Effectiveness of Vapor Corrosion Inhibitors Under Elevated Chloride Conditions for Aboveground Storage Tank Application

Pavan K. Shukla, Roderick E. Fuentes,
Andrew Nordquist, and Bruce J. Wiersma
Battelle Savannah River Alliance, LLC.
Aiken, South Carolina, 29808
USA

Ingrid Pederson
Enbridge
Enbridge Centre, 10175 101 Street NW
Edmonton T5J 0H3
Canada

ABSTRACT

The sand quality used to construct the tank pad is an important contributing factor to the rate of corrosion that occurs on the soil-side of the aboveground storage tanks (ASTs) floor plates. Clean sand that meets specific criteria provides the first line of defense for mitigation of tank floor corrosion. However, it has been observed that the sand quality used for some existing tanks differ greatly from the specifications provided in the API 651 standard; this could be partially due to initial sand quality not meeting the specification, and partially due to the environmental effects over time. For example, rain-water intrusion could lead to higher than the specified contents of corrosive species such as chloride. Tank operators are increasingly using vapor corrosion inhibitors (VCIs) either as a stand alone or in combination with cathodic protection (CP) for ASTs to mitigate soil-side corrosion. VCIs are delivered either through-the-floor or injected through the ports in the ring wall. Experimental studies were conducted to evaluate VCIs' performance at elevated chloride concentrations and to study the effectiveness of the delivery methods under extreme chloride conditions. The experimental work found that VCI performance is robust and not compromised due to high chloride levels, such as 300 ppm or more. The work also showed that the through-the-floor VCI delivery method is more beneficial compared to the through-the-sand-pad method when tank pad corrosivity is elevated.

Key words: Vapor Corrosion Inhibitors, Aboveground Storage Tank, Soil-Side Corrosion, API 651, Cathodic Protection.

INTRODUCTION

Soil-side corrosion of the bottom plates of aboveground storage tanks is one of the main reasons for the tank bottom failures. Literature data[1,2,3] and experimental work have shown that soil-side corrosion rates could reach as high as 50-100 mpy, indicating that soil-side corrosion could cause the tank-bottom failure in relative short periods, i.e., less than five years after initial installation or repairs.

Of the various corrosion causing species, chloride dominates for AST floors as demonstrated by the field coupon data published in a recent PRCI study.[4] In that study, the field samples indicated that chloride concentrations were typically less than 100 ppm, however there were a few exceptions. But most of the sand samples did not meet the API 651 chloride requirement.[5] Therefore, the effectiveness of VCIs at elevated chloride concentrations was studied. Following are the key points that were considered in this work. Two modes of VCI delivery were considered: (a) through-the-floor for out-of-service tanks, and (b) through-the-sand-pad for in-service tanks. VCI dosages depend on the soil chloride concentrations and were adjusted in proportion to higher level of chlorides. The most common ways to introduce VCIs into the tank pad include liquid slurry injection (prepared by mixing potable water with VCI) and dry powder application. Determining VCIs' migration characteristics are particularly important when VCIs are delivered through the ports located at discrete positions around the tank ring wall for the single bottom tanks, and around the dead shell of the double bottom tanks. The ports are 20-60 ft apart, and VCIs are pushed either directly through the port, or through a perforated tube installed at the ports; the perforated tubes extend into the sand pads and VCIs are released into the sand pad's interstitial space, along the length of the perforated tubes. In both scenarios of the through-port delivery, a plume is generated where VCI is released into the sand pad, followed by VCI migration from the plume front. VCIs' migration is aided by the process of chemical volatilization and diffusion for distribution of the inhibitor chemistry. None the less, VCI coverage of the tank bottom plate is determined by the extent of VCIs' migration in sufficient concentration that is effective for mitigating corrosion.

Field sand taken beneath a tank experiencing severe soil-side corrosion and commercially available playground sand were used to conduct tests to investigate VCI effects. Coupons were acid cleaned after completing exposure durations. Each coupon's material wastage data were analyzed to obtain surface average and deepest pit corrosion rates.

EXPERIMENTAL

A test matrix for the through-the-floor VCI was developed and is listed in Table 1. The following chloride levels were selected: (i) 300 ppm, (ii) 1000 ppm, (iii) 1500 ppm, and (iv) 3000 ppm. It was not necessary to conduct the control and VCI effect experiment at each chloride level because corrosion rates are expected to be mass-transfer controlled at elevated chlorides. Therefore, only three of the four chloride levels were selected for each category of experiments in Table 1. Field sand was used for the through-the-floor application method because the experiments did not require a large sand quantity. Sodium chloride and sodium sulphate salts were added to the field sand to achieve desired chloride and sulphate concentrations. An image of the experimental setup used for each test in Table 1 is presented in Figure 1(a).

Table 1
Test Matrix for the VCI Delivery Method Being Through-The-Floor

Chloride concentration	Control	VCI-A	VCI-B
Field Sand + 300 ppm chloride	Yes	Yes	Yes
Field Sand + 1000 ppm chloride	Yes	Yes	No
Field Sand + 1500 ppm chloride	Yes	No	Yes
Field Sand + 3000 ppm chloride	No	Yes	Yes

The test matrix for the through-the-sand-pad delivery method is listed in Table 2. These experiments required a larger amount of sand compared to the through-the-floor delivery method experiments. Therefore, commercially available playground sand was used. An image of the experimental setup is presented in presented in Figure 1(b).

Table 2
Test Matrix for the VCI Delivery Method Being Through-The-Sand-Pad

Chloride concentration	Control	VCI-A	VCI-B
Playground Sand + 300 ppm chloride	No	Yes	Yes
Playground Sand + 1000 ppm chloride	No	Yes	Yes
Playground Sand + 1500 ppm chloride	No	Yes	Yes
Playground Sand + 3000 ppm chloride	No	Yes	Yes

(a) (b)

Figure 1. (a) Image of the experimental setup used to evaluate effect of VCIs at elevated chloride levels using the field sand and through-the-floor delivery method. (b) Image of the experimental setup used to evaluate effect of VCIs at elevated chloride levels using the playground sand and through-the-sand-pad delivery method.

DATA AND RESULTS

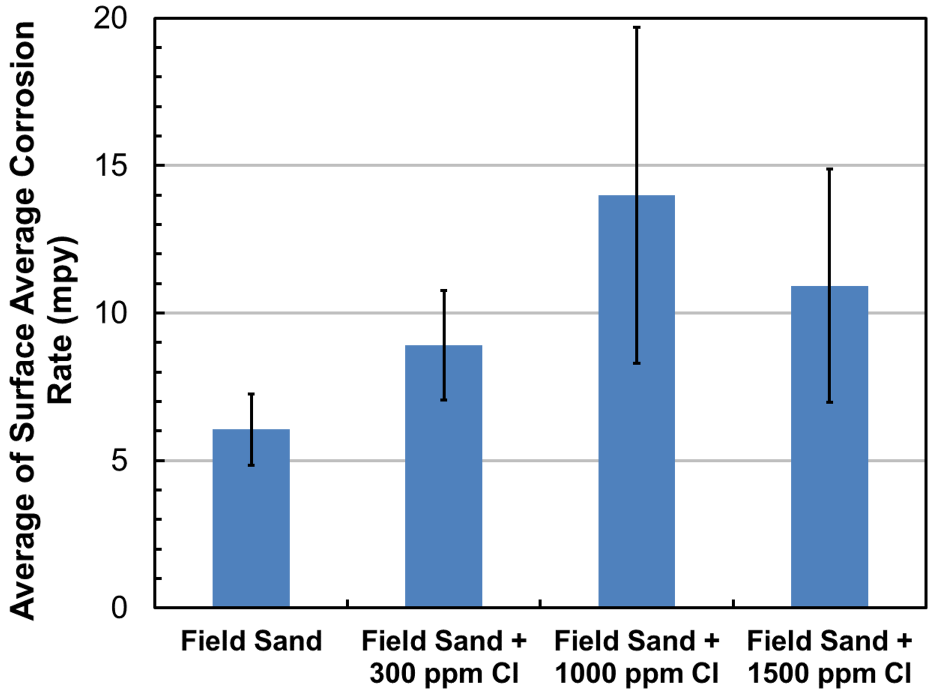
The coupons' corrosion rate data for the control tests are listed in Table 3; the table includes averages of surface average and deepest pit corrosion rates. The coupons corrosion rate data is graphically presented in Figure 2. The control tests data were used to determine the effect of chloride concentration on corrosion rates. To this end, the Student's t-test was used to determine significance of adding chloride concentration. Student's t-test provides a p-value; if the p-value is less than 0.05, this indicates that the effect is significant. The p-values for various combinations of the control tests are listed in Table 4.

Table 3
Control Tests Coupons Corrosion Rate Data

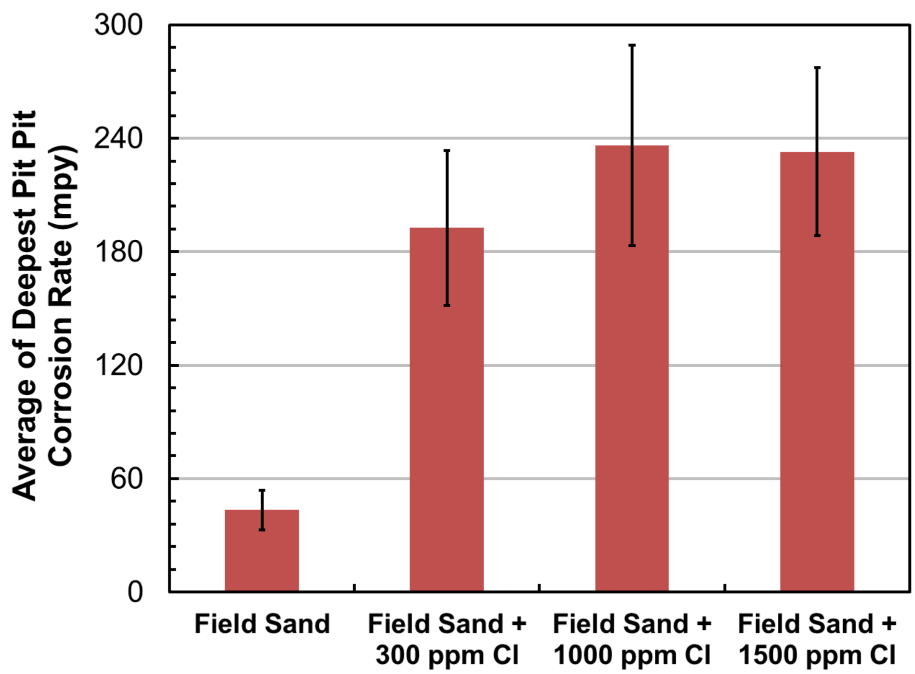
Chloride concentration	Average of surface average corrosion rate + standard deviation (mpy)	Average of deepest pit corrosion rate + standard deviation (mpy)
Field Sand*	6.1 ± 1.2	43.4 ± 10.5
Field Sand + 300 ppm chloride**	8.9 ± 1.9	192.6 ± 41.1
Field Sand + 1000 ppm chloride**	14.0 ± 5.7	236.3 ± 52.9
Field Sand + 1500 ppm chloride**	10.9 ± 4.0	232.8 ± 44.4
*Each data point is average of four coupons ** Each data point is average of six coupons		

Table 4
p-Values for Various Combinations of Control Test Electrolytes

Electrolyte Combination	p-value	
	Surface Average Corrosion Rate	Deepest Pit Corrosion Rate
Field Sand and Field Sand + 300 ppm chloride	0.02	1.6×10^{-4}
Field Sand and Field Sand + 1000 ppm chloride	0.02	1.9×10^{-4}
Field Sand and Field Sand + 1500 ppm chloride	0.03	7.0×10^{-5}
Field Sand + 300 ppm chloride and Field Sand + 1000 ppm chloride	0.08	0.23
Field Sand + 300 ppm chloride and Field Sand + 1500 ppm chloride	0.29	0.13
Field Sand + 1000 ppm chloride and Field Sand + 1500 ppm chloride	0.31	0.91



(a) Average of surface average corrosion rates



(b) Average of deepest pit corrosion rates

Figure 2. Average of (a) surface average and (b) deepest pit corrosion rates for the control test coupons. Standard deviations for corrosion rate data are represented by vertical black lines in each bar.

The following is inferred from the control experiments' corrosion rate data listed in Table 3 and p-values for various combinations in Table 4:

- Addition of chloride to 300 ppm or more resulted in significant increase in both surface average and pitting corrosion rates, and
- The pitting corrosion rate increased much more than the surface average corrosion rate with addition of chloride to 300 ppm or more, and
- There is no statistically significant difference between 300 ppm, 1000 ppm, and 1500 ppm chloride additions, indicating that the corrosion rates beyond 300 ppm chloride addition may be diffusion-controlled processes.

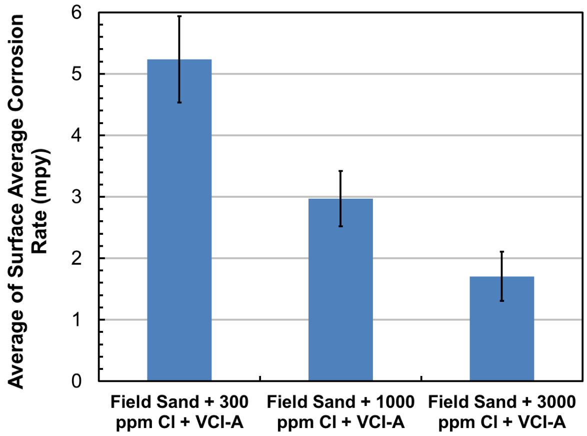
The corrosion rate data for the VCI dosed field sand plus chloride are listed in Table 5; the corrosion rate data in the table is graphically presented in Figure 3. The VCI-dosed field sand plus chloride corrosion rate data was compared to the control experiments using the Student's t-test; the p-values calculated student t-test are listed in Table 6; all of the listed p-values are below 0.05, indicating that reductions in both the both average and deepest pit corrosion rates are significant.

Table 5
Coupon Corrosion Rate Data for VCI Dosed Field Sand Plus Chloride for Through-The-Floor Delivery Method

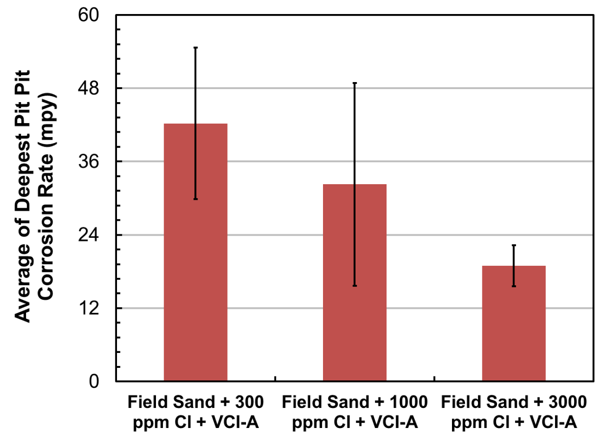
Chloride concentration	Average of surface average corrosion rate + standard deviation (mpy)		Average of deepest pit corrosion rate + standard deviation (mpy)	
	VCI-A	VCI-B	VCI-A	VCI-B
Field Sand + 300 ppm chloride + VCI*	5.2 ± 0.7	1.2 ± 0.3	42.2 ± 12.4	6.7 ± 2.0
Field Sand + 1000 ppm chloride + VCI*	3.0 ± 0.5	–	32.2 ± 16.6	–
Field Sand + 1500 ppm chloride + VCI*	–	0.6 ± 0.03	–	7.1 ± 5.1
Field Sand + 3000 ppm chloride + VCI*	1.7 ± 0.4	0.5 ± 0.4	18.9 ± 3.3	8.4 ± 2.2
*Each data point is average of six coupons				

Table 6
p-Values for Various Combinations of Control Test and VCI Dosed Field Sand Plus Chloride Electrolytes

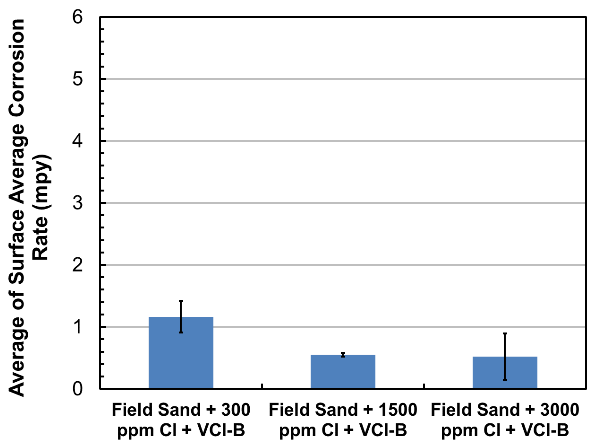
Electrolyte Combination	p-value	
	Surface Average Corrosion Rate	Deepest Pit Corrosion Rate
Field Sand + 300 ppm chloride and Field Sand + 300 ppm chloride + VCI-A	3.3×10^{-3}	1.5×10^{-4}
Field Sand + 300 ppm chloride and Field Sand + 300 ppm chloride + VCI-B	1.3×10^{-4}	1.0×10^{-4}
Field Sand + 1000 ppm chloride and Field Sand + 1000 ppm chloride + VCI-A	5.1×10^{-3}	1.1×10^{-4}
Field Sand + 1500 ppm chloride and Field Sand + 1500 ppm chloride + VCI-B	1.4×10^{-3}	5.5×10^{-5}



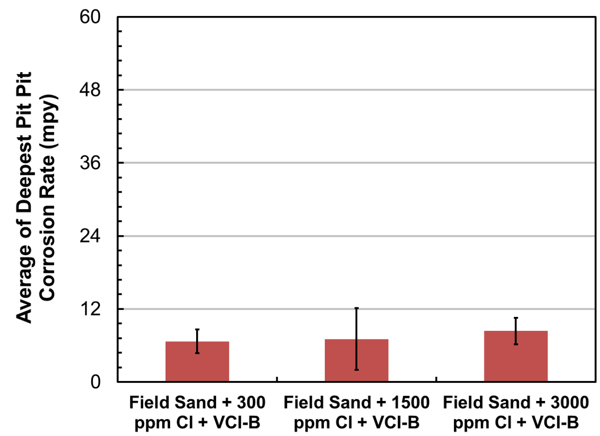
(a) Surface average corrosion rates for VCI-A addition



(b) Deepest pit corrosion rates for VCI-A addition



(c) Surface average corrosion rates for VCI-B addition



(d) Deepest pit corrosion rates for VCI-B addition

Figure 3. Average of (a) surface average and (b) deepest pit corrosion rates for field sand plus chloride plus VCI-A, and average of (c) surface average and (d) deepest pit corrosion rates for field sand plus chloride plus VCI-B. Standard deviations for corrosion rate data are represented by vertical black lines in each bar.

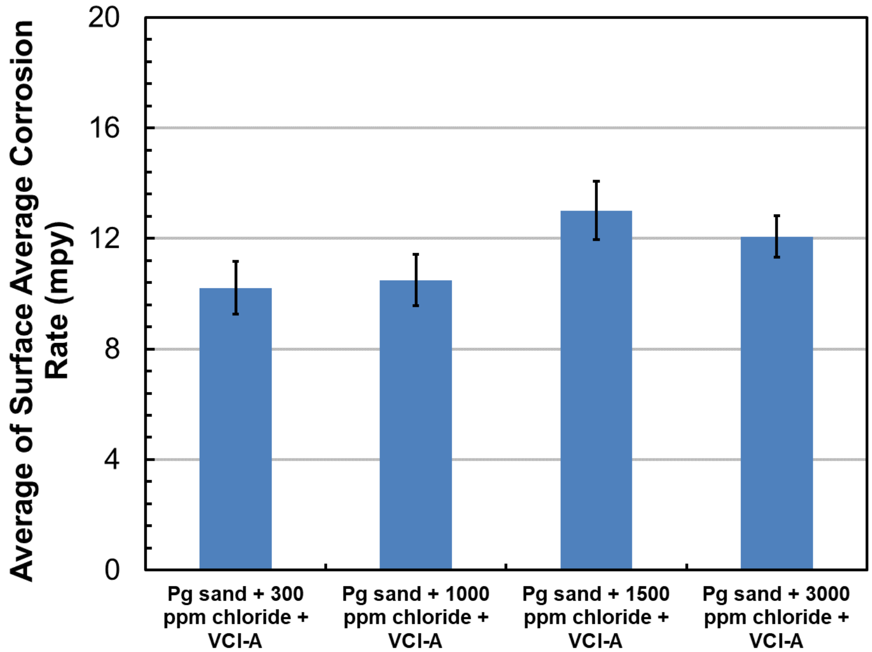
The corrosion rate data for the coupons in the VCI-dosed playground sand plus chloride are listed in Table 7; these data are for the VCI-delivery method being through-the-sand-pad. The corrosion rate data in Table 7 for VCI-A are graphically presented in Figure 4 and for VCI-B in Figure 5. The corrosion rates for the VCI-dosed playground sand plus chloride (through-the-sand-pad delivery method) are higher than the VCI-dosed field sand plus chloride, and in-fact VCI-dosed playground sand plus chloride corrosion rates are comparable to that of the control experiments conducted with field sand plus chloride. The Student's t-test was applied to calculate p-values between various combinations of VCI-dosed playground sand plus chloride and VCI-dosed field sand plus chloride. The p-values are listed in Table 8; all the listed p-values are below 0.05 for both surface average and deepest pit corrosion rates, indicating statistically significant difference between the through-the-floor and through-the-sand-pad corrosion rates.

Table 7
Coupon Corrosion Rate Data for VCI Dosed Playground Sand Plus Chloride for Through-The-Sand-Pad Delivery Method

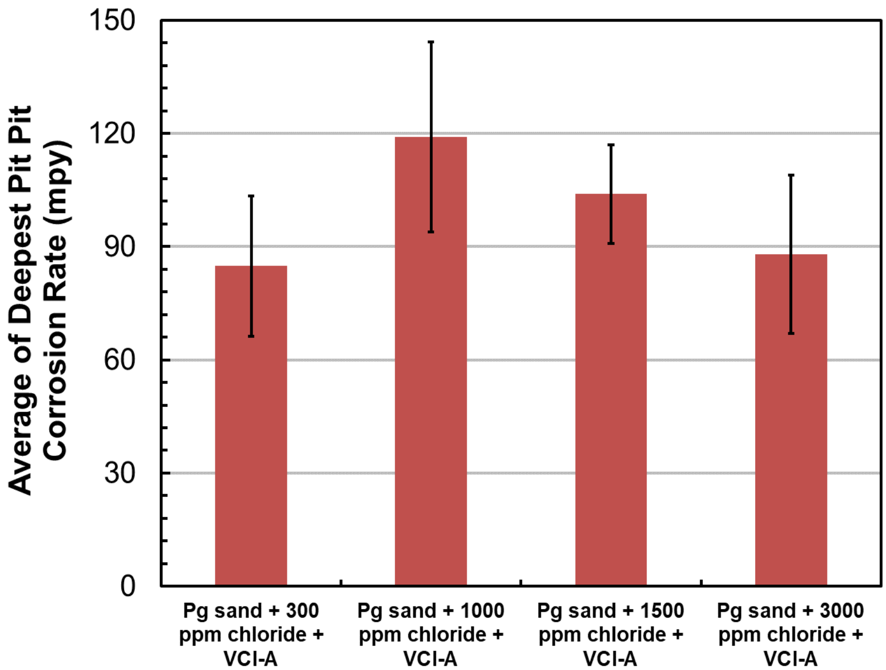
Chloride concentration	Average of surface average corrosion rate + standard deviation (mpy)		Average of deepest pit corrosion rate + standard deviation (mpy)	
	VCI-A	VCI-B	VCI-A	VCI-B
Playground Sand + 300 ppm chloride + VCI*	10.2 ± 0.9	13.5 ± 6.2	84.9 ± 18.6	79.4 ± 16.6
Playground Sand + 1000 ppm chloride + VCI*	10.5 ± 0.9	6.6 ± 0.7	119.0 ± 25.1	98.7 ± 17.1
Playground Sand + 1500 ppm chloride + VCI*	13.0 ± 1.1	6.1 ± 0.6	103.9 ± 13.0	79.9 ± 16.7
Playground Sand + 3000 ppm chloride + VCI*	12.1 ± 0.8	7.4 ± 0.8	87.9 ± 20.9	95.3 ± 21.8
*Each data point is average of six coupons				

Table 8
p-Values for Various Combinations of VCI Dosed Field Sand Plus Chloride and VCI Dosed Playground Sand Plus Chloride Electrolytes

Electrolyte Combination*	p-value	
	Surface Average Corrosion Rate	Deepest Pit Corrosion Rate
Field Sand + 300 ppm chloride + VCI-A and Playground Sand + 300 ppm chloride + VCI-A	2.2×10^{-6}	1.3×10^{-3}
Field Sand + 1000 ppm chloride + VCI-A and Playground Sand + 1000 ppm chloride + VCI-A	2.7×10^{-7}	7.1×10^{-5}
Field Sand + 3000 ppm chloride + VCI-A and Playground Sand + 3000 ppm chloride + VCI-A	3.2×10^{-9}	4.0×10^{-4}
Field Sand + 300 ppm chloride + VCI-B and Playground Sand + 300 ppm chloride + VCI-B	4.5×10^{-3}	1.1×10^{-4}
Field Sand + 1500 ppm chloride + VCI-B and Playground Sand + 1500 ppm chloride + VCI-B	2.2×10^{-6}	5.5×10^{-5}
Field Sand + 3000 ppm chloride + VCI-B and Playground Sand + 3000 ppm chloride + VCI-B	1.4×10^{-8}	1.8×10^{-4}
*Field sand was dosed through-the-floor method whereas playground sand was dosed through-the-sand-pad method		

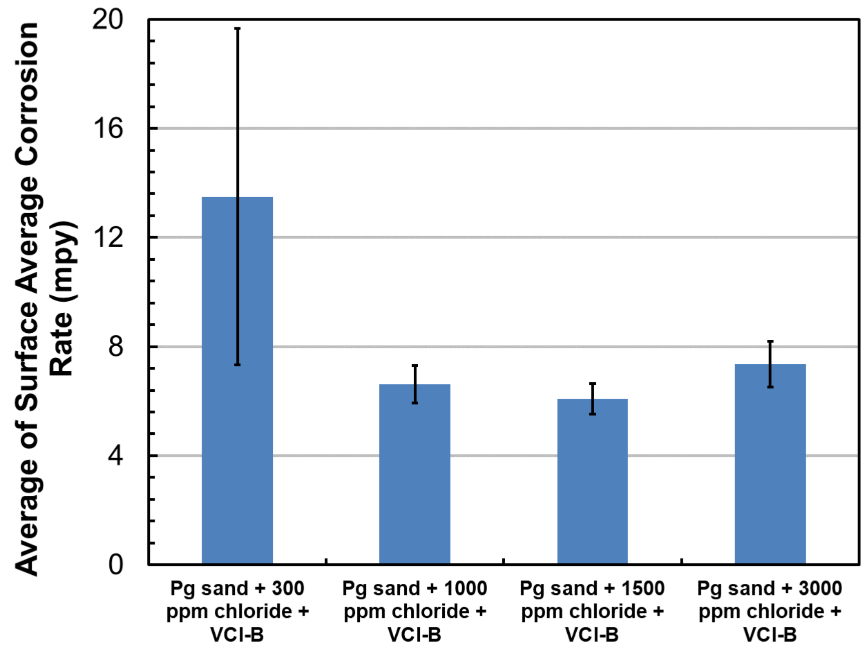


(a) Average of surface average corrosion rates

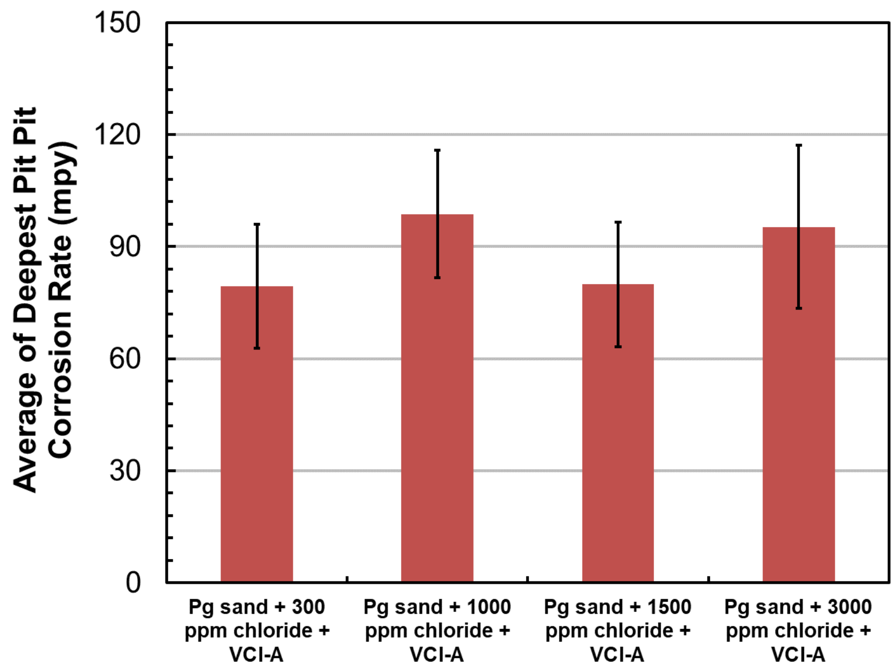


(b) Average of deepest pit corrosion rates

Figure 4. Average of (a) surface average and (b) deepest pit corrosion rates for the VCI-A dosed playground sand. Standard deviations for corrosion rate data are represented by vertical black lines in each bar. Playground sand is abbreviated as Pg sand in the x-axis labels.



(a) Average of surface average corrosion rates



(b) Average of deepest pit corrosion rates

Figure 5. Average of (a) surface average and (b) deepest pit corrosion rates for the VCI-B dosed playground sand. Standard deviations for corrosion rate data are represented by vertical black lines in each bar. Playground sand is abbreviated as Pg sand in the x-axis labels.

The following is inferred from the corrosion rate analysis and corresponding p-values.

- VCIs significantly reduce corrosion rates when applied through-the-floor delivery method in the field sand plus chloride electrolytes, and

- The surface average corrosion rates of the VCI-dosed playground sand plus chloride are comparable to that of the control experiments, however the deepest pit corrosion rates of the VCI-dosed playground sand plus chloride are lower than the control experiments.

Resistivity versus Corrosion Rate Data

Resistivity of the sand in each experimental setup was measured using the sand box four pin method as described in ASTM G57.[6] The sand resistivity data for the experiments conducted using the field sand is listed in Table 9. Similarly, the resistivity data for the experimental setup using the playground sand was also collected. Because of the large size of the experimental vessels used for the playground sand experiments compared to the field sand experiments, samples for the resistivity measurements were collected from the top, middle, and bottom of each tub; following this, each tub sand was mixed, and one additional sample was collected. Thus, four resistivity measurements were conducted for each playground sand experiment; the resistivity data is listed in Table 10. The resistivity versus surface average corrosion rate data for the field sand experiments are presented in Figure 6, and for the playground sand is in Figure 7; as seen in the figures, there is no correlation between the corrosion rates and resistivity. This observation proves the hypothesis that resistivity alone cannot be used as a corrosivity indicator for the sand pad.

Table 9
Sand Resistivity for the Experiments Setup Using the Field Sand and VCI Applied Through-The-Floor Delivery Method

Chloride concentration	Resistivity (Ω-cm)		
	Control	VCI-A	VCI-B
Field Sand + 300 ppm chloride	750	780	275
Field Sand + 1000 ppm chloride	370	235	Not applicable
Field Sand + 1500 ppm chloride	230	Not applicable	97
Field Sand + 3000 ppm chloride	Not applicable	100	59

Table 10
Sand Resistivity for the Experiments Setup Using the Playground Sand and VCIs Applied Through-The-Sand-Pad Delivery Method

Chloride Concentration	Resistivity (Ω-cm)		
	Control	VCI-A	VCI-B
Playground Sand + 300 ppm chloride	Not Applicable	Top: 3800 Middle: 1450 Bottom: 1550 Whole: 1750	Top: 2000 Middle: 610 Bottom: 290 Whole: 1100
Playground Sand + 1000 ppm chloride	Not Applicable	Top: 515 Middle: 235 Bottom: 210 Whole: 265	Top: 1650 Middle: 295 Bottom: 110 Whole: 450

Table 10
Sand Resistivity for the Experiments Setup Using the Playground Sand and VCIs Applied Through-The-Sand-Pad Delivery Method

Chloride Concentration	Resistivity (Ω-cm)		
	Control	VCI-A	VCI-B
Playground Sand + 1500 ppm chloride	Not Applicable	Top: 310 Middle: 150 Bottom: 130 Whole: 180	Top: 1600 Middle: 330 Bottom: 100 Whole: 330
Playground Sand + 3000 ppm chloride	Not Applicable	Top: 570 Middle: 105 Bottom: 78 Whole: 120	Top: 430 Middle: 160 Bottom: 77 Whole: 155

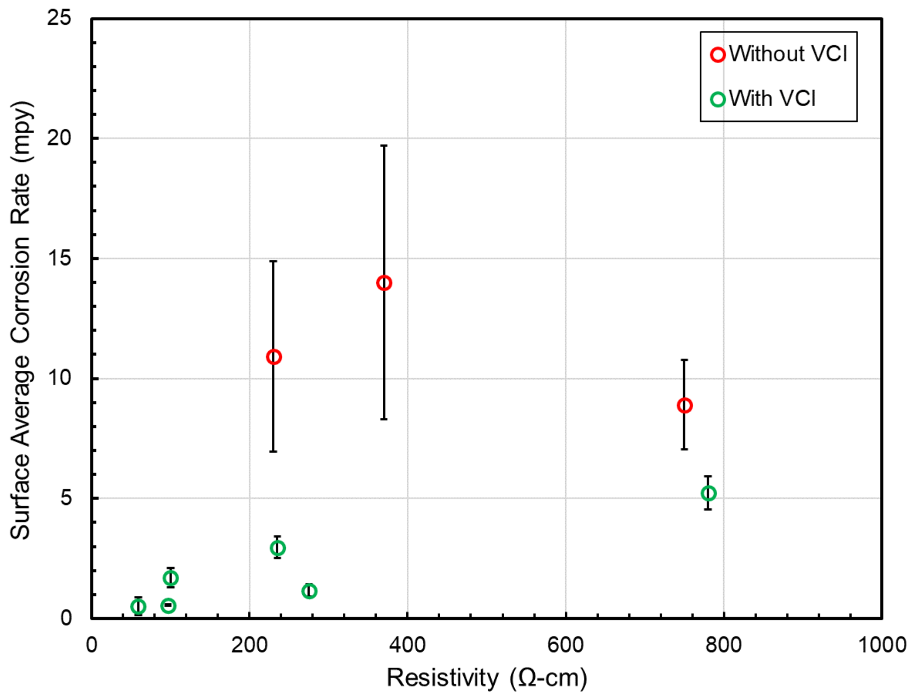


Figure 6. Resistivity versus surface average corrosion rate for the field sand experiments. Standard deviations for corrosion rate data are represented by vertical black lines for the data points.

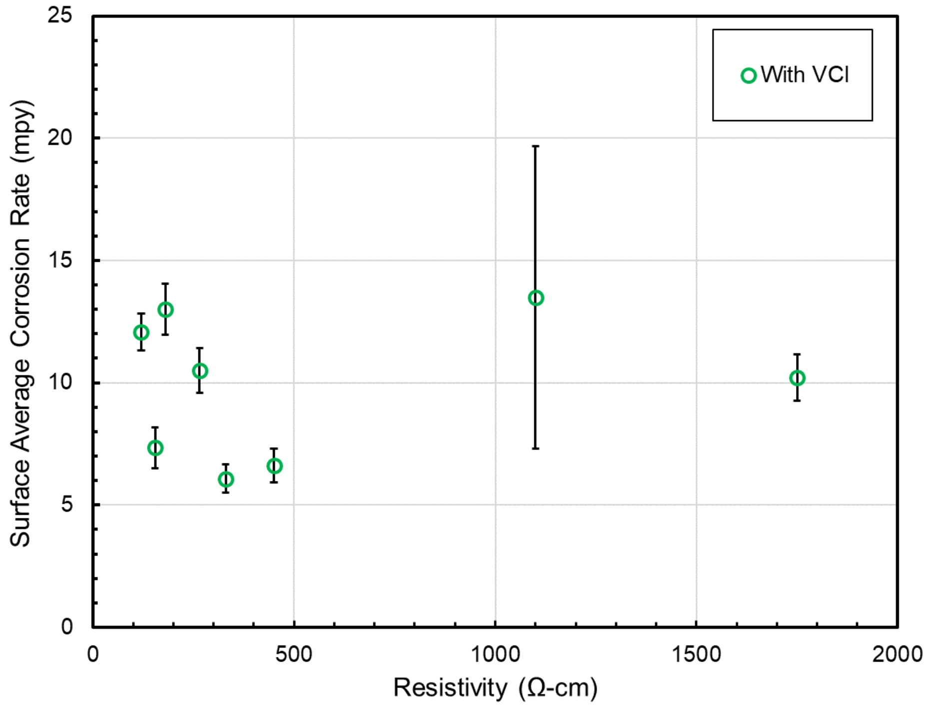


Figure 7. Resistivity versus surface average corrosion rate for the playground sand experiments. Standard deviations for corrosion rate data are represented by vertical black lines for the data points.

CONCLUSION

Coupon exposure experiments were conducted with field sand plus chloride (control), VCI-dosed field sand plus chloride, and VCI-dosed playground sand plus chloride. The added salts increased the chloride concentration of the field and playground sands by 300, 1000, 1500, and 3000 ppm. Addition of VCIs via the through-the-floor delivery method to field sand plus chloride environments resulted in significant reduction to both surface average and deepest pit corrosion rates. The surface average corrosion rates of the VCI-dosed playground sand plus chloride were comparable to that of control experiments, although pitting corrosion rates were reduced in the VCI-dosed playground sand plus chloride compared to the control tests. However, the p-values between the VCI-dosed field sand plus chloride and VCI-dosed playground sand plus chloride showed that both the surface average and deepest pit corrosion rates of the two sets of electrolytes are significantly different; this showed that through-the-floor VCI delivery method is more effective than the through-the-sand-pad for corrosion mitigation in high chloride sand pad conditions. Finally, an analysis of the resistivity versus surface average corrosion rate showed no correlation between the two quantities; this highlighted the fact that resistivity alone cannot be used as an indicator of the sand pad corrosivity.

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