



Article Electrochemical and Surface Characterisation of Carbon Steel Exposed to Mixed Ce and Iodide Electrolytes

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Abstract: The protection of ferrous metals in acidic environments is important in many industries. Extending the pH range of organic inhibitors to low pH has been achieved with the addition of iodide ions, which facilitate adsorption. It was of interest to see whether similar outcomes could be achieved with inorganic inhibitors. To this end, this paper examines the influence of potassium iodide addition on the level of corrosion protection provided by $Ce(NO_3)_3$ in 3.5% NaCl electrolytes over a pH range of 2.5 to 8. Potentiodynamic polarization was used to assess percentage inhibitor efficiency (*IE*%), and scanning electron microscopy, energy dispersive X-ray spectrometry, and X-ray photoelectron spectroscopy were used to characterize the corrosion product. It was found that KI alone provided only poor corrosion inhibition except at pH 2.5, where nearly 85IE% was achieved. Its addition to the cerium electrolytes was generally in excess of 90% and over 97% for the optimum concentration. The addition of KI seemed to change the mechanism of formation of corrosion products from predominantly Fe₂O₃ to a mixture of FeOOH, Fe₃O₄, and Fe₂O₃, which were more adherent. Corrosion protection was extended to pH 4, but under the conditions explored here, no additional protection was evident at pH 2.5.

Keywords: carbon steel; cerium (III) salt; pH; potassium iodide; synergistic effect

1. Introduction

In recent decades, there has been a strident interest in finding new inhibitors for corrosion prevention [1–5]. This search has been driven by a desire to find more environmentally friendly inhibitors to replace chemicals that represent environmental and health risks [6–10]. In this context, the authors recently reported on the combined effects of Ce and iodide ions for corrosion protection of aluminium alloy 2024-T3 and found a synergistic reaction between the two in acidic environments [11]. The choice of these two elements was based on the well-known protective properties of cerium compounds for aluminium alloys [12,13] and the enhancement effect of iodide ions on organic corrosion inhibitors for both Fe and Al alloys, particularly at low pH [14–21]. Protection at low pH involved a combination of two mechanisms: (i) the formation of insoluble Cu-iodides, particularly at inclusions (in this case Cu-containing intermetallic particles); and (ii) the adsorption of iodide ions onto the surface of hydrated oxide in competition with chloride ions. Thus, these results showed that the synergistic effects demonstrated by iodide ions on organic inhibitors could be extended to inorganic inhibitors.



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In the current paper, the authors examine whether these inhibition qualities are observed in the case of iron. Clearly, the mechanism of protection will be different with a ferrous metal. First, the formation of insoluble Cu-iodides will not play a role since Cu is not a major alloying component of mild steel. However, the adsorption of iodide ions in competition with chloride ions can still play a significant role in mitigating corrosion. Second, the presence of adsorbed iodide ions may facilitate the adsorption of cerium ions, thereby improving corrosion resistance. For ferrous metals and inorganic ions, iodide is reported to facilitate the formation of γ -Fe₂O₃ in NaNO₂ solutions [22]. It is widely reported that La ions provide better protection than cerium ions [4,23,24], which is attributed by Yasakau et al. as being due to differences in the protective properties of La and Ce hydroxides that form on the surface [24], although complexing may change this order [25]. Cerium nitrate has been investigated as an inhibitor of ferrous metal corrosion [26–28]. It was found that approximately 3×10^{-3} M of Ce(NO₃)₃ resulted in the maximum effect, producing a protective coating consisting of lepidocrocite and Ce(III) compounds consisting of mixed hydroxides and carbonates.

In our previous paper, it was proposed that cerium ions can adsorb onto "capping" iodide ions to form a 2D protective layer. The capping iodide ions are absorbed in preference to chloride ions, as reported in a number of studies [14,17,20,22,29,30]. To some extent, the further absorption of cerium ions onto the capping iodide ions will be independent of the substrate metal. To investigate this hypothesis further, potentiodynamic polarization studies supported by weight loss studies, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM)/energy dispersive X-ray spectrometry (EDS) were performed on mild steel samples exposed to 3.5 wt% NaCl electrolytes containing either potassium iodide, cerium nitrate, or a mixture of the two. It should be noted that the presence of nitrate ions in solution may play an active role in corrosion activation or protection since nitrate itself and its reduction products such as nitrite may also play a role [22,31,32]. Indeed, the reactions of nitrate with iron are widely researched [33] for the purposes of nitrate reduction in agricultural runoff [34]. In the corrosion field on carbon steels, much of the work with nitrates/nitrites is focused on concrete reinforcement in calciferous neutral-alkaline media where nitrite is considered a good inhibitor [31,35,36].

2. Materials and Methods

2.1. Materials and Chemicals

Mild steel with a nominal composition of 0.05 to 2.1% C, <1.65 Mn, <0.6% Si, 0.4 to 0.6% Cu, and up to 0.33% S was used in this study. All chemicals used were of analytical-grade quality. Cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, (99%)), potassium iodide, KI, (99.5%), and sodium chloride, NaCl, (99%) were obtained from Sigma–Aldrich. Electrolytes used in this study were prepared with (\leq 10 Ω ·cm) deionized (DI) water. Solutions were prepared with different pH values (2.5, 4, 7, and 8) by adjustment with hydrochloric acid and sodium hydroxide solutions.

As noted previously, adjustment at higher pH (pH 7 and 8) resulted in a small decrease in the level of Ce present at pH 7 and a larger decrease at pH 8. The decrease in dispersed cerium was accompanied by precipitate formation, which was identified as cerium carbonates and hydroxides based on Raman spectra [11]. Because nitrate was not observed in the precipitate but Ce was, the cerium/ NO_3^- ratio changed with pH adjustment. The effect is small at pH 7, but at pH 8 and at the highest nominal concentration of cerium, the NO_3^- to cerium ratio in solution is almost double the make-up ratio.

For SEM and XPS, samples were ground on SiC papers from 240, 600, 800, and 1200, then polished using diamond abrasives from 6 to 3 to 1 μ m to produce a mirror finish. The samples were then exposed to various electrolytes for a period of 24 h, this time being similar to the experimental time for the potentiodynamic polarization experiments. Upon removal, they were rinsed with distilled water and dried under ambient conditions. Sample surfaces had a mixture of appearances ranging from dull metallic (compared to the polished condition) where corrosion product was removed to regions where the corrosion product

was retained, where samples showed some level of ochre to red-brown corrosion product. These were in patches for the higher pHs, but there was complete coverage for samples exposed to the lowest pH solutions. For the samples exposed to electrolytes containing only Ce ions, there was evidence of pitting at pH 7 and pH 8.

2.2. Immersion Experiments

The carbon steel sheet was cut into coupons of $2 \text{ cm} \times 2 \text{ cm}$. The emery paper used to polish these coupons ranged in grade from 600 to 1000. These MS coupons were cleaned in an ultrasonic water bath before being acetone-degreased. MS coupons were initially weighed using an analytical balance with four decimal digits.

Then, at various times, these coupons were fully immersed in a 100 mL beaker containing 3.5% NaCl solutions without and with the addition of $Ce(NO_3)_3$ and KI. They were dried and weighed once again. To validate the correctness of the findings, experiments were repeated, and the average amount of weight reduction was noted.

The surface coverage and inhibition efficiency (*IE*%) were calculated using the following equations:

$$\theta = \left(\frac{Wt_b - Wt_{inh}}{Wt_b}\right) \tag{1}$$

$$IE\% = \left(\frac{Wt_b - Wt_{inh}}{Wt_b}\right) \times 100 \tag{2}$$

where Wt_{inh} and Wt_b are weight loss in the presence of additives and in their absence, respectively.

2.3. Electrochemical Polarization Measurements

Electrochemical measurements were performed using a conventional three-electrode cylindrical perspex cell containing 200 mL of electrolyte. Titanium mesh was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All experiments were performed at room temperature. The cleaned specimens were fixed in the electrochemical cell with an exposed area of 3.14 cm². Polarization studies were performed under computer control using a Solartron model 1280B potentiostat at a scan rate of 0.25 mV/s. Corrview software was used for analyzing the experimental data. Before recording the polarization curves, the working electrode was maintained at its corrosion potential for 30 min until a steady state was obtained.

The inhibition efficiency (*IE*%) was calculated using the following equation:

$$IE\% = \left(\frac{I_2 - I_1}{I_2}\right) \times 100\tag{3}$$

where I_1 and I_2 are the corrosion current densities of carbon steel in the presence and absence of inhibitors, respectively. The presence of any synergism between Ce(III) and iodide ions was determined using the synergism parameter, S, which was calculated using:

$$S = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \tag{4}$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \times \theta_2)$; θ_1 is the surface coverage of the iodide ions alone, θ_2 is the surface coverage of Ce(III) ions alone, and θ'_{1+2} is the measured surface coverage for Ce(III) ions in combination with the iodide ions.

2.4. X-ray Diffraction (XRD)

A Bruker D8 Advance A25 X-ray Diffractometer (Bruker, MA, USA) operating under CuK α radiation (40 kV, 40 mA) equipped with a Lynx Eye XE-T detector was employed to obtain the X-ray diffractograms from these samples. The samples were scanned over the 2 θ of range 5° to 130° with a step size of 0.02° and a count time of 1.6 s per step. They were spun at 15 RPM during data collection. Analysis was performed on the collected XRD

data using the Bruker XRD search match program EVA[™]6 (Bruker, MA, USA). Crystalline phases were identified using the ICDD-JCPDS powder diffraction database.

2.5. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos AXIS Ultra-DLD spectrometer (Kratos, Manchester, UK) with a monochromated Al K α source (1486.6 eV). Binding energies were referred to as C 1s, with a binding energy of 284.8 eV. The presence or absence of Ce(IV) in the samples was determined using the v" peak as described previously and depicted in Figure 1 [37]. Additionally, account was taken of the Fe Auger peaks, which occur between the 3d 5/2 and 3d 3/2 peaks (Figure 1a). The Fe 2p spectra were analyzed using curve fitting, taking into account Fe metal, oxides, and carbonate ($Fe(CO_3)_3$). In the case of the oxides, account was taken of all multiplets for Fe₂O₃, Fe₃O₄, and FeOOH as described by Biesinger et al. [38] as well as satellite peaks. Multiplet separation and relative intensities were fixed with respect to each other (Figure 1b). While the presence of all these multiplet peaks looks complicated, the analysis effectively only involves optimization of four peaks since the multiplets relative position and intensity are fixed against the first peak occurring in the series. The data presented later in the paper combines all multiplets, thus showing only a single peak for each iron oxide/hydroxide. Shirley backgrounds were used in all XPS analyses. In the case where significant levels of cerium were detected on the surface, a Ce-Auger component was fitted to the Fe 2p3/2 spectrum along with the other components at 716.5 to 717.5 eV. The half width of this peak was wide and encroached into the upper end of the multiplet structures of the Fe components.



Figure 1. (a) Ce 3d spectral region (green) and Fe Auger lines (red). The v^{'''} peak indactes the presence of Ce(IV). (b) Example of fitting of the Fe 2p3/2 peak with multiplets for Fe₂O₃, Fe₃O₄ and FeOOH after Beisinger et al. [39].

2.6. Scanning Electron Microscopy

An FEI Quanta 400 (FEI, Hillboro, OR, USA) field emission environmental SEM was employed for the examination of the samples studied using XPS. Images, spectra, and maps were collected at a 15 kV accelerating voltage and a probe current of approximately 0.7 nA. Samples were mounted using either carbon bags or conducting carbon tape. No metal or carbon layers were deposited on the samples to reduce charging. This approach was adopted to facilitate the identification of carbonates in the surface layer. The carbonates were inferred where the C K α signal increased significantly in intensity. Maps were typically collected for 17 h. Compositions were determined using standardless energy dispersive X-ray analysis using the ESPIRIT software (Bruker, MA, USA). For scatter plot analysis, hyperspectral map datafiles (Bruker ".bcf") generated using ESPIRIT were exported to an ".epmx" format and analyzed using Chimage software (CSIRO, Canberra, Australia).

3. Results

The approach adopted here was first to optimize the cerium concentration and then to examine the influence of the addition of iodide ions.

3.1. Inhibition as a Function of Cerium Concentration

Figure 2 shows PDP curves for mild steel in 3.5% NaCl without and with various additions of $Ce(NO_3)_3$. The corresponding parameters from the Tafel fitting of the curves are presented in Table 1. From Figure 2, it can be seen that the addition of $Ce(NO_3)_3$ to solution results in a reduction of cathodic current densities and the movement of E_{corr} to more negative values, resulting in a separation between E_{corr} and the pitting potential (E_{pit}). The changes in the cathodic arm may be due to a combination of reactions, including the reduction of oxygen, water, and the waters of hydration. Nitrate (or a reduction product such as nitrite) might be contributing to the changes in the cathodic arm. In nitrate solutions, E_{corr} has been reported to move to lower potentials, but the opposite is observed for nitrite [40]. These results are similar to previously reported results for carbon steel exposed to cerium chloride-based nitrate solutions [27,28,32], although the opposite has also been observed [41]. There is movement in both the anodic and cathodic arms, with E_{corr} generally decreasing. Dastgheib et al. [26] observed that E_{corr} moved to more negative values as the levels of $Ce(NO_3)_3$ increased and that the kinetics of the cathodic arm went through a minimum.



Figure 2. Polarization curves for the dissolution of carbon steel in 3.5% NaCl solution adjusted to pH = 7, in the absence and presence of different concentrations of Ce(NO₃)₃ at room temperature.

Ce(NO ₃) ₃ Moles	i _{corr} μA	E _{corr} mV	β_a	β _c	Θ	IE%
0	2.30	-420.30	38.78	-142.71	0.00	0.00
$1 imes 10^{-3}$	1.40	-441.73	52.18	-142.24	0.39	39.35
$3 imes 10^{-3}$	0.57	-427.06	34.11	-80.81	0.75	75.42
$5 imes 10^{-3}$	0.32	-548.52	39.87	-59.61	0.86	86.00
$7 imes 10^{-3}$	0.07	-527.46	24.12	-87.12	0.97	96.97
$10 imes 10^{-3}$	0.26	-509.21	24.77	-126.08	0.89	88.69

Table 1. The effect of concentration of Ce(III) cation on the corrosion current density (i_{corr}), the free corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (βa , βc) and inhibition percentage (*IE*%) of mild steel in neutral 3.5% NaCl solution at 25 °C.

Table 1 shows that i_{corr} decreases with increasing Ce(NO₃)₃ concentration up to 7×10^{-3} moles, above which it again increases. This is reflected in the PDP curve for 7×10^{-3} moles of Ce(NO₃)₃ which displays the lowest current density around E_{corr} of all the curves. The E_{corr} values themselves displayed a range of potentials, but all of these were lower than in NaCl alone, indicating some level of corrosion inhibition, as demonstrated in the column for *IE*% and also presented in Figure 3.



Figure 3. Effect of concentration of $Ce(NO_3)_3$ on the inhibition percentage (%) for corrosion of C-steel in neutral 3.5% NaCl solution (pH = 7).

The Ce(NO₃)₃ concentration of around 7×10^{-3} moles is nearly two orders of magnitude higher than the optimum reported for AA2024-T3, reflecting the differences between the two different metals [11]. The suppression of corrosion in aluminum alloys varies from one alloy to another but is generally marginally better than for steels above a minimum lathanide ion concentration [42]. This concentration is around twice that observed by [26]. The decrease in *IE*% at the highest Ce ion concentration has been attributed in the case of CeCl₃ to the reduction of waters of hydration which has become an important reaction [43].

3.2. Inhibition of Ce, and Ce+I-Electrolytes as a Function of pH

In this section, the corrosion inhibition of the optimum Ce(NO₃)₃ concentration of 7×10^{-3} moles is investigated as a function of pH between 2.5 and 8.0 (Table 2). In addition, data for 1×10^{-3} M is included as a double check on whether the optimum Ce concentration found at neutral pH is still valid across the pH range. For the pH 4, 7, and 8 ranges, the PDP curves in Figure 4 show that the introduction of $Ce(NO_3)_3$ to 3.5% NaCl largely causes changes to the cathodic arms. The nature of the changes is different for the two different concentrations of Ce ions. Specifically, the addition of 7×10^{-3} M Ce(NO_3)_3 tends to activate the cathodic arm at lower potentials, whereas at 1×10^{-3} M Ce(NO₃)₃, there is also some activation at the lowest potentials but some suppression of activity at potentials immediately below the OCP. The changes in the cathodic arm are likely related to the reduction of a number of species and their relative concentrations, e.g., oxygen, nitrate, possibly nitrite (from reduction of nitrate), waters of hydration for the cerium aquo-ion [44], and even $Ce(NO_3)^{2+}$, which will become more common at higher concentrations [45]. There is little difference between the cathodic arms of the PDP curves for the two concentrations at pH 2.5, but the *IE*% is considerably higher in the presence of 7×10^{-3} M Ce(NO₃)₃. However, it can be seen that the *IE*% is greatest where 7×10^{-3} M Ce(NO₃)₃ is present in solution at pH 4 and 7, and similar at pH 8. There is suppression on the anodic arm at all pHs for 7×10^{-3} M Ce(NO₃)₃, but a small level of activation at 1×10^{-3} M Ce(NO₃)₃. The suppression at higher concentrations may be due to the presence of nitrate ions in solution. At pH 8, there are two conditions in the solution that have changed, including the nitrate/cerium ratio, which has increased to near 6, and the fact that and the solution is more alkaline.

Table 2. Effect of pH on the corrosion current density (i_{corr}), the free corrosion potential (E_{corr}), Tafel slopes (βa , βc), inhibition percentage (*IE*%) for mild steel in 3.5% NaCl solution with and without addition of either 1×10^{-3} M or 7×10^{-3} M Ce(NO₃)₃ at 25 °C.

pН	Concentrations Ce(NO ₃) ₃ M	i _{corr} μA/cm ²	E _{corr} mV	$\substack{\beta_a \\ mV/dec^{-1}}$	$egin{array}{c} \beta_c \ mV/dec^{-1} \end{array}$	IE%
2 5	0	10.44	-669.36	47.84	-92.55	0.00
2.5	$1 imes 10^{-3}$	41.03	-629.96	29.08	-93.98	-292.79
4	0	3.62	-446.90	75.11	-147.34	0.00
4	$1 imes 10^{-3}$	3.82	-512.00	30.93	-37.57	-5.31
7	0	2.30	-420.30	38.78	-142.71	0.00
/	$1 imes 10^{-3}$	1.40	-441.73	52.18	-142.24	39.35
0	0	1.49	-522.51	37.58	-99.86	0.00
0	$1 imes 10^{-3}$	0.53	-750.94	89.08	-88.10	64.29
2 5	0	10.44	-669.36	47.84	-92.55	0.00
2.3	$7 imes 10^{-3}$	6.94	-552.59	69.92	-126.51	33.56
4	0	3.62	-446.90	75.11	-147.34	0.00
4	$7 imes 10^{-3}$	0.00	-537.81	39.73	-85.82	85.24
7	0	2.30	-420.30	38.78	-142.71	0.00
	$7 imes 10^{-3}$	0.07	-527.46	24.12	-87.12	96.97
8	0	1.49	-522.51	37.58	-99.86	0.00
	$7 imes 10^{-3}$	0.78	-458.36	13.25	-104.00	47.57

The addition of 0.1 M iodide and Ce ions to 3.5% NaCl is examined in Figure 5 as a function of pH, which summarizes the *IE*% for various Ce-electrolytes as a function of pH from analyses of the PDP curves. The *IE*% for the 0.1 M KI electrolyte, labeled as the I-electrolyte here, is also presented in Figure 5 as well as in Tables 3 and 4 At pH 2.5, no inhibition is provided by the addition of 1.0×10^{-3} M Ce or any of the mixed electrolytes. Indeed, the mixed electrolytes display only antagonism compared to either 7.0×10^{-3} M Ce or the I-electrolyte alone. At pH 4 and above, however, all the mixed electrolytes show improved *IE*% compared to the I-electrolyte and, in some instances, better performance than the Ce-electrolytes alone. As can be seen in Table 4, there is a small

degree of synergism displayed in the case where there is 7.0×10^{-3} M Ce and 0.1 M I. Interestingly, the I-electrolyte shows a quite good *IE*% at pH 2.5. This is the pH at which it is expected to act competitively with chloride ions from adsorption sites. However, the addition of 7×10^{-3} M increases the inhibition to just under 80%, which is higher than the inhibitor efficiency of up to 60% reported for cerium sulphate [46]. The synergy between I and Ce will be explored in more detail in the SEM section, where the distribution of both ions is examined in more detail. The co-location of these two ions will provide some insight into the co-operative mechanism between them.



Figure 4. Polarization curves showing the effect of pH on the dissolution of C-steel in 3.5% NaCl solution in presence of 1×10^{-3} M and 7×10^{-3} M Ce(NO₃)₃. (a) pH 8, (b) pH 7, (c) pH 4, and (d) pH 2.5.



Figure 5. Effect of pH on the inhibition efficiency percentage (*IE*%) of (**a**) 0.1 M KI, (**b**) 1×10^{-3} M and 7×10^{-3} M Ce(NO₃)₃ and (**c**) 1×10^{-3} M and 7×10^{-3} M Ce(NO₃)₃ both with 0.1 M KI for corrosion of C-Steel in 3.5% NaCl solution at room temperature.

Table 3. Effect of addition of KI on the inhibition efficiency (%) of C-Steel in 3.5% NaCl solution at pH 2.5 and at various concentrations of $Ce(NO_3)_3$ at room temperature.

IE%	
-292.79	
-37.67	
25.22	
59.24	
33.56	
84.60	
73.68	
	<i>IE%</i> -292.79 -37.67 25.22 59.24 33.56 84.60 73.68

Table 4. Effect of the presence of I in the Ce+I electrolyte on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion inhibition as a function of pH. Blank = 3.5% NaCl.

pН	Electrolytes	i _{corr} μA cm ⁻²	E _{corr} mV	IE%	S
2.5	Blank (3.5% NaCl)	10.44	_	0.00	
	$7 \times 10^{-3} \text{ M Ce(NO_3)_3} + 0.1 \text{ M KI}$	1.61	-487.78	84.60	1 1 /
	0.1 M KI	2.75	-559.61	73.68	1.14
4	Blank (3.5% NaCl)	3.62	-446.90	0.00	
	$7 \times 10^{-3} \text{ M Ce(NO_3)_3} + 0.1 \text{ M KI}$	0.51	-579.19	85.84	0.74
	0.1 M KI	2.58	-422.51	28.67	0.74
7	Blank (3.5% NaCl)	2.30	-420.30	0.00	
	$7 imes 10^{-3} \text{ M Ce}(\text{NO}_3)_3 + 0.1 \text{ M KI}$	0.19	-524.87	91.61	0.00
	0.1 M KI	0.58	-389.99	74.91	0.09
8	Blank (3.5% NaCl)	1.49	-522.51	0.00	
	$7 \times 10^{-3} \text{ M Ce}(\text{NO}_3)_3 + 0.1 \text{ M KI}$	0.20	-582.94	86.60	5 10
	0.1 M KI	1.95	-396.42	-30.35	5.10

3.3. SEM Characterisation of Surfaces Exposed to Electrolytes as a Function of pH at 24 h

The focus of characterization in this section moves onto examining the optimum Ce+I electrolyte $(7 \times 10^{-3} \text{ M Ce}(\text{NO}_3)_3 + 0.1 \text{ M KI})$ plus the individual Ce- $(7 \times 10^{-3} \text{ M Ce}(\text{NO}_3)_3)$ and I-(0.1 M KI) electrolytes of the same compositions. The aim is to characterize the type and distribution of insoluble corrosion products on the surface of mild steel after 24 h exposure to the I, Ce, and Ce+I electrolytes. Here the term "insoluble" is a reference to

the fact that soluble deposits on the surface have been removed because of rinsing with DI water.

Figure 6 shows low-magnification SEM images of the surfaces of mild steel after exposure to the various electrolytes at pHs ranging from 2.5 to 8.0. Generally, the corrosion product (CP) that developed on the surface was heterogeneous, with areas of heavy and light CP. The different compositions of electrolytes had their own unique features. After exposure to the I-electrolyte, the CP that developed was only loosely bound to the surface, so a significant fraction was removed during rinsing. The CP left after exposure to the I-electrolyte alone comprised mostly spherical particles with needle-like crystal growth, as seen in Figure 7a. In cases where there was a large amount of CP remaining on the surface, as seen in Figure 6, then it was composed of these types of particles. There were also areas with locally heavier deposits, reflecting local attacks.



Figure 6. Low-magnification secondary electron emission micrographs of typical features developed on the surfaces of specimens after 24 h exposure to the various electrolytes containing the specified inhibitors. Each Row is a different pH, which is indicated by the number. To provide some insight into typical features, the matrix and corrosion products are labeled "M" and "CP", respectively.



Figure 7. Images of different kinds of surface features that have been classified into embedded (color coded orange) and free precipitate (color coded green)—see text. (**a**) spherical polycrystalline features were observed in KI at all pH values. In 7×10^{-3} M Ce, there were (**b**) particles embedded into a solidified gel on the surface and (**c**) free particles. For 0.1 M KI + 7×10^{-3} M Ce, there were a range of particles, including (**d**) flaky particles emanating from, (**e**) solid particles embedded into a solidified gel on the surface, and (**f**) solid free particles, as well as (**g**) small spherical polycrystalline particles (at pH 2.5). (**h**) example of disbondment between embedded particles and solidified gel. (**i**) A third type of growth observed where cerium ions were present at some level was an adherent parallel plate-like structure.

The CP on the surfaces of samples exposed to the Ce-electrolyte was generally more adherent, but as with the I-electrolyte, there were areas of heavy and light deposits. Where CP remained on the surface, there were examples of particles embedded into a solidified gel on the surface as well as free particles (Figure 7b,c, respectively). In both cases, the presence of spherical particles suggests that they form around nuclei in solution, so the surface would not have an influence on their shape (i.e., make them non-spherical). With the embedded particles, it is proposed that they form within a gel layer on the surface but without influence from the surface, which would explain their spherical shape. It is assumed that as the gel dries, these particles become trapped in the resulting solidified material. The bond between the two does not appear to be strong, as disbondment can be observed between the two in many instances (e.g., Figure 7h). The spherical particles themselves seemed to form two classes, with one type being needle-like and the other having a flaky appearance. This appearance is consistent with the morphology of α -FeOOH and γ -FeOOH based on the needle-like and platelet structures, respectively [41,47]. There is a considerable difference in the sizes of the two features, with the solid particles formed in the gel typically being a few microns, whereas those formed in the solution are much finer. In addition, there was significant filiform corrosion at all pH values with exposure to the Ce-electrolyte. SEM examination of these features suggests that the filiform grew along the surface of the metal beneath a surface layer, which may well be the same gel in which the larger precipitates were formed. The structure within these filliforms showed domains of a regular lamellar structure, such as seen in Figure 7h, which form the filament tail. These lamellar are again typical of iron hydro-oxides and potentially green rusts since the environment within the filiform is likely to be anaerobic and the pH in the tail is likely to be

presumably due to the local environment in which they are formed. For the Ce+I electrolyte, the CP seemed heavier and more adherent than for either of the other two electrolytes. There were far fewer filiforms, which were replaced by more extensive coverage of the surface with other types of corrosion products. The number of different types of features was larger than for either the I or the Ce electrolytes and seemed to combine all the features of the individual solutions. Thus, there were a range of particles, including flaky particles emanating from the solidified gel (Figure 7d), solid particles embedded into a solidified gel (Figure 7e), free solid particles (Figure 7f), as well as small spherical particles with a polycrystalline needle-like structure (only observed at pH 2.5). A third type of growth, very similar to the structure observed in the filiforms (Figure 7i), was observed extensively across the surface and classified as surface growth (Figure 7i). Given that EDS analyses (see table in Appendix A.2) indicate a predominance of Fe and O with smaller amounts of other elements, it is suggested that this growth is a form of Fe-hydro-oxide. Since its appearance is similar to that in the filiforms, it is possible that it might be green rust, but its presence is unlikely because anaerobic conditions would be required for its formation and that it rapidly oxidized to either Fe₂O₃, α -FeOOH, or γ -FeOOH [47,48]. Examples of the typical compositions of these features are provided in Table A1.

alkaline [47-49]. Thus, there is a broad range of surface features with different appearances,

As noted above, the distribution of corrosion product on the surface of the samples was very heterogeneous, but some common features were observed and highlighted in Figure 7. For example, the central part of Figure 8 shows an SEM image of corrosion product after exposure to Ce+I electrolyte at pH 4 for 24 h. Some of the types of features depicted and described in Figure 7 are highlighted in the side images in Figure 8. The regions in pink have low but significant levels of I and less Cl, whereas those in mauve have a greater mixture of both ions based on the color mix. Indeed, those in pink were most often observed where much of the corrosion product had broken away and the Fe content was much higher, indicating a thin oxide. This suggests that iodide ions are interacting more with the surface of the mild steel than chloride ions. (This was also observed using XPS; see Section 3.5). The pastel yellow color is where there are higher levels of cerium. These types of sites are a mixture of claypan structures with/without precipitates on them. Importantly, many of the features identified in Figure 7 and highlighted in Figure 8 show a similar mauve color. This suggests that they may have similar compositions, and it may not be possible to uniquely identify them on the basis of composition alone.

Scatter plots were used to further explore whether these features had unique compositions. The scatter plots were constructed using the intensity of one element plotted against the intensity of another element (e.g., Fe to O). In this way, all points on a map are examined, and those with a common ratio (e.g., Fe/O) form a cluster in the scatter plot. An example is shown in Figure 9. The spectra for the regions labeled 1 to 6 in the map in Figure 8 are presented in Figure 9a. C, O, Fe, Cl, I, and Ce were detected in this series of spectra, and the positions of the main lines for each elemental X-ray series are presented in the figure. (Note: there are sum peaks detected in all spectra at some level.) The corresponding Fe-O, Ce-O, and Fe-Ce scatter plots for all pixels in the map are presented in Figure 9b using a "magma" color scale to indicate the density of points (orange and yellow are high density, and purple is low density). To the right of these whole-map scatter plots are scatter plots in grayscale (representing all the sample) with an overlay of blue points representing only the pixels that contribute to each of spectra $1 \rightarrow 6$ (each point represents the elemental ratio in an individual pixel enclosed by the white dashed circles in Figure 8). Looking at the Fe-O scatter plot for each, it is immediately clear that all spectra share largely common positions. On the Ce-O scatter plot, spectra from areas 1, 2, and 6 have more points that

are Ce-rich, but there are other points that also overlap with the other spectra that are Ce-poor. A similar situation exists for the Fe-Ce scatter plot, where all spectra occupy a similar space in the scatter plot, but the cerium-rich ones (1, 2, and 6) also extend along the Ce arm consistent with their higher cerium levels.



Figure 8. SEM and EDS analyses of corrosion products on the surface of mild steel after exposure to Ce+I -electrolyte (0.1 M KI + 7×10^{-3} M Ce(NO₃)₃) at pH 4 for 24 h. Central image is a composite of an SE image with superimposed O, Cl, Ce, and I elemental maps, with the color code highlighted in the image. There are four images of areas of interest, with positions indicated by the white dashed rectangles. The numbered dashed circles indicate where spectra have been collected and are presented below.

On the basis of these analyses, it can be concluded that it is not possible to definitively separate out, at a statistically significant level, these different features based on composition alone. This is not surprising given that the O/Fe ratios of Fe₂O₃, Fe₃O₄, FeOOH, and $[Fe(II)_{1-x}Fe(III)_x(OH)_2]^x$ (green rust anion) have O/Fe ratios of 1.5, 1.3, 2.0, and potentially >2.0 (if oxygen-containing cations are included), respectively. Given that there will also likely be waters of hydration, any differences in composition will be difficult to pick up using EDS.

On the other hand, for the purposes of interpreting the XPS data, it seems generally that cerium is associated more with larger particulates deposited on the surface of mud-crack structures or embedded into them; iodide is associated with some mud-crack structures as well as at the interface with the underlying metal; and there are "surface growths" that appear to be mainly iron-containing corrosion products such as Fe₂O₃, and Fe₃O₄, FeOOH.



Figure 9. (a) EDS spectra and (b) scatter plot analysis of the map collected from mild steel after exposure to $0.1 \text{ M KI} + 7 \times 10^{-3} \text{ M Ce}(\text{NO}_3)_3$ at pH 4 for 24 h, as depicted in Figure 8a. The numbers associated with each spectrum are depicted in Figure 8 and only the highest intensity line for each element in each series is labeled. (b) Fe-O, Ce-O, and Fe-Ce scatter plots using a magma color scheme to highlight where the greatest number of points fall and the corresponding points in blue for each spectrum.

3.4. X-ray Diffraction

Clearly, the SEM results indicate a crystallite structure within the corrosion product. X-ray diffraction was used to further characterize any crystalline phases on the sample surfaces with diffractograms for the three different electrolytes at pH 4 presented in Figure 10. Table 5 presents a qualitative assessment of the level of contribution of different phases to the overall composition of the corrosion product.



Figure 10. X-ray diffractograms collected from the surfaces of samples exposed to various electrolytes at pH 4. These patterns show the major lines of species observed for all samples, although the ratio of species varied with the pH of the electrolytes. Species included Fe metal (*), Lepidocrocite (Δ) and Akaganeite (\oplus). All peaks between 0 and 70° apart from the metal reflections are combinations of the two iron oxy-hydroxides.

Table 5. Summary of X-ray Diffraction Data for various samples, including I (0.1 M KI), Ce (7×10^{-3} M Ce(NO₃)₃) and Ce+I (mixture of compounds).

Sample	Lepidocrocite γ-FeOOH Red-Reddish Brown	Akaganeite β-FeOOH Metallic-Brown	Goethite α-FeOOH Brownish Yellow to Orange-Yellow	Luogufengite Fe ₂ O ₃ Rust-Red
Morphology	Scales aggregated into rossettes	Rod like		
		KI		
2.5	Major		Minor	
4.0	Major		Minor	
7.0	Trace		-	
8.0	Major		Minor	
		Ce		
2.5				
4.0	Major	Trace	-	Amorphous
7.0				
8.0	Major			
		Ce+I		
2.5	Major	Minor	-	Poorly Crystalline
4.0	Major	Major	-	Poorly Crystalline
7.0	Minor	Major	-	Poorly Crystalline
8.0	Minor	Major	-	Poorly Crystalline

Overall, the dominant phases present in the corrosion product were different polymorphs of FeOOH, namely lepidocrocite and akaganeite, with some minor amounts of goethite, the latter only observed on the surface exposed to the I-electrolyte. Akaganeite can contain chloride, but it is not clear how this extends to other halides such as iodide. While Ce was detected in the corrosion product using EDS, no crystalline phases containing Ce were identified, meaning that it must be present as either an amorphous phase or as very fine trace crystallites.

In the I-electrolyte and across the whole pH range, lepidocrocite was the major phase observed, with some minor amounts of goethite. Thus, the needle-like crystallites observed in SEM (Figure 7) on these surfaces can be identified with lepodocrocite. This morphology is consistent as other reports for lepodocrocite [50,51]. The chloride-containing akaganeite was not observed in the corrosion products developed in this electrolyte. In the Ce-electrolyte, lepidocrocite was, again, the major phase, with some traces of akaganeite and Fe₂O₃ formed at pH 4. Clearly, the conglomerate phase (observed using SEM and containing embedded particles) is poorly crystalline or amorphous since no characteristic reflections for any Ce-compounds were found. There were no minor traces of goethite observed. For the mixed Ce+I electrolyte, the mix of polymorphs of FeOOH was significantly different, with akaganeite being the major polymorph at pH 4.0, 7.0, and 8.0 and lepidocrocite being a major component at pH 2.5 and 4.0. Poorly formed hematite was observed at all pHs in this mixed electrolyte. Since lepidocrocite can only be formed through green rust, but akageneite can be formed by direct hydrolysis of ferric ions, the presence of this latter phase suggests a change in the pathway by which corrosion products are formed in the mixed electrolyte.

3.5. XPS Analyses

Having seen some general trends of elemental distribution based on the EDS mapping and identified the crystalline phases using XRD, it is easier to classify the observations made using XPS and try to understand some of the local chemistry of these sites.

Generally, Fe, O, C, and Cl were detected on all samples, and, in addition, either I, Ce, or both were detected on samples exposed to electrolytes containing these ions. As mentioned in the experimental section, XPS analyses of the Fe 2p3/2 peak were appropriately fitted using the multiplet structures of three different types of oxides/hydroxides: Fe₂O₃, Fe₃O₄, and FeOOH, with an example where the three different compounds are identified presented in Figure 11a. It is not possible to separate α -FeOOH (goethite) either β -FeOOH (16kageneite) or γ -FeOOH (lepidocrocite) in XPS. As a note, in the literature, it is common for single symmetric peaks to be used to fit these different oxide components, but clearly the shape for each type of oxide is not symmetric due to the multiplet structure (Figure 11a), thus stressing the importance of including the multiplet structure in fitting.



Figure 11. XPS spectra for (**a**) Background subtracted Fe 2p3/2 spectrum with fitted components including Fe₂O₃_green, Fe₃O₄—blue, and FeOOH—pink. Multiplet structure for each oxide has been added together to produce one peak). The Shirley background has been removed to isolate the peak shape. The inset shows the original spectrum. (**b**) C 1 s with fitted components as labeled.

Overall, a mixture of Fe-oxides/hydroxides was observed using XPS (Figure 12) on the surface, bearing a partial similarity to the observations reported for EDS and XRD. In addition, carbonate was detected on all samples, but because no crystalline carbonate phases were detected in XRD, the carbonate is assumed to be an adsorbed species. This species is not siderite (FeCO₃) based on the XPS curvefitting and is not incorporated into Figure 12. Thus, for the I-electrolyte, Fe_2O_3 and FeOOH (lepridocrocite from XRD) were the main components, with the amount of FeOOH reaching a minimum at mid pH and Fe_2O_3 reaching a corresponding maximum at mid pH (Figure 12a). The Fe_2O_3 must be amorphous or present as a thin layer because it was not detected in XRD. For the Ceelectrolyte, the overall trend was similar, but a larger percentage of Fe₂O₃ was generated at pH 4 (Figure 12b). The XRD indicated that the FeOOH was lepridocrocite but also that no Fe_2O_3 was observed, suggesting, as with the I-electrolyte, that it is amorphous or present as fine crystallites. In the Ce+I electrolyte, there are some subtle differences from the other two electrolytes (Figure 12c). First, there is significantly less FeOOH generated at low pH, but it is still mostly lepodrocite with a small amount of akageneite. The amount increases with pH, whereby a significant fraction of FeOOH is generated at neutral pH in the form of akageneite. There is a slight increase in Fe_3O_4 at lower pH. Significantly, there is a large increase in the amount of Fe₂O₃ generated at lower pHs, which XRD suggests could be luogifengenite (ε -Fe₂O₃).



Figure 12. Percentage of FeOOH, Fe_3O_4 , and Fe_2O_3 for the electrolytes: (**a**) iodide-electrolyte, (**b**) cerium-electrolyte, and (**c**) iodide and cerium electrolyte. Data is presented in pairs of colored bars, representing duplicates. The different colors codes indicate the different pH (2.5, 4, 7, 8). Color codes are the same across (**a**–**c**).

For the C 1s spectrum (Figure 11b), typical adventitious carbon peaks (C-C and C-O) arising from carbon contamination were observed [52]. However, there were two peaks of interest at higher binding energies. For the series of samples where only I⁻ was present in solution, a peak occurred at ~288.7 eV consistent with the presence of carbonate ions but not consistent with FeCO₃, which has a peak around 290.1 eV [38]. Moreover, the fitting of the corresponding Fe 2p3/2 spectra with FeCO₃ (incorporating full multiplet breakdown) resulted in a poorer fit to the data than with Fe₃O₄, suggesting that siderite was not present, leading to the conclusion that the carbonate ions might be adsorbed onto the surface of the oxides and/or FeOOH particles present in the corrosion product [47,48]. Bicarbonate is another possibility, with both the C1 s and the HBE O1 s having similar positions to Na and K bicarbonates [53]. This, however, cannot be considered a unique assignment. It should be noted that the presence of carbonate can be considered a contaminant since it is not a component of the electrolyte, but it is also a significant contribution to the XPS and therefore needs to be considered in the overall scheme. Indeed, Dastgheib et al. [26] and Forsyth et al. [4] attribute this species to a cerium (III) carbonate based on FTIR, with the likely source being HCO_3 from dissolved CO_2 in the electrolyte. In the case of the Ce and Ce+I electrolytes, an additional component was observed at ~289.7 eV, which is consistent with $Ce_2(CO_3)_3$ or $CeOCO_3$ [54]. The O 1s also showed a range of components that can be

broadly divided into (i) oxide (~529.5 eV), (ii) carbonates and hydroxides (~532 eV), and C-O and adsorbed water (>~533eV). Some of the detailed changes in these photoelectron spectra are discussed below.

With respect to composition, the O/Fe, Ce/Fe, Cl/Fe, and I/Fe results are presented in Figure 13 and full analyses expressed in elemental at.% are presented in Table 6. No nitrogen species were observed using XPS. As seen in the SEM section, samples generally had a loose corrosion product layer (labeled CP) on top of the carbon steel (labeled M for metal), so analyses were performed on both these regions where possible. The layer on the M-surface is likely to be most relevant for corrosion protection.



Figure 13. XPS analyses (at. %) for samples exposed to either 0.1 M I-electrolyte, 7×10^{-3} M Ce-electrolyte, or Ce+I electrolyte for 24 h. (a) O/Fe, (b) Ce/Fe, (c) Cl/Fe, and (d) I/Fe.

For the CP after exposure to I-electrolytes, there was a distinct difference in composition (Table 6) between the lower pH (2.5 and 4), where more Fe and O were detected, and pH 7 and 8. The O/Fe ratio (Figure 13a) was consistently around 1.5, implying that Fe₂O₃ was the main oxide present on the surface. The XPS fitting of the Fe 2p3/2 matched this analysis, as seen in Figure 12a. The Cl/Fe levels were similar for both sites across all pHs (Figure 13c) and were the lowest of all three electrolytes. The I/Cl ratio (Figure 13d) showed the same trend for both sites (CP and M), with higher ratios at pH 7 compared to lower pH.

Different trends were observed in the case of exposure to 7×10^{-3} M Ce ions, mainly because there were significant levels of Ce detected in both the CP as well as on the metal (Figure 13c). At low pH, around 3 at.% of Ce(III) was detected, but this increased at pH 4 and above to around 4 to 5 at.% in the CP and between 6.3 and 7.3 at.% in the metal. The presence of Ce(III) is largely consistent with the speciation analysis of cerium ions in solution, although some Ce(IV) might be expected at pH 2.5 [55]. Since the SEM/EDS results indicate that the highest levels of Ce were observed in the regions containing embedded particles, it can be assumed that much of the Ce detected in XPS is from these regions. Oxygen levels were consistently in the 38 to 40 at.% range for all the samples, but the O/Fe ratios were generally higher for the CP ($3.7 \rightarrow 4.3$) than the M ($2.0 \rightarrow 2.5$) (Figure 13a). This is largely due to the incorporation of Ce into both the CP as well as on

the metal surface, thus reducing the Fe at. % (Figure 13c), but there is also a contribution from the higher level of FeOOH observed from the XPS curvefitting. Most notably, the C concentrations in the CP and on the metal surface were twice as high as after exposure to the I-electrolyte, with the highest levels recorded at pH 7 and 8 (Table 6). The C 1s spectra for these samples showed that there were significant levels of carbonate formed at both types of sites. The strong correlation of the Ce and CO_3^{2-} can be seen in Figure 14b, where the normalized values are plotted against pH for the CP and M. The correlation between the two is obvious at pH 4 and above, and along with the C 1s binding energy of the carbonate component, it suggests the formation of either Ce₂(CO₃)₃ or Ce(OH)CO₃ since Ce(III) is the major component of the Ce3d spectra [26,54,56]. The strong correlation of the Ce and CO_3^{2-} contrasts with the I-electrolyte, where the CO_3^{2-} tends to reflect the Fe signal. It is interesting to note that although carbonate is not part of the electrolyte, it is present, particularly in the oxide layer described as M, and the levels follow a consistent trend.

Table 6. XPS elemental analyses in atomic percent for carbon steel exposed to 0.01 M NaCl containing various inhibitors including 0.1 M I, 7×10^{-3} M Ce and a mixture of both. CP = corrosion product and M = metal.

	pH 2.5		pH 4		pH 7		pH 8	
Element	СР	Μ	СР	Μ	СР	Μ	СР	Μ
				I-Electrolyte				
Fe	35.8 ± 0.5	34.4 ± 1.3	36.0 ± 0.4	29.2 ± 0.5	30.5 ± 0.5	30.8 ± 0.5	31.5 ± 1.0	30.8 ± 0.7
I (×10 ²)	1.51 ± 0.4	14.0 ± 0.7	2.0 ± 1.0	6.5 ± 1.5	17.0 ± 0.9	27.0 ± 9.0	14.5 ± 7.5	7.5 ± 0.5
0	51.8 ± 0.1	47.3 ± 1.9	52.3 ± 0.3	44.3 ± 0.3	42.0 ± 0.2	40.5 ± 0.1	46.9 ± 3.0	41.9 ± 0.1
С	11.7 ± 0.6	17.5 ± 2.1	11.0 ± 0.1	23.4 ± 1.0	24.6 ± 0.3	26.6 ± 0.5	20.7 ± 4.5	26.2 ± 0.9
Cl	0.33 ± 0.01	0.35 ± 0.10	0.22 ± 0.01	0.15 ± 0.15	0.09 ± 0.09	0.22 ± 0.04	0.26 ± 0.08	0.12 ± 0.05
				Ce-electrolyte	!			
Fe	21.6 ± 2.5	21.8 ± 4.7	16.6 ± 0.2	8.5 ± 0.4	14.8 ± 0.6	10.1 ± 0.1	16.1 ± 1.0	10.7 ± 0.6
Ce	3.0 ± 0.8	2.9 ± 0.4	5.4 ± 0.3	7.3 ± 0.1	4.1 ± 0.1	6.3 ± 0.1	4.6 ± 0.4	7.2 ± 0.2
0	39.9 ± 1.1	39.7 ± 1.8	38.4 ± 0.2	36.7 ± 0.3	39.7 ± 0.1	38.4 ± 0.3	40.4 ± 1.3	40.4 ± 0.5
С	34.8 ± 2.6	34.6 ± 6.0	39.1 ± 0.5	46.7 ± 0.1	40.6 ± 0.5	44.5 ± 0.3	38.5 ± 0.7	40.6 ± 0.7
Cl	0.39 ± 0.04	0.62 ± 0.06	0.19 ± 0.02	0.34 ± 0.01	0.30 ± 0.01	0.46 ± 0.01	0.33 ± 0.10	0.61 ± 0.06
			(Ce+I electrolyt	e			
Fe	34.9 ± 1.2	31.0 ± 2.1	32.2 ± 0.9	28.8 ± 0.8	32.1 ± 1.4	22.3 ± 2.3	31.6 ± 1.8	31.3 ± 3.3
Ce	-	0.5 ± 0.6	-	0.4 ± 0.3	0.5 ± 0.5	-	0.04 ± 0.03	1.0 ± 1.9
Ι	0.05 ± 0.01	0.25 ± 0.21	0.12 ± 0.03	0.16 ± 0.05	0.18 ± 0.10	0.16 ± 0.01	0.12 ± 0.02	0.08 ± 0.01
0	50.4 ± 0.86	44.4 ± 6.0	48.1 ± 1.3	48.6 ± 1.9	47.2 ± 2.0	40.2 ± 1.3	47.0 ± 0.8	47.3 ± 0.9
С	13.9 ± 1.7	19.4 ± 4.4	18.6 ± 2.0	19.8 ± 2.6	18.8 ± 2.5	32.5 ± 2.7	20.0 ± 2.9	19.0 ± 1.5
Cl	0.37 ± 0.17	0.27 ± 0.10	0.58 ± 0.14	0.33 ± 0.12	0.74 ± 0.34	0.29 ± 0.19	0.50 ± 0.08	0.42 ± 0.08



Figure 14. Normalized atomic percent for Fe, Ce, I, and CO_3^{2-} as a function of pH for the electrolytes containing (**a**) I, (**b**), Ce, and (**c**) Ce plus I. Vertical yellow regions indicate CP, whereas the white ones are for metal.

The results for the Ce+I electrolyte were quite different from those of either of the other two electrolytes. The SEM indicates that there was a wider variety of different morphologies for the corrosion product in these mixed electrolytes (Figure 7), and the XRD shows the appearance of akageneite instead of lepidocrocite. For the CP, the Ce/Fe ratios were much smaller than when Ce was the only inhibitor in the electrolyte. The highest Ce levels observed using EDS in the SEM were from the surface particulates and the embedded particles. The O/Fe and Cl/Fe ratios for Ce+I electrolyte falls between those of I and Ce electrolytes. The Cl/Fe in the case of Ce+I-electrolyte falls between the

other two electrolytes, suggesting that iodide impairs the incorporation of chloride into both the mud crack structure and the precipitates. In fact, the I/Cl ratio is close to 1 for the CP at pH 2.5 but between 0.2 and 0.5 for all other conditions. This figure is well above the value for the I-electrolyte, indicating an influence of the Ce ion on adsorption. On the M areas, high levels of Ce were detected in the Ce-electrolyte but lower levels for the Ce+I electrolyte. Again, this is similar to the EDS results on the matrix, where both Ce and I ions were detected, but the level of Ce was much lower in the presence of iodide ions. So both the EDS and the XPS results indicate that both iodide and cerium ions may be playing a combined role in protecting the surface of the matrix. Carbonate was detected on these surfaces, but the strong correlation between C and Ce seen in the Ce-electrolyte (Figure 14b) was not evident in the Ce+I electrolyte, thus suggesting a mixing of mechanisms with lower pHs looking more like the I-electrolyte and higher pHs displaying behavior more like the Ce-electrolyte (Figure 14c).

4. Discussion

Proposed pathways for the Fe-based protective layer (PL) and corrosion products (CP) are presented in Figure 15 and follow Suzuki [50] for major pathways for precipitation from Fe^{2+} and Fe^{3+} aquo species. Minor amounts of product may form via linkages excluded in Figure 15 and new linkages may also become apparent in other electrolytes [57]. These major pathways are the routes for the eventual formation of species such as FeOOH and Fe_2O_3 , which are considered the basic components of the PL. It should also be kept in mind that for the electrolytes containing Ce ions, the characterization techniques presented above indicate that there are parallel precipitation processes for these species, as discussed below.

The formation of any protective layer and corrosion products on mild steel is a complex process that starts with the oxidation of the underlying metal to form Fe^{2+} . From here, there can be further oxidation (Path I in Figure 15 and the formation of Fe(III) solution species. In parallel, there can be the formation of mixed Fe(II) and Fe(III) aquo-species (Path II in Figure 15). Along Path II, there is a further division based on pH: acidic pH 2.5 and 4, and neutral to alkaline pH 7, 8. These two regions represent a division in formation mechanism where, at the acidic pH, CP formation is probably via hydrolysis and deprotonation reactions of iron-aquo species, eventually resulting in the precipitation of magnetite (Fe_3O_4), but in alkaline solutions, corrosion product formation is via a green rust intermediate and the formation of lepidocrocite (γ -FeOOH) [48]. This is because green rust can only form above pH 6.0 because the FeO_6 octahedra (a basic constituent of GR and the hydro-oxide) dissolve at pH < 6 [47,48]. Obviously, the background pH is not as relevant as the local pH since lepidocrocite, which is formed only through green rust, was detected at all pHs in the I- and Ce-electrolytes, suggesting a locally higher pH than the background electrolyte in the case of the acid electrolyte. It is worth noting that in this study, the green rust precursors are likely to be type I green rusts such as hydrochloro green rust (GR1(Cl⁻)) and/or hydroxycarbonate green rust GR1(CO₃^{2–}). The carbonate-based green rust has been included because of the detection of carbonates, presumably resulting from the atmospheric contamination from absorbed CO₂. These precursors are transient species, with reports in the literature suggesting that $GR1(CO_3^{2-})$ completely dissolves 2 to 3 h after exposure to an oxidizing atmosphere [47]. Given that the exposures in this study are for 24 h, any GR should be fully converted to the end products. In the following, we look at how the presence of iodide and cerium ions might influence protective layer and corrosion product formation. While nitrate ions are present in two of the three electrolytes, there was no evidence of them (or nitrites or amines) in XPS, meaning that no conclusion on the role of nitrates or their reduction products can be drawn. It can be noted, however, that potentiodynamic polarization curves for electrolytes containing $Ce(NO_3)_3$ are different from simple nitrate (or nitrite) salt solutions, and the amount of lepidocrocite formed in the presence of $Ce(NO_3)_3$ no greater than in the iodide case (nitrate reduction would



facilitate lepidocrocite formation). This is largely due to the widespread deposition of cerium-based compounds.

Figure 15. Pathways for generation of protective layers and corrosion products for iron-containing species. Yellow arrows and "I" label indicate iodide-only electrolytes; green arrows and "Ce" label indicate Ce-only electrolytes; and blue arrows and "Ce+I" label are for electrolytes containing both Ce and I ions. Red-brown hatched outlines indicate precipitated products that can form either the protective layer, the corrosion product, or both, and the blue hatched outlines represent the solution species. This figure pertains to sites on the surface where Fe ions are generated, which are expected to be the anodes. At cathodic sites, there will be precipitation of Ce(III) compounds, which are largely expected to be Ce(OH)₃.

For the I-electrolyte, there is a weak correspondence between the iodide levels determined using XPS and the IE%. At low pH, there is good corrosion inhibition and higher iodide levels on the metal, and XPS showed that FeOOH was the dominant surface product, which XRD indicates is mainly lepidocrocite. As can be seen from the weight loss (Appendix A), the presence of iodide ions reduces weight loss at pH 2.5, indicating that iodide adsorption replacing adsorbed Cl⁻, which, from XPS, has the highest I/Cl ratio at this pH of all data reported in this work, inhibits iron dissolution. This mechanism is similar to that reported for AA2024-T3 [11] and reduces the overall production of ferrous and ferric ions. The FeOOH (lepidocrocite) eventually converts to γ -Fe₂O₃ through dehydration. The percentage of FeOOH is lower at pH 4, resulting in a lower *IE*%. The reason for this change is not entirely clear. There is a reduction in the I/Cl ratio, reflecting less adsorption of iodide ions, but the data suggests that the path via magnetite may be more favored. There is also the possibility of the formation of FeI_xO_y observed in I_2 corrosion in nuclear reactors [58], which may reduce the amount of FeO_6^- that is generated. At pH 7 and 8, the *IE*% increased (Figure 5) however, higher carbonate levels were also observed. This may indicate CP formation via $GR1(CO_3^{2-})$, where the carbonate has ended up adsorbed onto the surface of amorphous γ -Fe₂O₃ particles, noting that lepodocrocite and γ -Fe₂O₃ can only form through the green rust pathway [50]. These pathways are indicated by yellow arrows and labeled "I" in Figure 15. The generation of α -Fe₂O₃ requires thermal activation

(indicated by the red circle in Figure 15), such as forced hydrolysis at 100 $^{\circ}$ C [59]. It is not observed as an end product in this study.

In the Ce-electrolyte, there was a weak correspondence between Ce levels and the corrosion inhibition, suggesting that the presence of Ce in the gel on the surface, which, from XPS, may be a mixture of Ce-hydroxides and Ce₂(CO₃)₃ or Ce(OH)CO₃ (or CeOCO₃ if Ce(IV) is present), played some role in increasing the *IE*%. In this instance, it seems that the gel inhibits the formation of a widespread, iron-based protective layer, with CP confining these to much smaller regions on the surface (presumably the anodes). Moreover, for the regions where they are present, the XRD suggests a shift in the type of corrosion product that is generated at anodic sites, with amorphous Fe₂O₃ being generated. The development of two types of sites could be viewed as a separation of anodic (iron-based) and cathodic (Ce precipitation) sites on the surface, where at higher pH the surface oxides/hydroxides are more stable, and because of the higher pH there is more deposition of Ce compounds [55]. This is true for cerium systems as well as ferrous systems [60]. Clearly, where the gel is present on the surface, this seems to inhibit the formation of iron (hydro)oxide species, which would otherwise be the main species.

A major difference between the Ce-electrolyte and the Ce+I electrolyte is that the extensive areas covered by cerium-containing gel where filiform corrosion was observed in the former case were not observed in the latter case. The corrosion product in the tail of the filiform in the Ce-electrolyte case was similar in morphology to much of the general corrosion product that developed on the surface after immersion in the Ce+I electrolyte (classed as "surface growth" in Figure 7i).

One approach to interpreting this difference is that the presence of adsorbed iodide must interfere with the establishment of large-scale anodes and cathodes on the surface. The formation of Ce-rich regions in the Ce-electrolyte was proposed to occur largely over cathodic sites. The absence of this type of site in the Ce+I electrolyte suggests that the anode and cathodes are more localized when iodide is present and that anodic and cathodic activity is generally reduced (as reflected by the increase in *IE*%). The "surface growths" observed largely in the filiform corrosion on surfaces exposed to the Ce-electrolyte are widespread in the Ce+I electrolyte. Since it is not easily removed from the surface (not dissolved or washed off during rinsing), it is proposed that it provides greater protection to the surface than the CPs that develop after I- and Ce-electrolytes. From the XRD, the main difference between the Ce+I electrolyte and the others is the presence of Akageneite and the formation of either ε -Fe₂O₃, γ -Fe₂O₃ or both directly from Fe(II) and Fe(III) species through Fe₃O₄. (ε -Fe₂O₃ is likely to be formed in a path parallel to γ -Fe₂O₃ given that in both mineral [61] and biological systems [62] it seems associated with magnetite). The akageneite can only be formed through the Fe^{3+} route (path II, Figure 15), and according to Misawa et al. [63], chloride ions must be present. This suggests that for the Ce+I electrolyte the route via green rust formation is blocked. The "green rust" path (Path I) is likely to occur at cathodic sites where the pH can reach pH > 6. In the presence of cerium ions, these cathodes are likely to be deactivated by the precipitation of cerium products. Additionally, halides (Cl⁻ and I⁻) are reported to stabilize the tetragonal lattice of β -FeOOH. Thus, the combination of these two aspects favors the much greater stabilization of β -FeOOH over lepidocrocite obtained via the FeO_6^- route. It is also feasible that retention on the surface may be due to the lower solubility of iron-based compounds containing iodide compared to those containing chloride [64]. The data indicates that the protective layer formed through β -FeOOH leads to an improvement in adhesion and corrosion protection at pH 4. The small synergy observed between I and Ce and pH 4, 7, and 8 appears to be a result of the combination of cerium precipitates closing down cathodic sites, iodide adsorption suppressing iron dissolution, and perhaps iodide ions stabilizing β -FeOOH. Clearly, there is room for much more work to be performed on understanding the details of the switch to akageneite formation and the exact role of iodide and cerium ions in closing down the GR pathway.

5. Conclusions

The level of corrosion protection provided in 3.5% NaCl electrolytes by the addition of KI, Ce(NO₃)₃, and mixtures of the two was investigated over a range of pHs from 2.5 to 8.

- First, the optimum Ce concentration of 7×10^{-3} M at pH 7 was obtained by determining the inhibitor efficiency (*IE*%) from potentiodynamic polarization by examining a range of concentrations from 1×10^{-4} M to 10×10^{-3} M. An optimum of 97% was obtained for 7×10^{-3} M at pH 7.
- Next, the *IE*% at different pHs was determined for two Ce concentrations of 1×10^{-3} M to 7×10^{-3} M, confirming that 7×10^{-3} M Ce had the highest overall inhibitor efficiency across the pH range. The *IE*% of 0.1 M KI in 3.5% NaCl electrolyte was examined. It varied between 21% and 84%, with the latter observed at pH 2.
- The *IE*% of mixed was generally above 90%. The exception was at pH 2.5, where *IE*% was negative, i.e., there was promotion of corrosion. This was also reflected in weight loss experiments (see Appendix A). At higher pH values, *IE*% was similar to or better than the I- or Ce-electrolytes alone. Indeed, synergy was found between these two ions at pH 4, 7, and 8. Importantly, the mixture improved *IE*% at pH 4.
- At pH 4 and above, the formation of akageneite (β -FeOOH) was the dominant species as opposed to lepidocrocite observed in I-electrolytes and Ce electrolytes. γ -Fe₂O₃ was observed in both cases. This appears to form a very compact protective layer. Additionally, the widespread heterogeneous precipitation of cerium (III) compounds is probably mainly hydroxides since only Ce(III) was observed. As at pH 4, this was largely Ce(OH)₃. At pH 7 and 8, greater amounts of carbonate were observed, also indicating the presence of hydroxycarbonates. Iron carbonates were not observed in XRD or XPS. It should be noted that carbonate is not part of the electrolyte, and its presence was proposed to be due to the absorption of CO₂ from the atmosphere. Because it is a significant component of the surface oxides, it is reported here.

Author Contributions: M.A.E.-H. conceived the idea of using mixed iodide and cerium inhibitors to extend the range of protection of cerium solutions to a lower pH range and contributed to the writing of the paper. A.E.H. oversaw the XPS and SEM sample preparation and analyses and contributed to the writing of the paper. I.S.C. contributed to the design of the research program and the writing of the paper. C.D.E. performed the XPS analyses and contributed to the data interpretation. A.S. performed the XRD analyses. All authors have read and agreed to the published version of the manuscript.

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Appendix A

Appendix A.1. Weight Loss Measurements at pH 2.5

The reduction in corrosion activation through the presence of I in the Ce+I electrolyte at pH 2.5 raised the question of whether there might be a Ce(NO₃)₃ concentration where inhibition was observed. To investigate this further, weight loss measurements were performed as a function of time in 3.5% NaCl with and without 0.1 M KI plus various additions of Ce(NO₃)₃ ranging from 1.0 to 7.0×10^{-3} M. These results are presented in Figure A1.



Figure A1. Weight loss-time curves for the corrosion of C-Steel in 3.5% NaCl solution either in the presence or absence of different concentrations of $Ce(NO_3)_3$ and KI at room temperature at pH of 2.5.

The data in black in Figure A1 represents the baseline performance for weight loss in 3.5% NaCl at pH 2.5. It can be seen that for all Ce(NO₃)₃ concentrations at all immersion times, the weight loss is greater than that measured for the NaCl solution alone. Moreover, the level of weight loss increases with increasing Ce(NO₃)₃ concentration.

The addition of KI improves the situation. The baseline for performance for the comparison of mixtures of KI and Ce(NO₃)₃ in Figure A1 is KI alone (olive green) in a 3.5% NaCl solution, which shows the lowest weight loss. By comparison, it can be seen that for pH 2.5 at all Ce(NO₃)₃ concentrations and at all immersion times, the weight loss is greater than the baseline performance. Moreover, *decreasing* the Ce(NO₃)₃ concentration moves the performance towards that of KI alone, which provides the lowest weight loss in this time range, indicating that the addition of Ce(NO₃)₃ cannot improve the short-term weight loss. On the other hand, for times over 500 min, the weight loss of the combination is lower than in NaCl alone, indicating an improvement in inhibitor performance but not as good as KI alone. At longer times, the combined KI with Ce(NO₃)₃ solutions appear to converge, suggesting that at longer times, mixed inhibitor combinations may be better than KI alone, as seen in the PDP data, where synergy is observed at 24 h.

Appendix A.2. EDS Area Measurements of Individual Sites by Classification

In this appendix, individual EDS analyses for different features are presented. These analyses are based on spectra collected from each feature and are not point analyses. Thus, they represent some level of averaging compared to point analyses.

Feature Type	Fe	0	С	Ι	Ce	C1	S
	92.60 (S2)	1.51	2.19	-	-	0.02	-
	83.5 (S3)	3.0	12.7	-	-	-	-
	83.3 (S4)	3.2	12.7	-	-	-	-
	61.3 (S6)	17.1	19.2	-	1.9	0.09	0.05
Materia	55.4 (S7)	18.8	22.7	-	2.6	-	-
wiatrix	69.7 (S8)	9.7	19.1	-	0.92	-	-
	76.0 (S9)	4.5	18.0	0.01	0.16	-	0.05
	73.8 (S10)	12.4	13.2	0.02	0.03	0.08	-
	76.9 (S11)	13.4	8.4	0.05	0.22	0.2	-
	54.7 (S12)	3.4	12.5	-	-	-	-
	78.6 (S2)	20.24	2.70			0.06	-
	67.1 (S4)	11.45	20.3	-	-	0.06	-
Surface	32.8 (S7)	40.0	18.7	-	8.0	0.21	0.15
Particulates	25.6 (S7)	43.0	19.7	-	10.8	0.54	0.20
	37.9 (S9)	39.7	21.4	0.01	0.87	0.08	-
	42.8 (S11)	35.4	6.5	0.54	9.9	4.08	0.12
	31.2 (S6)	54.5	12.4	-	1.5	0.11	0.04
	35.9 (S7)	49.9	12.6	-	1.2	0.21	-
	32.7 (S10)	47.0	13.4	-	5.4	0.14	-
Flaky	41.9 (S11)	49.5	5.0	0.23	0.19	3.0	-
	39.9 (S12)	50.6	9.1	-	-	0.40	-
	38.0 (S12)	50.5	9.5	-	-	0	-
	34.7 (S12)	49.2	11.6	-	4.3	0.2	-
	32.6 (S6)	50.53	144.9	-	1.7	-	0.03
	24.8 (S7)	50.46	20.4	0.0	3.8	0.21	0.02
	39.9 (S8)	50.53	11.4	-	-	-	-
Mud Crack	76.0 (S9)	4.48	18.1	0.01	0.16	-	-
	34.3 (S10)	52.96	5.1	0.05	0.59	-	-
	53.7 (S11)	39.33	12.2	0.1	0.12	0.63	-
	34.6 (6)	46.21	16.2	-	2.2	0.41	0.03
	36.3 (6fi) *	45.5	15.6	-	0.95	1.3	0.02
	37.6 (S7)	50.98	10.8	-	0.28	-	-
	34.3 (S8)	50.0	14.3	-	0.66	0.47	-
Surface Growths	37.8 (S9)	39.5	21.3	0.01	0.87	0.08	-
	53.2 (S10)	34.65	11.5	0.12	0.37	1.9	-
	53.2 (S11)	40.25	5.1	0.02	0.46	0.19	-
	38.0 (S12)	50.53	9.5	-	-	0.385	-
	18.4 (S6)	53.59	18.1	0.01	9.6	0.21	0.1
Deschalter	29.4 (S8)	44.9	21.5	-	3.7	0.21	0.0
Particles	26.5 (S10)	51.84	18.7	0.54	1.4	0.9	-
Embedded	34.7 (S12)	49.22	11.6	-	4.3	0.20	-
	S7-dtmap						
* fi-filiform.							

Table A1. Examples Compositional Analyses of the different types of surace features in Atomic percent.

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