



Inhibitive effect of the Ce (III) chloride and nitrate on the corrosion resistance of Zn alloyed sacrificial coatings: Effect of alloying compounds of the sacrificial layer

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ABSTRACT

The corrosion protection of four different zinc-based sacrificial coatings alloyed with Al and Mg were investigated in 0.1 M NaCl with and without 5.10^{-3} M Ce (III) chloride and nitrate versus immersion time. The effect of Ce (III) chloride and nitrate salts were evaluated by Electrochemical Impedance Spectroscopy (EIS), potentiodynamic polarization measurements, SEM-EDS, and XRD analysis. Cerium salts showed the best effectiveness for HDG, followed by ZnAl, Zn and ZnAlMg coatings. The inhibition efficiency of Ce (III) ions was stable and higher than 82.5% for all types of substrate. Moreover, cerium chloride presented higher protection than cerium nitrate in long immersion time.

1. Introduction

Carbon steel is one of the most used materials in many industrial sectors due to its good mechanical properties [1,2]. Nevertheless, it exhibits a low resistance to corrosion resulting in a significant economic loss. Different solutions are employed to protect steel such as the cathodic or sacrificial protection method and/or organic coatings. The zinc-based sacrificial coating is the most used layer to provide sacrificial protection to the steel and to prolong the lifetime of metal structures [2–4]. However, the demand for a thinner coating, better corrosion protection, and a decrease in zinc consumption in some industries, particularly in the automotive and building industries, is increasing due to the rising cost of metals such as zinc [5–8].

In order to improve the corrosion resistance of the zinc coating and to meet various industry requirements, zinc-alloy coatings have been developed for several decades, such as zinc alloyed with aluminum. Adding aluminum to the zinc bath helps to prevent the Fe-Zn alloy formation. Therefore, Al alloyed Zn coating provides high cut edge corrosion protection [3].

Vu et al. [9] investigated the effect of the pH on the selective dissolution of Zn and Al from ZnAl coated galvanized steel. The results

indicated that the increase in local pH due to the cathodic reactions causes the selective dissolution of Al. The presence of Al^{3+} in the electrolyte preferentially enhances the formation of a more protective $ZnAlCO_3$ -LDH layer and later the simonkolleite (from pH=8) instead of ZnO on the ZnAl surface leading to an increase of the corrosion resistance of ZnAl coating.

In addition, magnesium is also presented as a potential alloying element for zinc-based coatings. Several studies have indicated that incorporating magnesium into the metal coating, alloyed or not with aluminum, enhances the corrosion resistance compared to hot-dip galvanized steel (HDG) [7,10–18].

Volovitch et al. [13,19] have studied the role of alloying elements (Al, Mg) in improving the corrosion resistance. They studied the corrosion mechanism and composition of corrosion products formed on zinc-based coatings in a chloride environment. Regarding ZnAlMg coating, the authors indicated that protective simonkolleite was first formed, followed by the double hydroxide layer (Zn-Al and/or Mg-Al LDH). The presence of these corrosion products was reported [15,16,19–22]. These products formed a denser and more compact structure resulting in a well adherent layer, preventing the ingress of aggressive species. Besides, the authors indicated that Mg^{2+} preferentially

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precipitates in the presence of carbonate, sulfate, or hydroxyle ions, thus stabilizing the protective simonkolleite and hindering the transformation of corrosion products into less protective ones such as ZnO [11,13,19–22]. This resistant protective layer is the main reason for the enhanced corrosion resistance of ZnAlMg coatings.

Schuerz et al. [10], showed that red rust appeared on the zinc coating surface after 100 h of salt spray testing and developed rapidly over the whole sample surface after 600 h. On the contrary, the surface of the ZnAlMg coating was covered by a stable and adherent aluminum-rich oxide layer [10,23] after 100 h of salt spray test. This prevented the corrosive attack and protected the coating against corrosion until 600 h of exposure. Moreover, no red rust was observed on the ZnAlMg surface over testing time.

Although zinc-based coatings provide a protective effect on steel, they are sensitive to be corroded in a humid and aggressive environment. Thus, corrosion inhibitors are used to slow down the degradation of sacrificial coatings and to increase the lifetime of the material.

Results from literature highlighted the corrosion protection effect of inhibitors such as cerium salts [24–29] to increase the lifetime of zinc or galvanized steel. The protective mechanism is explained by the formation of an insoluble cerium oxide/hydroxide film on the surface of cathodic areas due to pH increase. This insoluble hydr(oxide) layer consumes the produced OH^- at the cathodic sites, thus slowing down the dissolution of zinc in the anodic areas, and resulting in a decrease in the corrosion rate [25,27]. Arenas et al. [26] investigated the inhibition efficiency of cerium chloride in a concentration range from 100 ppm to 1000 ppm in 3.5% NaCl solution on HDG steel. The results demonstrated that the efficiency of cerium chloride (>250 ppm) was higher than 90% after 24 h of immersion and a yellow layer appeared on the surface, related to the mixture of Ce^{3+} and Ce^{4+} oxide/hydroxide. Kartsonakis et al. [24] found that cerium nitrate (500 ppm) showed a 99.3% inhibition efficiency for galvanized steel after 72 h of immersion in 0.05 M NaCl.

Besides, several studies have shown the influence of counter ions on the protective effect of Ce (III) salts for Al or its alloys. Rodić et al. [30] investigated the inhibition effect of different cerium salts on three types of substrates: pure aluminum, aluminum alloy AA 2024-T3, and AA 7075-T6. The authors indicated that the inhibition efficiency of cerium salts depends on various factors: the type of substrate (the composition of intermetallic particles in the alloy), the type of counter-ion, and the pH of the medium. Indeed, cerium acetate showed the best performance, followed by cerium nitrate and cerium chloride for the studied substrates. Moreover, the inhibition efficiency of Ce (III) salts rose from AA 2024-T3 to pure Al and was the highest for AA 7075-T6. Machkova et al. [31] reported the different efficiencies of Ce (III) salts regarding anti-corrosion protection of AA 2024. In a poorly concentrated medium (5.10^{-5} M), $\text{Ce}(\text{NO}_3)_3$ proved to be the most effective, followed by $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$, CeCl_3 and $\text{Ce}_2(\text{SO}_4)_3$. All species showed a similar protection mechanism by forming of Ce-hydroxides at the cathodic areas of the metallic surface. However, at higher concentration (10^{-2} M), Ce $(\text{NO}_3)_3$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$ behaved differently from the other two cerium salts with simultaneous acceleration of the cathodic reaction (due to the presence of NO_3^- which limited the formation of protective Cu_2O film on the re-deposited copper at the sample's surface as a result of the corrosion of the intermetallic particles Al_2CuMg) and inhibition of the anodic reaction. The counter ions of cerium salts affected not only the inhibition performance but also the inhibitive mechanism as well.

In the literature, some studies investigated the inhibitive effect of cerium salts for zinc or galvanized steel. However, a few of them are related to the use of these inhibitors in the case of alloyed zinc coating and to the influence of the alloying elements, especially Al and Mg in ZnAl and ZnAlMg sacrificial coatings. Moreover, these investigations principally focused on the corrosion inhibitive ability of cerium cation, while the effect of counter-ions on the inhibition efficiency of cerium has not been studied and reported for zinc substrates and Zn-based coatings. Therefore, this work investigated the influence of alloying elements (Al

and Al-Mg) on the inhibitive effect of Ce (III) for four different Zn-based sacrificial coatings: Zn (obtained by electrodeposition), HDG (hot-dip galvanized steel), ZnAl (galvan) and ZnAlMg. Moreover, the influence of the counter-ion on the corrosion inhibition of cerium salts for different coatings was evaluated. The corrosion performance was investigated by electrochemical measurements (OCP, EIS, polarization curves). A surface analysis (SEM/EDS and XRD) was performed after 24 h of immersion in the aggressive environment with and without inhibitors.

2. Experimental methods

2.1. Materials

In this work, HDG, ZnAl and ZnAlMg coatings were supplied by ArcelorMittal, Belgium. In comparison, Zn coatings were obtained by electrodeposition from a 0.77 M zinc sulfate (VWR Chemicals) solution at 40 °C, adjusted at pH=2 by adding sulfuric acid with a direct current density of 50 mA/cm² [28]. HDG, ZnAl, and ZnAlMg substrates were first degreased with acetone, and then all four substrates were dipped in an alkaline commercial solution (Gardoclean®) at 50 °C for 30 s to remove residual traces of oxide before experiments. The thickness of the layers and their chemical composition were investigated by a Hitachi SU8020 FE-SEM. The roughness of top layers was measured by optical profilometry with a NanoJura instrument. 10 mm length scans were performed at a scan rate of 100 µm/min. The thickness, the roughness and the coating composition of top layers are presented in Table 1.

2.2. Electrochemical measurements

The corrosion behavior of the sacrificial coatings in the electrolyte with and without inhibitors was investigated by Open Circuit Potential (OCP) measurements, Electrochemical Impedance Spectroscopy and potentiodynamic polarization. A three-electrode system was employed using a flat cell of 300 mL, composed of a Saturated Calomel Electrode (SCE) as the reference electrode, a platinum grid as the counter-electrode, and the studied substrate (1 cm² exposed) as the working electrode. EIS tests were performed at OCP and room temperature. A frequency range of 100 kHz to 10 mHz was applied with a perturbation amplitude of 10 mV by using a Solartron Analytical ModuLab potentiostat. The electrolyte was 0.1 M NaCl (NaCl, VWR Chemicals). The inhibitors were cerium chloride ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, VWR Chemicals, 98.5%) and cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ Aldrich, $>99\%$) at a concentration of 5.10^{-3} M. These concentrations were selected based on a previous study [28]. In the case of cerium chloride, the amount of sodium chloride was adjusted to control the chloride ion concentration at 0.1 M. Actually, in the cerium chloride solution, only cerium can be considered as an inhibitive species. In the cerium nitrate, cerium and nitrate are mentioned as inhibitive species in the literature [24,25,27,32,33]. Besides, the pH of the 0.1 M NaCl electrolyte was adjusted at pH = 7 by adding 0.01 M NaOH. While in the case of cerium containing electrolytes, the pH values measured were quite similar and slightly acidic with pH values of 5.66 (CeCl_3) and 5.44 ($\text{Ce}(\text{NO}_3)_3$). Each test was repeated at least twice to confirm the reproducibility.

The anodic polarization measurements were carried out from a narrow interval around the open circuit potential (-0.03 V/OCP) to $+0.7$ V/OCP at a scan rate of 0.2 mV/s with a stop condition fixed at 10^{-3}

Table 1

The main composition of the top surface of the different sacrificial coatings.

Coating	Thickness (µm)	Ra (µm)	Coating composition (wt%)		
			Zn	Al	Mg
Zn	8.5 ± 0.5	1.05	97.1	0	0
HDG	11 ± 0.2	0.87	92.1	1.2	0
ZnAl	21 ± 0.3	1.22	89.2	9.4	0
ZnAlMg (ZAM)	29.6 ± 0.5	0.01	83.7	7.1	4.0

A/cm². Each test was repeated at least twice to confirm the reproducibility.

2.3. Surface characterization

The surface morphology and the chemical composition of the sacrificial coatings before and after immersion tests were examined by a Field Emission Scanning Electronic Microscope (FE-SEM, Hitachi SU8020) coupled to an Energy Dispersive X-ray spectrometer analyzer (EDS). EDS mapping was performed to determine the elemental distribution in the observed micrographs.

XRD measurements were carried out via a Bruker D5000 device with CoK radiation ($\lambda = 0.1789$ nm) at a scanning rate of 1°/min in the 2 θ range from 10° to 70° to identify the crystallographic structure of the products formed on the surfaces.

3. Results and discussion

3.1. Characterization of sacrificial coatings

The thickness, the roughness and the composition of the four commercial sacrificial coatings applied on steel substrate are summarized in Table 1. The data indicate that the alloying element content in each layer is different: the Zn layer consists in pure Zn; while the HDG, ZnAl and ZnAlMg layers are composed of Zn + 1.2 wt% Al, Zn + 9.4 wt% Al and Zn + 7.1 wt% Al + 4.0 wt% Mg, respectively.

Fig. 1 presents the surface morphology of all four substrates and the EDS mappings of HDG, ZnAl, and ZnAlMg coatings obtained by SEM analysis at high resolution (5000x) and EDS analysis respectively. Regarding the EDS mapping of HDG, ZnAl, and ZnAlMg coatings, the Zn

element was homogeneously distributed on all surfaces. However, Al distribution was heterogeneous on the HDG surface due to its low concentration, while this alloying element was homogeneously present on the ZnAl and ZnAlMg surfaces. Besides, a quite heterogeneous distribution of Mg was observed on the ZnAlMg surface. Concerning the SEM images, with higher alloying element content, the surface morphology of ZnAl and ZnAlMg coatings was more uniform than that of Zn and HDG coatings. From the surface morphology (Fig. 1) and the roughness values measured by optical profilometry (Table 1), the ZnAlMg layer presented the lowest roughness value. All the substrates came from an industrial continuous line and were skin passed. The skin passed gave a specific structure to the metallic coatings. The structure was depending on the skin pass roller as previously shown [34].

Then, Fig. 2 reveals the morphology and EDS mapping of the cross-section of the coatings. Regarding EDS mapping images, the Zn element is uniformly dispersed in the cross-section of all layers. In the case of the HDG layer, Al accumulated mainly in the interface between steel and the Zn layer, participating to the inhibition of the intermetallic growth in the Zn bath. Meanwhile, Al was evenly dispersed in two different regions, with a high and low Al content in both ZnAl and ZnAlMg layers. Besides, EDS mapping showed an uneven distribution of Mg in the cross-section of ZnAlMg coating, it was absent in several zones, namely zinc-rich phases. This distribution of alloying elements generated heterogeneous microstructures of ZnAl and ZnAlMg coatings. The typical microstructure of ZnAl coating consists in two phases: the zinc-rich phase and the Zn-Al phase. However, the microstructure of ZnAlMg is more complex with the zinc-rich region and intermetallic particle phases such as MgZn₂ which was confirmed by XRD analysis on the top surface (Fig. 8(d)). The presence of these microstructures in ZnAl and ZnAlMg agrees with the reports in the literature [3,10,11,35].

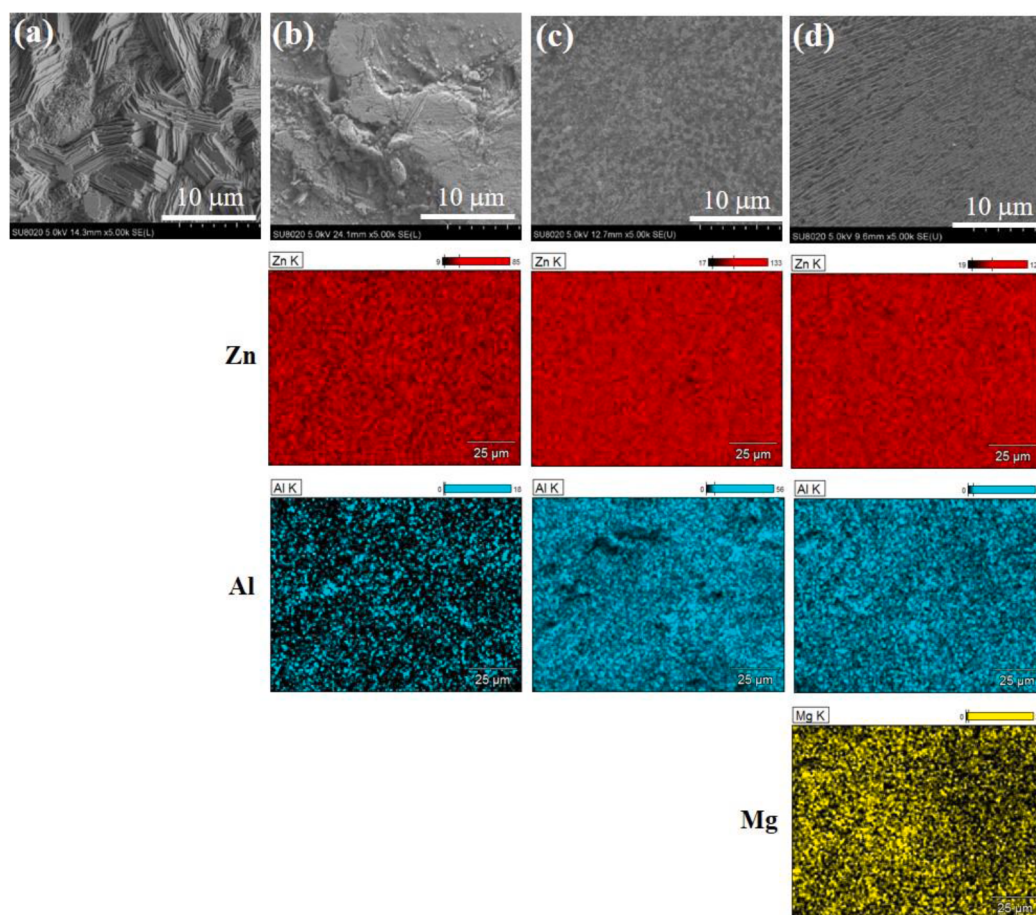


Fig. 1. SEM images and EDS mapping of Zn (a), HDG (b), ZnAl (c), and ZnAlMg (d) coatings before immersion experiment.

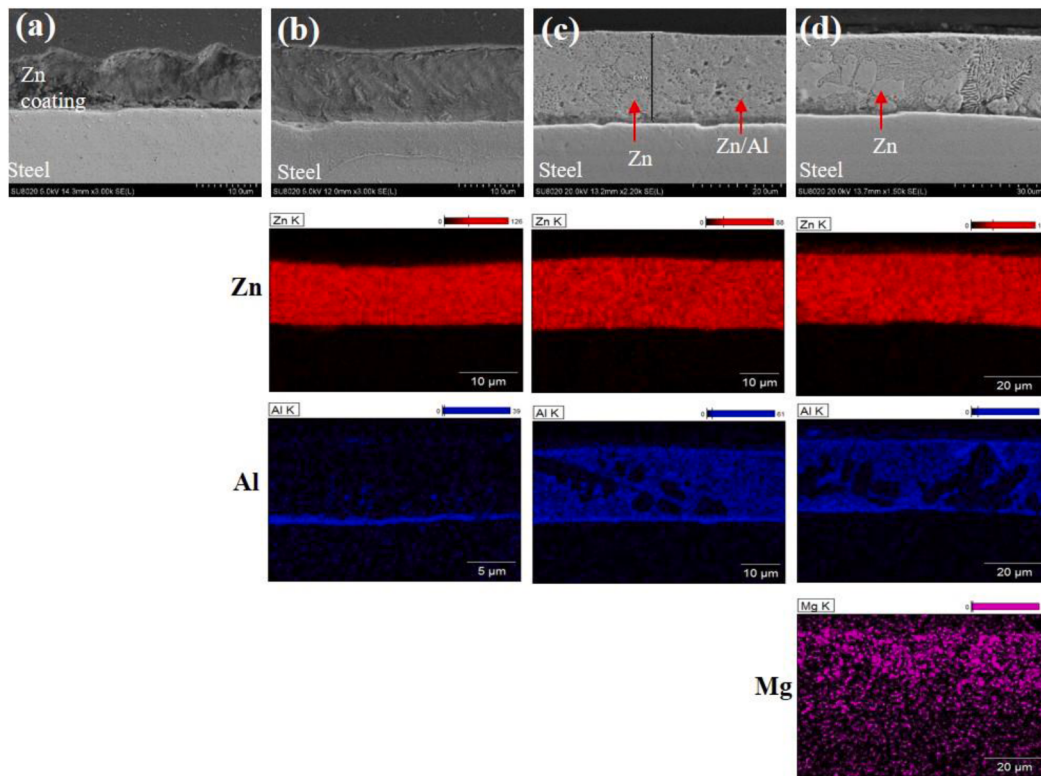


Fig. 2. The morphology and EDS mapping of the cross-section of Zn (a), HDG (b), ZnAl (c), and ZnAlMg (d) coatings.

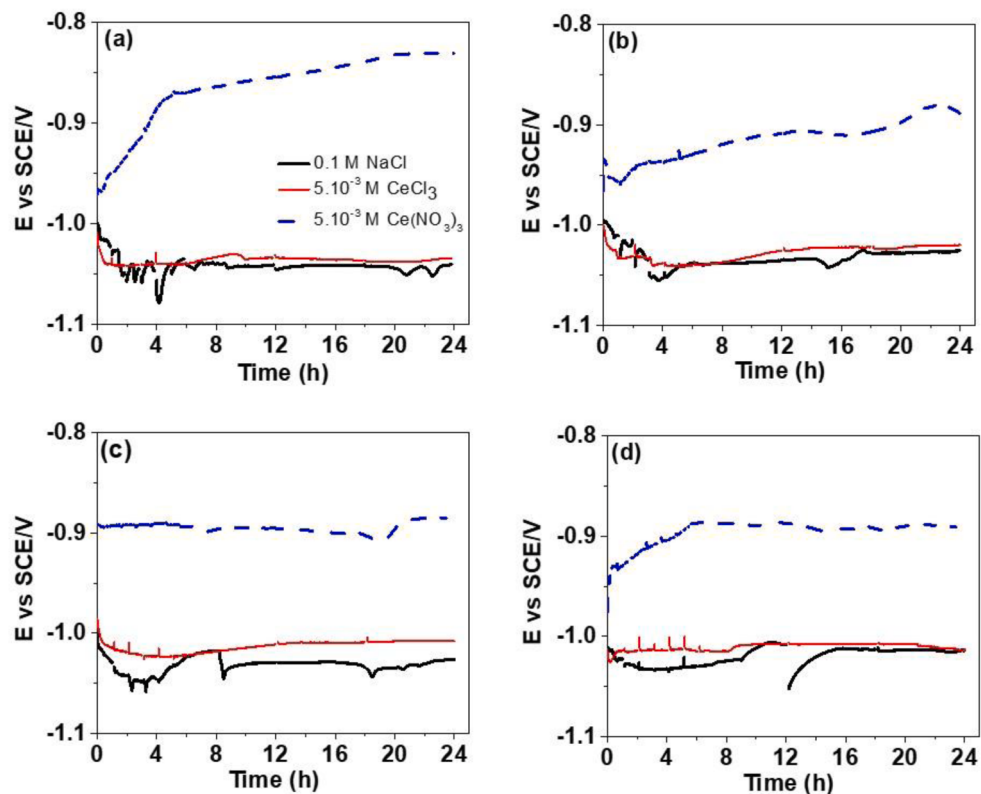


Fig. 3. OCP evolution of Zn (a), HDG (b), ZnAl (c), and ZnAlMg (d) coatings immersed in 0.1 M NaCl without and with 5.10^{-3} M cerium salts.

3.2. Effect of cerium salts on the corrosion of sacrificial coatings

3.2.1. Corrosion behavior in 0.1 M NaCl containing cerium salts

The OCP evolution of all the coatings (Zn, HDG, ZnAl, and ZnAlMg) was followed during immersion time in 0.1 M NaCl with and without cerium salts as shown in Fig. 3. As can be seen, in the reference solution, the OCP values for all four substrates were relatively similar; they rapidly decreased with an oscillation between -1025 mV/SCE and -1075 mV/SCE (for Zn and HDG coatings) during the first 2 h and remained stable at about -1050 mV/SCE for Zn coating, -1025 mV/SCE for HDG and ZnAl coatings, and the highest at about -1014 mV/SCE for ZnAlMg coating. Regarding the presence of CeCl_3 , the OCP values for all four substrates gradually decreased during the initial 2 h and remained stable in the presence of CeCl_3 in the electrolyte. In the presence of $\text{Ce}(\text{NO}_3)_3$, the potential rose before reaching a plateau at about -850 mV/SCE after more than 4 h for Zn and ZnAlMg coatings, respectively, with an oscillation between -900 and -950 mV/SCE for HDG coating, while it remained stable during immersion time for ZnAl coating. $\text{Ce}(\text{NO}_3)_3$ showed higher OCP values for all substrates than CeCl_3 . The positive shift could reduce the corrosion rate and indicate the

typical behavior of anodic inhibitors. Moreover, it confirmed the importance of nitrate anion contained in the solution where Cl^- ions are added in the same concentration and highlighted that nitrate anion can probably act as an anodic inhibitor species and give a synergistic effect with cerium cations.

The anodic polarization curves of four samples recorded after 24 h in 0.1 M NaCl and for Zn, HDG, ZnAl, and ZnAlMg coatings recorded after 24 h in 0.1 M NaCl with inhibitors are reported in Fig. 4. Regarding the results recorded of all four substrates after 24 h of immersion in 0.1 M NaCl (Fig. 4(a)), the HDG, ZnAl, and ZnAlMg coatings showed a lower anodic current density than that of the Zn coating. Moreover, a plateau of about 40 mV was observed in the case of the ZnAl and ZnAlMg layers, probably due to the oxide formation on the surface, limiting the corrosion process [30,36]. These results indicated that adding alloying elements into the substrates, especially in the case of ZnAl and ZnAlMg coatings, could inhibit the anodic reaction.

In the presence of CeCl_3 , a plateau was highlighted for all four coatings with a decrease in corrosion current density, probably related to the formation of a protective layer, which inhibited the anodic and cathodic reactions and slowed down the corrosion rate [24,25,36]. No

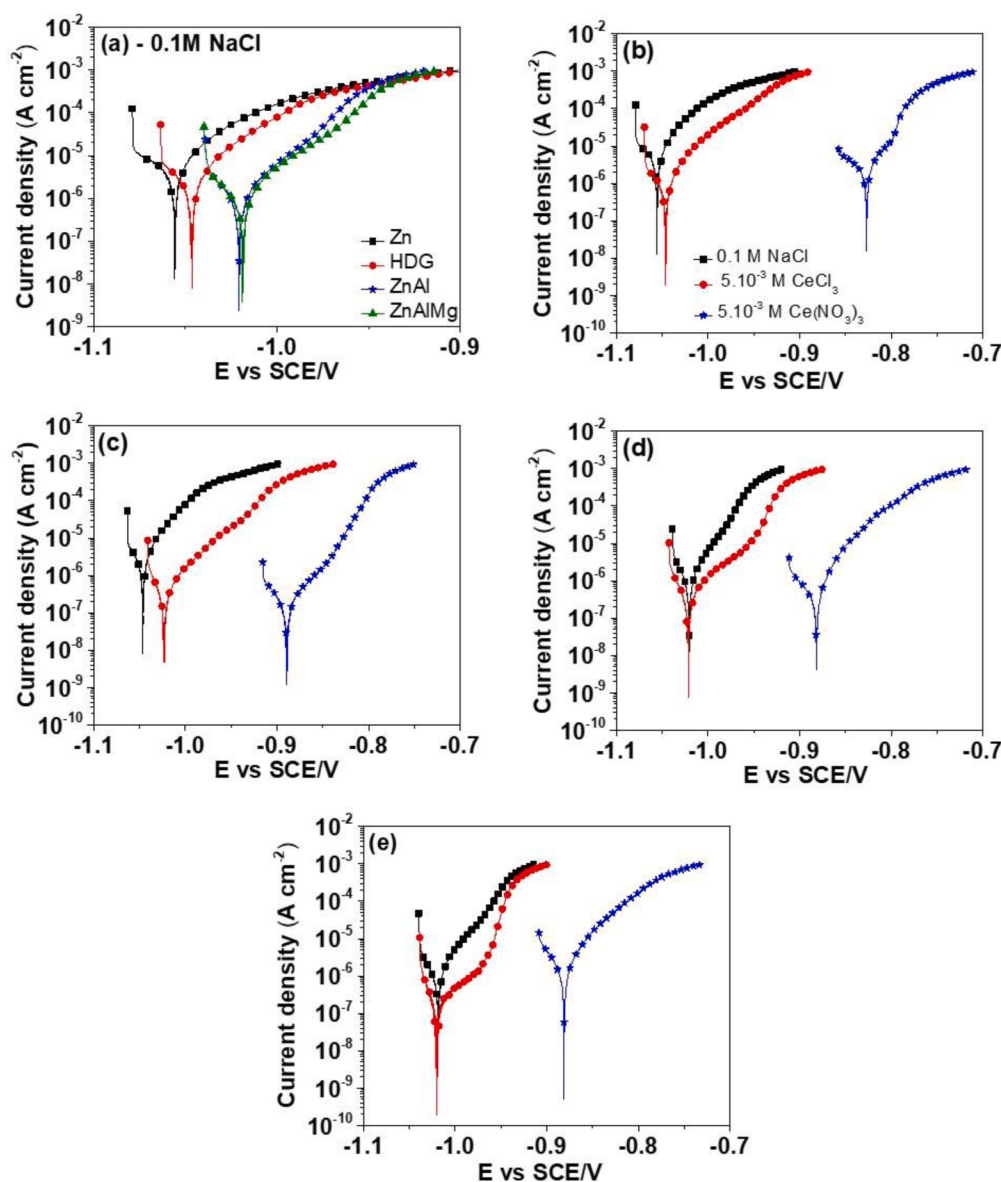


Fig. 4. Anodic polarization curves obtained for all four substrates (a) after 24 h of immersion in 0.1 M NaCl, and for Zn (b), HDG (c), ZnAl (d), and ZnAlMg (e) coatings after 24 h of immersion in 0.1 M NaCl with 5.10^{-3} M cerium salts.

significant change in the corrosion potential is observed in presence of CeCl_3 . Whereas in the presence of $\text{Ce}(\text{NO}_3)_3$, the potential is shifted towards more positive values for the four substrates, relating to the anodic inhibitive effect of NO_3^- [32,33] in agreement with reports in the literature [37,38]. Besides, a narrower plateau is observed only for Zn and HDG coatings. Lower current densities were achieved for Zn, HDG, and ZnAl substrates, while the presence of $\text{Ce}(\text{NO}_3)_3$ showed an insignificant decrease in corrosion current density compared to the blank solution in the case of ZnAlMg coating, meaning a poor protection. This slight decrease in corrosion current density may be related to the microstructure of ZnAlMg layer and the simultaneous and antagonist properties (inhibition of the cathodic reaction and acceleration of the intermetallic particles dissolution) of $\text{Ce}(\text{NO}_3)_3$, which will be discussed in the next part.

It noted that the potentiodynamic polarization measurements were scanned in a pH range from 5.44 to 7 and that the anodic polarization curves were recorded in a potential range from around a narrow interval of the open circuit potential (-0.03 V/OCP) ($> -1.1 \text{ V/SCE}$) to -0.7 V/

SCE. Thus, with the respect to the Pourbaix diagram of zinc [39], in the cathodic branches (30 mV lower than OCP) of all the polarization curves, the dissolved O_2 reduction takes place but not significantly and does not affect the anodic branch. Moreover, in the investigated potential range, anodic dissolution mainly occurs. In addition, it is important to note that the Tafel method was not recommended to accurately determine the corrosion current density (i_{corr}) values, the polarization resistance (R_p), or the Tafel slope via the linear fitting of the polarization curves [24,31] because there is no clear linear region in the anodic branches to calculate the corrosion current density. The Tafel plots can be only rigorously used when the limiting step is the charge transfer. This is not the case for the corrosion of zinc substrates in neutral chloride solution. Furthermore, the Tafel method can be only used for yields an average uniform corrosion rate, not appreciated for localized corrosion (corrosion pitting, etc...), which could appear in the zinc coating, especially in the case of zinc alloy coatings. Besides, with the scan rate application (0.02 mV/s), Machkova et al. [31] indicated that the low scan rate ($< 1 \text{ mV/s}$) expressed the current deviations, which

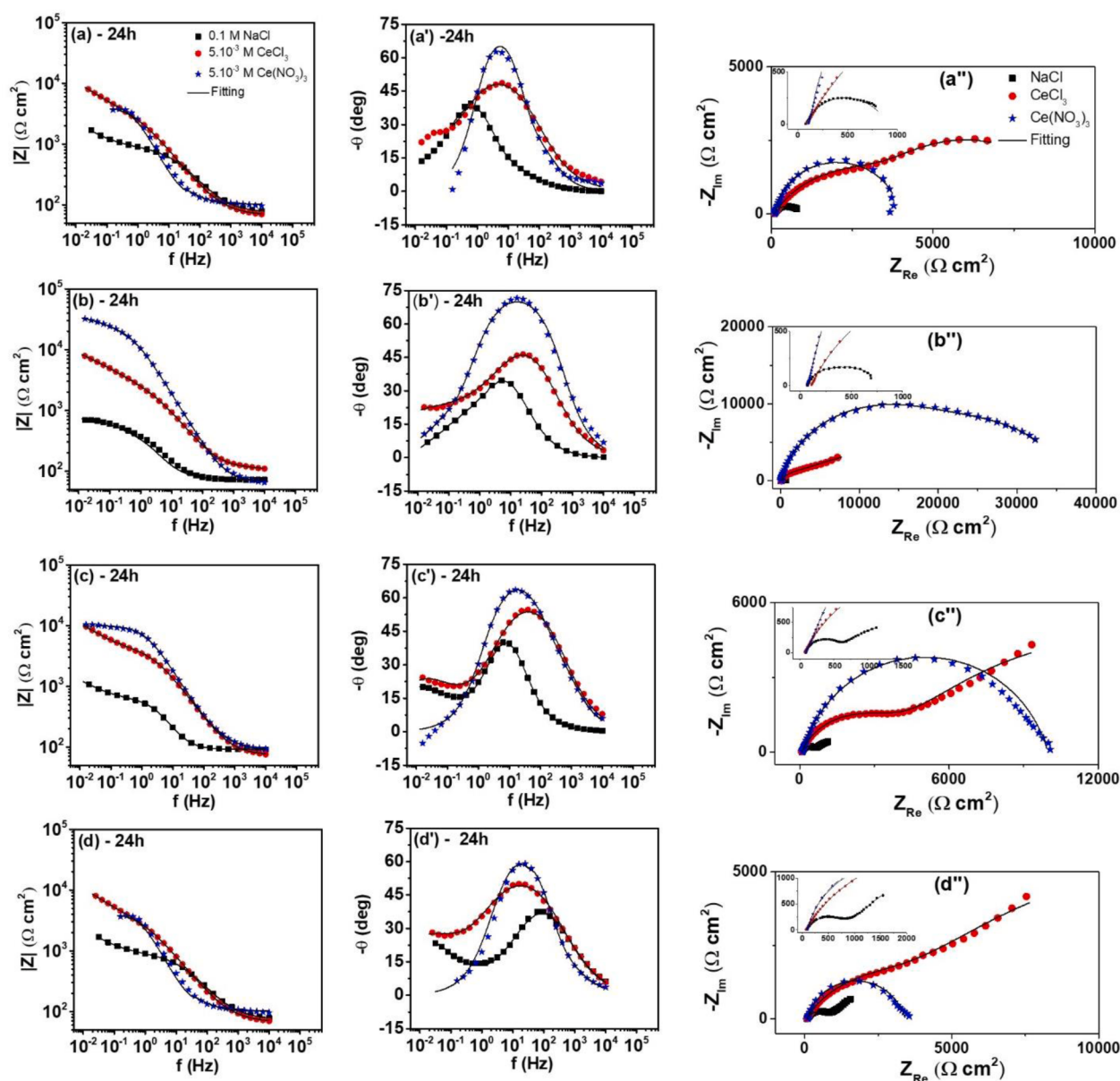


Fig. 5. Bode and Nyquist diagrams of Zn (a, a', a''), HDG (b, b', b''), ZnAl (c, c', c''), and ZnAlMg (d, d', d'') coatings after 24 h of immersion in 0.1 M NaCl without and with 5.10^{-3} M cerium salts.

could not provide the precise value of corrosion current density. Thus, in this study, the polarization method was only employed to qualitatively estimate the inhibitive behavior of inhibitors.

Fig. 5 presents Bode and Nyquist diagrams obtained for Zn (a, a', a''), HDG (b, b', b''), ZnAl (c, c', c'') and ZnAlMg (d, d', d'') coatings after 24 h of immersion in 0.1 M NaCl without and with inhibitors. As can be seen, in the blank electrolyte, the phase diagrams for Zn and HDG coatings were characterized by a broad time constant in the medium-low frequencies range, which is associated with the corrosion process [24]. Moreover, the broadening of this time constant may related to the growth of corrosion products [40]. Meanwhile, two time constants in low and medium frequency areas were clearly observed for ZnAl and ZnAlMg layers. The first one was located in the low frequency range and was related to the charge transfer and the double layer capacitance. The second one in the medium frequency range was associated to the formation of a corrosion protective film on the surface [24,28,36,41,42].

In the presence of cerium salts, two time constants were observed for all substrates (Fig. 5). In the presence of CeCl_3 , the first one was located in the low-frequency part and related both the corrosion process and the formation of a zinc oxide/hydroxide layer while the second one at medium frequencies would be associated with the formation of a cerium hydr(oxide) film on the surface [24,28,36,41,42], limiting the oxygen reduction and the corrosion rate [27]. Indeed, after 24 h of exposure, a thin yellow film was observed on the Zn surface, attributed to a mixture of Ce^{3+} and Ce^{4+} [25,27]. However, in the presence of $\text{Ce}(\text{NO}_3)_3$, the time constant at low frequency was not well defined. Moreover, the time constant at the medium frequency range presented the highest angle phase in absolute value, at about -70° , related to the protective film formed on the surface [36,40]. In addition, in presence of both cerium salts, a higher impedance value is obtained in the low frequency range compared to the blank solution, indicating an inhibitive effect of cerium salts regarding the corrosion of Zn, HDG, ZnAl coatings. However, in the case of ZnAlMg, CeCl_3 produced a relatively higher impedance to the substrate than the blank solution, whereas $\text{Ce}(\text{NO}_3)_3$ showed limited protection for ZnAlMg (Fig. 5(d)), which is correlated with the polarization results.

To quantify the electrochemical parameters of the system without and with inhibitor, the EIS spectra were numerically fitted, using the equivalent circuits (EEC) conducted by software ZSim Win 3.50 and shown in Fig. 6. The constant phase element (CPE) denoted as Q is used to replace pure capacitance. Generally, the equivalent circuit of all systems included five components. Fig. 6(a) presented all four substrates after 24 h immersion in the chloride solution without inhibitor consisting of resistance solution (R_s), the resistance and the capacitance of the zinc oxides and/or the oxide/hydroxide layer formed on galvanized surface at the medium frequencies (R_{ox} - Q_{ox}), and the charge transfer resistance, and a double layer capacitance associated with the time constant in the low frequency range (R_{ct} - Q_{dl}). Besides, Fig. 6(b) modeled for all four substrates after 24 h of immersion in the chloride medium in the presence of cerium salts. It is composed of the solution resistance (R_s), the capacitance of the cerium oxide film in the medium frequency range (R_{inh} - Q_{inh}), and the components R_{ct} - Q_{dl} in the low frequencies related to the corrosion process. The obtained fitting results were tabulated in Table 2. The quality of the impedance fit was characterized

by errors in each EEC parameter value of 1–5%.

As can be seen, the charge transfer resistance R_{ct} increased from Zn to ZnAlMg coatings in the blank solution. The values were about 719, 587, 1746 and 1505 $\Omega\cdot\text{cm}^2$, respectively, proving the higher corrosion resistance of ZnAlMg and ZnAl layer compared to Zn and HDG coating, as expected. Furthermore, the resistance of metal oxide film on the zinc-based surface was different, with the highest values obtained for the ZnAlMg (801 $\Omega\cdot\text{cm}^2$) layer, followed by ZnAl (525 $\Omega\cdot\text{cm}^2$), HDG (306 $\Omega\cdot\text{cm}^2$), and Zn (97 $\Omega\cdot\text{cm}^2$) coatings. These results revealed that the metal oxide film formed on the ZnAl and ZnAlMg layers exhibited the best barrier properties, followed by Zn, and HDG coatings. These better barrier properties could be related to the composition and the nature of metal oxide films such as protective simonkolleite or layer double hydroxide (LDH), which are commonly mentioned as corrosion products formed on ZnAl and ZnAlMg coatings [15,16,20,22].

Regarding the solution with cerium salts, a significant increase in the charge transfer resistance R_{ct} with a decrease in Q_{dl} values (lower than 1 or 2 orders of magnitude) was observed for all substrates compared to the blank electrolyte, indicating the higher corrosion resistance and anticorrosive behavior in presence of cerium salts. It may be remarked that the presence of CeCl_3 demonstrated higher R_{ct} for all samples (except the HDG layer) compared to $\text{Ce}(\text{NO}_3)_3$. Moreover, CeCl_3 exhibited the highest R_{ct} for the ZnAlMg layer (18,600 $\Omega\cdot\text{cm}^2$), followed by HDG (14,400 $\Omega\cdot\text{cm}^2$), ZnAl (10,000 $\Omega\cdot\text{cm}^2$), and Zn (4250 $\Omega\cdot\text{cm}^2$) coatings. Meanwhile, $\text{Ce}(\text{NO}_3)_3$ presented the highest R_{ct} for HDG (23,600 $\Omega\cdot\text{cm}^2$) coating, followed by ZnAl (9580 $\Omega\cdot\text{cm}^2$), ZnAlMg (3455 $\Omega\cdot\text{cm}^2$), and Zn (3331 $\Omega\cdot\text{cm}^2$) layers. The higher R_{ct} values correspond to higher corrosion resistance [24].

Based on charge transfer resistance (R_{ct}), the inhibition efficiency, η (%) was calculated following Eq. (1) [24] and is presented in Table 3.

$$\eta = \left(\left(R_{ct}^{inh} - R_{ct}^0 \right) / R_{ct}^{inh} \right) \times 100\% \quad (1)$$

In which: R_{ct}^{inh} and R_{ct}^0 are the charge transfer resistance with inhibitors and without inhibitors for the same immersion time in the electrolyte.

Table 3 indicates that the inhibition efficiency of cerium salts after 24 h of immersion in 0.1 M NaCl for all types of substrates. CeCl_3 provided higher effectiveness than $\text{Ce}(\text{NO}_3)_3$ for all coatings (except HDG layer). Cerium chloride species was the most efficient for HDG (95.9%) and ZnAlMg (91.9%), followed by Zn (83%) and ZnAl (82.5%) layers, respectively. Besides, $\text{Ce}(\text{NO}_3)_3$ presented an improved protection than CeCl_3 for HDG substrates (97.5%) and presented lower protection for ZnAl (81.7%), Zn (78.3%), and especially for ZnAlMg (56.4%) coatings. As can be observed, although CeCl_3 offered a high protection for ZnAlMg, $\text{Ce}(\text{NO}_3)_3$ exhibited limited protection for ZnAlMg (56.4%) after 24 h of immersion. This poor performance may be related to the microstructure of ZnAlMg (intermetallic particles- MgZn_2 phase) and the effect of counter-ion (NO_3^-).

In comparison between the two cerium salts, the effective protection of both cerium salts for each sample (Zn, HDG, and ZnAl layers) was not significantly different. Meanwhile, $\text{Ce}(\text{NO}_3)_3$ acts in a different way to CeCl_3 for ZnAlMg coating. In addition, the inhibition efficiency of cerium salts was different for each substrate, suggesting that the corrosion protection of cerium salts depends on the type of substrate,

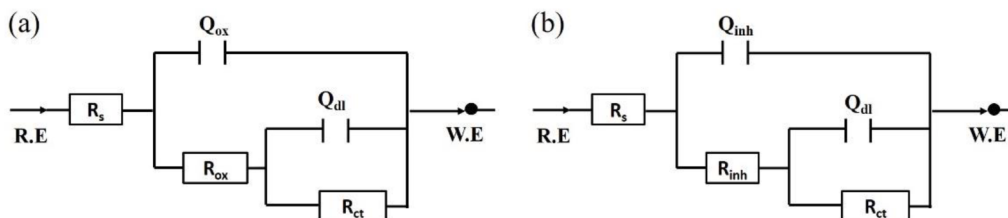


Fig. 6. Equivalent electrical circuits used to fit the EIS data for all four sacrificial coatings.

Table 2Fitting results of impedance spectra recorded for Zn, HDG, ZnAl and ZnAlMg coatings in 0.1 M NaCl without and with 5.10^{-3} M inhibitors.

	R_s ($\Omega \text{ cm}^2$)	$R_{ox/inh}$ ($\Omega \text{ cm}^2$)	n	$Q_{ox/inh}$ ($\text{Fcm}^{-2} \text{ Sn}^{-1}$)	R_{ct} ($\Omega \text{ cm}^2$)	n	Q_{dl} ($\text{Fcm}^{-2} \text{ Sn}^{-1}$)	$ Z _{10 \text{ mHz}}$ ($\Omega \text{ cm}^2$)
Zn-NaCl	81.0	97.3	0.67	1.3×10^{-3}	719.9	0.70	2.65×10^{-4}	804.5
Zn-CeCl ₃	88.7	5108	0.67	1.48×10^{-4}	4250	0.91	1.07×10^{-4}	7499.1
Zn-Ce(NO ₃) ₃	95.9	368.2	0.60	3.01×10^{-4}	3331	0.84	1.98×10^{-4}	2937.9
HDG-NaCl	71.6	306.3	0.77	3.73×10^{-4}	587	0.65	3.31×10^{-3}	693.7
HDG-CeCl ₃	111.8	2148	0.72	3.34×10^{-5}	14,400	0.42	2.35×10^{-4}	8762.9
HDG-Ce(NO ₃) ₃	64.9	12,830	0.84	1.63×10^{-5}	23,600	0.74	8.57×10^{-5}	33,284.0
ZnAl-NaCl	90.5	525.9	0.86	1.68×10^{-4}	1746	0.61	5.23×10^{-3}	1272.5
ZnAl-CeCl ₃	75.6	4275	0.74	3.01×10^{-5}	10,000	0.65	4.71×10^{-4}	11,137.3
ZnAl-Ce(NO ₃) ₃	92.4	3040	0.84	1.05×10^{-5}	9580	0.84	6.14×10^{-5}	10,059.3
ZnAlMg - NaCl	78.2	801.7	0.69	5.37×10^{-5}	1505	0.56	2.36×10^{-3}	2316.3
ZAM-CeCl ₃	74.9	4480	0.67	7.50×10^{-5}	18,600	0.59	4.49×10^{-4}	11,159.0
ZAM-Ce(NO ₃) ₃	90.6	236	0.81	1.54×10^{-5}	3455	0.98	3.42×10^{-5}	3614.4

Table 3Inhibition efficiency (%) calculated from R_{ct} values for different sacrificial coatings after 24 h of immersion in 0.1 M NaCl with 5.10^{-3} M inhibitors.

	Inhibition efficiency – η (%)	
	Cerium chloride	Cerium nitrate
Zn	83.0	78.3
HDG	95.9	97.5
ZnAl	82.5	81.7
ZnAlMg	91.9	56.4

and the type of anion. These results agree with the report in the literature for Al and its alloys. A better resistant protection for the longer exposure time of CeCl₃ in comparison with Ce(NO₃)₃ was presented for the AA7075-T6 substrate [37]. Moreover, the effect of the counter-ion and the type of substrate regarding the inhibition efficiency of cerium salts was confirmed for Al and its alloyed by Rodić et al. [30].

From EIS results, cerium salts proved to be the most effective inhibitors for HDG, followed by ZnAl, Zn, and ZnAlMg, respectively.

The high effectiveness of cerium salts for HDG steel or pure zinc was also reported in literature [24,26,27]. Arenas et al. [26], reported that CeCl₃ (>250 ppm) provided high inhibition efficiency (>90%) for HDG steel in 3.5 wt.% NaCl by potentiodynamic polarization method. Kartsonakis et al. [24], investigated the corrosion behavior of HDG steel

versus immersion time in 0.05 M NaCl without and with 500 ppm Ce(NO₃)₃ by EIS measurements. The results indicated that Ce(NO₃)₃ exhibited high performance with an efficiency around 98.5% for HDG steel after 3 h of immersion. Moreover, the efficiency slightly increased (99.3%) after 72 h of exposure. However, the inhibitory effect of cerium salts has often been studied individually, without the comparison with other cerium salts, as well as the effect of the counter anion. Thus, it is necessary to understand the influence of counter anion of cerium salts. In addition, this work is also one of the first studies on the inhibitory effect of different cerium salts (as soluble inhibitors) on zinc alloys, especially on ZnAl and ZnAlMg coatings. Thus, it provides an overview of the inhibitive behavior of two cerium salts for zinc alloy substrates, especially for ZnAl and ZnAlMg layers, as well as the influence of Al and Mg alloying elements on the corrosion behavior of the zinc-based substrates in the presence of cerium salts.

3.2.2. Surface characterization of sacrificial coatings after immersion in 0.1 M NaCl containing cerium salts

The typical crystal morphologies determined on the surfaces of all coatings after 24 h of exposure to the electrolyte (0.1 M NaCl) without and with cerium salts are shown in Fig. 7. The EDS analyses of all substrates are summarized in Table 4. As can be seen, the morphologies of all coatings after 24 h of immersion exhibited several changes compared to the original morphologies due to the presence of corrosion products.

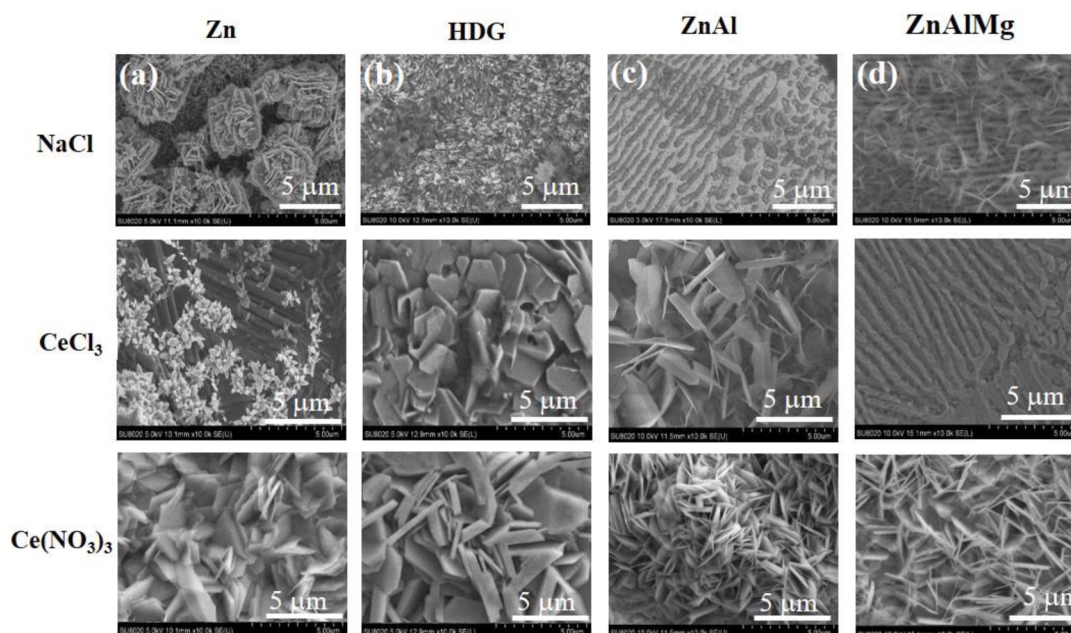


Fig. 7. SEM images of Zn (a), HDG (b), ZnAl (c) and ZnAlMg (d) surfaces after 24 h of immersion in 0.1 M NaCl without and with 5.10^{-3} M cerium salts.

Table 4

EDS analysis (wt%) of the locations indicated in Fig. 7 after 24 h of immersion in 0.1 M NaCl with and without 5.10^{-3} M inhibitors.

		C	O	Zn	Al	Mg	Ce	Cl
NaCl	Zn	1.3	18.6	80.1	–	–	–	–
	HDG	1.7	24.7	68.4	2.3	–	–	0.5
	ZnAl	1.7	4.0	88.1	6.2	–	–	–
	ZnAlMg	1.6	19.1	73.8	3.5	2.0	–	–
NaCl + CeCl ₃	Zn	1.0	14.3	74.6	–	–	10.1	–
	HDG	6.9	19.2	51.4	1.1	–	13.3	7.6
	ZnAl	3.9	20.1	40.7	4.3	–	30.2	0.8
	ZnAlMg	1.7	6.6	77.8	4.9	3.6	5.0	0.4
NaCl + Ce(NO ₃) ₃	Zn	1.7	22.9	55.9	–	–	9.8	9.7
	HDG	2.1	22.6	61.5	–	–	1.7	12.2
	ZnAl	2.2	24.1	58.6	2.4	–	1.5	11.3
	ZnAlMg	2.4	26.6	52.3	0.1	4.9	0.3	13.3

Moreover, after immersion, the surface structure of each layer presented different types of crystals.

In the blank solution, needle and flower-like morphologies were observed on the surface of the Zn and HDG coatings, while a plate-like corrosion product was detected on the surface of the ZnAlMg layer. However, no crystal morphology was observed on the surface of ZnAl. In addition, EDS analysis revealed that Zn and O are the main elements detected on the four sample surfaces. Moreover, on the Zn and HDG coatings, the Zn:O molar ratio is around 1:1, which is ordinary related to the zincite (ZnO) growth [19]. Nonetheless, the amount of O detected decreases to 4 wt% in the case of ZnAl coatings.

XRD analyses performed on Zn (a), HDG (b), ZnAl (c), and ZnAlMg (d) coatings after 24 h of exposure in the electrolyte with cerium salts are shown in Fig. 8. The metallic zinc peaks are detected on all layers.

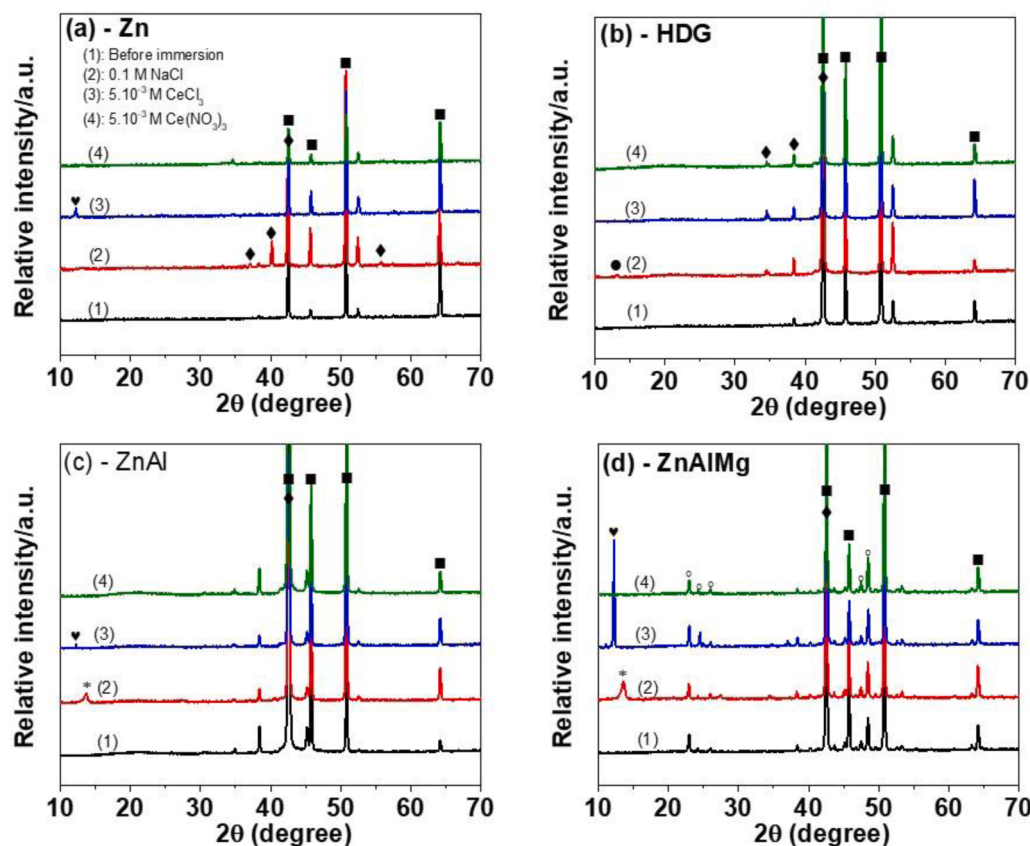


Fig. 8. XRD pattern of the Zn (a), HDG (b), ZnAl (c) and ZnAlMg (d) coatings after 24 h of immersion in 0.1 M NaCl without and with 5.10^{-3} M cerium salts. Peaks marked with ■, ○ are related to the Zn, and MgZn₂ and ◆, ♥, ★, * are attributed to ZnO, Ce₂(CO₃)₃·2H₂O, Zn₅(OH)₈Cl₂·H₂O, and Zn₅(OH)₈Cl₂·H₂O/ Zn₆Al₁₂(OH)₁₆(CO₃²⁻)₄·4H₂O (LDH), respectively.

not similar, which may be related to the nature of the alloying elements, and the growth of crystals due to the protective mechanisms on each surface. Furthermore, different crystal shapes are observed on the same type of coating, in the CeCl_3 and $\text{Ce}(\text{NO}_3)_3$ solutions.

Concerning the electrolyte with CeCl_3 , the flower shapes were evenly dispersed over the Zn surface while staked crystal plaque was observed on HDG and ZnAl surfaces. However, there is no difference in surface morphology of ZnAlMg compared to the unexposed sample. A thin yellow film was observed by a visual analysis on Zn, HDG, ZnAlMg, and ZnAl (thickest film) surfaces which is associated to a mixture of Ce^{3+} and Ce^{4+} [25,27] and the thicker yellow film, the higher Ce^{4+} content. The fact that, EDS analysis (Table 4) confirmed a significant amount of oxygen and cerium on the surface of all substrates can be related to the formation of cerium protective film on the surface of coatings, providing active protection from corrosion for substrates. Indeed, the XRD patterns (Fig. 8) indicated the presence of cerium carbonate ($\text{Ce}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$) (JCPDS No.00-030-0295) on the surface of all coatings (except HDG) which was identified at diffraction peak at $2\theta \approx 12.6^\circ$. The intensity of this peak is much stronger on the ZnAlMg surface, indicating the pronounced growth of ($\text{Ce}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$) on this surface. The appearance of cerium carbonate could result in the reaction between $\text{Ce}(\text{OH})_3$ with carbon dioxide dissolved in the solution. Meanwhile, zincite was found on HDG coating instead of ($\text{Ce}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$).

Regarding the electrolyte containing $\text{Ce}(\text{NO}_3)_3$, SEM images (Fig. 7) presented typical rod-like and plate-like morphologies of corrosion products on all the surfaces. Indeed, in combination with the EDS data, the plate-like or rod-like morphologies showed a molar ratio of Zn:O:Cl around 5:8:2, corresponding to simonkolleite in the case of Zn, HDG, and ZnAl coating. In addition, the formation of Mg-modified simonkolleite on the ZnAlMg surface was proposed due to the molar ratio of Zn:Mg:O:Cl from the plate-like structure near 4:1:8:2, which was previously reported by Volovitch et al. [19], and Thierry et al. [46]. However, these proposed based on EDS analyses are not in agreement with the XRD results, which determined mainly zincite in place of simonkolleite on all samples. In addition, the presence of Mg^{2+} and Al^{3+} in the aggressive medium could influence the crystallization of corrosion products, resulting in different shapes and sizes of ZnO [19, 47]. Interestingly, ($\text{Ce}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$) was not found on all substrates in the electrolyte with $\text{Ce}(\text{NO}_3)_3$. These results suggested that the main cerium products formed on all coatings may be $\text{Ce}(\text{OH})_3/\text{Ce}(\text{OH})_4$, which existed in amorphous form [48]. Therefore, they could not be characterized by XRD analysis.

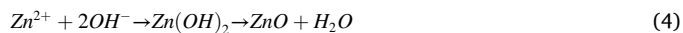
3.3. Discussion

3.3.1. The formation of corrosion products in electrolyte without and with inhibitors

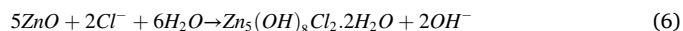
The EIS results revealed that ZnAl and especially ZnAlMg coatings presented more protection than conventional Zn and HDG coatings in sodium chloride solution. Several authors reported the better protection offered by ZnAl and ZnAlMg due to the formation of stable corrosion products as simonkolleite and/or LDH [13,23]. Indeed, XRD measurements indicated the formation of simonkolleite on HDG coatings and simonkolleite/LDH on ZnAl and ZnAlMg layers. For ZnAlMg coating, during the corrosion process, the intermetallic particle MgZn_2 is the most active phase and unstable in the pH range of 2.5 to 12.5. Thus, it corrodes preferentially causing the formation of Mg^{2+} and Zn^{2+} ions due to anodic reactions (Eq. (2)) [11,30], while the oxygen reduction occurs in the cathodic site (Eq. (3)).



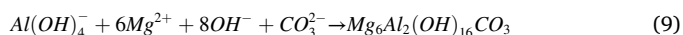
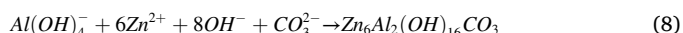
The generation of OH^- led to the increase of local pH, resulting in the formation of corrosion products Eqs. (4) and (5):



Based on the Pourbaix diagram of magnesium [39]), the precipitation of $\text{Mg}(\text{OH})_2$ occurs in an alkaline medium (at about pH = 10). This $\text{Mg}(\text{OH})_2$ formation significantly reduced OH^- ions, resulting in a decrease in the local pH, which allows the precipitation of insoluble $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (described as Eq. (6)) and could contribute to an increase in the thermodynamic stability of simonkolleite with a protective nature [15], preventing the transformation of simonkolleite into ZnO.



Besides, as suggested in literature [13,23], the formation of LDH (pH > 10) due to the Al dissolution could be presented Eqs. (7), 8 and (9):



The absence of simonkolleite/LDH on the HDG, ZnAl and ZnAlMg coatings immersed in the solution with cerium salts may be associated with the solubility product and the pH value. The solubility product of $\text{Ce}(\text{OH})_3$ ($K_{sp} = 1.6 \times 10^{-20}$) is lower than the value of $\text{Zn}(\text{OH})_2$ ($K_{sp} = 3 \times 10^{-16}$), $\text{Al}(\text{OH})_3$ ($K_{sp} = 2.7 \times 10^{-11}$), and of $\text{Mg}(\text{OH})_2$ ($K_{sp} = 1.8 \times 10^{-11}$) (in the case of ZnAlMg coating) [49,50]. Therefore, the formation of $\text{Ce}(\text{OH})_3$ on the top surface of the substrate in the solution containing Ce^{3+} is preferred. This process slowed down the cathodic reaction, thus suppressing the anodic dissolution. Hence, the concentration of ions Zn^{2+} and Al^{3+} in the environment decreased, driving the reduction in capacity of simonkolleite/LDH formation. In addition, the formation of LDH happened at alkaline medium (pH > 10) [11]. Besides, Ogle et al. [51] presented that the formation of simonkolleite occurred at a neutral medium (about pH = 6–7), while the precipitation of ZnO formed at pH value higher than 7–8. Moreover, the HYDRA-MEDIUM modeling [28] with $[\text{Ce}^{3+}] = 5 \text{ mM}$, $[\text{Cl}^-] = 15 \text{ mM}$ and $[\text{CO}_3^{2-}] = 5 \text{ }\mu\text{M}$ indicated that $\text{Ce}(\text{OH})_3$ could be obtained at pH value superior than 7. Therefore, the formation of $\text{Ce}(\text{OH})_3$ could hinder the formation of ZnO and/or $\text{Al}(\text{OH})_3$, preventing the formation of simonkolleite/LDH. These proposals could explain the absence of simonkolleite/LDH on HDG, ZnAl and ZnAlMg layers in the solution containing cerium salts compared with the corrosion product formed on the zinc-based coating in the blank solution.

3.3.2. Effect of counter ion on the effectiveness of cerium

Cerium is well known as an inhibitor for zinc, sacrificial coating based on Zn, aluminum and its alloys [24,27,31]. The protective mechanism was proposed for the formation of cerium hydr(oxide) film on the cathodic area, leading to reduction of the global corrosion rate. Nitrate anion is considered as an inhibitor to protect steel, aluminum and its alloys from corrosion [32,33,52,53].

In this work, the performance of cerium and the effect of counter-ion (NO_3^-) were investigated in chloride medium for different sacrificial coatings based on zinc. The presence of NO_3^- enhanced the protective corrosion in short immersion time. However, the inhibition efficiency of $\text{Ce}(\text{NO}_3)_3$ decreased for ZnAlMg coating in prolonged immersion time. This poorer protection may be associated with the microstructure of ZnAlMg.

Indeed, Jiang et al. [54] indicated that the Zn and Mg selective dissolution increased in the presence of 0.03 M NO_3^- in 0.01 M H_3PO_4 medium, while the presence of NO_3^- inhibited the Al dissolution in the coating. The preferred Zn and Mg dissolution in the presence of NO_3^- may associated with the oxidizing strength of the $\text{NO}_3^-/\text{NO}_2^-$ couple, which was also reported for aluminum alloy AA7075-T6 by Foley et al.

[52,53]. The authors suggested that accelerated effect of NO_3^- may be related to the presence of NH_3 formed by the cathodic reactions. These chemical reactions could be described according following reactions:

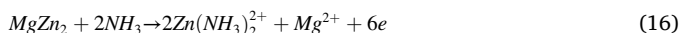
Anodic reactions:



Cathodic reactions:



The reaction between intermetallic particles with NH_3 :



This complex is relatively soluble (with the equilibrium constant $K_{\text{stability}} = 2.89 \times 10^9$) and accelerates the corrosive attack. Whereas, in the presence of $\text{Ce}(\text{NO}_3)_3$, Ce^{3+} could consume OH^- generated in cathodic sites, forming cerium hydr(oxide) film on the surface. This protective film served as a barrier to protect the substrate against corrosion. Therefore, $\text{Ce}(\text{NO}_3)_3$ would simultaneously accelerate the anodic dissolution of intermetallic MgZn_2 and inhibit the cathodic reaction of the corrosion process, resulting in poor inhibitive protection for ZnAlMg in prolonged immersion time. This simultaneous property of $\text{Ce}(\text{NO}_3)_3$ was reported for AA 2024 aluminum alloy at the concentration of 10^{-2} M by Machkova et al. [31].

4. Conclusion

This work evaluated the corrosion performance of the four different Zn based sacrificial coatings alloyed with Al and Mg in 0.1 M NaCl solution and the inhibitive effect of two cerium salts on the corrosion resistance of zinc alloy sacrificial coatings.

This study confirmed the improved properties obtained for the ZnAlMg alloys during immersion due to simonkolleite/LDH growth and its protective properties.

Ce (III) obtained by adding cerium chloride with the same chloride concentration compared to the reference solution provided a higher protection after 24 h of immersion in comparison with cerium nitrate for all Zn, ZnAl and ZnAlMg substrates. Nevertheless, an improvement of the corrosion performance is observed in the presence of the nitrate anions for the HDG coatings due to the anodic synergistic effect. The cerium nitrate exhibited a poorer protection in longer immersion time for ZnAlMg coatings due to its dissolution effect on the magnesium rich phase.

The results indicated that Ce (III) exhibits high inhibition efficiency on different sacrificial coatings. The inhibitive effect of cerium salts was highest for HDG, followed by ZnAl , Zn, and the lowest for ZnAlMg coating. Moreover, the effectiveness of cerium salts depends on the substrate and the counter-anion.

CRedit authorship contribution statement

T.T. Nguyen: Investigation, Methodology, Validation, Writing – original draft. **C. Arrighi:** Methodology, Validation. **T.T. Thai:** Methodology, Validation, Writing – review & editing. **L. Dangreau:** Investigation, Validation. **M.F. Gonon:** Investigation, Validation. **A.T. Trinh:** Methodology, Validation, Writing – review & editing, Supervision. **M.-G. Olivier:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Funding acquisition.

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.

Data availability

Data will be made available on request.

Acknowledgments

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