

# EVALUATING THE CORROSIVITY OF CHEMICAL DEICERS: AN ELECTROCHEMICAL TECHNIQUE

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**Abstract:** This paper presents a novel electrochemical technique to rapidly evaluate the corrosivity of chloride-based deicers for winter highway maintenance. Potentiodynamic polarization curves were measured in the ranges of  $E_{\text{corr}} \pm 150$  mV. Corrosion parameters were calculated on the basis of potential (E) versus current density (i) characteristics in the range of  $E_{\text{corr}} \pm 70$  mV (weak polarization). The Tafel slopes were approximated by fitting the anodic and cathodic curves to two polynomials and then taking their derivative at  $E_{\text{corr}} \pm 60$  mV, respectively.

First, the experiments were conducted in salt solutions with chloride concentration of 0.5M, representative of five deicer categories, i.e., NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl+10wt.% MgCl<sub>2</sub>, and NaCl+20wt.% MgCl<sub>2</sub>. Then, the inhibiting efficiency of three different chemicals on steel corrosion in NaCl+10wt.% MgCl<sub>2</sub> was investigated. The experiments were performed at room temperature with carbon steel coupons, for both potentiodynamic polarization and gravimetric measurements. For the solutions investigated, the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) were found useful to predict the result of gravimetric test at reasonable accuracies. The electrochemical technique was able to rapidly evaluate the corrosivity of deicer products in the presence and absence of corrosion inhibitors, and with some improvements, it is expected to supplement the existing gravimetric corrosion test.

**Keywords:** Deicer; Corrosion rate; Potentiodynamic; Corrosion tests; Weak polarization.

## 1. Introduction

Chloride-based chemicals play a key role in ensuring safe winter-driving conditions, especially for highways enduring cold and snowy weather. The common chemical deicers include sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>), and calcium chloride (CaCl<sub>2</sub>), and they are widely used for anti-icing, de-icing and pre-wetting operations [1]. These chemical deicers are arguably a great concern for their corrosive effects on motor vehicles and the transportation infrastructure.

The Pacific Northwest Snowfighters (PNS), an Association of transportation professionals for British Columbia, Washington, Idaho, Montana, Oregon, and Colorado, has implemented testing protocols and guidelines for new product qualification for deicers. A central feature of these requirements is the presence of corrosion inhibitor in all deicers, and the qualification and evaluation of all deicers by a modified NACE corrosion test. The NACE/PNS test is based on a gravimetric method that entails cyclic immersion of multiple parallel coupons for 72 hours on a custom design machine. For quality assurance and litigation purposes, a faster, more reliable technique is desirable to evaluate the corrosivity of chemical deicers.

Electrochemical techniques may provide an attractive alternative to the gravimetric method in terms of allowing rapid determination of corrosion rate of metals and revealing information pertinent to the corrosion mechanism and kinetics. However, the challenge lies in the fact that electrochemical techniques generally give information on the instantaneous corrosion rate (or corrosion resistance), while the gravimetric method gives the average corrosion rate over a

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period of time. The relationship between the two types of corrosion rate, if any, is not necessarily linear or self-evident, especially when various types of corrosion inhibitors are added to the aqueous solution. The corrosion inhibitors act by different mechanisms (anodic, cathodic, or mixed type) and some may act faster than others.

Linear polarization resistance (LPR) and Tafel polarization measurements were found capable of indicating the effect of inhibitor injection on the corrosion rate of carbon steel in natural seawater [2]. In many practical applications, the use of LPR (within  $E_{\text{corr}} \pm 15$  mV) could be preferred due to its simplicity [3,4]. However, there are concerns over its validity and reliability when LPR is used to quantify the corrosion rate, as it is prone to measuring errors of the test instrument and other variations. For Tafel polarization (beyond  $E_{\text{corr}} \pm 150$  mV), the limitation is that the applied external perturbation may lead to significant change in the surface state of electrodes, in the solution composition, or in the controlling corrosion mechanism and kinetics [5].

Weak polarization offers advantages over LPR and Tafel polarization measurements, as it studies the corrosion behavior of the metal close to its natural state without requiring high-end test instruments. It has been, however, computation-intensive, in order to obtain electrochemical parameters of corrosion processes by fitting the weak polarization curves. For instance, Gauss-Newton and Levenberg-Marquardt methods were applied for curve-fitting [6,7]. To alleviate that, a 4-point method was used to determine the corrosion of carbon steel and assess the effects of corrosion inhibitors, which obtained results consistent with Tafel polarization in the optimum polarization region of -50 to -10 mV and 10-50 mV [8]. Based on the authors' experience, nonetheless, the results obtained using a few data points on the polarization curves could suffer from their sensitivity to the measuring errors.

This paper aims to establish an easy-to-implement, practical electrochemical technique for the fast evaluation of corrosivity of various chloride-based deicers, based on potentiodynamic polarization in the weak polarization region.

## 2. Experimental Method

The salt solutions investigated include those with chloride concentration of 0.5M, representative of five PNS deicer categories, i.e., NaCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, NaCl+10wt.% MgCl<sub>2</sub>, and NaCl+20wt.% MgCl<sub>2</sub>. The corrosion inhibitors investigated include sodium monofluorophosphate (MFP), barium metaborate (BMB), and disodium  $\beta$ -glycerophosphate (DGP). All chemicals were from Sigma-Aldrich. In addition, three actual deicer products were provided by the Montana Department of Transportation (MDT) for testing. Both gravimetric and electrochemical experiments were performed at room temperature (72-75°F), with the MDT deicers diluted to a 3wt.% solution as specified by the NACE/PNS protocol and the salt solutions tested directly.

The gravimetric corrosion tests were conducted by the Analytical Laboratories, Inc. (Boise, ID), following the NACE/PNS corrosion rate test protocol. The protocol was developed by PNS based on the NACE-TM-01-69 standard (revised 1976), which involves cyclic immersion (10 minutes in the solution followed by 50 minutes exposed to air) for 72 hours followed by a measurement of weight loss. The weight loss result in MPY (milli-inch per year) was translated into a percentage, or percent corrosion rate (PCR), in terms of the solution corrosivity relative to a eutectic salt brine. The coupons used were TSI washer steel and met ASTM F 436, Type 1, with a Rockwell Hardness of C 38-45.

The electrochemical experiments used carbon steel coupons from Metal Samples, Inc. (Munford, AL), each 1.6 cm in diameter and polished to 600 grit. Table 1 lists the nominal

elemental composition of these C4130 coupons as provided by the vendor. For each coupon, it was first cleaned with cotton and distilled water, then with chloroform, and dried. Then, the steel coupon was mounted onto the reactor, a Princeton Applied Research Model K0235 Flat Cell, which allows an area of 1 cm<sup>2</sup> to be exposed to the solution. The Flat Cell also features a silver/silver chloride reference electrode and a platinum-on-niobium counter electrode. No stirring was provided for the electrochemical tests, each of which used 300 ml of solution.

Table 1. The nominal elemental composition (wt.%) of C4130 coupons

Fe	Cr	Mn	C	Si	Ni	Mo	Cu	Al	P	S
Balance	0.970	0.490	0.310	0.250	0.180	0.170	0.150	0.024	0.023	0.009

The electrochemical measurements were carried out using a computer-controlled Faraday MP Potentiostat from the Obbligato Objectives, which enables software filtering and Ohmic drop compensation for polarization curves. For each solution of interest, the open circuit potential (OCP) of working electrode, i.e., the corroding steel, was monitored for 40 minutes to allow it to stabilize. Then, cyclic voltammetry (CV) was applied in the range of OCP±100 mV in order to determine the Ohmic drop due to the electrolyte resistance and to identify the range of the corrosion potential ( $E_{corr}$ ). At time of 60 and 70 minutes, cathodic stripping voltammetry (CSV) were applied twice in the range of  $E_{corr}$ ±150 mV. All electrochemical experiments used the sweep rate of 6.7mV/s for potential scan.

The surface morphology of a steel coupon from electrochemical testing in the 0.5M NaCl solution was studied using an environmental scanning electron microscope. The coupon was rinsed with distilled water and dried for 72 hours before surface analysis.

### 3. Mathematical Model

For weak polarization of steel in the salt solutions, the polarization due to mass transfer or ohmic drop is either negligible or can be compensated. Therefore, the relation between current density ( $i$ ) and potential ( $E$ ) on the polarization curve is governed by the following equation:

$$i = i_{corr} \left\{ \exp \frac{2.3(E - E_{corr})}{b_a} - \exp \frac{2.3(E - E_{corr})}{b_k} \right\} \quad (1)$$

where  $E_{corr}$  and  $i_{corr}$  are the corrosion potential and corrosion current density,  $b_a$  and  $b_k$  are the anodic and cathodic Tafel slope, respectively.

The corrosion electrochemical parameters including  $E_{corr}$ ,  $i_{corr}$ ,  $b_a$  and  $b_k$ , can be used not only to determine the instantaneous corrosion rate but also to unravel the corrosion mechanism and kinetics governing the corrosion processes. In order to obtain such information from potentiodynamic polarization curves, this paper presents an approximation method in place of the numerical solution. First,  $E_{corr}$  is interpolated as the potential where the current density is zero on the CSV curve.

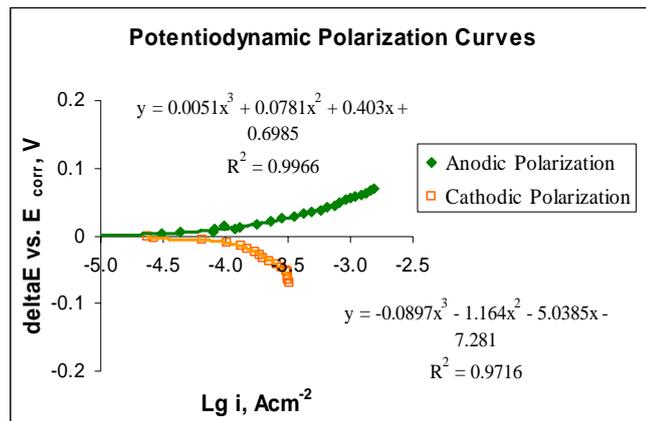


Figure 1. An example potentiodynamic polarization curve, showing the curve fitting in the weak polarization region

As illustrated in Figure 1, the anodic and cathodic polarization curves are then plotted as overpotential ( $\Delta E$ ) versus the logarithm of current density ( $\text{Lgi}$ ), in the polarization range of  $\pm 70$  mV (weak polarization region). The anodic and cathodic curves are then fitted to two polynomials, respectively. In Figure 1, the values of R-square indicate how well the curves were fitted, with 1 as best fit and 0 as worst fit. Once the curves are fitted, the Tafel slopes,  $b_a$  and  $b_k$ , can be approximated by taking the derivatives of the polynomials at overpotential of  $\pm 60$  mV, respectively. Based on  $b_a$  and  $b_k$ , the value of Tafel constant B can be calculated.

Finally,  $i_{\text{corr}}$  can be obtained following the rule of Tafel linear extrapolation, which is expressed in the following equations:

$$\Delta E_a = A_a + b_a \lg i_a \quad (2)$$

$$\Delta E_k = A_k + b_k \lg i_k \quad (3)$$

where  $\Delta E_a$  and  $\Delta E_k$  are anodic and cathodic overpotential, and  $i_a$  and  $i_k$  are anodic and cathodic current density, respectively. Replacing  $\Delta E_a$  and  $\Delta E_k$  with 60 and -60 mV in equations (2) and (3) respectively, we can obtain the values of  $A_a$  and  $A_k$ . Then, replacing  $\Delta E_a$  and  $\Delta E_k$  with 0, we can obtain the values of  $\lg i_a$  and  $\lg i_k$  at  $E_{\text{corr}}$ . If the values of  $\lg i_a$  and  $\lg i_k$  at  $E_{\text{corr}}$  are very close to each other, their average gives the logarithm of  $i_{\text{corr}}$ .

Table 2. The corrosion electrochemical parameters and corrosivity of various deicer solutions

Deicer ID	$E_{\text{corr}}$ (V, Ag/AgCl)	$b_a$ (mV)	$b_k$ (mV)	B (mV)	$i_{\text{corr}}$ (mA/cm <sup>2</sup> )	PCR, Measured	PCR, Predicted	Error
NaCl	-0.698	66.6	294.9	23.63	0.111	99.1	103.3	4.3%
MgCl <sub>2</sub>	-0.645	100.3	174	27.67	0.089	56.5	63.9	13.1%
NaCl+10%MgCl <sub>2</sub>	-0.631	71.4	143.2	20.71	0.095	68.1	58.1	-14.7%
NaCl+20%MgCl <sub>2</sub>	-0.652	93.3	136.4	24.09	0.095	75	68.3	-8.9%
CaCl <sub>2</sub>	-0.671	52.2	219.6	18.33	0.333	98.5	100.7	2.3%
4+10mM DGP	-0.47	66	113.7	18.16	0.096	19.5	22.5	15.6%
4+50mM MFP	-0.458	157.1	120.7	29.68	0.080	20.9	20.7	-0.8%
4+2mM BMB	-0.618	94.2	100.7	21.16	0.043	45.7	45.5	-0.4%
MDT 34	-0.184	76.7	188.5	23.72	0.173	15	16.6	10.6%
MDT 46	-0.252	117.7	128.3	26.7	0.164	17.9	15.7	-12.5%
MDT 47	-0.266	114.1	135.9	26.96	0.167	16.3	15.7	-3.5%

#### 4. Results and Discussion

Table 2 lists the corrosion test results of various deicer solutions, including the 0.5M [Cl<sup>-</sup>] salt solutions in the absence and presence of three corrosion inhibitors as well as three actual deicer products used by MDT. All calculations of corrosion electrochemical parameters were performed in a spreadsheet without programming. The R-square for weak polarization curve fitting was found mostly higher than 0.90, and the coefficient of variance for  $\lg i_a$  and  $\lg i_k$  was found mostly lower than 2%. These findings indirectly validate the proposed approach to obtaining corrosion electrochemical parameters from weak polarization curves.

For each solution, the electrochemical testing was performed in less than two hours, long before a conventional weight change would be measurable. As shown in Figure 2, the typical size of a larger corrosion site on the carbon steel surface is around 10 microns in diameter.

The relationship between the instantaneous corrosion rate (expressed as  $i_{\text{corr}}$ ) and the average corrosion rate (expressed as PCR), was neither linear nor self-evident. A closer examination of the data in Table 2, however, led to some interesting observations. There is a nonlinear relationship between PCR and  $E_{\text{corr}}$  (as illustrated in Figure 3) and a linear relationship between

$\text{Lg}(\text{PCR})$  and  $\text{Lg}(i_{\text{corr}}) - 5E_{\text{corr}}$  (as illustrated in Figure 4). Based on these observations, the authors identified a stronger linear relationship ( $R^2 = 0.9784$ ) as described by the following equation:

$$\text{Lg}(\text{PCR}) = 4.312E_{\text{corr}}^2 + 2.188E_{\text{corr}} + 0.187\text{Lg}(i_{\text{corr}}) + 1.619 \quad (4)$$

Figure 5 shows that the PCR values predicted via equation (4) are in good agreement with the measured values.

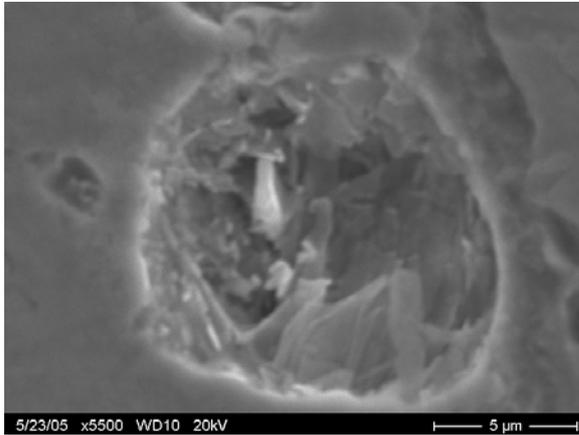


Figure 2. Scanning electron microscope view of a corrosion site on the carbon steel surface

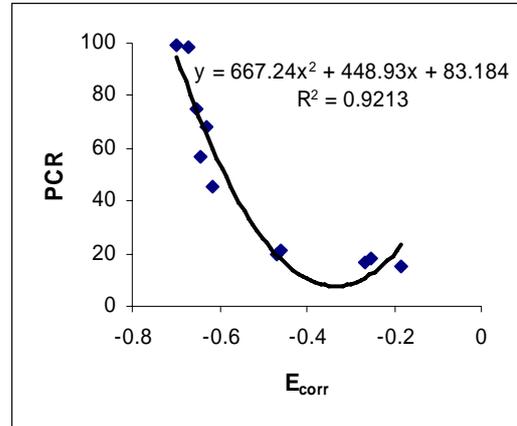


Figure 3. PCR as a function of  $E_{\text{corr}}$

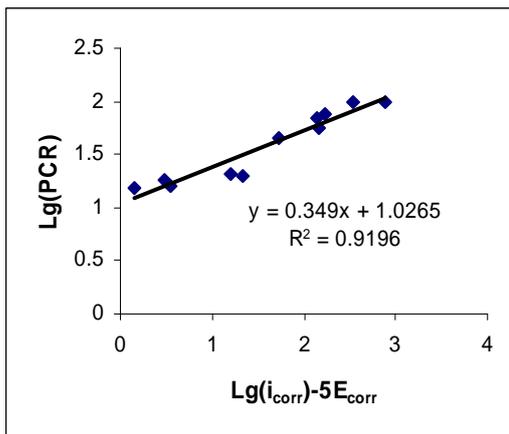


Figure 4.  $\text{Lg}(\text{PCR})$  as a function of  $\text{Lg}(i_{\text{corr}}) - 5E_{\text{corr}}$

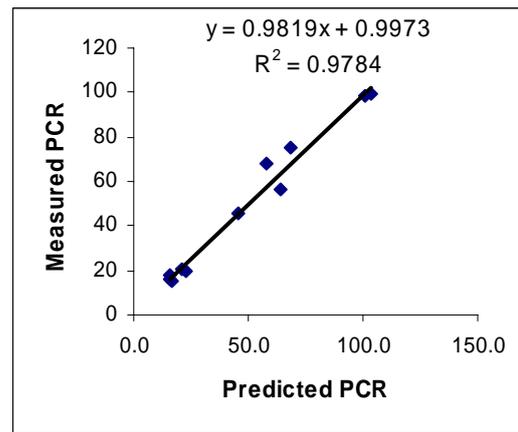


Figure 5. Relationship between predicted and measured PCRs

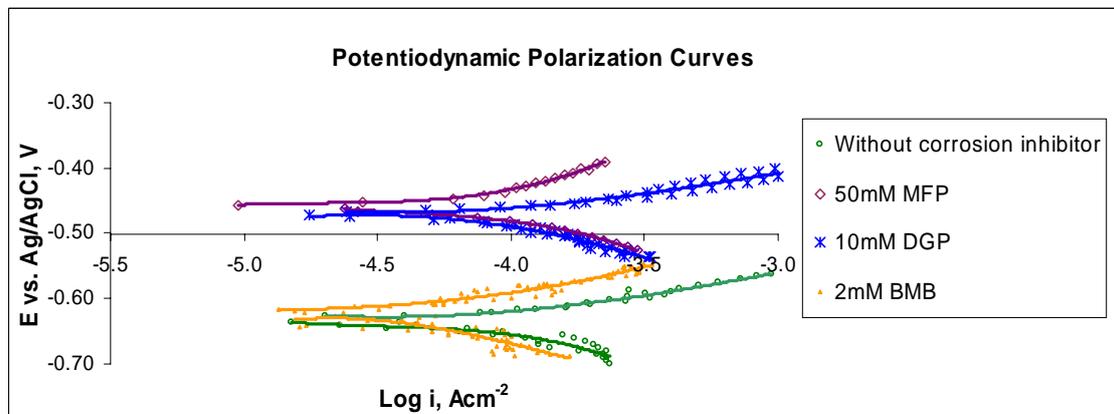


Figure 6. Polarization curves of the 0.5M  $[\text{Cl}^-]$  NaCl+10wt.%  $\text{MgCl}_2$  solution with or without corrosion inhibitors, obtained through CSV

Figure 6 shows potentiodynamic polarization curves of the 0.5M [Cl<sup>-</sup>] NaCl+10wt.% MgCl<sub>2</sub> solution with or without corrosion inhibitors, obtained through CSV. Such polarization curves are expected to provide “signature” information pertinent to the corrosion behavior of steel in the inhibited or non-inhibited solution and to be used for quality assurance of deicer products. The polarization curves also revealed the corrosion inhibition mechanism of different chemicals. For instance, adding 10mM DGP or 50mM MFP both shifted potential in the positive direction, offering certain levels of inhibition for the corroding steel. This is consistent with previous studies on these chemicals [9,10].

To further improve the reproducibility of electrochemical tests, the authors are planning to use the wire beam electrode (WBE) to replace the one-piece working electrode. The working surface of WBE consists of an array of mini-electrodes insulated from each other, allowing more statistically reliable results [11].

## 5. Conclusions

This paper presents a novel electrochemical technique to rapidly evaluate the corrosivity of chloride-based deicers for winter highway maintenance. For the solutions investigated, the corrosion potential and corrosion current density were found useful to predict the result of gravimetric test at reasonable accuracies. The electrochemical technique was able to rapidly evaluate the corrosivity of deicer products in the presence and absence of corrosion inhibitors, and with some improvements, it is expected to supplement the existing gravimetric corrosion test.

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