

Effectiveness of Vapor Corrosion Inhibitors Under Bacterial Activity for Aboveground Storage Tank Application

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ABSTRACT

Bacterial activity is known to influence corrosion and can result in increasing soil-side corrosion of the aboveground storage tanks (ASTs) floor plates. Association for Materials Protection and Performance (AMPP) defines this phenomenon as Microbiologically Influenced Corrosion (MIC). It has been hypothesized that vapor corrosion inhibitors (VCIs) can not only function in presence of bacterial activity but can also function as biocides. Experiments were conducted to study the effect of bacterial activity on corrosion in the sand pad conditions and effect of VCIs in mitigating MIC. Various bacteria cultures were grown using commercially available culture media, and coupon exposure tests were performed with field sand mixed with the culture media. To this end, control and VCI-dosed electrolytes were prepared using the field sand plus bacteria cultures. Pre- and post-test bacteria concentration estimation and measurements, respectively, in the VCI-dosed electrolytes indicated that VCIs do not function as biocides, however, VCIs are highly effective for mitigating corrosion in presence of bacterial activity.

Key words: Vapor Corrosion Inhibitors (VCIs), Aboveground Storage Tank, Soil-Side Corrosion.

INTRODUCTION

Soil-side corrosion of the bottom plates of aboveground storage tanks is one of the main reasons for 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, e.g., less than five years after initial installation or repairs.

Bacterial activity is known to influence and frequently increase corrosion. AMPP defines this phenomenon as Microbiologically Influenced Corrosion (MIC). An industry sponsored study⁴ was recently conducted to understand the effect of MIC on soil-side corrosion. In addition, the study objective also evaluated the effectiveness of VCIs in mitigating soil-side corrosion in the presence of MIC. To this end, numerous experiments were conducted to study the effect of bacterial activity on corrosion and effect of VCIs in mitigating MIC. Following are the key points that were applied in this work: various bacteria cultures were grown using commercially available culture media, coupon exposure tests were performed with field sand mixed with the culture media.

Mitigation of MIC in the environment with various dosages of VCI was investigated. Each coupon's material wastage data were analyzed to obtain surface average and deepest pit corrosion rates, the data was analyzed to evaluate effectiveness of VCIs in mitigating the soil-side corrosion of AST floors.

EXPERIMENTAL

A list of bacterial culture media is provided in Table 1. The media cultures are identified using the labels, also listed in Table 1. Control experiments were conducted using the field sand plus culture media. In addition, VCI effect experiments were conducted using the field sand plus culture media plus VCI. The test matrix for control and VCI effect experiments is listed in Table 2.

Table 1
Bacteria Culture Media Used to Grow Bacterial Colonies

Media	Label
Sulphate reducing bacteria	SRB-culture
General anaerobic bacteria	GAB-culture
Aerobic acid bacteria	AAB-culture-with-air
Anaerobic acid bacteria	AAB-culture-without-air
Mixed-bacteria-culture	Mixed-bacteria-culture

Table 2
Test Matrix to Study VCI Effect in Presence of Bacterial Activity

Bacteria Culture Media	Control	VCI-A	VCI-B
SRB-culture	Yes	Yes	Yes
GAB-culture	Yes	Yes	Yes
AAB-culture-with-air	Yes	No	No
AAB-culture-without-air	Yes	No	No
Mixed-bacteria-culture	Yes	Yes	Yes

Each control experiment was setup using the following steps. First a fixed amount of field sand was weighed and placed in a plastic container. Then a portion of a bacteria culture was mixed with potable water, and the resulting mixture was added in the container. Five coupons were placed in each container such that coupons exposed surfaces were in contact with the sand. Coupons were extracted after approximately six months of exposure. Each VCI effect experiment was setup using the following steps. A fixed amount of field sand was weighed and placed in a plastic container. Then, a portion of bacteria culture was mixed with potable water and the resulting mixture was added to the container. Following this, the respective VCI amount was mixed potable water, and the resulting product was added to the container. The coupons in the VCI effect experiments were also exposed for six months. The coupons were acid cleaned and analyzed for material wastage. The BART method [8] was used to measure the bacteria count. The bacteria count was measured in each culture, and in the VCI effect experiments after completion.

The field sand from the control experiments was reused to determine efficacy of VCIs concentrations lower than the recommended in mitigating MIC. To this end, additional bacteria cultures and VCIs were

added to the sand of control experiments. The amount of VCIs were used to test the efficacy of the lower VCI concentrations. VCI-A was mostly used for the lower concentration VCI effect experiments, and only one experiment was conducted using VCI-B; lower than recommended VCI-A dosages were used for all the of the VCI cultures, but VCI-B was used only for the mixed bacteria culture.

EXPERIMENTAL DATA AND RESULTS

The bacteria count in each culture is listed in Table 3. The listed bacteria concentrations were obtained using the BART test. It is noted that the total bacteria culture in the last column of Table 3 is simply numerical sum of the Columns 2-4 entries.

Table 3
Bacteria Concentrations in Various Culture Media

Bacteria Culture Medium	Heterotrophic Aerobic Bacteria (CFU/mL)	Acid Producing Bacteria (CFU/mL)	Sulphate Reducing Bacteria (CFU/mL)	Total bacteria Culture (CFU/mL)
SRB-culture	1.4×10^4	5.4×10^6	5.0×10^5	5.91×10^6
GAB-culture	1.4×10^4	6.1×10^4	6.0×10^3	8.1×10^4
AAB-culture-with-air	8.2×10^4	6.1×10^4	6.0×10^3	1.49×10^5
AAB-culture-without-air	8.2×10^4	6.1×10^4	6.0×10^3	1.49×10^5
Mixed-bacteria-culture	8.2×10^4	5.75×10^5	1.15×10^5	7.72×10^5

The following are inferred from the bacteria counts in the various media:

- Sulphate reducing bacteria (SRB) grew in substantial concentration in the SRB culture, however, both heterotopic aerobic and acid producing bacteria also grew the SRB culture. The total count in the SRB culture was the highest.
- Moderate amounts of SRB and acid producing bacteria (APB) grew in the GAB-culture and in both the AAB-cultures.
- Significant levels of Heterotrophic Aerobic Bacteria (HAB) and APB grew in the mixed bacteria culture; however, SRB was also present in the mixed-bacteria culture.

The bacteria levels were also measured in the tap water and field sand, and in the VCI effect experiments post-test. The tap water bacteria concentration was negligible. Various bacteria concentrations in the field sand and in the VCI-dosed field sand plus bacteria culture for the test matrix in Table 2 are listed in Table 4. A sum of the three bacteria concentration for each VCI-dosed field sand plus bacteria culture is also listed in rightmost column in Table 4. It is noted that there could be other bacteria strains that were not included in the measurements, therefore, the absolute total bacteria concentrations are expected to be higher than the values listed in the rightmost column of Table 4.

Table 4
Post-Test Bacteria Concentrations in Field Sand and VCI-Dosed Field Sand

Electrolyte	Heterotrophic Aerobic Bacteria (CFU/g)	Acid Producing Bacteria (CFU/g)	Sulphate Reducing Bacteria (CFU/g)	Total Bacteria Culture (CFU/g)
Field sand	0	1.4×10^4	0	1.4×10^4
VCI-A dosed field sand plus SRB culture	1.1×10^6	2.6×10^4	1.2×10^4	1.1×10^6
VCI-A dosed field sand plus GAB culture	1.0×10^6	3.0×10^4	1.2×10^4	1.07×10^6
VCI-A dosed field sand plus mixed culture	1.2×10^6	1.7×10^5	1.3×10^4	1.39×10^6
VCI-B dosed field sand plus SRB culture	1.1×10^6	1.6×10^5	2.6×10^3	1.24×10^6
VCI-B dosed field sand plus GAB culture	1.2×10^5	8.7×10^3	1.2×10^4	1.41×10^5
VCI-B dosed field sand plus mixed culture	1.1×10^6	1.6×10^5	1.2×10^4	1.2×10^6

The initial bacteria concentrations based on the culture's concentrations and mixing amounts were calculated. The calculated bacteria concentrations are listed in Table 5; the rightmost column values in Table 5 are simply the sum of the three bacteria strains. The initial calculated bacteria concentrations are graphically compared to the post-test bacteria concentrations. Different labels are used to succinctly denote various electrolytes. The electrolyte labels are listed in Table 6. The calculated pre-test and measured post-test heterotrophic aerobic, acid producing, and sulphate reducing bacteria concentrations are presented in Figure 1(a), Figure 1(b), and Figure 1(c), respectively. The pre- and post-tests sums of the three bacteria strains are graphically compared in Figure 1(d). The logarithmic y-axis scale is used to represent the data in the figures, thus a step change in the presented data values is tenfold increase in the bacteria concentration.

The following is deduced from the pre-test calculated and post-test measured bacteria concentrations in the VCI-dosed electrolytes:

- HAB concentrations increased to approximately 10^6 CFU/g in all six VCI-dosed field sand plus bacteria culture electrolytes,
- APB concentrations increased in five of the six VCI-dosed field sand plus bacteria culture electrolytes, slight reduction occurred in the VCI-B dosed field sand plus GAB,
- SRB concentrations increased in five of the six VCI-dosed field sand plus bacteria culture electrolytes, with post-test SRB concentrations being approximately 10^4 CFU/g. A slight reduction occurred in the VCI-B dosed field sand plus SRB culture.

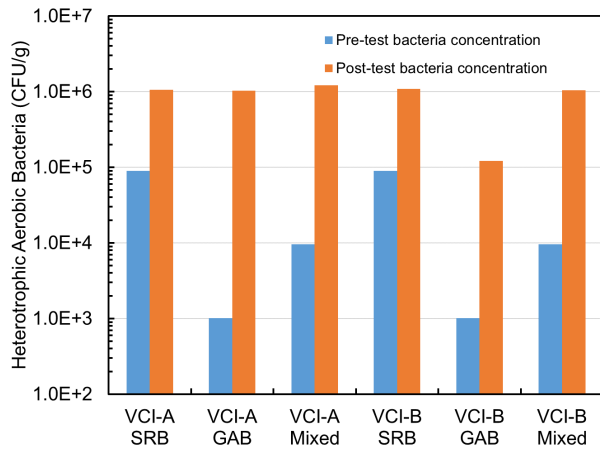
Table 5
Calculated Pre-Test Bacteria Concentrations in VCI-Dosed Field Sand

Electrolyte	Heterotrophic Aerobic Bacteria (CFU/g)	Acid Producing Bacteria (CFU/g)	Sulphate Reducing Bacteria (CFU/g)	Total Bacteria Culture (CFU/g)
VCI-A dosed field sand plus SRB culture	9.0×10^4	1.4×10^4	8.3×10^3	1.13×10^5
VCI-A dosed field sand plus GAB culture	1.0×10^3	1.4×10^4	1.0×10^2	1.51×10^4
VCI-A dosed field sand plus mixed culture	9.6×10^3	1.5×10^4	1.9×10^3	2.69×10^4
VCI-B dosed field sand plus SRB culture	9.0×10^4	1.4×10^4	8.3×10^3	1.13×10^5
VCI-B dosed field sand plus GAB culture	1.0×10^3	1.4×10^4	1.0×10^2	1.51×10^4
VCI-B dosed field sand plus mixed culture	9.6×10^3	1.5×10^4	1.9×10^3	2.69×10^4

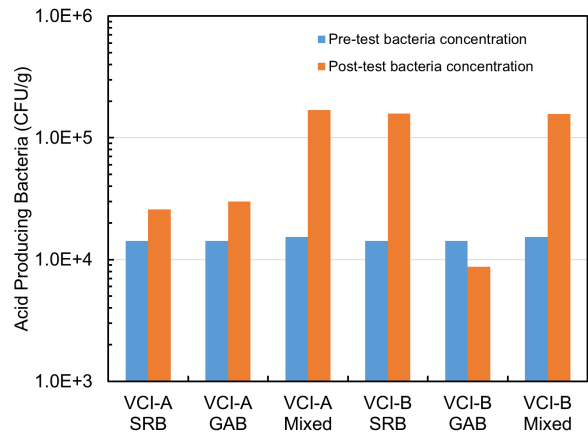
Table 6
Abbreviated Labels for the VCI-Dosed Electrolytes

Electrolyte	Chart Label
VCI-A dosed field sand plus SRB culture	VCI-A SRB
VCI-A dosed field sand plus GAB culture	VCI-A GAB
VCI-A dosed field sand plus mixed culture	VCI-A Mixed
VCI-B dosed field sand plus SRB culture	VCI-B SRB
VCI-B dosed field sand plus GAB culture	VCI-B GAB
VCI-B dosed field sand plus mixed culture	VCI-B Mixed

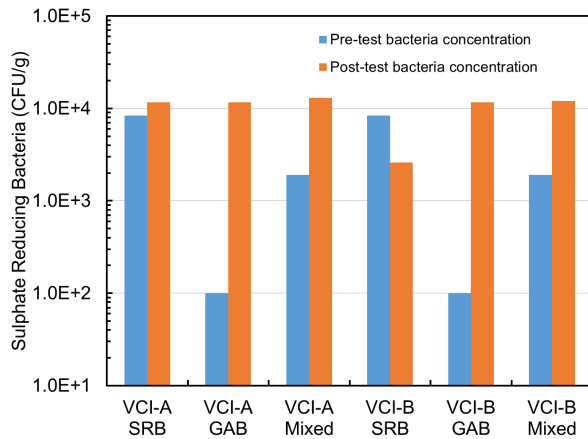
Given that the bacteria count typically increased during the test, it is clear that VCIs do not function as biocides. The presence of the bacteria was further evident by the fact that fungus, mold, and slime formed at the sand pad surface after completion of the test. Images of the sand pads for field sand plus VCI dosed experiments for the recommended and below recommended VCI levels are presented in Figure 2 and Figure 3, respectively; as seen in the figures, the sand pad surfaces are covered with the fungus, slime, and mold throughout the surfaces.



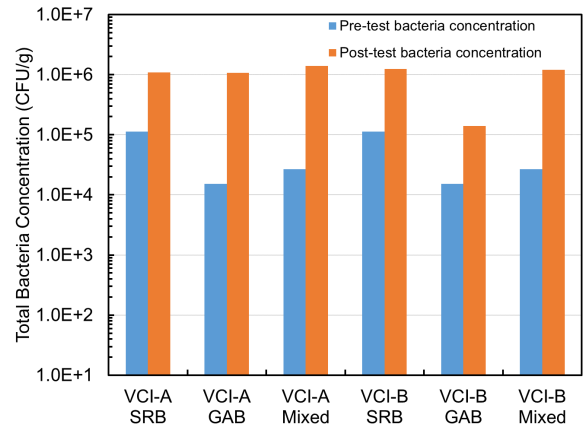
(a) Heterotrophic Aerobic Bacteria



(b) Acid Producing Bacteria



(c) Sulphate Reducing Bacteria



(d) Total Bacteria Concentration

Figure 1. Calculated initial and post-test measured (a) heterotrophic aerobic bacteria, (b) acid producing bacteria, and (c) sulphate reducing bacteria concentrations in the VCI-dosed electrolytes. Sums of the three strains in the VCI-dosed electrolytes are depicted as (d) total bacteria concentrations.

Coupons' corrosion rate data for the field sand plus bacteria culture, i.e., control tests, are listed in Table 7. The corrosion rate is graphically presented in Figure 4. Abbreviated labels are used to denote various control electrolytes; the abbreviated labels are listed in **Error! Reference source not found.**

The surface average corrosion rates of the field sand plus SRB and field sand plus GAB cultures are higher than the rest. Student's t-test was used for evaluation of the differences in the surface average corrosion rates of the various control electrolytes. The surface average corrosion rate p-values for various combinations of the control electrolytes are listed in Table 9. The deepest areapitting corrosion rate of the field sand, field sand plus SRB, field sand plus GAB, and field sand plus mixed cultures was approximately 50 mpy, whereas that of field sand plus AAB aerobic and field sand AAB anaerobic are approximately 22 and 27 mpy, respectively. The surface average corrosion rate p-values for various combinations of the control electrolytes are listed in Table 10.

Table 7
Control Tests Coupons Corrosion Rate Data

Control Electrolyte	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 plus SRB-culture**	12.7 ± 2.0	47.8 ± 22.7
Field Sand plus GAB-culture**	11.5 ± 3.2	47.0 ± 22.7
Field Sand plus AAB-culture**-aerobic	5.0 ± 0.8	21.2 ± 2.2
Field Sand plus AAB-culture**-anaerobic	5.6 ± 1.6	26.8 ± 2.2
Field Sand plus mixed-bacteria-culture**	5.5 ± 0.8	50.9 ± 13.8
*Each data point is average of four coupons		
** Each data point is average of five coupons		

Table 8
Abbreviated Labels for the Control Electrolytes

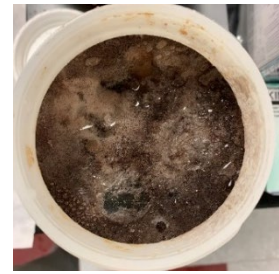
Electrolyte	Chart Label
Field Sand	Field Sand
Field Sand plus SRB-culture	Control SRB
Field Sand plus GAB-culture	Control GAB
Field Sand plus AAB-culture-aerobic	Control AAB Aerobic
Field Sand plus AAB-culture-anaerobic	Control AAB Anaerobic
Field Sand plus mixed-bacteria-culture	Control Mixed



(a) VCI-A SRB



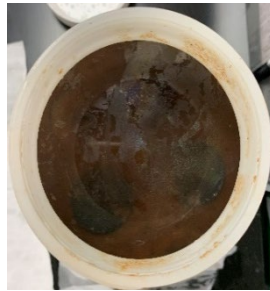
(b) VCI-A GAB



(c) VCI-A Mixed



(d) VCI-B SRB



(e) VCI-A GAB



(f) VCI-A Mixed

Figure 2. Images of the sand pad surface after exposure duration for the bacteria plus VCI experiments where VCI dosages were at the recommended levels.



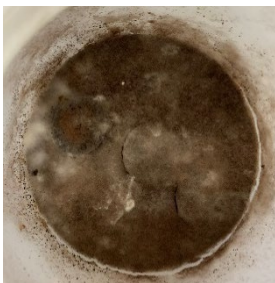
(a) Lower VCI-A SRB



(b) Lower VCI-A GAB



(c) Lower VCI-A AAB
Aerobic



(d) Lower VCI-A AAB
Anaerobic

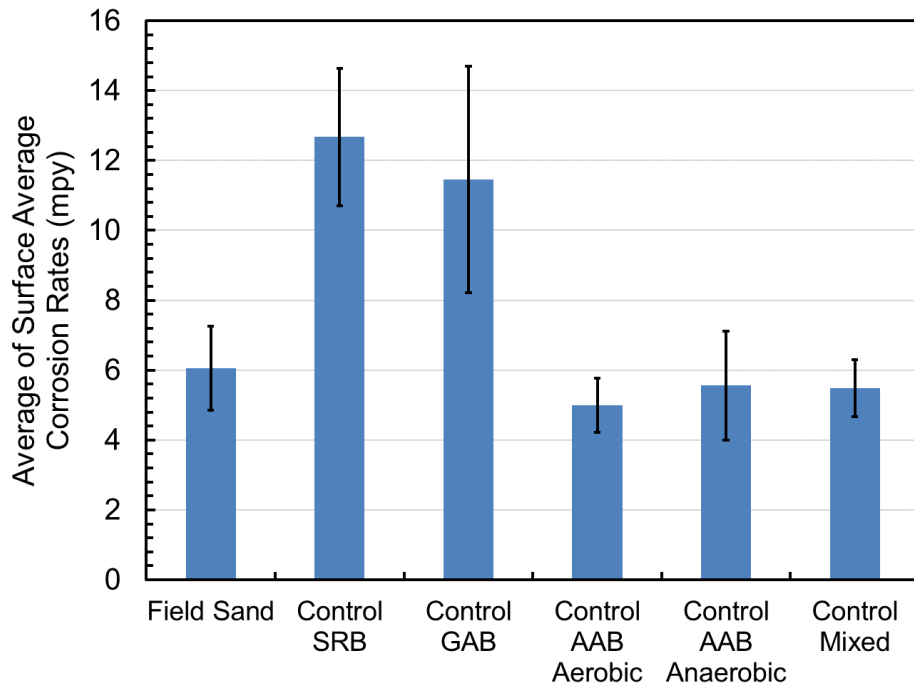


(e) Lower VCI-A Mixed

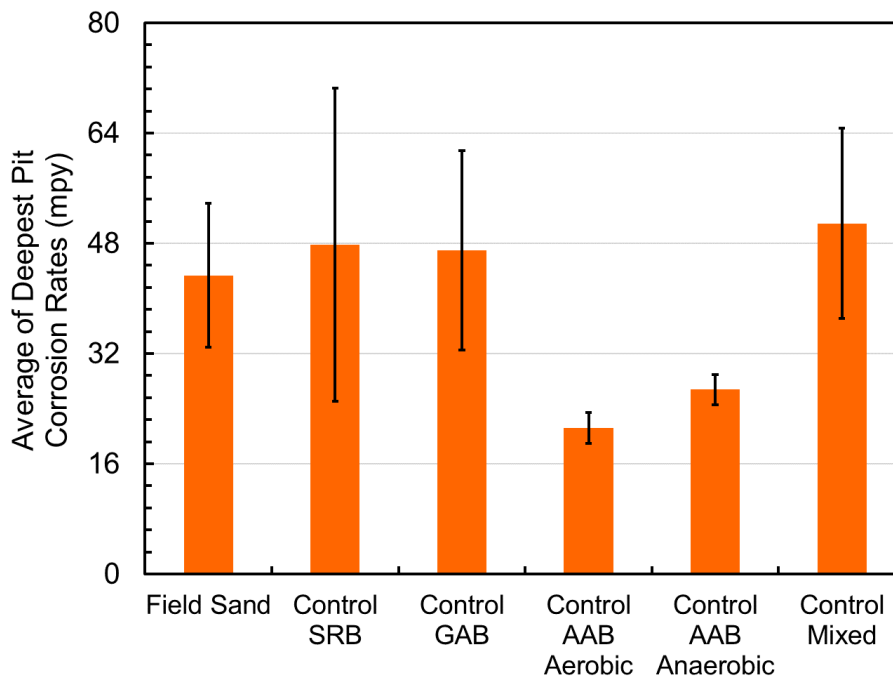


(f) Lower VCI-B Mixed

Figure 3. Images of the sand pad surface after exposure duration for the bacteria plus VCI experiments where VCI dosages were below the recommended levels.



(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 of the coupons exposed to field sand plus bacteria cultures. Standard deviations for corrosion rate data are represented by vertical black lines in each bar.

The following observations are deduced from the p-values listed in Table 9 and Table 10.

- Control SRB and Control GAB coupons surface average corrosion rates are statistically similar, and are significantly different compared to the rest, and

- Field sand, Control AAB aerobic, Control AAB anaerobic, and Control Mixed electrolytes' surface average corrosion rates are statistically similar, and
- The deepest pit corrosion rates of the field sand, Control SRB, Control GAB, and Control Mixed electrolytes are statistically similar. Similarly, the deepest pit corrosion rates of the Control AAB aerobic and Control AAB anaerobic are statistically similar.
- The p-value of the Control AAB anaerobic electrolyte with respect to Control SRB is 0.11, indicating marginal similarity in the deepest pit corrosion rates of the two electrolytes. This marginal similarity occurred due to large standard deviation of the Control SRB coupons.

The surface average and deepest pit corrosion rate data of the control electrolytes showed that surface average corrosion is more severe in Control SRB and Control GAB electrolytes compared to the rest, and pitting corrosion is more severe in field sand, Control SRB, Control GAB, and Control Mixed electrolytes compared to the rest.

Table 9
Surface Average Corrosion Rate p-Values for Various Combinations of the Field Sand plus Bacteria Culture Control Electrolytes

Electrolyte	Electrolyte					
	Field Sand	Control SRB	Control GAB	Control AAB Aerobic	Control AAB Anaerobic	Control Mixed
Field Sand	1	5.4×10^{-4}	1.7×10^{-2}	0.19	0.61	0.46
Control SRB	5.4×10^{-4}	1	0.50	3.8×10^{-4}	2.8×10^{-4}	4.9×10^{-4}
Control GAB	1.7×10^{-2}	0.5	1	9.7×10^{-3}	1.1×10^{-2}	1.3×10^{-2}
Control AAB Aerobic	0.19	3.8×10^{-4}	9.7×10^{-3}	1	0.49	0.36
Control AAB Anaerobic	0.61	2.8×10^{-4}	1.1×10^{-2}	0.49	1	0.91
Control Mixed	0.46	4.9×10^{-4}	1.3×10^{-2}	0.36	0.91	1

Note: p-value less than 0.05 means statistically significant difference between two groups with 95% probability. All p-values less than 0.05 are in red fonts to highlight those compared to the rest.

Table 10
Deepest Pit Corrosion Rate p-Values for Various Combinations of the Field Sand plus Bacteria Culture Control Electrolytes

Electrolyte	Electrolyte					
	Field Sand	Control SRB	Control GAB	Control AAB Aerobic	Control AAB Anaerobic	Control Mixed
Field Sand	1	0.71	0.68	2.2×10^{-2}	4.8×10^{-2}	0.38
Control SRB	0.71	1	0.95	5.8×10^{-2}	0.11	0.80
Control GAB	0.68	0.95	1	1.5×10^{-2}	3.4×10^{-2}	0.67
Control AAB Aerobic	2.2×10^{-2}	5.8×10^{-2}	1.5×10^{-2}	1	4.2×10^{-3}	7.9×10^{-3}
Control AAB Anaerobic	4.8×10^{-2}	0.11	3.4×10^{-2}	4.2×10^{-3}	1	1.7×10^{-2}
Control Mixed	0.38	0.80	0.67	7.9×10^{-3}	1.7×10^{-2}	1

Note: A p-value less than 0.05 means statistically significant difference between two groups with 95% probability. All p-values less than 0.05 are in red fonts to highlight those compared to the rest.

The surface average and deepest pit corrosion rates of the coupons in various VCI-dosed field sand plus bacteria cultures are listed in Table 11; the corrosion rate data is for the for the test matrix in Table 2. The VCI amounts for the corrosion rate data in Table 11 were at the recommended dosages. The coupons surface average corrosion rates are lower than 0.25 mpy for all VCI-dosed electrolytes, and deepest pit corrosion rates are lower than 5 mpy for all VCI-dosed electrolytes except for the VCI-B dosed sand plus mixed culture. The deepest pit corrosion rate for the VCI-B dosed sand plus mixed culture is 2.9 ± 3.4 mpy, the standard deviation is higher than the mean value; this happened because of one of the coupon's deepest pit corrosion rate was 7.9 mpy and other three coupons' deepest pit corrosion rate was less than 2 mpy. Nonetheless, overall, it is clear that VCIs are highly effective for mitigation of both surface average and deepest pit corrosion rates in presence of bacteria. Both surface average and deepest pit corrosion rates in VCI-dosed electrolytes are an order of magnitude lower than the control electrolytes; this obviates the need to use the Student t-test to establish significance of the difference.

The surface average and deepest pit corrosion rates of the coupons in various VCI-dosed field sand plus bacteria cultures for the VCI concentrations being lower than the recommended values are listed in Table 12. The surface average corrosion rates listed in Table 12 are sub-mils and deepest pit corrosion rates are near about 1 mpy; the corrosion rates for the recommended and below recommended VCIs dosages are found to be comparable in presence of bacterial activity.

Table 11
Coupon Corrosion Rate Data for VCI-Dosed Field Sand plus Bacteria Cultures for the Recommended Concentrations of VCIs

Electrolyte	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
VCI dosed field sand plus SRB culture* (silver)	0.19 ± 0.03	0.08 ± 0.02	0.8 ± 0.2	1.9 ± 1.5
VCI dosed field sand plus GAB culture* (golden)	0.04 ± 0.01	0.05 ± 0.01	1.3 ± 1.0	0.7 ± 0.1
VCI dosed field sand plus mixed culture*	0.07 ± 0.00	0.17 ± 0.07	0.8 ± 0.3	2.9 ± 3.4

*Each data point is average of four coupons

Table 12
Coupon Corrosion Rate Data for VCI-Dosed Field Sand plus Bacteria Cultures for the VCIs Concentrations Lower than the Recommended Values

Electrolyte	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
VCI dosed field sand plus SRB culture* (silver)	0.16 ± 0.02	–	1.2 ± 0.6	–
VCI dosed field sand plus GAB culture* (golden)	0.16 ± 0.04	–	0.8 ± 0.3	–
VCI dosed field sand plus AAB-culture-aerobic* (green)	0.11 ± 0.01	–	0.5 ± 0.1	–
Field Sand plus AAB-culture-anaerobic* (blue)	0.11 ± 0.01	–	1.1 ± 0.2	–
VCI dosed field sand plus mixed culture*	0.31 ± 0.06	0.15 ± 0.01	1.1 ± 0.3	1.5 ± 0.4

*Each data point is average of five coupons

CONCLUSION

VCIs were tested for their ability to mitigate microbiologically influenced corrosion. Different growth media were used to culture various bacteria strains. Control and VCI-dosed electrolytes were prepared using the field sand plus bacteria cultures. Pre and post-test bacteria concentration estimation and measurements, respectively, in the VCI-dosed electrolytes indicated that VCIs do not function as biocides, however, VCIs are highly effective in mitigating corrosion in the presence of bacterial activity.

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