Study of local Na⁺ and Cl⁻ distributions during the cut-edge corrosion of aluminum rich metal-coated steel by scanning vibrating electrode and micro-potentiometric techniques

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ABSTRACT

Scanning vibrating electrode technique (SVET) and micro-potentiometric pH measurements were performed simultaneously to study the cut-edge corrosion of aluminum-rich metal-coated steel. Different areas of pH and anodic/cathodic activity were identified and the analyzed corrosion products were linked to the values of pH measured at regions of precipitation. A step further into the understanding of the corrosion mechanism in the cut-edge is based on the knowledge concerning the movement of the ions which take part in the corrosion process.

Local and in situ concentration of the ions of the supporting electrolyte, 0.005 M NaCl, were recorded over the cut-edge of metal-coated steel. In this frame, zinc, aluminum and zinc/aluminum metal-coated steel samples were studied by micro-potentiometry with Cl⁻ and Na⁺ selective microelectrodes. Either Cl⁻ or Na⁺ distribution was mapped simultaneously with monitoring current density by SVET in continuous immersion. Interesting though unexpected finding is the depletion of Cl⁻ in anodic sites and its accumulation in cathodic sites. Along with this, an increase of Na⁺ concentration occurs in anodic sites and Na⁺ content decreases in cathodic sites over the steel. Such distribution is explained by formation of Cl⁻ and OH⁻ containing corrosion products and charge compensation effects. The described Cl⁻ distribution was partly confirmed by ex situ analysis of corrosion products performed by SEM-EDX and Raman spectroscopy.

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1. Introduction

Since the 1960s, many efforts have been made with the aim of searching for alternatives of the classical zinc galvanized steel products [1,2]. The volatile price of zinc and the leaching effect while exposed to high chloride concentrations, feeds the markets demand of more versatile products. One of the methods proposed to increase the corrosion resistance of zinc coatings, was the addition of aluminum to the alloy baths in the metallization process. A new family of Zn/Al metal-coated steel products, were introduced in the markets in the 1970s with aluminum contents in the metal coating from 5 to 55 wt% [3]. These products could supply a higher corrosion performance in comparison with zinc coated steel products due to the addition of the sacrificial protection properties supplied by zinc and the high barrier properties provided by aluminum [4–7].

However, these products, while in service, show special sensitivity to corrosion in cut-edges exposed to the atmosphere.

The corrosion process taking place in the cut-edge has been widely studied by many authors [8–21]. It is generally accepted that in galvanized steel products, a galvanic coupling is established between the metal coating (anode) and the steel substrate (cathode). The activation of this galvanic coupling is highly influenced by an unfavorable anode to cathode ratio [8].

The local initiation and propagation of corrosion in the cut-edge, has focused attention on the application of localized electrochemical techniques. One example of a local technique widely used in the last years for the study of corrosion is the scanning vibrating electrode technique (SVET), which measures local potential differences due to the ionic fluxes produced above the sample during corrosion. Developed by biologists in its present form [22,23], SVET was adapted for corrosion studies by Hugh Isaacs in the 1980s [24,25]. Since then it has been used to study many aspects of cut-edge corrosion as its initiation in coil coated products [9], the effect of differential aeration due to the change of porosity [10] or photodegradation [11], the link to the microstructural changes [26,12],
the effect of corrosion inhibitors [13,14] and modeling of cut-edge corrosion [15,27]. However, SVET cannot differentiate the chemical nature of the species present in an electrical field. Potentiometry with ion-selective micro-electrodes provides information about local effective concentration (activity) of specific ions in solution (e.g., H+) making possible tracing changes in the acid-base equilibria associated with the electrochemical processes [28–30,8,15,31–42]. Mg2+, Zn2+, Na+ and Cl− selective microelectrodes have also been reported to be used for studying localized corrosion [29,43–46,33,47,48,42].

Important role of local pH on the propagation and passivation of corrosion processes at cut-edge as well as on precipitation and distribution of corrosion products was described by Thébault [36,15], who performed consecutive SVET and local pH measurements with glass-capillary micro-electrode over the cut-edge of hot dip galvanized steel. Recently, Lamaka [30] proposed the combination of SVET and micro-potentiometry (e.g. SIET: scanning ion-selective electrode technique) to perform quasi-simultaneous measurements that allow characterizing the electrochemical processes in terms of potential/current as well as in terms of distribution of different chemical species correlated in space and time. In our previous work [28], the effect of aluminum contents in cut-edge corrosion has been studied in three different specimens in terms of local pH and current density distribution. The high corrosion rates found on hot dip aluminized cut-edge sample were explained by the low pH of precipitation of Al corrosion products that cannot block the cathodic reaction in contrast to Zn-based corrosion products. A link could be established between the corrosion products detected by different surface analysis techniques and the products thermodynamically stable at the pH measured by SIET.

A step further into the investigation of corrosion processes is the availability of information concerning the distribution of ionic species locally and in situ. This source of information has big value for the prediction and the modeling of corrosion processes. Nguyen studied the distribution of chloride ions at the coating/metal interface by using glass-capillary double barreled electrodes [44]. Lin measured the accumulation of Cl− in the anodic sites on stainless steel and on a Cu–Pt couple [43]. Lamaka recorded simultaneous pCl and pH maps over anodically polarized Pt wire and observed an increase of Cl− activity and decrease of Na+ activity over the Pt current source [29]. In all these works, the increase of Cl− activity in the anodic areas was justified by compensation of surplus of positive charge induced by accumulated H+.

This work aims at better understanding of the corrosion mechanisms at the cut-edge by measuring local concentrations of free Cl− and Na+ in solution. In this frame, micro-potentiometric measurements with Na+ and Cl− selective glass-capillary microelectrodes were performed. Each micro-potentiometric measurement was coupled with simultaneous mapping of local ionic current density acquired by SVET. Measurements have been performed in 0.005 M NaCl under continuous immersion in three different metal-coated steel systems with aluminum contents in the metal coating varying from 0.5 through 55 to 100 wt%. Right after immersion, the corrosion products formed were analyzed by SEM-EDX and Raman spectroscopy. Finally, a mechanism to explain the ion distribution at the cut-edge is proposed.

2. Experimental

2.1. Samples

Three metal-coated steel products with varying content of aluminum were studied. The metal coating compositions are shown in Table 1. The steel substrate thickness was 0.4 mm while the metal coatings had thickness of 15 μm in hot dip galvanized system, 20–25 μm for hot dip Al–Zn galvanized steel and 40 μm in the case of hot dip aluminized steel. For SVET–SIET measurements, the metal samples were cut into 0.45 mm band and mounted in an epoxy resin. Then, they were gradually polished in several steps using 120 μm and 320 μm sand papers and finished in two steps on a cloth with 9 μm and 3 μm diamond suspensions.

![Image](image-url)

**Table 1** Metal coating composition in wt%.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Zn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot dip galvanized</td>
<td>0.5</td>
<td>99.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Hot dip Al–Zn</td>
<td>55.0</td>
<td>43.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Hot dip Al</td>
<td>100.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
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</table>

2.2. Micro-potentiometric and scanning vibrating electrode technique measurements

A commercial scanning vibrating electrode technique equipment (manufactured by Applicable Electronics, Inc.) and controlled by ASET software (Science Wares, Inc.) was used to perform SVET and micro-potentiometric (SIET) measurements. This set-up allows for quasi-simultaneous measurements of local current density and local ion concentration as described in Ref. [30]. The vibrating probe of SVET and the glass-capillary microelectrode were positioned at a distance of 50 μm in order to avoid the cross-talk effect and break of the glass electrode by the vibrating probe and excessive solution stirring. A time lag between acquiring each current density and micro-potentiometric data-point was only 2.1 s. Thus, one SVET–SIET scan yielded two independent maps showing ionic current density and ion distribution. All experiments were performed in a Faraday cage at room temperature (24 ± 3 °C). Experiments were performed during continuous immersion in 0.005 M NaCl for 24 h, mappings were obtained every hour. Insulated Pt-Ir micro-probes (MicroProbes for Life Science) with platinum black deposited on a spherical tip of 15 μm diameter were used as vibrating electrodes for the SVET measurements. The probe was positioned 100 ± 3 μm above the surface, vibrating in the planes perpendicular (Z) and parallel (X) to the sample’s surface. The amplitude of vibration was 32 μm (peak to peak), vibration frequencies of the probe were 124 Hz (Z) and 325 Hz (X). Only the data collected at the vibration perpendicular (Z) to the sample was considered and presented in this work.

The local activity of Na+, Cl− and H+ was detected by using ion-selective microelectrode (ISME) in potentiometric mode. The glass-capillary microelectrodes were positioned 50 ± 5 μm above the surface. The membrane cocktails of Na+ and Cl− selective microelectrodes used in this work were recently optimized for corrosion related studies. The membrane of Cl−–ISME was composed of tridodecymethylammonium chloride and 2-nitrophenolylctyl ether. The membrane of Na+-SME consisted of bis[(12-crown-4)methyl]dodecyltrimethylammonium chloride and 2-nitrophenolylctyl ether. The membrane of Na+-SME consisted of bis[(12-crown-4)methyl]dodecyltrimethylammonium chloride and 2-nitrophenoyctyl ether. The membrane of Na+-SME consisted of bis[(12-crown-4)methyl]dodecyltrimethylammonium chloride and 2-nitrophenolylctyl ether. All the reagents for membrane cocktail were Selectophores® grade products from Fluka. The details of membrane composition of pH-selective microelectrode and its analytical characteristics are presented in Ref. [31]. All three ISME possessed the Nernstian response.
ISME were made of single-barrelled, standard-wall (330 μm) borosilicate glass capillaries with an outer diameter of 1.5 mm. The P-97 Flaming/Brown Micropipette Puller, (Sutter Instruments Company) was used to shape the cone tip. The diameter of the orifice of the tip was 2.0 ± 0.5 μm. The capillaries were silanized by injecting 200 μL of N,N-dimethyltrimethylsilylamine in a glass preparation chamber at 220 °C. The silanized glass micropipettes were first back-filled with an inner reference solution and then tip-filled with a selective ionophore-based oil-like membrane cocktail. The column length of the membrane was about 50–100 μm. The inner filling solution was 0.05 M NaCl. An Ag/AgCl wire was inserted into the electrolyte to provide reference electrode electrical contact. A homemade Ag/AgCl electrode with agar stabilized 0.05 M NaCl worked as external reference electrode. IP2A amplifier (input resistance >10^15 Ω) was used to record the potential values. Micro-potentiometric measurements were performed in rather dilute solution, 0.005 M NaCl solution under open circuit potential conditions. Hence, no difference between the concentration and activity of ions of interest was drawn in this work. The drift of the potential of the ISME was eliminated by taking a reference potential reading in the bulk solution before each SIET scan.

2.3. Surface analysis

Corrosion products analysis was performed after immersion by Raman spectroscopy and SEM-EDX. Raman spectra were obtained using a DILOR XY Laser Spectrometer. Green Ar+ laser radiation at 514.5 nm and red He/Ne laser at 632.8 nm were used as excitation lines. With a magnification of x50, spots of 2 μm^2 were analyzed. A JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) coupled with a JEOL Dry SD Extra X-ray detector was used to study the elemental composition of the formed corrosion products. A electron beam energy of 15 keV was applied for EDS mappings.

3. Results

3.1. Local Cl−, Na+ and scanning vibrating electrode technique measurements

Typical distributions of Na+ and Cl− concentration recorded simultaneously with ionic current density are shown together with the optical micrograph in Fig. 1. The contours on the cut-edge samples indicated in the SVET and SIET maps identify the areas corresponding to the metal coating and the steel substrate. This facilitates the ascription of activity shown in the SVET and ion distribution maps to the metal coating and steel areas shown in the optical images. X and Y coordinates in the data maps represent the size of the mapped area in μm. Measured concentrations of Na and Cl are presented as −log10(ion concentration), also known as pCl and pNa, by analogy with pH.

Cathodic activity is present along the steel substrate whereas anodic activity is localized in the metal coating. This is in line with previous reports [12,49–52,10] and with our measurements performed on the same samples [28].

The distribution of concentration of Na cations and Cl anions over the corroding cut-edge sample is presented here for the first time. Fig. 1 shows that the lower pCl values (higher chloride concentration) are found in the middle of the steel substrate, while Cl− depletion is observed in the metal coating showing correlation with the SVET mapping. The opposite situation is revealed for
Na distributions. The lower pNa values (higher Na⁺ concentration) correlate with the areas showing anodic activity in the SVET mapping. These Cl⁻ and Na⁺ ion distributions have been detected since the beginning of the immersion till its end for the three studied metal-coated systems. In total 68 maps of Na⁺ and over 90 maps of Cl⁻ distribution were recorded for three different samples. For each of these maps corresponding current density distribution was also acquired. These correlations between SVET and ion distribution mappings will be discussed further.

The interest of this study is focused on the local ionic distribution and its correlation with current density and pH distribution. To treat such massive amount of generated data, the maximum and the minimum value of chloride and sodium ion distributions [28,53–55], were extracted from each map and plotted versus the time of immersion, see Fig. 2. Note that high Cl⁻ and low Na⁺ concentration corresponded to cathodic sites (identified as such by SVET) in all the acquired maps. Correspondingly, low Cl⁻ and high Na⁺ concentration were always observed in anodic sites. It was also remarked that none of the tested samples became passive after 24 h of immersion. Fig. 3 presents the local current density distributions for hot dip galvanized, hot dip Al–Zn and hot dip Al samples after 24 h of immersion. The evolution of current density distribution measured here did not differ from the one reported in our previous work [28]. Differences can be observed for each ion: maximum and minimum concentrations of free sodium in solution showed very slight variation in time, usually between 0.0046 and 0.0054 M. No differences can be observed as a function of the system measured.

The evolution of free chloride concentration shows rather different pattern than the one recorded for Na. For hot dip galvanized steel, [Cl⁻] is rather constant value between 0.0030 ± 0.0005 and 0.0065 ± 0.001 M apart from two points at the beginning and at the end of the measurements. Chloride concentration there increases to 0.05 M in cathodic area and decreases to 0.001 M in anodic area. For hot dip Al–Zn sample, measured chloride values are rather high in cathodic area and low in anodic sites compared to two other samples. Maximum [Cl⁻] values show an increase of [Cl⁻] from 1 to 2.5 h and a new one from 7 to 12.5 h. From this time until 23 h, the maximum [Cl⁻] decreases until being stable around 0.02 ± 0.005 M. Minimum [Cl⁻] varies between 0.001 and 0.003 M. For hot dip Al sample, the [Cl⁻] values vary in the region narrowest among all tested samples: between 0.0039 ± 0.0008 and 0.0058 ± 0.0005 M in anodic and cathodic sites correspondingly.

The changes of potential difference measured by ISME in this work were less than 6 mV in case of Na⁺ measurements (ΔpNa < 0.1) and ca. 6–100 mV in the case of Cl⁻ measurements (0.1 < ΔpCl < 1.6). This is much narrower range compared to the regular pH micro-potentiometric measurements for corroding systems where the potential changes in the range of 200–450 mV as pH changes from 5 to 9 or rarely from 3.6 to 12 [28,8,29]. Thus, any sudden potential drift which, unfortunately, is an intrinsic property of ISME may result in a significant error of measured pNa and pCl. To account for the possible potential drift and to eliminate this problem, a reference reading of potential was taken before starting each potentiometric measurement. Acquired data was corrected for the observed shift of the potential. Hopefully most of the micro-potentiometric maps acquired in this work are free of potential shift problems. This can be indirectly verified by observing the trends of the maximum and minimum concentrations of Na⁺ and Cl⁻ as a function of time. Mirror like change of maximum and minimum concentration (increase of maximal concentration accompanied by decrease of minimal concentration relatively the bulk solution) is an evidence for the absence of potential shift. Co-directional increase or decrease of minimal or maximal concentrations may suggest the potential shift that was not corrected.

The issues of the IR drop should also be considered when small potential changes are measured. In the work of Nazarov [45], a study was performed to rule out the influence of the IR drop on the measurements performed with Cl⁻ and Na⁺-selective micro-electrodes used in present work.

3.2. Corrosion product analysis

After 24 h of immersion in the electrolyte, the first differences between the systems were remarked visually: in hot dip galvanized steel and hot dip Al–Zn, white corrosion products formed half-circles on the steel substrate. In the case of hot dip Al, red corrosion products dominated over the white products precipitated on the steel surface in the shape of the same half-circles. Dissolution of Fe occurs from the Fe rich layer of metal coating that is formed when dipping is performed [56–59].

EDX analysis performed on the products formed on hot dip galvanized steel showed the presence of high concentration of Zn, O and Cl in the products formed. By Raman spectroscopy, the presence of Zn5(OH)8Cl2 in the white corrosion products could be confirmed by the peaks appearing at 258, 395 and 3492 cm⁻¹ [60]. Characteristic bands of ZnO could also be detected on the rings of products formed and in the middle of the steel substrate.

On hot dip Al–Zn, EDX mappings showed the presence of zinc containing products on the steel substrate while aluminum was mainly found on the metal coating and in its vicinity. High chloride concentration was detected on the metal coating as it can be observed in Fig. 4. Mixtures of ZnO and β-Zn(OH)2 were detected by Raman spectroscopy in measurements performed on the products.
formed on the steel. Al–O mode from diaspore (AlO(OH)) found at 220 cm$^{-1}$ [61] and the broad band identified between 2800 and 3000 cm$^{-1}$ confirmed the presence of aluminum corrosion products.

In the case of hot dip Al, EDX mappings revealed that aluminum products were mainly located in the interior side of the rings of products while iron and oxygen were mainly located in the periphery of the rings. Local points of chloride concentration were detected on the metal coating areas where rings of products were centered. The presence of mixtures of haematite (α-Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) was confirmed by the strong Raman peaks observed at 220, 285 and 670 cm$^{-1}$ [62]. Lepidocrocite (γ-FeOOH) was detected in the areas between the metal coating and the steel substrate. The possible masking of Al–O signatures from aluminum products is not rejected as the previously described peaks from iron products fall in the same range of wavenumbers.

4. Discussion

As shown in Section 3, free chloride in solution shows a maximum concentration in the middle of the steel substrate, where cathodic activity takes place. This result was supported by comparison with EDX mappings. Fig. 5a displays a SIET mapping of free Cl for hot dip Al specimen measured after 24 h in 0.005 M NaCl which is compared with an EDX Cl elemental mapping of the same area obtained ex situ after immersion. The dotted line in Fig. 5 depicts the areas where a decrease of chloride concentration is observed in the SIET mapping while accumulation of this element is detected in the same area under ex situ conditions. Local depletion of Cl$^{-}$ over anodic zones is caused by the precipitation of Cl$^{-}$ containing corrosion products that leads to consumption of Cl$^{-}$, locally, around the sites where precipitation takes place. In contrast, free Na$^{+}$ accumulation was observed in areas where high concentration of Cl was observed in the EDX mappings – Fig. 5b. Therefore, a correlation can be established between in situ and ex situ measurements. A number of authors claimed that chloride ions accumulate in the anodic sites [24] and accelerate propagation of localized corrosion [44,43]. Important, that anodic sites are usually acidified due to the hydrolysis of Me$^{n+}$ cations formed there. Therefore, increase of Cl$^{-}$ concentration [29,43,44] is explained by Cl$^{-}$ migration to the sites with high amount of H$^{+}$ (and Me$^{n+}$) to compensate the surplus positive charge and maintain the charge balance. In our recent work [28] pH distribution was measured over cut-edge hot dip Al–Zn, hot dip Al and hot dip galvanized samples. Predictably, anodic sites where found to be acidified (pH from 4.0 to 6.2) and cathodic sites where alkaline (pH 9.6 ± 1.0) – see Fig. 6b. One would expect accumulation of Cl$^{-}$ in anodic sites (accompanied by depletion of Cl$^{-}$ in cathodic areas, accumulation of Na$^{+}$ there and depletion of Na$^{+}$ in anodic sites) over cut-edge hot dip Al–Zn, hot dip Al and hot dip galvanized samples as well. However, the measurements performed in this work clearly showed opposite distribution: depletion of Cl$^{-}$ and preferential location of Na$^{+}$ in anodic areas (metal coating) while Cl$^{-}$ was mainly present in the cathodic ones (steel substrate). This notwithstanding the results of present work and ones reported in [29,43,44] cannot be called contradictory. The variation of the ion distribution found in this work is attributed to the precipitation of OH$^{-}$ and Cl$^{-}$ containing corrosion products like Zn$_2$(OH)$_3$Cl$_2$ and Al(OH)$_2$Cl. In the work of Lamaka [29] Cl$^{-}$ and Na$^{+}$ were measured over polarized Pt wire, thus no corrosion products were produced there. Lin [43]
mapped Cl⁻ distribution over stainless steel undergoing crevice and pitting corrosion, where Cl⁻ contain corrosion products were not formed.

According to the SEM-EDX and Raman analysis and in agreement with the thermodynamic diagrams [63], Fig. 7, chloride-containing corrosion products, Zn₅(OH)₆Cl₂ and Al(OH)₃Cl, are formed at lower pH, hence closer to the acidified anodic sites. Hydroxide and oxide species, Al(OH)₃, Zn₅(CO₃)₂(OH)₆, γ-FeOOH, α-Fe₂O₃, Fe₃O₄, ZnO and Zn(OH)₂ precipitate at higher pH, over cathodically active area.

The explanation for the recorded distribution of Cl⁻ and Na⁺ monitored in this work can be proposed (Fig. 8) as follows:

- A galvanic coupling is established between the metal coating, which generates Al³⁺ and/or Zn²⁺ cations and the steel substrate where oxygen reduction produces OH⁻.
- Precipitation Al(OH)₃Cl (and Zn₅(OH)₆Cl₂) occurs close to anodic sites as was detected by SEM-EDX and Raman spectroscopy. This precipitation leads to local depletion of free Cl⁻ ions in solution in the anodic areas.
- As a part of Al(OH)₃Cl and Zn₅(OH)₆Cl₂ precipitation, cations Al(OH)₂⁺ and Zn₅(OH)₆²⁻ also are taken out of the anodic sites and local negative charge that is being created in such a way is compensated by increase of local Na⁺ concentration.
- In cathodic sites, OH⁻ is consumed to produce Al[OH]₃, Zn₅(CO₃)₂(OH)₆, γ-FeOOH, α-Fe₂O₃, Fe₃O₄, ZnO and Zn(OH)₂. Decrease of OH⁻ is compensated by the local increase of Cl⁻ and decrease of Na⁺ to maintain the charge balance.

In Fig. 2, the maximum and minimum Na⁺ and Cl⁻ concentrations are shown. It can be observed that the amplitude of deviation of Cl⁻ concentration from the value of the bulk solution is considerably higher than that of Na⁺. The average delta for Cl⁻ variation is 0.015 to −0.003 M while average delta for Na⁺ is only ± 0.0002 M. This can be explained by the higher mobility of Cl⁻ ions (K_{Cl⁻} = 7.91 × 10⁻⁸ m² s⁻¹ V⁻¹) compared to Na⁺ (K_{Na⁺} = 5.19 × 10⁻⁸ m² s⁻¹ V⁻¹) [64]. Additionally, in charge compensating competition, Cl⁻ moves co-directionally with equally charged but faster OH⁻ (K_{OH⁻} = 20.50 × 10⁻⁸ m² s⁻¹ V⁻¹), while Na⁺ moves co-directionally with even faster H⁺ (K_{H⁺} = 36.25 × 10⁻⁸ m² s⁻¹ V⁻¹). Comparing the ratio of ion mobilities of Na⁺/H⁺ versus Cl⁻/OH⁻, it is clear that the one of the positive ions is almost the double than the one of Cl⁻/OH⁻ (K_{H⁺} : K_{Na⁺} = 6.98 vs. K_{OH⁻} : K_{Cl⁻} = 2.59). Therefore, the charge compensating ability of Na⁺ is lower than that of Cl⁻.
A drastic change of the concentration of \( \text{Cl}^- \) at the beginning and at the end of the measurement in hot dip galvanized was observed (see Fig. 2). The only explanation for these 'jumps' of \( \text{Cl}^- \) is the localized corrosion. Note, that the \( \text{Cl}^- \) and \( \text{Na}^+ \) evolution reported for each system were reproducible in all the repeated measurements. Some deviations of the absolute values of \( \text{Cl}^- \) and \( \text{Na}^+ \) at a certain time were detected. However, the trends were the same: \( \text{Cl}^- \) values for hot dip galvanized steel varied in rather wide range, variation of \( \text{Cl}^- \) for hot dip Al was lower than that for the two other samples, and finally, \( \text{Cl}^- \) in the cathodic area of hot dip Al–Zn kept being higher than for the other two samples.

The higher maximum concentration of \( \text{Cl}^- \) observed for hot dip Al–Zn in Fig. 2 is rather difficult to explain at the moment. Perhaps, the differential dissolution of zinc and aluminum hydroxides may contribute to it [65,66,29].

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**Fig. 5.** Comparison between (a) pCl mapping and EDX mapping for Cl on hot dip Al and (b) pNa mapping and EDX mapping for Cl measured on hot dip Al–Zn after 24 h of immersion in 0.005 M NaCl.

**Fig. 6.** pH and SVET mapping on hot dip Al–Zn after 3 h of immersion in 0.005 M NaCl.

**Fig. 7.** Logarithm of activity as a function of pH for hot dip Al–Zn at \( t=25 \) °C and average ionic strength 0.1 M. The following concentrations were considered: \([\text{Zn}^{2+}] = [\text{Al}^{3+}] = 5 \times 10^{-3} \) M and \([\text{CO}_3^{2-}] = 5 \times 10^{-5} \) M. Corrected values of \( K \) were used for the following reactions: \( 5\text{Zn}^{2+} + 2\text{Cl}^- + 8\text{H}^+ + \text{Zn}_x(\text{OH})_y(\text{Cl})_z \log K = -34.5 \) instead of \(-38.5 \) and \( 5\text{Zn}^{2+} + 2\text{Cl}^- + 6\text{H}^+ + \text{Zn}_x(\text{OH})_y(\text{CO}_3)_z \log K = -5.4 \) instead of \(-9.69 \) that are used by Medusa software. These newer constants were calculated based on the data provided in [36]. Additionally to the complexes existing in the software database, aluminum hydroxychlorides \( \text{Al(OH)Cl}_y \) and \( \text{Al(OH)_3Cl} \) complexes were added to the Hydra-Medusa database. Corresponding stability constants were calculated based on literature [67] and fed in the software.
5. Conclusions

Local distribution of Cl$^-$ and Na$^+$ has been successfully measured in situ in the cut-edge of three different specimens. The coupling with surface analysis techniques is required for a better understanding and interpretation of the corrosion process and the chemistry involved. Together, local electrochemical techniques and surface analysis allowed establishing a link between in situ and ex situ measurements which provide valuable information in the further understanding of the cut-edge corrosion mechanism.

The distribution of Na$^+$ and Cl$^-$ in the studied conditions showed similar behavior independently on the aluminum content in the metal coating. The mechanism proposed, justified the presence of Cl$^-$ in the middle of the steel substrate and the presence of chloride in the metal coating based on charge balance which in these systems and in the imposed conditions was highly affected by the precipitation of corrosion products.

The values of Cl$^-$ concentrations observed seemed to be influenced by the nature of the metal coating. This variation was attributed to the different composition of the corrosion products formed.

Further work is oriented towards the assessment of information concerning the point formation of corrosion products. This can be of great importance for corrosion prediction and numerical modeling.

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