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Corrosion resistance of hot-dip galvanized steel in simulated soil solution: A factorial design and pit chemistry study



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ABSTRACT

The soil corrosion of widely applied galvanized steel structures, such as power transmission towers, must be considered to prevent harm to their structural integrity and to mitigate the high costs associated with early failure. A full two-level factorial design was used to evaluate the relative significance of various influencing factors on the underground corrosion of hot-dip galvanized steel. Experiments were performed in simulated soil solutions. The effects of temperature and the concentrations of chloride, sulfate, bicarbonate and citric acid were evaluated using statistical analysis of the results. Using analysis of variance, temperature, citric acid and chloride were found to be individually significant. Also, temperature/citric acid and temperature/chloride significantly interacted to increase the corrosion rate. The lead-in pencil electrode technique was used to further evaluate the impact of the above mentioned factors on the dissolution behavior of the Zn coating. The results revealed that chloride and citric acid affect salt film formation at the pit bottom, while temperature alters the dissolution kinetics by changing the diffusion coefficient of the dissolving Zn(II) species. Moreover, the effect of bulk solution dissolved oxygen concentration on the corrosion rate of the galvanized steel was modeled. It was found that oxygen concentration does not have a dominant effect on the overall corrosion behavior of galvanized steel. Rather, the effect of temperature is dominant.

1. Introduction

Hot-dip galvanized steel is widely used in the electric power utility industry for power transmission and distribution structures because of its suitable service life in many atmospheric and underground conditions [1,2]. The Zn coating protects the underlying carbon steel substrate via the formation of a passive layer and simultaneously by providing a sacrificial anode. Recently, efforts have been made in the electric power transmission and distribution industry, in North America and throughout the world, to build smart structures to integrate with or replace the older electric utility networks. However, there are still many aging steel structures that could remain in service with proper maintenance. For instance, the British Columbia Power Authority (BC Hydro) currently owns more than 79,000 km of transmission and distribution lines, with over 22,000 transmission steel structures and 100,000 transmission wood pole structures (the latter with galvanized steel anchors) in British Columbia. Most of these structures were erected approximately 30-40 years ago and require maintenance. Such maintenance, to be effective over the 944,000 m² of jurisdictional area, requires prioritization and thus an understanding of the important corrosion rate determining material related and environmental factors.

In general, transmission towers are designed for decades of service, due to the relatively low corrosion rate of the Zn coating. However, under certain conditions the corrosion rate of Zn coatings is considerable, and it may threaten the integrity of the galvanized steel structure, thus limiting its service life. Therefore, evaluating below-grade corrosion of galvanized steel transmission towers is of pivotal importance.

The corrosion of galvanized steel occurs in three successive steps [3]. First, corrosion initiates by dissolution of the Zn coating, followed by formation of Zn corrosion products that reduce the overall corrosion rate of the Zn coating. In stage 2, after localized consumption of the Zn coating, corrosion of the steel substrate takes place. The final stage starts when the Zn coating is completely consumed, and the bare steel substrate corrodes as a carbon steel covered with corrosion products. Although atmospheric corrosion of galvanized steel has been the subject of numerous studies [4–7], its underground corrosion has received less attention [8]. In spite of numerous previous research studies, many aspects of underground corrosion still remain unclear, because soil is a complex, porous and discontinuous environment constituted by inorganic and organic solid phases, a liquid aqueous phase, air and other

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Received 8 April 2019; Received in revised form 23 October 2019; Accepted 27 October 2019 Available online 10 November 2019 0010-938X/ © 2019 Elsevier Ltd. All rights reserved. gas phases [9]. There are as many factors that influence soil corrosivity as there are soil types, moisture contents, positions of the water table, soil resistivities, soluble ion concentrations, soil pHs, oxidation-reduction potentials and microorganisms [10]. Although soil water and oxygen content have been considered the most important factor influencing the corrosion rate of an underground steel structure [11,12], soil resistivity and pH critically influence the corrosion behavior of a buried steel structure [13]. Using a numerical model, it was shown that differential aeration can lead to severe corrosion of a buried pipeline [14].

Two common approaches are employed to study soil corrosion: conducting research in the field [12,15] or performing experiments under laboratory conditions [16,17]. Simulated soil solution has been used to study the influence of the physicochemical properties of soil on the corrosion behavior of buried steel [18-20]. In general, a simulated soil solution contains Cl⁻, SO₄²⁻, and HCO₃⁻ [21]. These species are normally selected to mimic the electrolyte in contact with an underground metallic structure, however, the effect of dissolved O₂ is often neglected in simulated soil solution studies. Soil organic content has been shown to have a significant impact on the corrosion behavior of steel, either directly by metal complex formation [22,23] or indirectly by providing nutrients to microorganisms that cause microbially assisted corrosion [24]. Like salt content and texture, soil organic content varies significantly for different types of soils. Organic acids, such as citric and oxalic acid are believed to be involved in a number of processes occurring in the rhizosphere, where plant root secretions and microorganisms' activities directly affect the organic content of soil [25].

Investigating the main factors influencing the soil corrosion of galvanized steel and the possible interactions between the various factors that may affect it is of great importance to determine the service life (and potential maintenance schedule) of buried structures as well as the design of new Zn-based coatings. Running a one-factor-at-a-time approach is inefficient, especially when the number of factors is considerable. Moreover, this method does not account for possible factor interactions. Design of Experiments (DoE) using statistical methods provides an efficient approach to explore the effect of each factor and potential interactions to optimize the system [26]. Moreover, DoE can elucidate the influence of a relatively wide range of each factor [27,28], which for soil corrosion studies provides an important broad perspective.

It has been reported that the corrosion of galvanized steel usually initiates as localized corrosion [29]. Soils contain chlorides and sulfates and, with good aeration, tend to induce localized corrosion - often pitting corrosion [30]. Pitting corrosion was observed for a long exposure atmospheric corrosion study of galvanized steel in different environments from rural to marine to industrial [4]. From a practical perspective, the pitting corrosion of galvanized steel is of importance as it leads to perforation of the Zn coating and exposure of the substrate steel to the corrosive environment. Moreover, pitting corrosion, like other types of localized corrosion, is characterized by restricted mass transfer, which results in accumulation and eventually precipitation of dissolution products [31]. Such products further influence the dissolution kinetics of galvanized steel [29]. The corrosion products that form on Zn are mainly composed of Zn oxide and hydroxide [32] as well as basic Zn salts including anions such as chloride, sulfate, and carbonate [33,34]. Models developed for pit dissolution of Zn and Zn coatings propose that active dissolution of Zn takes place within the pit, while cathodic oxygen reduction occurs on the surrounding areas i.e. outside of the pit [3,4,29].

During pitting of a metal, two regimes of growth can be identified: active/ohmic-controlled dissolution at lower potentials and diffusioncontrolled dissolution at higher potentials [35]. While the former can be studied directly using a conventional electrochemical method and a bulk electrode, the latter requires a specific experimental setup to simulate the restricted mass transfer condition within the pit cavity. The lead-in pencil electrode technique has been developed to study the dissolution kinetics of metals and alloys during diffusion-controlled dissolution [31,36,37]. In this method, the pit chemistry is evaluated through a 1D pit developed by dissolution of a thin wire embedded in an isolated support [38]. Because of the restricted geometry of the pit cavity, pit solution saturates with dissolving metal cations during 1D pit dissolution. Consequently, a metal salt film precipitates at the pit bottom, which directly affects the dissolution kinetics [31].

The corrosion behavior of Zn and Zn coatings during atmospheric corrosion have been studied extensively [39,40] and have mostly been related to the presence of chloride, sulfate, and carbonate [4]. However, the effect of temperature, especially at subfreezing temperatures, has received less attention [41]. Similarly, studies focused on soil corrosion of galvanized steel have neglected the influence of temperature on underground corrosion [11,42]. Considering British Columbia's varied climate and vegetation, research is required to address the effect of soil parameters as well as the influence of temperature on the underground corrosion of galvanized steel. In the present paper, a full two-level factorial design is employed to investigate possible factors like temperature, chloride, sulfate, bicarbonate and citric acid affecting the underground corrosion of galvanized steel power transmission towers installed in British Columbia. There are, of course, other soil parameters that may affect the corrosion behavior of buried galvanized steel. However, testing for the effects of all of these parameters requires a very large experimental setup. Most importantly, it is known that some of these factors are inter-dependent (e.g. soil resistivity is a function of soil moisture and soluble salt content). However, in factorial design of experiments, one can only consider independent variables.

2. Experimental

2.1. Design of experiments

A two-level factorial design method was used to determine the most important effects on the corrosion current density of galvanized steel. With this approach, a linear relationship is assumed between the factors and the response, although perfect linear behavior is not always required [43]. Temperature, chloride, sulfate, bicarbonate and citric acid concentration were considered and studied based on a fully randomized run order. Table 1 shows names and units for each factor. In this Table, the coded values of -1, 0 and +1 indicate low, center and high levels for each factor, respectively. The effects of these factors were quantified using 2⁵ factorial design, including 32 experiments plus 5 additional experiments at the center point. The center points were added to check the curvature of data set and provide an independent estimation of the error [43]. The corrosion current density (i_{corr}) was the response. The effect of bulk solution dissolved oxygen concentration on the corrosion behavior of the galvanized steel in simulated soil solution was evaluated using thermodynamic models and the assumption of oxygen diffusion limited corrosion.

The lower and upper values for chloride, sulfate, bicarbonate and citric acid were selected based on the characterization of soil samples collected from 10 different locations on Vancouver Island, British Columbia, Canada. The pH of the collected soil samples varied from 4.9 to 5.8; thus, the effect of pH was not considered in the DoE. The pH of the test solutions varied between 3.7 to 3.9. Before each corrosion test,

Table 1

Factor values used for factorial design. -1, 0 and +1 indicate the coded values for low, center and high levels of the factors, respectively.

Factor	Unit	Low level (-1)	Center (0)	High level (+1)
Chloride Sulfate Bicarbonate Citric acid Temperature	M M M °C	0.001 0.001 0.001 0.001 - 5	0.005 0.005 0.005 0.005 10	0.01 0.01 0.01 0.01 25

the pH of the test solution was adjusted to 5.2 by adding 0.1 M NaOH. The temperature range was chosen to coincide with the temperature change that an underground galvanized steel structure might experience in British Columbia. Multiple regression analyses through the least squares method were used to analyze the experimental data. Analysis of variance (ANOVA) was performed to evaluate the significance of the terms and the adequacy of the model.

2.2. Corrosion experiments

A commercially hot-dip galvanized steel sheet received from the British Columbia Power Authority (BC Hydro) with an average coating thickness of 95 μ m and average coating mass of 678 g/m² was used for the corrosion experiments. 1 cm diameter coins were cut out of the asreceived galvanized steel. The samples were initially degreased with ethanol and rinsed with deionized water without any further surface treatment. For each corrosion experiment, a freshly prepared sample was used. Subsequent to each test, the sample surface was visually examined. If any evidence of crevice corrosion was detected, the result was discarded, and the test was repeated. A sample holder comprising a copper wire, a Teflon holder (0.785 cm² electrode surface area exposed to the test solution) and a vinyl tube was used to provide the electrical connection. The corrosion behavior of the galvanized steel was evaluated using potentiodynamic polarization in a conventional threeelectrode cell. Before each polarization, the open circuit potential (OCP) of the sample was recorded for 3600 s, letting the system approach a steady-state condition (i.e. the variation of OCP was less than 5 mV over a 10 min time period [44]). Then, the sample was polarized from -500 mV to 700 mV with respect to the OCP at a potential scan rate of 0.167 mV/s. The corrosion current density was obtained using the Tafel extrapolation method from potentiodynamic polarization curves. Analytical grade reagents and distilled water were used to prepare the test solutions. All corrosion experiments were conducted in a water-jacketed cell open to air. The test solution was not stirred. An Ag/AgCl reference electrode and a platinum wire were used as the reference electrode and the counter electrode, respectively. All test solutions were prepared using analytical grade chemicals and deionized water.

To verify the occurrence of pitting corrosion after immersion in simulated soil solution, a hot-dip galvanized steel sample was immersed in 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃ + 0.005 M citric acid at 10 °C (the center point of the factorial design) for 4 weeks. Then, the sample was rinsed in deionized water and air-dried. Afterward, the surface morphology and cross-section of the sample was evaluated using scanning electron microscopy (SEM). The metallographic preparation technique for hot-dip galvanized steel proposed by Jordan et al. [45] was used for the cross-sectional evaluation.

To evaluate the effect of solution chemistry and temperature on the dissolution behavior of galvanized steel, the lead-in pencil electrode technique was used. To do so, the conditions leading to the highest and the lowest corrosion current density plus the center point were selected. It has been shown that the corrosion rates of pure Zn and hot-dip galvanized steel are comparable [4]. Therefore, commercially pure Zn (99.0 %) was used for artificial pit studies. The pencil electrodes were prepared using the method described in detail elsewhere [38]. The polarization sequence for the artificial pit studies included polarizing the pencil electrode at +250 mV (Ag/AgCl) for some time (from 1800s to 3000 s, depending on test temperature), followed by immediate switching of the potential to -500 mV (Ag/AgCl) for 1 s to dissolve the salt film precipitated during polarization at high anodic potential. Then, the potential was switched back to +250 mV (Ag/AgCl) for 300 s. Next, the potential was reversely ramped towards more negative potentials at a scan rate of 5 mV/s until reaching open circuit corrosion. Each artificial pit test was repeated 5 times.



Fig. 1. a) Typical open circuit potential plot vs. time, b) typical potentiodynamic polarization plot. The arrow indicates the pitting potential. Both plots were obtained for commercial hot-dip galvanized steel in 0.005 M NaCl + $0.005 \text{ M Na}_2\text{SO}_4 + 0.005 \text{ M NaHCO}_3 + 0.005 \text{ M citric acid at 10 °C}$ (*i.e.* center point of DoE).

3. Results

3.1. Factorial design

Fig. 1 show an OCP vs. time plot and a potentiodynamic polarization plot for galvanized steel obtained in 0.001 M NaCl + 0.001 Na₂SO₄ + 0.01 M NaHCO₃ + 0.001 M citric acid at 20 °C. A change of OCP of less than 5 mV over a 10 min period was the criterion used to determine steady-state [44]. As Fig. 1.a shows, the potential changes most rapidly at the beginning of the immersion. As the metal/solution interface approaches steady-state, the rate of variation of the potential decreases. In all polarization curves, the cathodic branch was oxygen reduction diffusion limited, while the anodic branch was mixed activation/diffusion-controlled. Both branches were extrapolated to the corrosion potential to determine *i*_{corr}.

In nearly all experiments, the corrosion attack was initiated in the form of pitting. The pitting potential is indicated with an arrow in Fig. 1.b. Pitting corrosion has previously been observed during atmospheric corrosion of Zn and hot-dip galvanized steel [4,29]. Fig. 2 shows SEM images of the hot-dip galvanized steel sample immersed in $0.005 \text{ M} \text{ NaCl} + 0.005 \text{ M} \text{ Na}_2\text{SO}_4 + 0.005 \text{ M} \text{ Na}\text{HCO}_3 + 0.005 \text{ M} \text{ citric}$





Fig. 2. SEM images of hot-dip galvanized steel sample after 4 weeks immersion in 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃ + 0.005 M citric acid at 10 °C (*i.e.* center point of DoE): a) surface morphology (the arrows indicate corrosion pits), b) cross-sectional analysis (pit is indicated by dashed-line).

acid at 10 °C for 4 weeks. The surface morphology and cross-sectional images show corrosion pits, suggesting that the corrosion of the Zn coated steel initiates in the form of pitting corrosion. Using a rotating disk electrode, it was shown that in the pH range of 4-6, the corrosion of Zn is controlled by diffusion of oxygen from the bulk solution to the electrode surface [46]. The cathodic branch of the potentiodynamic polarization curve shown in Fig. 1.b indicates diffusion-controlled behavior, implying that the oxygen reduction reaction is the main cathodic reaction. This behavior was observed for all potentiodynamic polarization curves. The corrosion current density, calculated using the Tafel extrapolation method, was the response. Table 2 summarizes the randomized set of the experiments in coded form and the measured icorr response. ANOVA was performed to statistically evaluate the significance of the factors. This analysis, which tests the relationship between the factors and the response variability, allows one to obtain deviation from the mean. Subsequentially, ANOVA is used to test the null hypothesis [26]. This was performed by calculating the sum of the squared deviations from the mean because of the main effects or interactions and dividing this sum by the degree of freedom. If neither a change of the factors or the interactions affects the response, then the null hypothesis holds. However, if the mean square of a particular factor or an interaction is greater than the mean square due to error, the null hypothesis does not hold. Table 3 summarizes the ANOVA results for the model used to estimate the corrosion rate of the galvanized steel

in the simulated soil solution. The significant factors or interactions can be identified by *F*-value by comparing the mean square of a factor or an interaction to the residual mean square. If the *p*-value is less than 0.05, then the effect is considered significant [43]. As Table 3 shows, temperature, citric acid, chloride, the interaction between temperature and citric acid and the interaction between temperature and chloride are significant. The model *F*-value of 102.47 implies that the model is significant and there is only 0.01 % chance that such a large *F*-value is because of experimental noise. Moreover, Lack of Fit and curvature are not significant, meaning that the linear assumption of the model holds true. The model expressed in terms of the coded factors is as follows.

$$i_{corr} = 4.20 + 0.81X_1 + 1.45X_2 + 2.90X_3 + 0.55X_1X_3 + 0.95X_2X_3$$
(1)

where X_1, X_2 , and X_3 are chloride, citric acid, and temperature in coded form, respectively.

Fig. 3 shows the Pareto chart for the model, which graphically presents the statistical significance of the factors and interactions based on their effect on $i_{\rm corr}$. Two t-limits were shown in the Pareto chart that is based on Bonferroni corrected t and a standard t for individual effects tests (i.e. t-value limit). All effects that are above the Bonferroni limit are certainly significant and should be added to the model, while all effects that are below the *t*-value are not likely to be significant [43]. Effects ranked between the Bonferroni limit and t-value limit are possibly significant. As Fig. 3 shows, temperature is the most significant factor, followed by citric acid, temperature/citric acid interaction, chloride and temperature/chloride interaction. Moreover, Fig. 3 shows that there are two effects that fall between the Bonferroni limit and tvalue limit, which are the third order interaction between chloride, citric acid and temperature and interaction between chloride and citric acid. The ANOVA suggests that these two effects are not significant, therefore, only those effects that are above the Bonferroni limit were considered significant for the model.

Fig. 4 shows a normal probability plot of externally studentized residuals calculated from the model, which verifies whether the residuals follow a normal distribution. This plot graphically illustrates the goodness of the fit of the model. R-squared (R²), Adjusted R-squared (R_{adi}^2) and Predicted *R*-squared (R_{Pre}^2) values are also shown in Fig. 3. As can be seen, R^2 is 0.944, which is reasonably close to 1. Moreover, the difference between R_{adj}^2 and R_{Pre}^2 is less than 0.2, confirming that the model is fitting the data accurately and that it can be reliably used to interpolate the response [43]. Furthermore, all data points shown in Fig. 4 are scattered evenly around a straight line without any definite pattern, which suggests that residuals follow a normal distribution and no transformation of the response is required. A plot of actual (measured) corrosion current density vs. the predicted response values is shown in Fig. 5. In this plot the data points are evenly split by the 45degree line, indicating a good fit between the experimental results and the outcomes of the model [47].

Fig. 6.a and 6.b show the 3D surface plot of i_{corr} as a function of temperature and citric acid concentration at low and high levels of chloride, sulfate and bicarbonate concentration, respectively. The 3D graphs are presented to evaluate the relationship between the independent variables and the response [48]. The 3D plots show that both temperature and citric acid concentration have a significant effect on $i_{\rm corr}$ and the maximum $i_{\rm corr}$ is expected when temperature and citric acid concentration are at high levels. At a constant temperature, -5 °C for example, $i_{\rm corr}$ increased from $0.55\,\mu\text{A/cm}^2$ to $1.54\,\mu\text{A/cm}^2$ with an increase in citric acid concentration from 0.001 M to 0.01 M. This effect is more pronounced when the temperature is elevated. Similarly, at a given citric acid concentration, icorr rises sharply with increasing temperature. For instance, in the presence of 0.001 M citric acid, icorr increased from $0.55 \,\mu\text{A/cm}^2$ to $2.87 \,\mu\text{A/cm}^2$ when temperature increased from -5 °C to 20 °C. These findings agree with those previously reported for the effect of temperature and citric acid on the corrosion resistance of galvanized steel. Padilla and Alfantazi [41] have shown that increasing temperature from -5 °C to 25 °C significantly increases

Table 2 Factor values used for factorial design in coded form and i_{corr} as the response.

Standard experiment sequence	Randomized experiment sequence	Factor A (chloride)	Factor B (sulfate)	Factor C (bicarbonate)	Factor D (citric acid)	Factor E (temperature)	Response (i _{corr} , μA/ cm²)
36	1	-1	-1	-1	-1	1	3.91
26	2	1	-1	1	1	1	12.07
12	3	0	0	0	0	0	5.16
34	4	1	1	-1	-1	1	6.70
37	5	1	-1	1	-1	1	4.44
19	6	1	-1	-1	1	-1	2.10
5	7	0	0	0	0	0	4.85
11	8	-1	1	-1	1	1	8.09
20	9	1	-1	1	1	-1	1.44
31	10	1	-1	-1	1	1	9.14
32	11	-1	-1	1	-1	-1	0.38
4	12	0	0	0	0	0	4.49
35	13	-1	1	-1	1	-1	2.02
25	14	-1	-1	-1	1	1	7.11
1	15	0	0	0	0	0	3.39
7	16	1	-1	-1	-1	1	5.62
24	17	-1	1	-1	-1	1	3.99
23	18	-1	1	1	-1	-1	0.59
33	19	-1	-1	1	-1	1	3.87
30	20	1	1	1	1	1	11.88
27	21	-1	-1	-1	-1	-1	0.52
22	22	1	1	1	-1	1	5.01
8	23	1	-1	-1	-1	-1	1.06
10	24	1	1	-1	1	-1	2.24
2	25	-1	1	1	1	-1	1.83
16	26	1	-1	1	-1	-1	1.01
15	27	-1	-1	1	1	1	6.82
3	28	1	1	-1	1	1	12.87
9	29	-1	1	-1	-1	-1	0.65
28	30	0	0	0	0	0	2.92
14	31	-1	-1	-1	1	-1	1.20
13	32	-1	-1	1	1	-1	1.18
21	33	1	1	1	1	-1	2.40
29	34	1	1	1	-1	-1	1.13
17	35	-1	1	1	-1	1	4.09
6	36	-1	1	1	1	1	8.00
18	37	1	1	-1	-1	-1	1.18

the corrosion current density of galvanized steel in 3.5 wt% NaCl solution. Soriano and Alfantazi [22] have reported the detrimental effect of citric acid on the corrosion behavior of galvanized steel. Fig. 7.a and. b show the 3D surface plots of the effect of temperature and chloride concentration on $i_{\rm corr}$ at low and high levels of citric acid, sulfate and bicarbonate concentration, respectively. Similar to Fig. 6, the significant effect of temperature on $i_{\rm corr}$ is evident, especially at high citric acid concentrations (Fig. 7.b).

3.2. Lead-in pencil electrode studies

The corrosion current density presented as the response for the DoE in the previous section was obtained using the Tafel extrapolation method from potentiodynamic polarization curves. For the DoE experiments, $i_{\rm corr}$ represents the dissolution rate in the active dissolution

state *i.e.* under charge transfer control. In the presence of corrosion products, however, the dissolution will be diffusion-controlled due to accumulation of, and restricted mass transfer through corrosion products [38,49]. The lead-in pencil electrode technique was used to study the effect of simulated soil solution on the dissolution of galvanized steel during diffusion-controlled corrosion [49]. Fig. 8 presents the current density vs. time curve obtained from pencil electrode polarization in 0.005 M chloride + 0.005 M sulfate + 0.005 M bicarbonate + 0.005 M citric acid at 10 °C (experiment 15 or the center point of factorial design in Table 2). The graph shown in Fig. 8.a, which is a typical current density vs. time for an artificial pit [50], is divided into two parts. From the onset of the test up to 2100s (from point A to B), the current density was measured during polarization at a constant potential of +250 mV (Ag/AgCl). From point B to C, the current response was recorded during a potential backscan at a scan rate of 5 mV/s, so

Table 3	
Summary of ANOVA for the model based on full factorial design.	

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	Prob > F	
Model	395.23	5	79.04	102.47	< 0.0001	Significant
Chloride	21.18	1	21.18	27.46	< 0.0001	"
Citric acid	66.86	1	66.86	86.68	< 0.0001	"
Temperature	268.41	1	268.41	347.98	< 0.0001	"
Chloride/Temperature	9.76	1	9.76	12.66	0.00126	"
Citric acid/ Temperature	29.00	1	29.00	37.59	< 0.0001	"
Curvature	7.43×10^{-3}	1	7.43×10^{-3}	9.64×10^{-3}	0.92	Not significant
Residual	23.14	30	0.77	-	-	-
Lack of Fit	19.44	26	0.74	0.80	0.68	Not significant
Pure Error	3.69	4	0.92	-	-	-



Rank

Fig. 3. The Pareto chart for the model graphically presents the statistical significance of the factors and interactions. Bonferroni and *t*-value limits are shown as well.



Fig. 4. Normal probability plot of externally studentized residuals calculated from the model. R^2 , R^2_{adj} and R^2_{Pre} values suggest that the model is accurately fitting the data.

the pit passed through two regimes of dissolution, *i.e.* diffusion control and activation/ohmic control, as shown in Fig. 7.b in more detail. The current fluctuations in Fig. 8.a at 1800s are real and happened due to dissolution and reprecipitation of the salt film during stepping of the potential to -500 mV (Ag/AgCl) and stepping back the potential to +250 mV (Ag/AgCl) [38]. The limiting current density (i_{lim}) was considered to be the current density between the diffusion-controlled and the activation/ohmic-controlled dissolution [51]. At i_{lim} the pit surface is salt-free, however, the pit solution is still saturated with the dissolving metal cations (*i.e.* Zn (II)) [31]. During diffusion-controlled dissolution, the current density is virtually potential independent for some



Fig. 5. A Plot of actual vs. predicted corrosion current density. The data points are evenly split by the 45-degree line, suggesting a good fit between the experimental results and the model results.

time, as Fig. 8.b shows. This is followed by a small peak and a linear decrease with decreasing potential. The small peak just before the linear part of the curve (*i.e.* activation/ohmic controlled dissolution) is a result of loss of the salt film formed during diffusion-controlled dissolution [52,53]. During the diffusion-controlled dissolution, the pit surface is covered by a metal salt film and dissolution is controlled by diffusion of dissolving metal cations through the salt film [54]. During the active/ohmic-controlled condition, however, dissolution occurs on a salt-free pit surface [51].

At $i_{\rm lim}$, one can measure the dissolution kinetics by applying Fick's first law in combination with Faraday's law, assuming that the bulk concentration of the dissolving cations is zero [36,50], as follows:

$$D. C_{\rm S} = \frac{l_{\rm lim}\delta}{n\rm F} \tag{2}$$

where *D* is the diffusion coefficient of metal cations (here Zn (II)), C_S is the saturation concentration of metal cation, δ is the pit depth, *n* is the oxidation state of the metal and F is Faraday's constant. δ was calculated by integration of the current vs. time curve and by applying Faraday's law [50]. When the pit is deep enough, the diffusion length of dissolving metal cations is assumed to be the pit depth. Gaudet et al. [54] have shown that the linear part of a plot of diffusion-limited current vs. inverse of pit depth indicates the minimum pit depth for which this assumption holds true. Using their approach, the minimum pit depth of 140 µm was calculated for the pure Zn electrode in the simulated soil solution.

Using Eq. 2, $D.C_S$ values were calculated and summarized in Table 4 for three different simulated soil solutions that resulted in the highest and the lowest i_{corr} as well as the center point from DoE: experiments 28, 11 and 15, respectively (see Table 2). All $D.C_S$ values shown in Table 4 were measured at $\delta = 450 \pm 10 \,\mu$ m, which is well beyond the minimum pit depth for diffusion-controlled dissolution of Zn in simulated soil solution. Comparing the chemical composition of experiments 28, 11 and 15, it is evident that experiment 28 had the highest temperature, chloride, sulfate and citric acid concentration, which suggests, based on the results of DoE, the most aggressive environment. On the other hand, experiment 11 had the least aggressive test condition. As Table 4 shows, the higher the i_{corr} , the greater the value of $D.C_S$. This implies that the aggressiveness of the environment affects both active dissolution and diffusion-controlled dissolution.

Fig. 9 shows the pit depth vs. the square root of time for experiments



Fig. 6. 3D surface plots of *i*_{corr} as a function of temperature and citric acid concentration: a) low levels of chloride, sulfate and bicarbonate concentration, b) high levels of chloride, sulfate and bicarbonate concentration.



Fig. 7. 3D surface plots of *i*_{corr} as a function of temperature and chloride concentration: a) low levels of citric acid, sulfate and bicarbonate concentration, b) high levels of citric acid, sulfate and bicarbonate concentration.



Fig. 8. Current density vs. time curves obtained from Zn pencil electrode polarization in 0.005 M chloride + 0.005 M sulfate + 0.005 M bicarbonate + 0.005 M citric acid at 10 °C: a) potentiostatic polarization at +250 mV (Ag/AgCl) (from point A to point B) followed by potential backscan at a scan rate of 5 mV/s (from point B to point C). b) Potential backscan part in more detail.

Table 4

 $i_{\rm corr}$ and *D*.*C*_S values for experiments 28, 11 and 15 of DoE. Each *D*.*C*_S shows the mean value and the standard deviation calculated from 5 experiments at the same condition. Pit depth at $i_{\rm lim}$ was 450 \pm 10 µm for all conditions.

Experiment	28 (highest $i_{\rm corr}$)	11 (lowest i_{corr})	15 (center point)
i _{corr} (μA/cm²)	12.87	0.38	3.39
D.C _S (mol/	7.60 × 10 ⁻⁸ (±	$3.63 imes 10^{-8}$ (\pm	5.89 × 10 ⁻⁸ (±
cm.s)	2.78 × 10 ⁻⁹)	$1.07 imes 10^{-8}$)	2.67 × 10 ⁻⁹)

28, 11 and 15 obtained during potentiostatic polarization of the Zn electrode at + 250 mV (Ag/AgCl) for 1800s. A linear increase of δ with $\lor t$ indicates that the dissolution is diffusion-controlled in the presence of a salt film at the pit bottom [55]. The slope of δ vs. $\lor t$, which is proportional to *D*.*C*_S, increased with increasing aggressiveness of the environment. Similarly, for a given time, the pit depth was increased as the aggressiveness of the environment increased.

4. Discussion

4.1. Simulated soil solution

Temperature, citric acid, chloride, and their interactions are the most significant factors on the corrosion rate of galvanized steel, as



Fig. 9. Pit depth vs. \sqrt{t} for experiments 28, 11 and 15 of DoE obtained during potentiostatic polarization at + 250 mV (Ag/AgCl) for 1800s.

Fig. 3 shows. Temperature affects the corrosion behavior via changing O₂ solubility, diffusion coefficients and the enthalpy of reactions. The effect of temperature on O₂ solubility will be discussed in detail later. Moreover, solution resistance is dependent on temperature and increases dramatically below freezing [41]. It is likely that the observed icorr at low temperature levels was a result of a lowered diffusion coefficient of dissolving Zn (II) and a high solution resistance. It was previously shown that, among soil organic matter, citric acid has the most detrimental influence on the corrosion resistance of galvanized steel [22]. Citric acid accelerates metal dissolution by formation of metal organic complexes [23,56]. The corrosion of Zn and galvanized steel in the presence of chloride has been studied extensively for atmospheric corrosion [4,29,41,57,58] and in soil environments [41]. The composition and structure of the passive film formed on Zn is directly associated with the presence of various ions in the electrolyte and separation of anodic and cathodic processes [4,59]. For example, it was previously shown that in a carbonate-containing solution, a thick insulating zinc oxide inner and a porous zinc hydroxycarbonate outer layer form, which hinder the dissolution reactions [34]. Moreover, for Zn and galvanized steel, it has been reported that sulfate to carbonate ratio has an important effect on the composition and morphology of the corrosion products, as the formation of corrosion products is governed by corrosion processes [23]. It is believed that the presence of bicarbonate facilitates the propagation of localized corrosion attack via the formation of a porous zinc hydroxyl carbonate [29]. The results shown in Figs. 5-7 suggest that sulfate and bicarbonate had a negligible effect on the corrosion current density of galvanized steel in the simulated soil solution, although the effect of these factors is probably more important for atmospheric corrosion [4]. One possible explanation for this observation is that the variation of sulfate and bicarbonate was not significant in comparison to the detrimental influence of temperature, citric acid, and chloride concentration.

4.2. Pit chemistry

Any observed change of $D.C_{\rm S}$ with bulk solution composition and temperature can be explained with a change in metal salt solubility or diffusion coefficient. First, let us consider a constant *D*. Under this assumption, any change in $D.C_{\rm S}$ is only associated with a change in $C_{\rm S}$. Therefore, any parameter that alters metal salt solubility affects the dissolution kinetics. The solubility of a metal salt decreases in the presence of a common-ion. This phenomenon, known as the commonion effect, is the main mechanism for observed decreases of $D.C_{\rm S}$ with bulk solution composition [60,61]. Moreover, the presence of a corrosion inhibitor [50] or an accelerator [36] is believed to influence metal dissolution by modifying the salt film composition. Furthermore, in a pure chloride bulk solution, it was shown that the salt film precipitates as a metal chloride (e.g. ZnCl₂ for a Zn electrode) [62]. Compared to pure chloride solutions, the simulated soil solution contains more ligands, therefore, it is highly likely that the metal salt film formed during 1D pit dissolution in simulated soil solution was a mixture of more complex, ligand containing salts. Such salts would have a lower solubility (lower C_s) than ZnCl₂ because of the common-ion effect. To verify this hypothesis, D.C_s in 0.005 M ZnCl₂ solution at 25 °C at a pit depth of 450 μ m was measured and found to be 11.84 \times 10⁻⁸ mol/cm.s, which is greater than that of experiment 28 (7.60×10^{-8} mol/cm.s). This implies that the common-ion effect is not the only possible reason for a decreasing $D.C_{\rm S}$ for the Zn electrode. The formation of a mixed salt film instead of ZnCl₂ in the simulated soil solution is also a reasonable assumption [62]. Therefore, both the composition and solubility of the metal salt formed in the simulated soil solution should be different from a pure chloride containing solution. However, changing C_s via a change in the bulk solution composition is not the only possible mechanism for the observed dissolution kinetics.

For Zn, it was shown that an assumption of a constant D is not accurate [49] because of the unusual transport behavior of Zn (II) [63], probably due to its high tendency for complexation [64]. For a Zn pencil electrode, Nakhaie and Asselin [49] have shown that D.Cs decreases with increasing bulk chloride concentration via decreasing diffusion coefficient and metal salt solubility. Moreover, solution viscosity effect on D is found to be significant [65]. In a concentrated solution, D decreases because of increasing solution viscosity. However, the results shown in Table 4 contradict this behavior, most likely because of the influence of temperature on D. Moreover, for a given bulk solution composition, it was found that increasing temperature increases the dissolution kinetics of Zn due to an increase of D [38]. In addition, it is known that at a higher temperature metal salt solubility increases. Therefore, diffusion takes place in a more concentrated solution, which in turn decreases D. On the other hand, D increases with increasing temperature. It is believed that the latter effect is more important for the measured dissolution kinetics than the former [51]. Considering the effect of the bulk solution on viscosity and diffusion coefficient, one expects that $D.C_{\rm S}$ should decrease by increasing the concentration of chemical species in the bulk solution. However, the results shown in Table 4 suggest quite the opposite, as the species concentration in experiment 28 was considerably higher than that of experiments 11 and 15.

In general, the increased dissolution kinetics observed when the solution became more aggressive was due to modifications of both the diffusion coefficient and the salt film solubility. On the one hand, increasing solution concentration resulted in decreasing $C_{\rm S}$ because of the common-ion effect, and decreasing *D* due to increasing solution viscosity. On the other hand, both $C_{\rm S}$ and *D* increased at elevated temperatures. Comparing the bulk solution compositions, it is evident that experiment 28 had higher temperature, chloride, sulfate and citric acid concentration than experiments 11 and 15. Although higher solution concentration results in decreasing the dissolution kinetics, experiment 28 showed a higher $D.C_{\rm S}$ value. This suggests a strong influence of temperature on the dissolution kinetics, most likely due to an increase of diffusivity. This finding supports the results from DoE, suggesting that temperature is the most significant factor controlling the corrosion resistance of the galvanized steel in the simulated soil solution.

4.3. The effect of temperature and ionic solutes on dissolved O_2 and the corrosion rate

In a near neutral electrolyte, oxygen reduction is the dominant cathodic reaction controlling the corrosion rate of Zn and Zn coatings. The oxygen reduction reaction is controlled by oxygen mass transport to the electrode surface [66], when the corrosion current density approaches the limiting current density for oxygen reduction (i_{lim,O_2}), as

follows:

$$J_{\rm lim,O_2} = \frac{4FD(C_{O_2} - C_{O_2,\rm air})}{d}$$
 (3)

where $C_{O_2,air}$ is the atmospheric oxygen concentration (typically about 8 ppm) and *d* is the thickness of the surface diffusion layer. The limiting current density, which is a measure of oxygen availability around the buried hot-dip galvanized steel, is a function of soil porosity and moisture content. The time-dependent oxygen concentration (C_{O_2}) within the soil under isothermal and isobaric conditions can be obtained by solving Fick's first and second laws as follows, respectively [67,68]:

$$F = -D_{\text{eff},O_2} \frac{\partial C_{O_2}}{\partial z} = -\theta_{\text{eq}} D^* \frac{\partial C_{O_2}}{\partial z}$$
(4)

$$\frac{\partial C_{O_2}}{\partial t} = -D^* \frac{\partial^2 C_{O_2}}{\partial z^2} - K_r^* C_{O_2}$$
(5)

where D_{eff,O_2} is the effective diffusion coefficient of O_2 in soil, z is the vertical distance under the soil surface, D^* equals $D_{\text{eff},O_2}/\theta_{\text{eq}}$, K_r^* is the reaction rate coefficient, t is time, and θ_{eq} is the equivalent porosity defined by [67]:

$$\theta_{\rm eq} = \theta_{\rm a} + {\rm H}\theta_{\rm w} \tag{6}$$

where is θ_a volumetric air content, H is Henry's constant (approximately 0.03 at 25 °C), and θ_w is the volumetric water content. The diffusion of O₂ occurs in both air and water phases and can be estimated using a semi-empirical equation as follows [263]:

$$D_{\text{eff},O_2} = \frac{1}{p^2} [D_{\text{air},O_2} \theta_a^k + H D_{\text{water},O_2} \theta_w^k]$$
⁽⁷⁾

where *p* is the soil porosity, k is a constant (approximately 3.3), D_{air,O_2} and D_{water,O_2} are the oxygen diffusion coefficient in air ($\approx 1.8 \times 10^{-5}$ m²/s) and water ($\approx 2.5 \times 10^{-9}$ m²/s at 25 °C), respectively. Moreover, $\theta_a = p - \theta_w$ and $\theta_w = pS_w$ (where S_w is the soil's degree of saturation). Therefore, Equation 7 becomes:

$$D_{\rm eff,O_2} = \frac{1}{p^2} [D_{\rm air,O_2} (p(1 - S_{\rm w}))^k + H D_{\rm water,O_2} (pS_{\rm w})^k]$$
(8)

Using Eqs. 4–8 one can estimate oxygen accessibility at the electrode surface within the soil [14].

It has been shown that the corrosion of Zn in the pH range of 4-6 is controlled by diffusion of oxygen from the bulk solution to the electrode surface [46]. Oxygen diffusion in air is very fast, and thus, the oxygen diffusion within the water phase of soil is rate determining. Further, the use of a naturally aerated solution (i.e. open to the atmosphere) provides the most aggressive condition for oxygen delivery to the electrode surface that one could obtain in a soil environment. Thus, the experiments conducted here simulate the most aggressive oxygen delivery condition that is possible in soil. Moreover, oxygen solubility in soil's aqueous phase depends on several factors, such as soil soluble salt content and temperature. Therefore, the effect of bulk oxygen concentration on the corrosion behavior of galvanized steel was not considered in the DoE. As is usual in oxygen reduction-limited corrosion, it is assumed that the concentration of oxygen at the electrode surface is 0 [46,69]. In other words, oxygen diffusion from the bulk solution to the electrode surface is the rate determining step (limiting current density), as Eq. 2 shows.

The O_2 concentration within the soil water phase depends on the partial pressure of oxygen in the atmosphere in contact with the solution, the solution temperature and the presence of ionic solutes. In an open system, it is known that the corrosion rate of steel increases with temperature, reaches a maximum, and decreases [70]. The presence of the maximum corrosion rate as temperature rises is a combination of an increasing diffusivity of O_2 counteracted by a decreasing O_2 solubility. In the presence of an inorganic solute *I*, C_{aq} decreases because water has



Fig. 10. Predicted oxygen solubility behavior, calculated from the thermodynamic model (see Appendix A) for different bulk solution concentrations. A: 0.001 M NaCl + 0.001 M Na₂SO₄ + 0.01 M NaHCO₃; B: 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃ and; C: 0.01 M NaCl + 0.01 M Na₂SO₄ + 0.001 M NaHCO₃.

less ability to accommodate the dissolved O_2 . Several experimental and modeling attempts have been made to correlate O_2 solubility to temperature and solution concentration. Tromans [70–72] has successfully developed a thermodynamic model to predict O_2 solubility as a function of temperature, O_2 partial pressure (P_{O_2}) and inorganic electrolyte solutes, as follows:

$$C_{\rm aq} = k' P_{\rm O_2} \tag{9}$$

where k' is a constant determined by temperature and inorganic solute concentration explained in detail in appendix A. Using the Tromans model, $(C_{aq})_{I}/P_{O_2}$ was calculated for different bulk solution concentrations and this is shown in Fig. 10. In this Figure, A, B, and C represent solution concentrations of 0.001 M NaCl + 0.001 M Na₂SO₄ + 0.01 M NaHCO₃, 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃, and 0.01 M NaCl + 0.011 M Na₂SO₄ + 0.001 M NaHCO₃, respectively. These bulk solution concentrations were chosen to represent experiment 11 (lowest i_{corr} of DoE), experiment 15 (center point of DoE), and experiment 28 (highest i_{corr} of DoE), respectively. As can be seen, $(C_{aq})_{I}/P_{O_2}$ declines with increasing temperature and bulk solution concentration, however, it is less temperature sensitive for high bulk solution concentration (*i.e.* A).

To find the temperature dependence of the corrosion current density, one might combine Eqs. 3 and 9, which results in:

$$i_{\rm corr} \propto \frac{Dk' P_{\rm O_2}}{d}$$
 (10)

In a stagnant electrolyte, *d* remains reasonably constant. Thus, by knowing k', the corrosion rate at any $T(r_T)$ relative to a reference temperature can be estimated. For instance, using the corrosion rate at 298 K (r_{298}) as the reference temperature, the relative corrosion rate at *T* is given by:

$$r_T / r_{298} = \left(\frac{Tk' P_{O_2}}{\eta}\right)_T / \left(\frac{298k' P_{O_2}}{\eta}\right)_{298}$$
(11)

where η is viscosity of water. Fig. 11 illustrates the predicted relative corrosion rate of the galvanized steel determined with Eq. 11. A, B, and C in Fig. 11 refer to 0.001 M NaCl + 0.001 M Na₂SO₄ + 0.01 M NaHCO₃, 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃, and 0.01 M NaCl + 0.01 M Na₂SO₄ + 0.001 M NaHCO₃, respectively. For temperature *T*, the predicted relative corrosion rate for conditions A, B, and C were calculated as follows:



Fig. 11. Predicted relative corrosion rate (dimensionless ratio) as a function of temperature calculated for different bulk solution concentrations. A: 0.001 M NaCl + 0.001 M Na₂SO₄ + 0.01 M NaHCO₃; B: 0.005 M NaCl + 0.005 M Na₂SO₄ + 0.005 M NaHCO₃ and; C: 0.01 M NaCl + 0.01 M Na₂SO₄ + 0.001 M NaHCO₃.

$$r_T / r_{298} = i_{\rm corr, T} / i_{\rm corr, 298} \tag{12}$$

where $i_{\text{corr},T}$ and $i_{\text{corr},298}$ were calculated from the DoE model using Eq. 1 (*i.e.* DoE model in the form of coded terms). This behavior is more pronounced in less concentrated bulk solution. In other words, in a relatively dilute simulated soil solution, increasing temperature has a greater effect on the corrosion rate than in concentrated solutions.

Increasing temperature results in decreasing O_2 solubility and, hence, should lead to decreasing i_{corr} (Eq. 3). However, Fig. 11 shows the opposite result, *i.e.* increasing corrosion rate with increasing temperature. This implies that O_2 solubility does not have a dominant effect on the overall corrosion behavior of galvanized steel in simulated soil solution. Rather, the effect of the oxygen diffusion coefficient is more important, which agrees with the findings of the artificial pit studies, as discussed previously.

4.4. The significance of findings for underground corrosion of galvanized steel power transmission towers

British Columbia has a diverse climate and its biogeoclimatic conditions are classified in 14 distinct zones, where 8 are classified as having cold (mean annual soil temperature 2 < 8 °C) to extremely cold (mean annual soil temperature < -7 °C) soil temperature [73]. Moreover, a difference of 10–15 °C was reported for daily soil temperature on a clear day during summer in the interior of British Columbia [74]. Results from DoE suggest that temperature is the most significant factor affecting the corrosion rate of galvanized steel in simulated soil solutions. Therefore, a galvanized steel structure installed in British Columbia has a different underground corrosion behavior compared to those reported for relatively warmer locations. Moreover, using empirical models developed to predict the soil corrosion rate of galvanized steel might underestimate the service life of galvanized steel assets installed in British Columbia, as they are based on corrosion data collected from warmer locations [75].

According to the American Association of State Highway and Transportation Officials (AASHTO), an aggressive soil is defined as having either: an chloride concentration greater than 100 ppm, an sulfate concentration greater than 200 ppm, soil resistivity lower than 3000 Ω .cm, a pH outside the range of 5–10, or organic content more than 1 % [76]. A survey of up to 20 years of service life for galvanized steel structures buried in different soils has shown that structures buried in soils out of AASHTO limits experience considerably higher

corrosion rates, which are related to either higher chloride or sulfate concentrations, a low pH or high soil organic content [77]. For soil with the resistivity of more than 3000 Ω .cm, the AASHTO model predicts that the corrosion rate of a Zn coating would be $1.0\,\mu\text{A}/\text{cm}^2$ (or a corrosion rate of $15 \,\mu$ m/year) [77]. Although this model was found to be conservative, it predicts cumulative metal loss less than 2000 µm after 75 years of service life for a galvanized steel [75]. The low and high levels of chloride, sulfate and citric acid concentration shown in Table 1 covers both the non-aggressive and aggressive soil AASHTO criteria. The results listed in Table 2 for the DoE in simulated soil solution suggest that when temperature, chloride and citric acid concentration are at low levels, $i_{\rm corr}$ is less than 1.0 μ A/cm². However, by increasing either chloride or citric acid concentration to a high level, *i*_{corr} increases to greater than $1.0 \,\mu\text{A/cm}^2$, even when the temperature is low. Moreover, at the high level of temperature, $i_{\rm corr}$ is greater than 3.0 μ A/cm², regardless of chloride and citric acid concentration, which is above the acceptable AASHTO corrosion rate limit [41]. This reinforces the significant effect of temperature on the dissolution kinetics of galvanized coatings, which was confirmed by the artificial pit studies as discussed previously.

Soils with high resistivity (low moisture and soluble salt content) usually have very low corrosivity, even at elevated temperatures. For example, soils with resistivity more than 10,000 Ω .cm are categorized as negligibly corrosive based on NACE soil corrosivity classification [78]. Most soils in British Columbia, however, have considerably lower resistivity, which make them more corrosive. Consequently, the effect of temperature on corrosion resistance of a buried galvanized steel structure in British Columbia would be more pronounced than that of a structure installed in warmer, but drier locations. Moreover, it is known that soil aeration and moisture content vary for different types of soils. The results from DoE and oxygen solubility modeling suggest that temperature and the presence of inorganic solutes greatly influence oxygen solubility. Different parts of the foundation of a transmission tower are exposed to electrolyte with different levels of oxygen content due to variation of soil temperature, salinity, and porosity, which can accelerate corrosion in areas with less oxygen access because of differential aeration.

Overall, one can link the results presented in this paper to underground corrosion of galvanized steel transmission towers from two viewpoints. First, the significance of influencing factors on soil corrosion of galvanized coatings are elucidated. Second, these same factors affect the localized corrosion of Zn, which is known to trigger the deterioration of galvanized coatings.

It should also be noted that a transmission tower installed in British Columbia experiences a non-linear annual corrosion rate because of seasonal temperature changes. During cold months, the corrosion rate is low even at high soil soluble salts and organic content, while during warm months the corrosion rate is high even in a soil with low levels of soluble salts and organic content. For example, results of DoE show that for 0.001 M chloride + 0.001 M sulfate + 0.001 M bicarbonate + 0.001 M citric acid at -5 °C and 25 °C, the corrosion rate will be 7.84 µm/year and 58.60 µm/year, respectively. Although, the main objective of the present study was to better understand the soil corrosion of buried galvanized steel structures installed in British Columbia, the findings presented here are not limited to British Columbia and can be extended to similar soil and climatic conditions.

5. Conclusions

Simulated soil solution was used to assess underground corrosion behavior of hot-dip galvanized steel power transmission towers. A full two-level factorial design was employed to identify the most significant factors and interactions influencing the corrosion rate of the galvanized steel. The effects of chloride, sulfate, bicarbonate, citric acid and temperature were evaluated. The range of each factor was selected to mimic soil and climate conditions in British Columbia and the corrosion current density was the factorial design response. ANOVA was used to analyze the statistical significance of the results. It was shown that the model is significant, while the curvature is not, implying that the model accurately fits the data and can reliably be used to interpolate the response. Using ANOVA, temperature, citric acid, the interaction between temperature and citric acid andchloride, and the interaction between temperature and chloride were identified as the most significant factors on the corrosion current density of galvanized steel. In contrast, ANOVA showed that sulfate and bicarbonate had a negligible effect on *i*_{corr}. At the low level of chloride, citric acid and temperature the corrosion current density was below the AASHTO corrosion rate limit for buried galvanized steel (*i.e.* $1.0 \,\mu$ A/cm²). However, at high levels of temperature, *i*_{corr} was well above the AASHTO limit, implying the important negative effect of increasing temperature on the corrosion resistance of buried galvanized steel.

The pit chemistry was evaluated using the lead-in pencil electrode technique. It was found that temperature affects the dissolution kinetics of the Zn coating via increasing the diffusion coefficient of dissolving metal cations. Moreover, other factors, such as citric acid and chloride concentration, in particular, change the pit chemistry and most likely the composition of the salt film. The dissolution kinetics were affected by bulk solution concentration and temperature. While increasing bulk solution concentration hindered the dissolution kinetics by lowering the solubility of the metal salt due to the common-ion effect, increasing temperature overcame this effect by increasing the diffusion coefficient of the dissolution products. Moreover, thermodynamic modeling predicted that oxygen solubility decreases with increasing temperature and bulk solution concentration of chloride, citric acid and sulfate. Thus, a decrease in corrosion current density might be expected from these parameter changes alone. However, experimental results showed that icorr increased with temperature and bulk solution concentration of chloride, citric acid and sulfate. This contradiction clearly demonstrates that the oxygen diffusion coefficient, rather than the oxygen solubility. has a dominant effect on the overall corrosion rate of galvanized steel in simulated soil solution. Similar behavior is expected for buried galvanized steel in soil, where, compared to other parameters such as soil oxygen content, temperature has a dominant effect influencing the overall corrosion rate via changes in the oxygen diffusion coefficient.

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

Declaration of Competing Interest

Please check the following as appropriate:

All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

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Appendix A. Supplementary data

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