemental analysis of 11000 ppm soil.

Element	Mass Norm. [%]
Carbon	7.90
Oxygen	33.60
Magnesium	0.53
Aluminum	16.00
Silicon	2.77
Sulphur	0.78
Zinc	36.57
Potassium	0.23
Calcium	0.19
Titanium	0.04
Iron	1.39

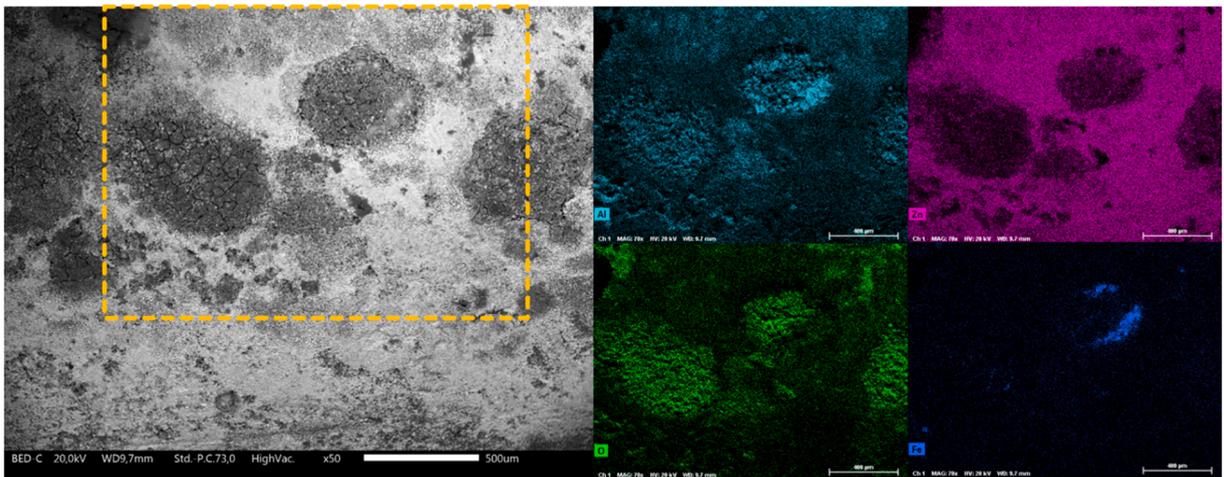


Fig. 10. SEM EDXS map of the elements connected with the corrosion process of 11000 ppm sample.

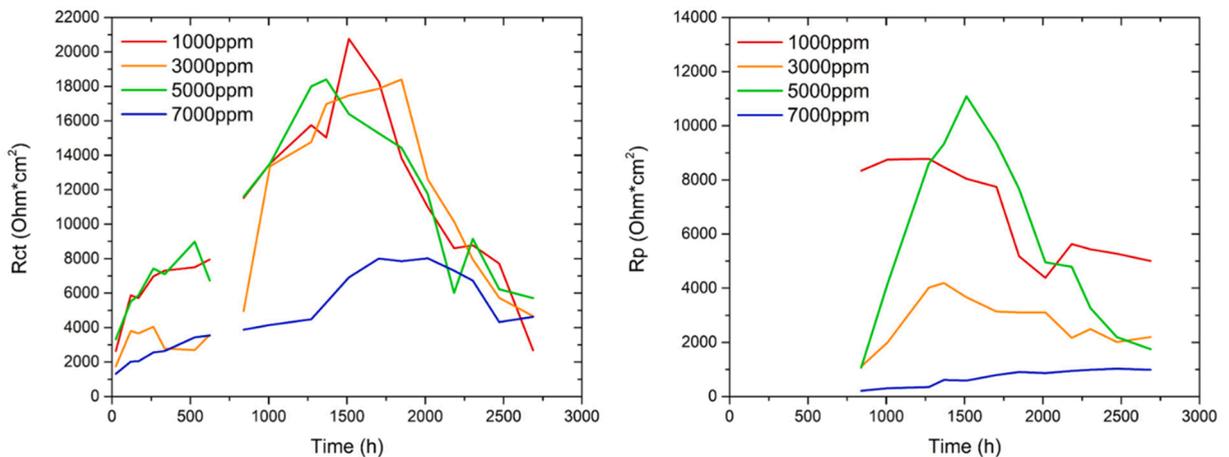


Fig. 11. variation of Rct and Rp, on the left and on the right, respectively, as a function of the immersion time for samples in soil with different chloride concentration.

(10.26%). Therefore, the external layer is covered by Zn-Al corrosion products. Regarding the other elements, only calcium (4.18%) and silicon (2.73%) have a significant concentration derived by the soil, while the content of iron is very low (less than 1%), hence corrosion process was not sufficient to reach the intermetallic layer formed by Zn-Fe alloy. Differently, the elemental analysis of 7000 ppm wire presents a very high amount of zinc (59.44%) and oxygen (23.47%), while the aluminum content (6.31%) results to be reduced respect to the 1000 ppm sample. However, the most interesting aspect is the very significant increase of iron concentration

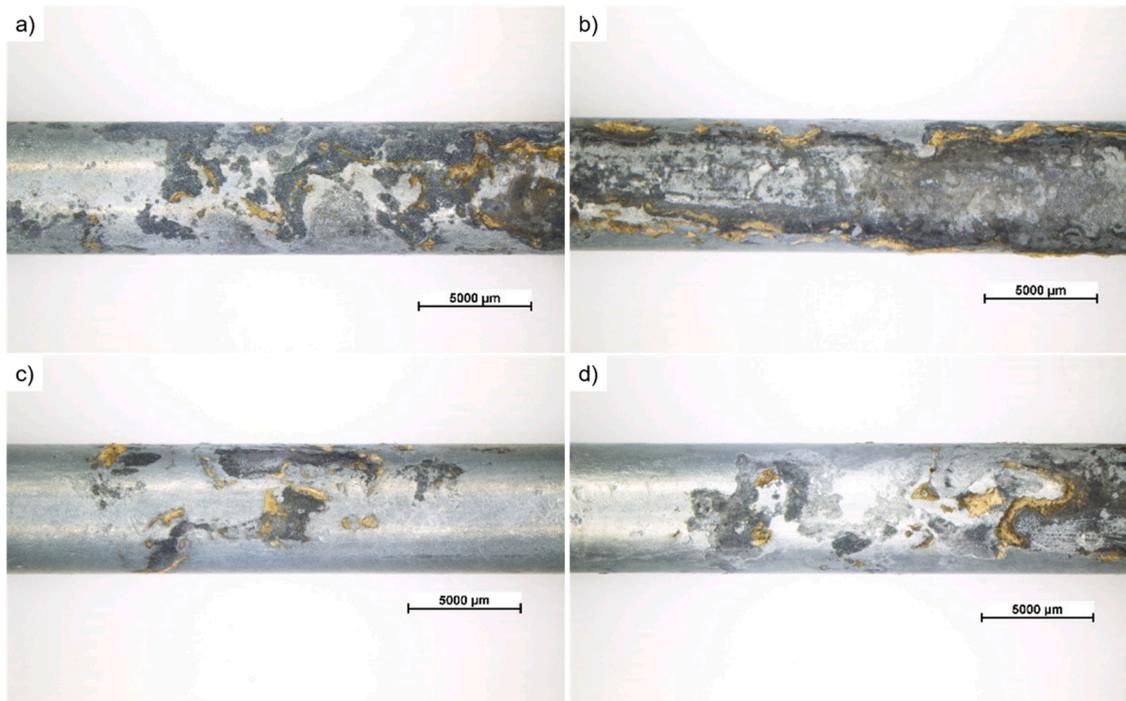


Fig. 12. optical images of the galvanized steel wires without corrosion products. a) 1000 ppm, b) 3000 ppm, c) 5000 ppm and d) 7000 ppm.

Table 9
elemental analysis of 1000 ppm and 7000 ppm soils.

Element	Mass Norm. [%] - 1000 ppm	Mass Norm. [%] - 7000 ppm
Oxygen	27.78	23.47
Magnesium	0.65	/
Aluminum	10.26	6.31
Silicon	2.73	0.30
Sulfur	0.79	0.46
Zinc	52.15	59.44
Potassium	0.46	0.57
Calcium	4.18	1.08
Chlorine	0.17	0.34
Iron	0.83	8.07

(8.07%) respect to the other samples. Therefore, the corrosion process, thanks to the more important effect of chlorides, in some spots was able to reach the Zn-Fe intermetallic alloy or even the steel substrate.

The maps of the elements connected with the corrosion process of the wire immersed in the soil containing 7000 ppm of chlorides are reported in Fig. 13. Oxygen is present predominantly on the edges, while aluminum, zinc and iron are concentrated mainly in the central region. The greater content of these last three elements can lead to define that the zone at the centre represents the intermetallic layer of the galvanized coating composed mostly by Zn-Fe alloy with presence of Al. This can be demonstrated even by the low presence of oxygen and the consequent poor formation of zinc and aluminum corrosion products. In addition, three specific central spots show an even more intense concentration of iron and aluminum and at the same time a reduction in the amount of zinc. Hence, in these regions the coating was probably completely corroded producing the direct contact between the steel substrate and the soil.

3.5. Comparison between first and second sets of soils

The analysed corrosion morphology, as expected, was completely different between the two type of environments. The addition of chlorides led to a localization of the corrosion process, while the sulphates produced a generalized corrosion that was approximately uniform on whole surface. The optical microscope observations clearly showed this progressive change in the corrosion mechanism: indeed, the least critical soil of the second set (containing 7000 ppm of sulphates and 1000 ppm of chlorides) was subjected to a uniform corrosion, similarly to the samples containing only sulphates, while the subsequent gradual increase of chloride concentration in the other wires led to a localized corrosion process.

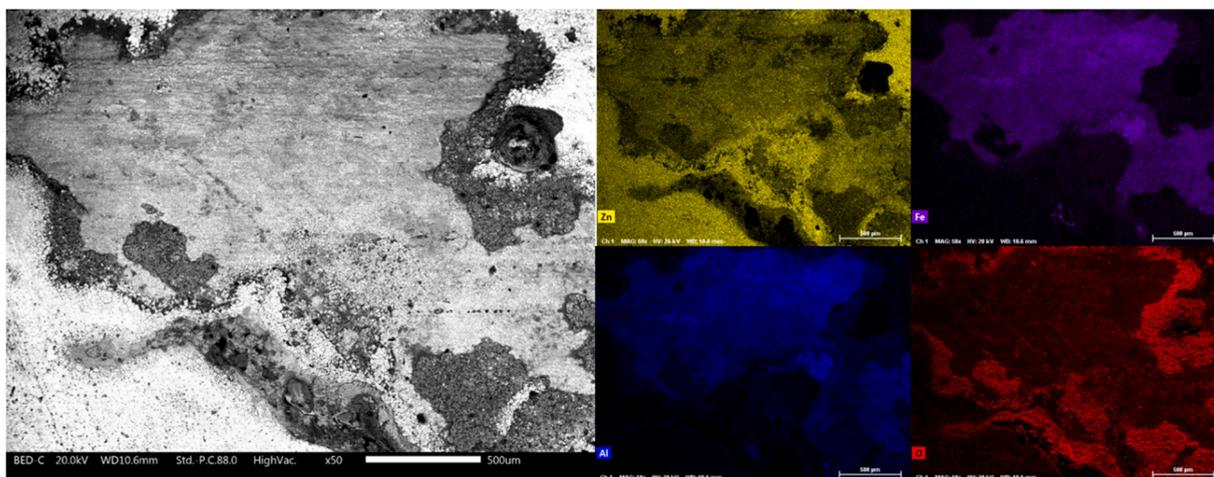


Fig. 13. SEM EDXS map of the elements connected with the corrosion process of 7000 ppm soil.

By comparing the corrosion currents obtained by potentiodynamic analysis obtained in soils, the current values evidenced the influence of greater content of salt in promoting higher corrosion current and consequently more intense corrosion rate. In particular, the effect of sulphates seemed to be more detrimental respect to chlorides, confirmed by the higher shift of potentiodynamic curves considering an increase of sulphates. In any case, the influence of chlorides on I_{corr} can be noted taking as reference the sample of the first set with a sulphate concentration equal to 7000 ppm and by observing the subsequent increment of I_{corr} following the increase of chlorides content applied in the second set of soils.

The free corrosion potential variation between the two sets of environments during the immersion time was very similar. Nevertheless, different amounts of chlorides and sulphates had different effects on the corrosion behavior of galvanized steel wires. In particular, the presence of chloride was more critical for the corrosion of the surface of the wires.

Indeed, the results obtained by means of the SEM analysis and the examination of the sample sections after immersion in soils containing only sulphates revealed that the zinc coating was still present on whole surface without ever reaching the intermetallic layer. Differently, the synergy of the presence of two salts (especially with sulphate content of 7000 ppm and chloride content of 7000 ppm), led to the penetration of the corrosion process into the galvanized coating up to the Zn-Fe layer and even up to the steel substrate in specific points of the surface.

4. Conclusions

This work aims to study the corrosion process of galvanized steel wires buried in soil. In detail, the various experimental analyzes were performed in order to investigate the influence of the chemical characteristics of the soil on corrosion behavior of hot-dip galvanized steel. Specifically, the contribution of two critical factors of the soil was evaluated, such as the concentration of sulphates and chlorides.

The test revealed that the presence of sulphates introduced a generalized corrosion, approximately uniform on the surface of wire, that became more severe following the increasing of their concentration in the soil. In any case, the corrosion process was not enough vigorous to cause the significant degradation of the zinc coating.

Differently, the addition of chlorides produced the progressively formation of a localized corrosion phenomenon, according to the increment of chloride content, which was able to penetrate the external layer reaching the steel substrate, significantly reducing the durability offered by the hot-dip Zn-Al coated steel.

Therefore, the introduction in the soil of these salts forced the corrosion process, mostly due to the synergistic effect that occurred when both chloride and sulphates were present at the same time. This aspect results very critical for buried structures that in general must have a service life of several tens of years, considering that the immersion time in case of this study was more or less of 4 months. However, it is necessary to highlight that the soil used for the testing was subjected to an addition of amount of chlorides and sulphates that can be rarely found in natural soils.

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CRediT authorship contribution statement

Stefano Rossi: Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing. **Mattia**

Pinamonti: Data curation, Formal analysis, Investigation, Validation, Writing – original draft. **Massimo Calovi:** Data curation, Methodology, Visualization, Writing – original draft; 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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References

- [1] E. Del Angel, R. Vera, F. Corvo, Atmospheric corrosion of galvanised steel in different environments in Chile and Mexico, *Int. J. Electrochem. Sci.* 10 (2015) 7985–8004.
- [2] Y. Li, Y. Ji, G. Wu, W. Yang, Q. Wang, X. Li, Study on Atmospheric Corrosion Behavior of Q235 Galvanized steel in Substation. 2016 International Forum on Mechanical, Control and Automation (IFMCA 2016), Atlantis Press., 2017, pp. 542–549.
- [3] R. Vera, F. Guerrero, D. Delgado, R. Araya, Atmospheric corrosion of galvanized steel and precipitation runoff from zinc in a marine environment, *J. Braz. Chem. Soc.* 24 (2013) 449–458.
- [4] Priyotomo G., Nuraini L., Prifiharni S., Royani A., Sundjono S., Gunawan H. et al. Atmospheric Corrosion Behavior of Carbon Steel and Galvanized Steel after Exposure in Eretan and Ciwaringin, West Java Province, Indonesia. *Indonesian Journal of Chemistry*.20:1032–1043.
- [5] X. Zhong, R. Liang, G. Liu, W. Pan, Zinc coating on steel by atmosphere plasma spray and their anti-corrosion behavior, *Mater. Lett.* (2022), 131825.
- [6] J.W. Krzywicki, Zinc coatings: steel's corrosion inhibitor: multifaceted finish serves dual purpose in shielding steel substrates from atmospheric exposure while offering cathodic protection, *Met. Finish.* 104 (2006) 28–37.
- [7] I. Kovalenko, D. Laskin, A. Trifonova, The impact of zinc coating specifications on corrosion resistance and durability of steels, *Mater. Sci. Forum.: Trans. Tech. Publ.* (2019) 740–745.
- [8] G. Jiang, G. Liu, T. Shang, W. Qiu, Corrosion Properties of Steel Sheet with Zinc-Base Alloy Coatings. TMS 2019 148th Annual Meeting & Exhibition Supplemental Proceedings, Springer., 2019, pp. 949–957.
- [9] A. Marder, The metallurgy of zinc-coated steel, *Prog. Mater. Sci.* 45 (2000) 191–271.
- [10] F.C. Porter, Zinc handbook: properties, processing, and use in design, Crc Press, 1991.
- [11] G.A. El-Mahdy, A. Nishikata, T. Tsuru, Electrochemical corrosion monitoring of galvanized steel under cyclic wet–dry conditions, *Corros. Sci.* 42 (2000) 183–194.
- [12] A.P. Yadav, A. Nishikata, T. Tsuru, Degradation mechanism of galvanized steel in wet–dry cyclic environment containing chloride ions, *Corros. Sci.* 46 (2004) 361–376.
- [13] 14713–2:2020 UEI. Zinc Coatings—Guidelines and Recommendations for the Protection against Corrosion of Iron and Steel in Structures—Part 2: Hot Dip Galvanizing. ISO. 2020:14713–2.
- [14] I. Odnevall Wallinder, C. Leygraf, A critical review on corrosion and runoff from zinc and zinc-based alloys in atmospheric environments, *Corrosion* 73 (2017) 1060–1077.
- [15] D. Persson, D. Thierry, O. Karlsson, Corrosion and corrosion products of hot dipped galvanized steel during long term atmospheric exposure at different sites world-wide, *Corros. Sci.* 126 (2017) 152–165.
- [16] K.C. Brady, M.J. Greene, D.I. Bush, A review of the durability of soil reinforcement, *ISRM Int. Symp. : OnePetro* (2000).
- [17] Y. Chen, Practical analysis and design of mechanically-stabilized earth walls—I. Design philosophies and procedures, *Eng. Struct.* 22 (2000) 793–808.
- [18] V. Padilla, P. Ghods, A. Alfantazi, Practical model for three-stage corrosion behavior of galvanized steel reinforcement in soil, *Corrosion* 69 (2013) 509–521.
- [19] A. Królikowska, L. Komorowski, P.L. Bonora, Pitting corrosion of hot-dip galvanized coatings, *Materials* 13 (2020) 2031.
- [20] X.G. Zhang, Corrosion and electrochemistry of zinc (Springer Science Business Media, LLC), Plenum Press., New York, 1996.
- [21] J.F.D. Stott, G. John, *Corros. Soils Shreir's*. Corros. 2 (2010) 1149–1168.
- [22] I.S. Cole, D. Marney, The science of pipe corrosion: a review of the literature on the corrosion of ferrous metals in soils, *Corros. Sci.* 56 (2012) 5–16.
- [23] P. Pedeferra, M. Ormelisse, *Corrosion science and engineering*, Springer., 2018.
- [24] H.Y. Shiu, R.W. Cheung, Long-term durability of steel soil nails in Hong Kong, *HKIE Trans.* 15 (2008) 24–32.
- [25] D. Nakhaie, A. Kosari, J. Mol, E. Asselin, Corrosion resistance of hot-dip galvanized steel in simulated soil solution: a factorial design and pit chemistry study, *Corros. Sci.* 164 (2020), 108310.
- [26] Transportation CDo. Corrosion guidelines. Sacramento 2003.
- [27] Beckham TL, Sun L., Hopkins TC. Corrosion evaluation of mechanically stabilized earth walls. University of Kentucky Transportation Center; 2005.
- [28] Nations FaAOotU. Soil testing methods. Rome 2020.
- [29] Transportation TDo. Determining chloride and sulphate contents in soil. Austin 2014.
- [30] P.R. Lang, Y. Liu, *Soft matter at aqueous interfaces*, Springer, 2016.
- [31] C. Bini, G. Sartori, M. Wahsha, S. Fontana, Background levels of trace elements and soil geochemistry at regional level in NE Italy, *J. Geochem. Explor.* 109 (2011) 125–133.
- [32] Fierotti G., Mancini F., Ugolini F. In nome del Suolo.
- [33] Fontana MG, Greene ND. *Corrosion Engineering*. 1967.
- [34] S. Lameche-Djehghaba, A. Benchettara, F. Kellou, V. Ji, Electrochemical behaviour of pure aluminium and Al–5% Zn alloy in 3% NaCl solution, *Arab. J. Sci. Eng.* 39 (2014) 113–122.
- [35] J.R. Macdonald, E. Barsoukov, *Impedance spectroscopy: theory, experiment, and applications*, John Wiley & Sons, 2018.
- [36] H. Gerengi, K. Schaefer, H.I. Sahin, Corrosion-inhibiting effect of Mimosa extract on brass-MM55 corrosion in 0.5 M H₂SO₄ acidic media, *J. Ind. Eng. Chem.* 18 (2012) 2204–2210.
- [37] V. Padilla, A. Alfantazi, Corrosion performance of galvanized steel in Na₂SO₄ and NaCl solutions at subfreezing temperatures, *Corrosion* 69 (2013) 174–185.
- [38] S. Bonk, M. Wicinski, A.W. Hassel, M. Stratmann, Electrochemical characterizations of precipitates formed on zinc in alkaline sulphate solution with increasing pH values, *Electrochem. Commun.* 6 (2004) 800–804.
- [39] F. Rosalbino, E. Angelini, D. Macciò, A. Saccone, S. Delfino, Application of EIS to assess the effect of rare earths small addition on the corrosion behaviour of Zn–5% Al (Galvan) alloy in neutral aerated sodium chloride solution, *Electrochim. Acta* 54 (2009) 1204–1209.
- [40] V. Padilla, A. Alfantazi, Corrosion film breakdown of galvanized steel in sulphate–chloride solutions, *Constr. Build. Mater.* 66 (2014) 447–457.
- [41] E. Diler, B. Rouvellou, S. Rioual, B. Lescop, G.N. Vien, D. Thierry, Characterization of corrosion products of Zn and Zn–Mg–Al coated steel in a marine atmosphere, *Corros. Sci.* 87 (2014) 111–117.

- [42] V.P. Perez, A. Alfantazi, Effects of oxygen and sulfate concentrations on the corrosion behavior of zinc in NaCl solutions, *Corros., J. Sci. Eng.* (2012) 68, 035005-1–11.
- [43] S. Liu, H. Sun, L. Sun, H. Fan, Effects of pH and Cl⁻ concentration on corrosion behavior of the galvanized steel in simulated rust layer solution, *Corros. Sci.* 65 (2012) 520–527.
- [44] H. Sun, S. Liu, L. Sun, A comparative study on the corrosion of galvanized steel under simulated rust layer solution with and without 3.5 wt% NaCl, *Int J. Electrochem Sci.* 8 (2013) 3494–3509.