Application of Vapor Phase Corrosion Inhibitors for the Contaminated Environments

For:

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By

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Enviromentally Safe VpCI®/MCI® Technologies

Eight USDA biobased corrosion inhibitors (EcolineVpCI-642, VpCI-605L, VpCI-605PS, VpCI-645, VpCI-705 Bio, FlashCorr, 706MM, and Ecoline Biobased Nanogrease) were evaluated in this study to optimize the best combination of inhibitors to minimize the corrosion of multi-metallic component systems that are exposed to contaminated salt solutions. Laboratory studies presented in this study, showed the effectiveness of vapor phase corrosion inhibitor products in both fresh and salt water applications. Corrosion test results confirmed the effectiveness of these vapor phase corrosion inhibitors in various water chemistries including fresh and salt water. Average corrosion rate dropped from ~10 mpy for salt contaminated solutions to less than 0.4-1.2 mpy when various inhibitors were added. It is worth mentioning the effectiveness of these inhibitors is remarkable in fresh clean water (less than 0.4 mpy).

Exposure of the steel samples to these inhibitors did not show any loss in mechanical properties. Both strength and ductility of the low carbon steel samples were maintained even in a long duration immersed condition. However, only VpCI 605L showed some adverse effects on aluminum alloys, brass and galvanized steel.

The vapor-inhibiting ability (VIA) corrosion rating per TM-208 indicated that the control sample had Grade 0, while VpCI-642, VpCI-645 and VpCI-605L ratings were Grade 3. These observations indicate that these inhibitors have vapor-inhibiting ability.

VpCI FlashCorr and VpCI 605PS inhibitors demonstrated to be very effective in calcium chloride solution.

Ecoline Biobased Nanogrease electrochemical impedance spectroscopy results showed that this newly developed nanogrease is very effective in lowering the corrosion rate of steel samples (less than 0.01 mpy). Coated UNS G10180 steel with Ecoline Biobased Nanogrease showed no sign of any corrosion when exposed to salt spray corrosion tests for more than 2,000 hours (ASTM B117). Electrochemical impedance spectroscopy (EIS) of UNS G10180 steel in 1.0% VpCI 707 (Fuel additive) inhibitor in salt contaminated solution showed effectiveness in lowering the corrosion rate of steel samples.

Langmuir Adsorption Model was used to calculate the adsorption energy for these inhibitors. The adsorption energy was about -21,520 to -24,970 J/mol, indicating a strong physisorption mechanism.

Application of an inhibitor in any water system requires compliance with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES). These corrosion inhibitors investigated are water-based, biobased, environmentally friendly, and can be effective replacements for toxic nitrite, chromate or hydrazine base inhibitors. They satisfy all the required environmental compliance.

Introduction

With a shortage of fresh water resources, seawater may be used in recirculating cooling water systems and hydrostatic pressure tests of pipeline and storage tanks [1-3]. Seawater as industrial circulating cooling water can relieve the constraint of a clean water shortage and rapid development of industries [4]. But seawater is an electrolyte solution with multiple salts, mainly 3.0%~5.0% sodium chloride, pH value about 8, and a higher percentage of oxygen [1]. Due to its chemistry, seawater easily corrode pipelines. So the key of seawater utilization is to solve piping and equipment corrosion problems in the seawater environment by modifying its chemistry with the addition of corrosion inhibitors.

Corrosion and corrosion inhibition of steel have received enormous attention for the recirculating cooling water system [5-7.] The common methods to control and prevent equipment corrosion is to use resistant materials, to use cooling water anticorrosion coatings, to increase pH value of the cooling water operation and to add corrosion inhibitors [6-9]. Among these methods, using resistant materials can protect metal equipment effectively, but the expense is too high. The technology of anticorrosion coating method is complex and this method applies to local anticorrosion in the system. Increasing water pH passivates mild steel. Adding corrosion inhibitors can protect the system and it is economical and practical [7]. After the completion of a hydrostatic test, the water must be discharged, often with environmental considerations due to toxicity or excessive chemicals when inhibitors are added [8].

The development of seawater corrosion inhibitors has changed from inorganic to organic chemistry, from single to multiple compounds, from single inhibition type to mixed inhibition type and other electrochemistry method combination processes [8-10]. Many organic molecules exhibit high anticorrosion potential, but they pollute the environment during their synthesis and applications [7-9]. The effect of single seawater corrosion inhibitor is unsatisfactory in general, so two or several types of compounds coordinate to improve inhibition efficiency.

Therefore, to control corrosion and bacterial growth in the pipeline during hydrostatic pressure test and future storage, the test water may be treated with corrosion inhibitors and other chemical compounds to manage and control corrosion activities. Commonly used chemicals are biocides which kill the microorganisms and prevent the formation and growth of bacteria and other organisms in the seawater, corrosion inhibitors used to retard general corrosion when residual oxygen is available and oxygen scavengers used to reduce the amount of oxygen available for corrosion and bacterial growth. Different classes of corrosion inhibitors may be used to protect systems from corrosion, including inorganic or organic. Inorganic inhibitors include nitrites, phosphorous based and others. Organic inhibitors are the products formulated from molecules constructed from of carbon, hydrogen, oxygen and nitrogen atoms. Vapor-phase corrosion inhibitors (VCI) described in this paper are organic based blends. The mechanism of the corrosion protection of organic inhibitors includes the formation of a thin, sometimes a few molecular layers on the metal, which is a protective barrier to aggressive ions [4-5]. In the majority of cases, organic components form a physical bond with the metal substrate. Formulations can include components with other functionalities for added protective capabilities. The main difference of the VCI products versus non-VCI products, is the presence in the formulation of an ingredient with moderately high vapor pressure that can prevent corrosion in the vapor space without applying VCI directly to the metal surface [9-10]. The typical examples of this class are organic amines and their salts with carboxylic acids (amino-carboxylates). The advantage of VCI are that the volatilized molecules can access hard to-reach spaces. When they reach the metal, VCI attach to it by the active group, creating a strong physisorption mechanism. After the completion of a hydrostatic test, the water must be discharged, that must be in compliance with environmental restrictions. It is required compliance with the Clean Water Act and the National Pollutant Discharge Elimination System (NPDES) [8].

RESEARCH OBJECTIVES

The main objective of this program was to study corrosion behavior of steel samples to demonstrate effective corrosion protection of different vapor phase corrosion inhibitors including EcolineVpCI-642, VpCI-605L and PS, VpCI-645, VpCI-705 BIO, FlashCorr, 707, and Ecoline Biobased Grease against aggressive attack from high chloride environment. The program include: Study DC and EIS electrochemical corrosion behavior of carbon steel in aggressive chloride solution and addition of inhibitors. Monitoring corrosion rate (mpy) of steel pipe samples and ER probes for ninety days using stagnant solution condition using with and without inhibitor addition. Post-test evaluation of surface condition of exposed samples using Light microscopy, scanning electron microscopy (SEM/EDAX) and XPS analysis.
The list of the inhibitors include: VpCI 645 (lot 96216), VpCI 705 Bio (lot 91917), VpCI 605L, (Lot 91907), Ecoline VpCI 642, (lot 91877), M 605 PS, (lot 92516-1), FlashCorr VpCI, (Lot 079816), Ecoline Biobased Nanogrease, (lot 91927) and VpCI 707, (lot 91887). Properties of each inhibitor investigated in this project are summarized below:

VpCI-645 is a unique, concentrated formulation that protects ferrous and non-ferrous metals from corrosive solutions containing chlorides. The product is designed to provide corrosion protection in fresh water, salt water, brine and other highly corrosive solutions containing dissolved halogens. As a concentrated formulation, VpCI-645 offers low dosage effectiveness as a treatment for a wide variety of marine and process applications requiring economical corrosion inhibition for fresh and saltwater. VpCI-645 is effective as a replacement for nitrite- and chromate-based formulations and hydrazine-based oxygen scavengers. Being environmentally safe to use, VpCI-645 helps solve the problem of disposal, particularly for large quantities of water. VpCI-645 provides effective corrosion protection against aggressive attack from high chloride solutions. VpCI-645 effective for a broad range of applications to stop aggressive corrosion from fresh and salt water, brine, chloride and other dissolved halogens. This corrosion inhibitor is Biodegradable, environmentally friendly, nitrite- and amine-free. It can provide Multi-metal protection and readily water-soluble liquid for easy application. Its solubility is not affected by pH range and salt concentration levels. Typical applications include: Closed circuit cooling and heating systems containing brines or water, Desalination plants, Prevents water-bottom corrosion in oil storage tanks and ballast tanks of ship and offshore platforms, Wet lay-up of boilers, pipelines, vessels, and Pulp and paper process equipment.

EcoLine VpCI-642 is a Biobased corrosion inhibitor specially designed for hydrotesting with seawater. The addition of EcoLine VpCI-642 allows seawater to be safely utilized without the danger of premature corrosive equipment failure. EcoLine VpCI-642 effectively protects the ferrous metals in contact with the corrosive, high-chloride fluid by

forming a protective layer on metal surfaces and inhibiting cathodic corrosion reactions. Its low dosage of 0.3-0.75% by volume makes it economical and cost-competitive. As a USDA certified Biobased product, EcoLine® VpCI®-642 is also an eco-conscious option for corrosion protection during offshore hydrostatic testing. Chiefly derived from renewable resources, it contains 93% USDA certified Biobased content. It provides an excellent replacement for more hazardous products containing nitrite, chromate, and hydrazine. EcoLine VpCI-642 is also biodegradable with an environmentally friendly profile that makes disposal of large quantities of used hydrotesting water more likely to comply with local regulations. Once the treated water is drained, corrosion protection of the vessel can be extended by rinsing with fresh water containing 0.5 percent by weight of VpCI-609.
Major benefits of EcoLine VpCI-642: Specially designed for corrosion protection of ferrous metals against aggressive attack from a high chloride environment, water-soluble for easy dilution, Biobased and biodegradable and Nitrite and amine free.
EcoLine VpCI-642 is not limited to hydrotesting and can be used as a low dosage treatment for a wide variety of other applications. This includes corrosion protection during wet lay-up of carbon steel vessels containing saltwater, brine, or high chloride/halogen-content water.

VpCI-705 Bio is specially formulated for use as a multifunctional fuel additive to biodiesel and other bio-fuels. It serves as a corrosion inhibitor, fuel stabilizer, and water emulsifier for biodiesel, diesel, and gasoline. VpCI-705 Bio provides corrosion protection, lubricity and elastomer protection for bio-based fuels. As a fuel stabilizer, this product provides better engine performance. VpCI-705 Bio provides excellent corrosion protection for all of the common engineering metals used in automotive fuel systems including aluminum, aluminum die cast and zinc die cast alloys, tin plated surfaces, copper, ferrous alloys, cast iron and solder. VpCI-705 Bio gives unique multi-metal corrosion protection in all phases: liquid, interface and vapor phases above and below the fuel level. VpCI-705 Bio provides protection in liquid and vapor phase and at liquid/air interface. It has passed the rust test in accordance to MIL-I-25017 and ASTM D665-92. VpCI-705 Bio is in form of liquid, easy to blend and Fuel stabilizer allows better engine performance. VpCI-705 Bio does not contain trace metals, chlorides, chromates, nitrites or phosphates. It does not form corrosive combustible products and Absorbs water in tank and fuel line

M-605 L and M 605 PS are corrosion inhibitors designed specifically as additives to prevent corrosion due to chlorides. M-605 L and PS can also be used in closed loop cooling systems containing brine solutions. M-605 L and PS provide protection to ferrous alloys. M-605 L and M-605 PS are non-toxic, environmentally friendly, and contain no chromate, nitrite, or phosphate inhibitors. These products satisfy the Pacific NorthWest States (PNS), Department of Transportation requirements as an additives for deicers and pass their corrosion tests when added to a deicer at concentration level of 5% by weight.

EcoLine Biobased NanoGrease powered by Nano VpCI is a multipurpose Biobased grease with superior corrosion protection properties for carbon steel applications. It is formulated from vegetable oils, lithium-based thickener, extreme pressure additives, and corrosion inhibitors. It contains 86% USDA certified Biobased content and is listed as part of the USDA BioPreferred®federal purchasing program.

EcoLine Biobased grease offers dual lubrication and corrosion protection for a variety of metal-to-metal applications. In addition to protecting metals through direct contact, it also protects metals in surrounding hard-to-reach cavities through vapor phase corrosion inhibiting action. EcoLine Biobased grease is especially valuable for protecting and lubricating metals exposed to harsh corrosive conditions and can be used under a broad range of operating temperatures. This grease is stable in a broad range of operating temperatures and is effective in high pressure applications. EcoLine Biobased grease is an effective corrosion protection in contact phase and vapor phase.
EcoLine® Biobased grease can be used as a lubricant and/or protect at the Metal-to-metal contact areas for the lubricating sleeves, ball and roller bearings, vehicle/equipment chassis and enclosed hard-to-reach cavities.

VpCI 707 (VpCI 706mm) is specially formulated for use as an additive for diesel and biodiesel fuels. The product provides superior corrosion protection for ferrous metal surfaces in contact with the fuel, as well as the surfaces above the fuel level. Adding VpCI 707 to diesel tanks before shipment protects heavy equipment fuel tanks and systems from corrosion during storage, shipment, and equipment use. This lowers the risk of monetary loss and customer dissatisfaction from corrosion claims. Because VpCI 707 is fully compatible with diesel and biodiesel and does not affect engine performance, the additive can be used in the tank during engine operation. The engine can be safely started in order to drive heavy equipment in and out of the shipping or storage compartment for easier loading and unloading. VpCI 707 can also be left in the diesel tanks for continued corrosion protection during storage and operation for truck or heavy equipment. Typical applications are fuel tanks and fuel systems. It can be used in operation, storage, and shipment and fully compatible with diesel and biodiesel fuels to provide protection in liquid and vapor phase, and at liquid/air interface. It does not contain trace metals, chlorides, chromates, nitrites, or phosphates. VpCI®-706 was specifically designed for protection of carbon steel.

FlashCorr VpCI is a highly effective, non-toxic, environmentally safe cleaner that removes and neutralizes even the harshest of salt build-up from any metal surface. FlashCorr VpCI represents an environmental and economic breakthrough in corrosion prevention. FlashCorr VpCI enables superior protection of metal surfaces from corrosion. It has a unique ability to neutralize and remove salt deposits such as sodium chloride and other deicing salts and naturally occurring contaminants as well as protect from further salt exposure and flash rust.
FlashCorr VpCI is a blend of surfactants, chelating agents, and corrosion inhibitors used for removing salts from commercial and marine equipment. It is nonflammable, nitrite-free, non-toxic, and does not cause disposal problems. It also contains inhibitors to protect metal parts from corrosion after cleaning salt deposits remain. FlashCorr VpCI can be applied to sand blasted, water blasted, and wire brushed surfaces in order to stabilize and protect against flash-corrosion before application of primers, paints, and protective coatings. This product greatly reduces application costs and improves

adhesion, thus allowing effective and long-term performance of protective coatings systems.

FlashCorr VpCI is excellent for winter season use for everyday cleanup of salt permeated equipment but also will serve as a perfect solution for end of season storage of winter equipment. It is a nitrite- and amine-free and Contains an inhibitor package for protection of ferrous and, aluminum alloys. It leaves no residual film and will not affect paint adhesion qualities. It prevents flash rust and can be applied to a wide range of machinery and equipment It also has no adverse effects on glass, plastics, and rubber. It can be used as an additive to water rinse after salt quenching.

Table 1: shows the current Biobased label status of these inhibitors awarded with a USDA Biobased label.

Product	Status of USDA Biobased label*
Ecoline VpCI-642	93%, Awarded
VpCI-605 L	<40% not eligible
VpCI-605 PS	98%, Awarded
VpCI-645	93%, Awarded
VpCI-705 BIO	80%, Awarded
FlashCorr	64%, Awarded
VpCI 707 (706mm)	<54%; not eligible
Ecoline bio-base grease	86%, Awarded

*Based on the test method ASTM D6866 (Organic carbon has C-H bonds and often C-C bonds). Biobased products are derived from plants and other renewable agricultural, marine, and forestry materials. Biobased products provide an alternative to conventional petroleum derived products and include a diverse range of offerings such as construction, janitorial, and grounds-keeping products specified and purchased by Federal agencies, to personal care and packaging products used by consumers every day.

EXPERIMENTAL PROCEDURE

Corrosion behavior of the low carbon steel (UNS G10180 steel), 304 stainless steel (UNS S30400), Brass UNC C36000, galvanized steel and Aluminum 2024 Alloy (UNS A2024) were investigated exposed to the different VpCI products in salt solutions using electrochemical techniques, and total immersion tests followed by post tensile tests. , Vapor-inhibiting ability (VIA, NACE TM 208-2018) also was conducted on the low carbon steel (UNS G10180 steel) exposed to Ecoline VpCI-642, VpCI-645, and VpCI-605 L.

Electrochemical polarization standards per ASTM-G61 (Cyclic polarization), Polarization resistance/Corrosion rate measurements, and electrochemical impedance spectroscopic techniques were used to evaluate the behavior of these inhibitors on the different alloys in different chloride solutions. Electrochemical experiments were conducted using Gamry PC4/750 Potentiostat /Galvanostat/ZRA instrumentation and DC105 corrosion test software. Samples were polished (1.0 um Alumina powder), placed in a flat cell and tested in deionized water solutions containing 1.0% or 3.5% NaCl plus 1.0% VPCI inhibitor. The choice of corrosion inhibitors for this study was made based on their functions and effectiveness in different aqueous solutions. Ecoline VpCI-642, VpCI-645, VpCI-605 L, VpCI-705 BIO, VpCI-605PS, FlashCorr, VpCI707, Ecoline bio-base grease; have demonstrated to inhibit corrosion of low carbon steel when exposed to contaminated aqueous environments . These inhibitors are combination of film formers and vapor corrosion inhibitors. The main ingredients are Biobased salts of amines and organic acids of different chemical structure and triazole. The main function of this product is formation of a protective film with some vapor corrosion inhibition action. All these inhibitors are Biobased with potentially biodegradable and surface modifiers.

The samples were pre-treated prior to the experiments by polishing with silicon carbide paper (240, 320, 400, 600, and fine polishing with 1.0 um Almina powder), degreased in acetone for 5 minute in ultrasonic bath, then rinsed with ethyl alcohol and dried in desiccator at room temperature. The corrosion inhibitors were different USDA Biobased labeled (based on ASTM D6866, Organic carbon has C-H bonds and often C-C bonds). These corrosion inhibitors were remixed with different dosages (1.0%) in order to find out the optimum proportional relation for an effective protection. The salt solutions were prepared based on 1.0% NaCl or 3.5% NaCl solutions. For certain inhibitors corrosion behaviors were compared in both CaCl2 and NaCl solutions.

The corrosion behavior of different metallic samples were investigated using electrochemical impedance spectroscopy (EIS) in different salt concentrations. The experiments were conducted using commercially available systems for EIS and DC corrosion tests. EIS Bode plots were created from the data obtained using the potentiostatic technique. By comparing the bode plots, changes in the slopes of the curves were monitored as a means of establishing a trend in the R_p value over time. To verify this analysis, the R_p values were also estimated by using a curve fitting algorithm on both Nyquist and Bode plots. In these plots, the R_p and R_Ω combined values are displayed in the low frequency range of the bode plot and the R_Ω value can be seen in the high frequency range of the bode plot. The diameter of the Nyquist plot is a measure of the R_p value. During this investigation, changes in the polarization resistance (R_p) of these alloys were monitored to ascertain the degree of effectiveness for these inhibitors to lower corrosion rate.

The NACE TM 208-2018 Standard Test Method was also used to evaluate the vapor-inhibiting ability (VIA) of various forms of VCI. [11]. This laboratory test method evaluates the vapor-inhibiting ability (VIA) of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces. The VIA corrosion test method provides for standard conditions in a test jar of water-saturated, warm air without the presence of accelerating contaminants. The combination of (1) vapor transport across a gap containing air, water vapor and VCI, and (2) corrosion protection are evaluated in this test method. The VIA tests consist of four steps of sample conditioning or saturation for 20 hours at 22 ^{o}C, cooling cycle at 2^{o}C, pre-warming at 50^{o}C, followed by three hours at 22 ^{o}C for specimen conditioning. After the last three hour conditioning period, the steel samples were inspected for visible water condensation. Following verification of water condensation on each sample, visual examination of the surface was done and microscopic observation was conducted to determine the corrosion rating for each sample. The corrosion criteria for rating steel specimens consist of grade 0 through grade 4. To have a valid test, the control sample must have grade 0; samples with no inhibitor received worst grade. The control samples consistently rated a grade 0 for all VIA tests, therefore, validating the test method. Relative humidity and the temperature of each test jar were monitored by inserted sensors and data logging software. Post-test evaluation of surface condition of exposed samples using digital Light microscopy, scanning electron microscopy (SEM/EDS analysis) and XPS analysis.

Experimental Results and Discussions

Cyclic Polarization Behavior

Figures 1-6 show the polarization behavior for UNS G10180 steel in 1.0% inhibitor (different VCI products) in different salt solutions. All the conducted test results are included in Appendices A-D. The most noticeable changes are the positive shift in the breakdown potential and expansion of the passive range for these alloys when inhibitors were added. These inhibitors showed to be acting as effective cathodic inhibitors. The inhibitor changed the reactivity by reducing the pH level, increased the passivation range significantly, and was beneficial in reducing localized corrosion damages. As demonstrated in these polarization curves, extension of the passive zone contributes to the stability of the protective oxide film over a wider electrochemical range, resulting in a more stable passive film, and shift of the critical pitting potential to more positive anodic potential levels. Figure 7 shows the contribution of these inhibitor addition to lower corrosion rate for ferrous alloys in different salt solution.

Table 2 shows effects of these inhibitor addition in different salt solution for different metallic alloys. Figures 8-11 demonstrate the changes of corrosion rate for different inhibitors (VpCI 642, VpCI645, VpCI 606L and VpCI705Bio). Results showed that all these inhibitors are very effective in lowering corrosion rate. However, VpCI 605L showed it had adverse effect on Al-alloys, brass and galvanized steel. Therefore, it should be warned to not apply this inhibitor to the system that have these alloys. Figures 12-14 show the significant drop in ductility of 7075 Al-alloy when it was immersed in 1.0% VpCI 605L solution for 28 days. However, no significant changes was observed for any of the ferrous

alloys. Electrochemical tests also showed similar adverse effects for VpCI605L on Al-alloy, galvanized steel and Brass alloy.
Electrochemical tests on the VpCI705Bio showed that this inhibitor is extremely an effective inhibitor in short term exposure duration. However, in long term stagnant exposure due to partitioning effects, metallic samples showed susceptibility to localized corrosion in presence of this inhibitor. In the recirculating that mixing and maintaining a uniform distribution of all chemical ingredients is achievable, this inhibitor can be very functional and provide excellent protection (corrosion rate less than 0.5 mpy).

Figure 15 shows electrochemical behavior of UNS G10180 steel in 1.0% VpCI FlashCorr Inhibitor at different aqueous solutions. Results showed that this inhibitor is very effective in calcium chloride solution. Similar results were observed for the VpCI 605PS Inhibitor at CaCl2 aqueous solution (Figure 16). Results showed that these two inhibitors are very effective in calcium chloride solution compared with sodium chloride solution.

Sample & Solution	Corrosion Rate, mpy			
	VpCI 642	VpCI 645	VpCI 605L	VpCI 705Bio
304 3.5% NaCl, Control	0.10	0.10	0.10	0.10
304 3.5% NaCl + VpCI	0.02	0.04	0.02	0.03
304 1% NaCl, Control	0.05	0.05	0.05	0.05
304 1% NaCl + VpCI	0.02	0.02	0.02	0.02
2024 3.5% NaCl, Control	1.80	1.80	1.80	1.80
2024 3.5% NaCl + VpCI	0.06	0.08	31.20	0.03
2024 1% NaCl, Control	0.08	0.08	0.08	0.08
2024 1% NaCl + VpCI	0.03	0.02	24.50	0.01
Brass 3.5% NaCl, Control	2.28	2.28	2.28	2.28
Brass 3.5% NaCl + VpCI	0.14	0.11	0.88	0.08
Brass 1% NaCl, Control	0.33	0.33	0.33	0.21
Brass 1% NaCl + VpCI	0.12	0.05	0.78	0.08
Zn/steel 3.5% NaCl, Control	12.00	12.00	12.00	12.00
Zn/steels 3.5% NaCl + VpCI	3.20	0.17	14.20	2.93
Zn/steel 1% NaCl, Control	4.30	4.30	4.30	4.30
Zn/steels 1% NaCl + VpCI	1.10	0.03	1.44	0.55
Steel 3.5% NaCl, Control	8.50	8.50	8.50	8.50
Steel 3.5% NaCl + VpCI	3.26	0.64	2.01	1.78
Steel 1.0% NaCl, Control	7.30	7.30	7.30	7.30
Steel 1.0% NaCl+ VpCI	0.51	0.41	0.87	1.10

Table 2: Summary of corrosion rate measurements (mpy) for different alloy in different inhibitors (1.0% VpCI addition).

Electrochemical impedance spectroscopy (EIS) behavior of UNS G10180 steel in 1.0% VpCI 707 (Fuel additive) Inhibitor in salt aqueous solution is demonstrated in Figure 16. Results showed that this inhibitor as a fuel additive is very effective in lowering corrosion rate of steel samples. Therefore, it is highly recommended to use to protect the engine. Figure 18 show the electrochemical impedance spectroscopy (EIS) behavior of coated

UNS G10180 steel with Ecoline Nanogrease inhibitor in different salt aqueous solution. Results showed that this newly developed Nanogrease is very effective in protecting of steel samples. The coated UNS G10180 steel samples with Ecoline Nanogrease Inhibitor showed no sign of any corrosion when exposed to salt spray corrosion tests for more than 2,000 hours (ASTM B117).

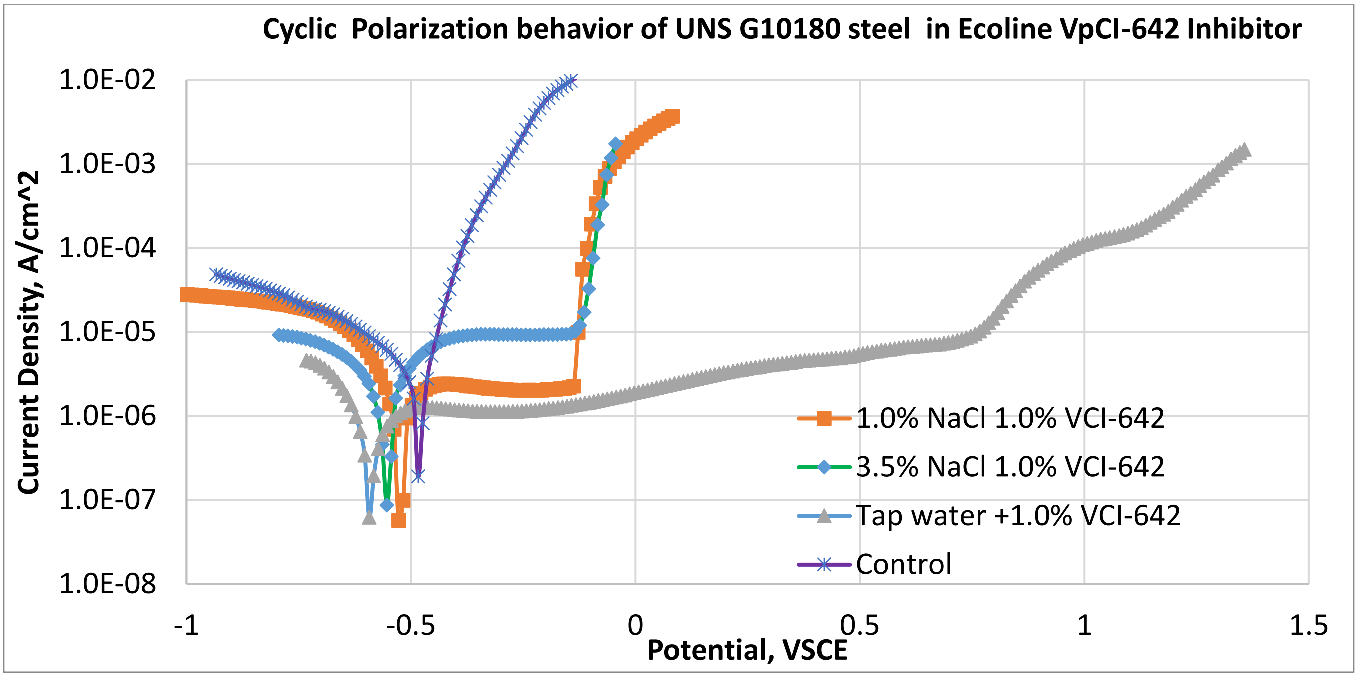


Figure 1: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI 642 Inhibitor at different aqueous solutions.

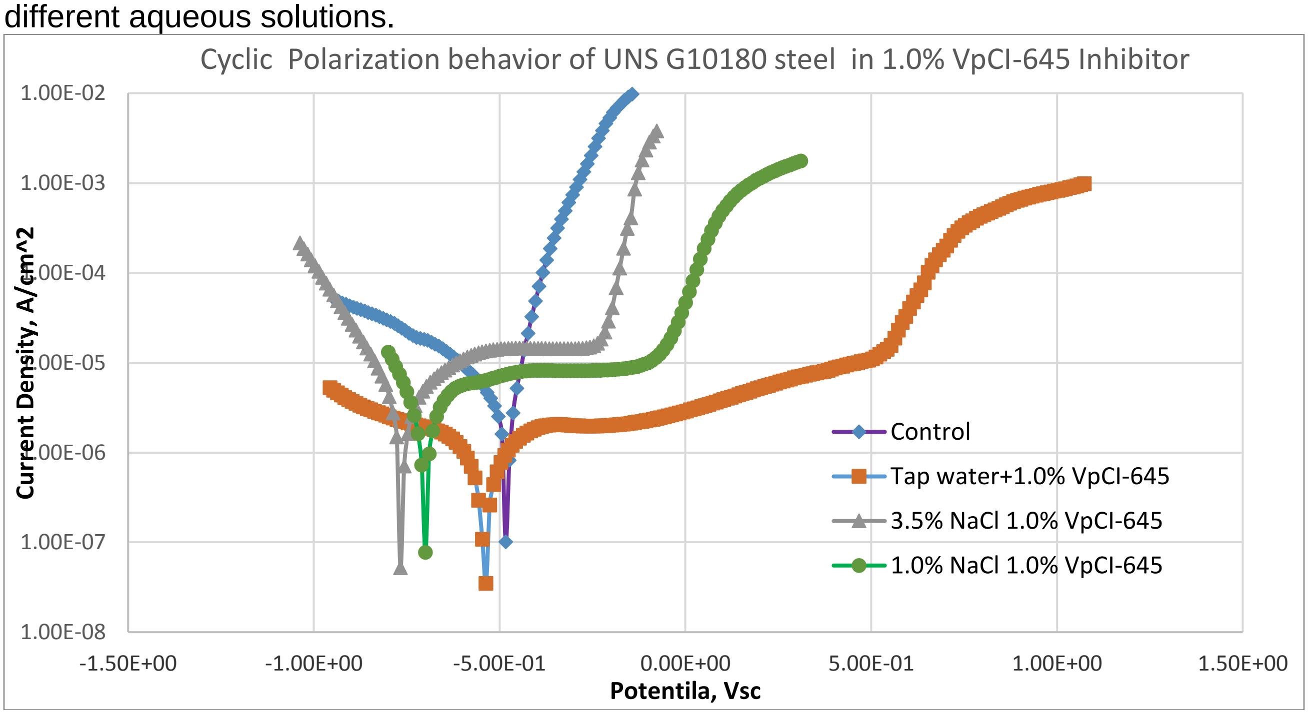


Figure 2: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-645 Inhibitor at different aqueous solutions.

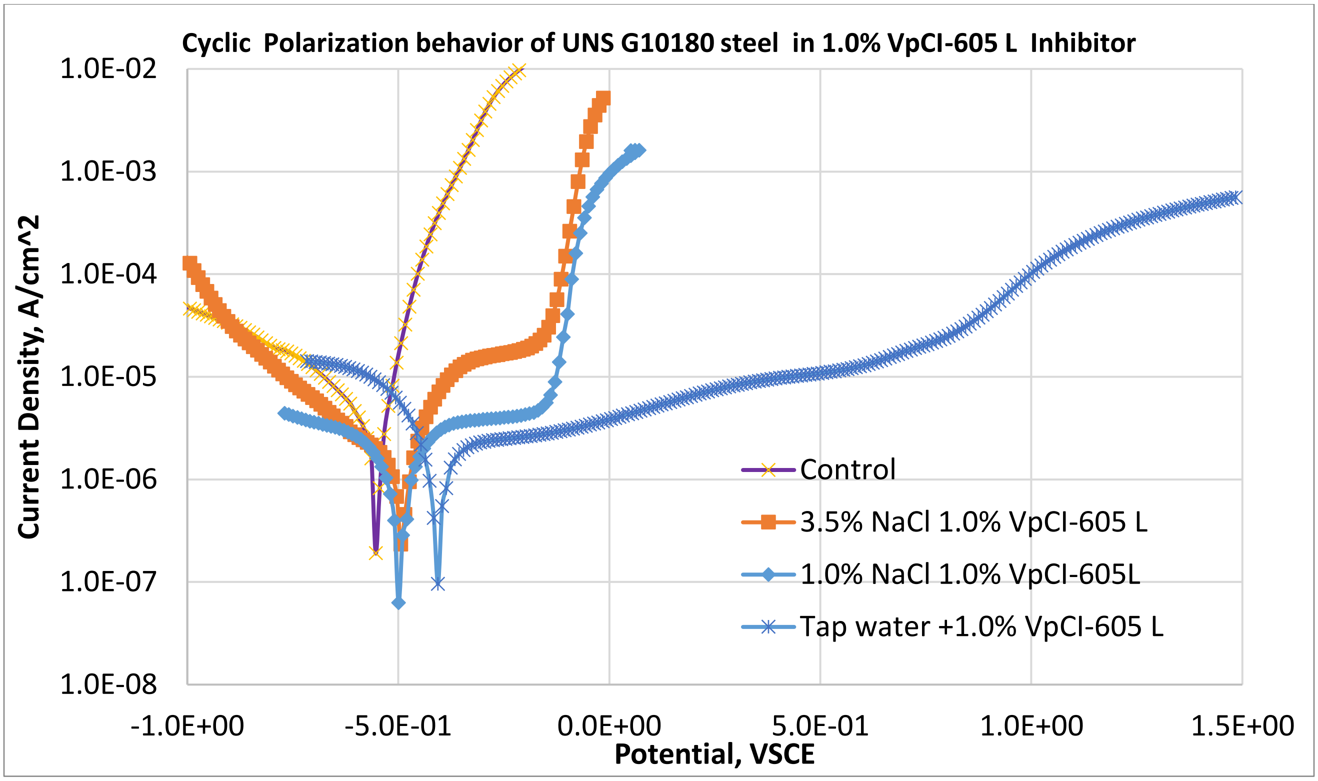


Figure 3: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-605 L Inhibitor at different aqueous solutions.

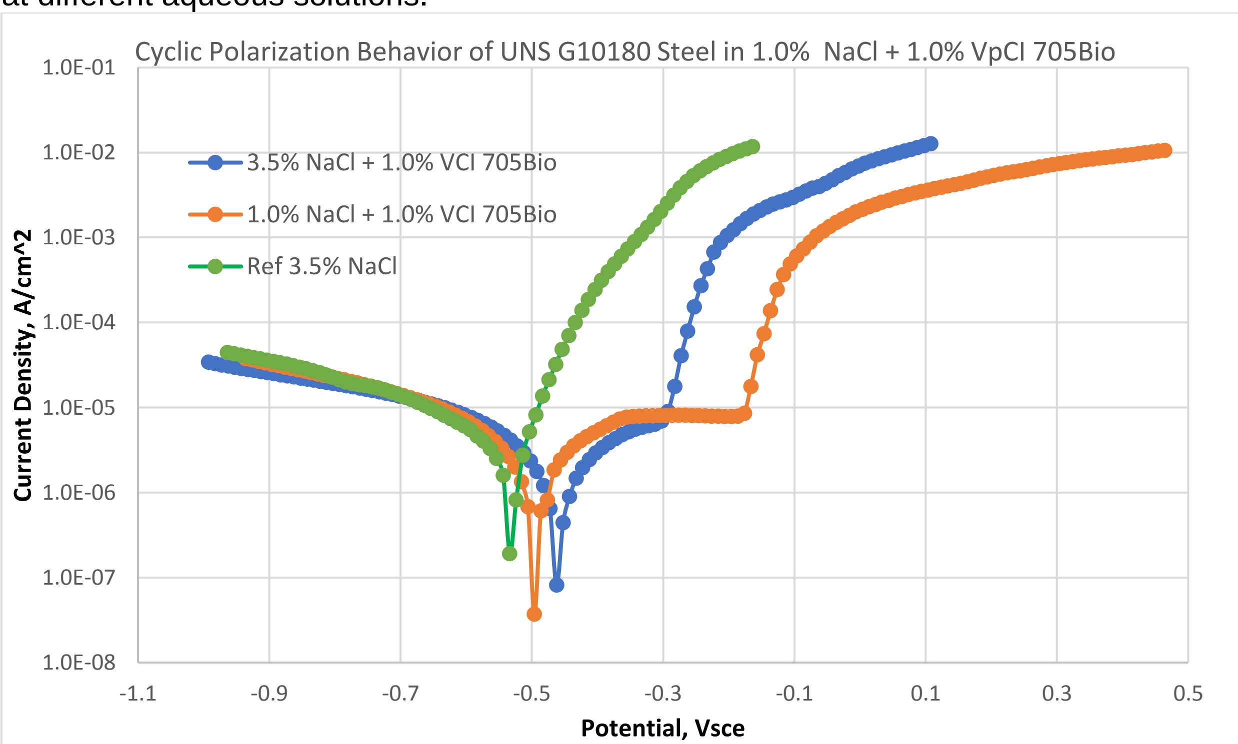


Figure 4: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-605 L Inhibitor at different aqueous solutions.

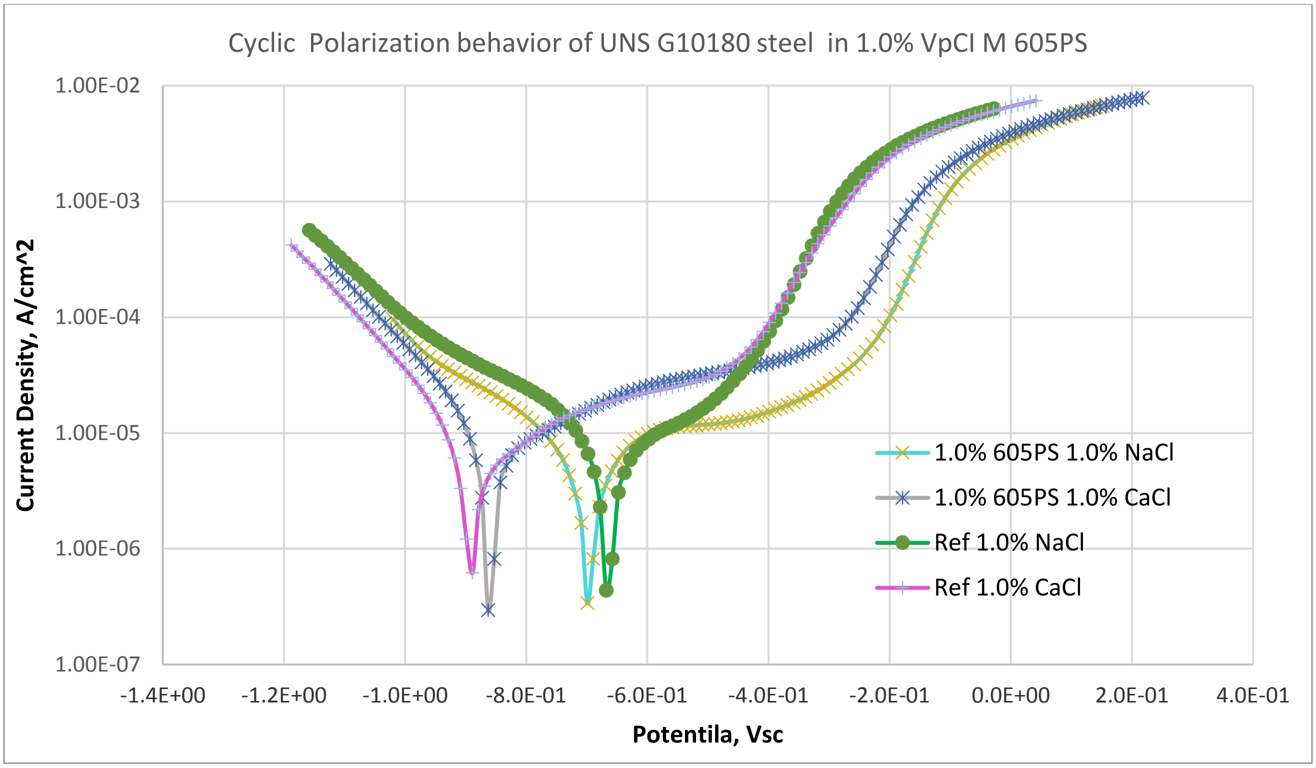


Figure 5: Comparison of Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI-605 L Inhibitor at different aqueous solutions.

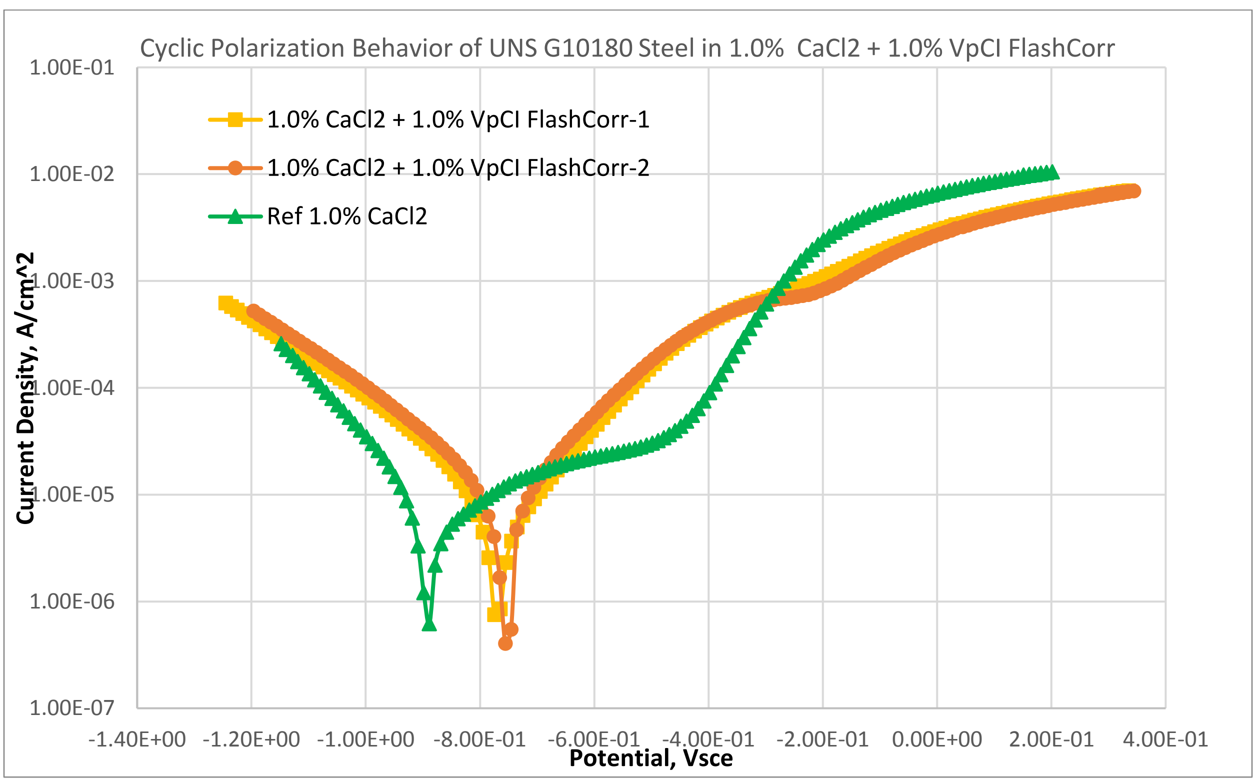


Figure 6: Comparison of Cyclic Polarization behavior of UNS G10180 steel in 1.0% VCI FlashCorr Inhibitor in CaCl2 aqueous solutions.

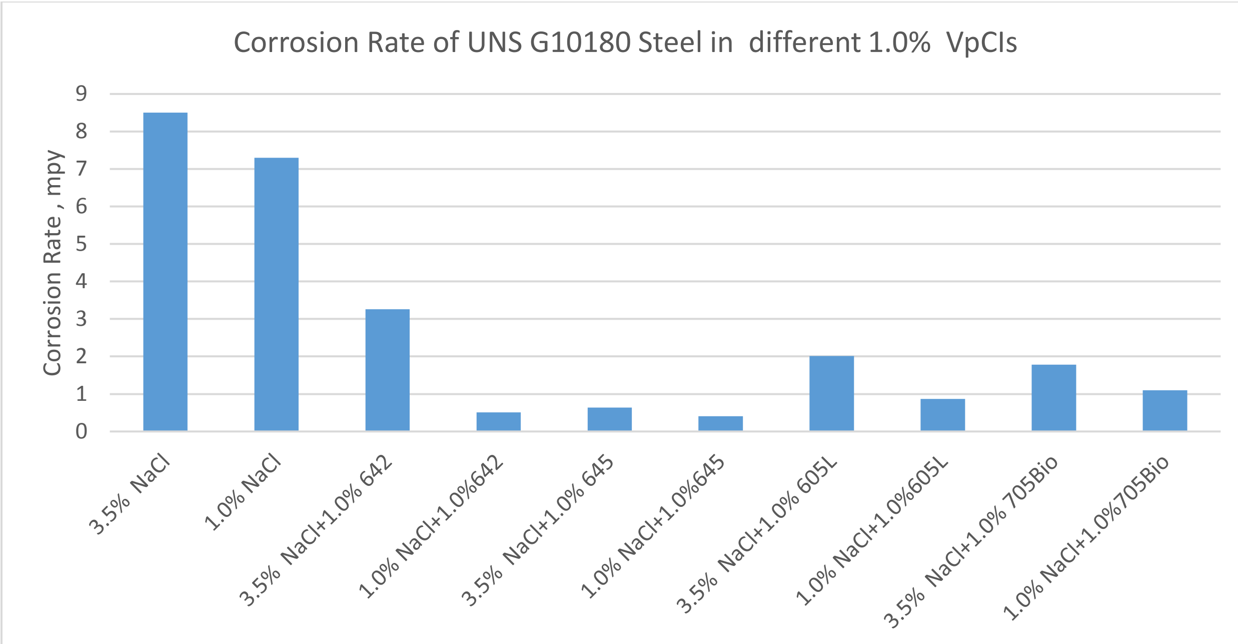


Figure 7: Comparison of corrosion rate of UNS G10180 steel in different aqueous solutions, showing significant decrease in corrosion rate in presence of different inhibitors.

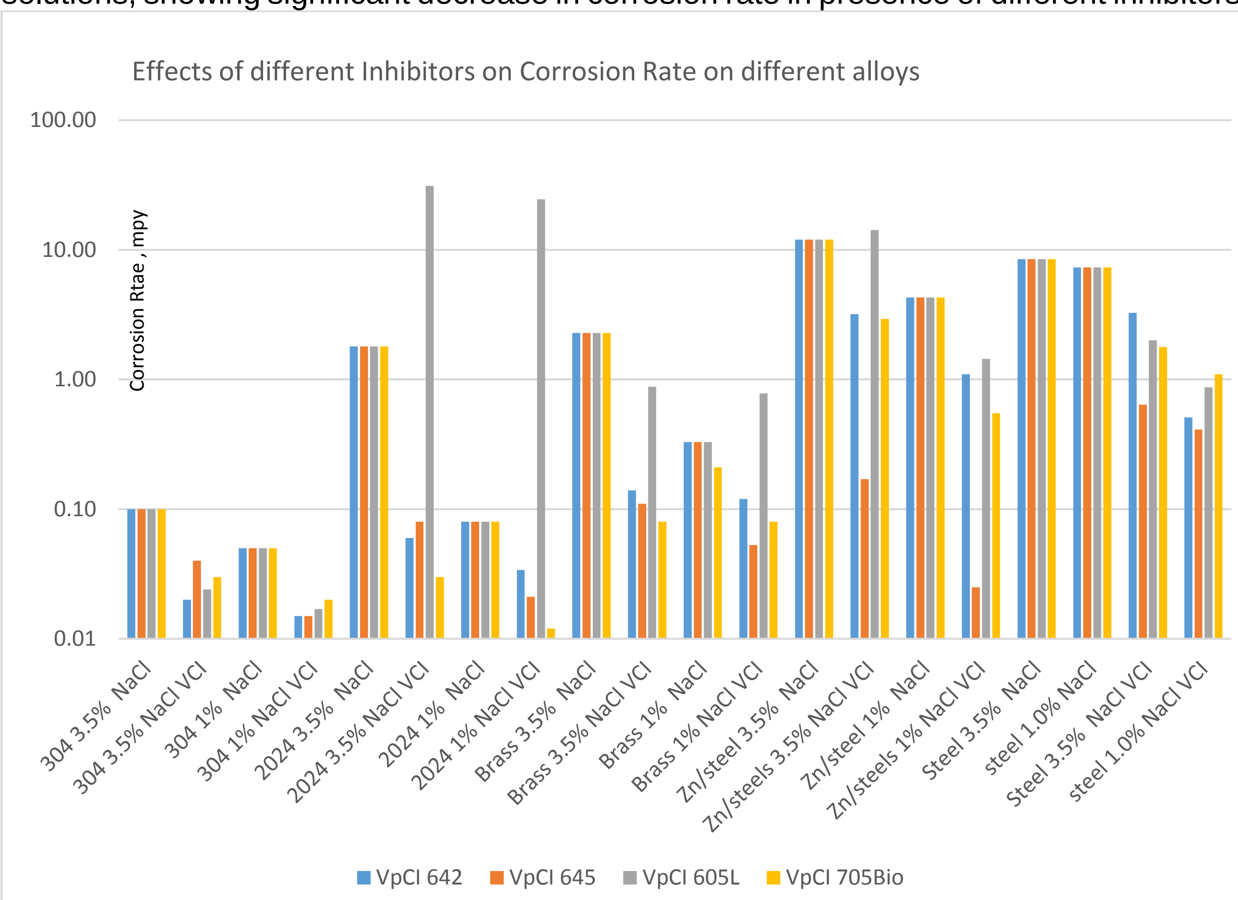


Figure 8: Summary of corrosion rate measurements (mpy) for different alloy in different inhibitors.

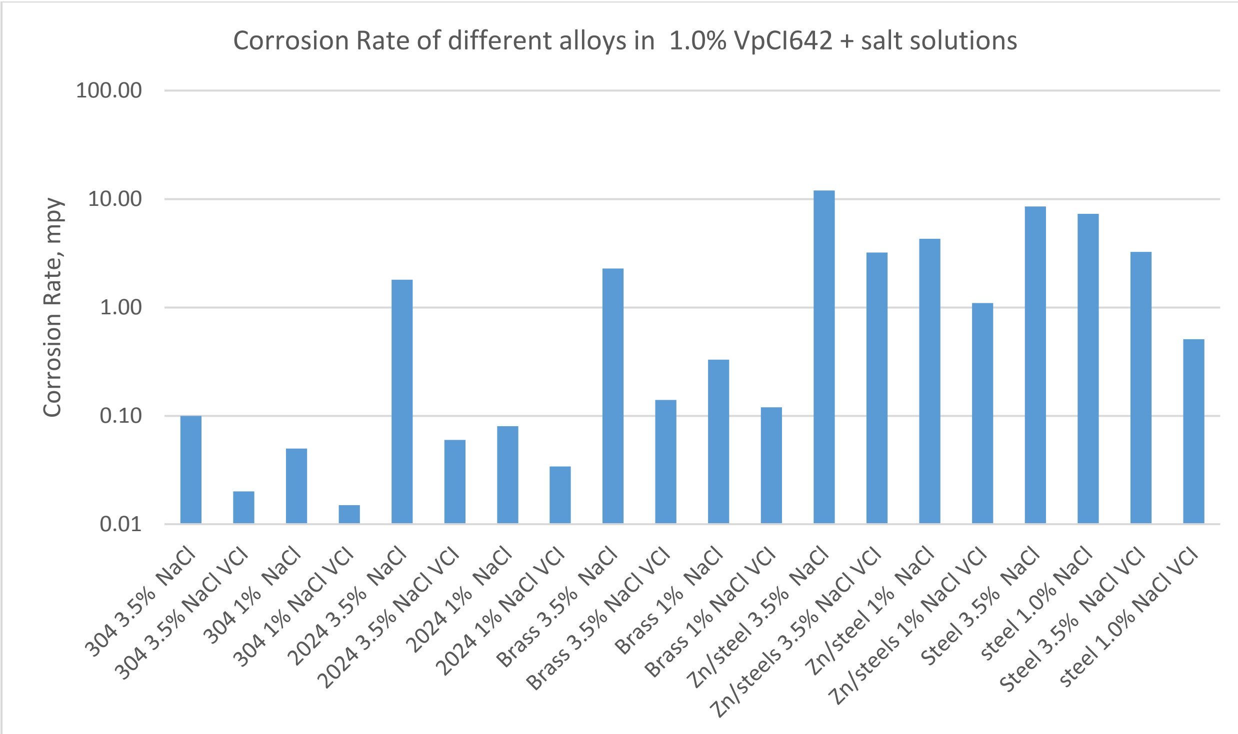


Figure 9: Comparison of corrosion rate of different alloys in different aqueous solutions, showing VpCI642 significant decrease corrosion rate of all exposed alloys.

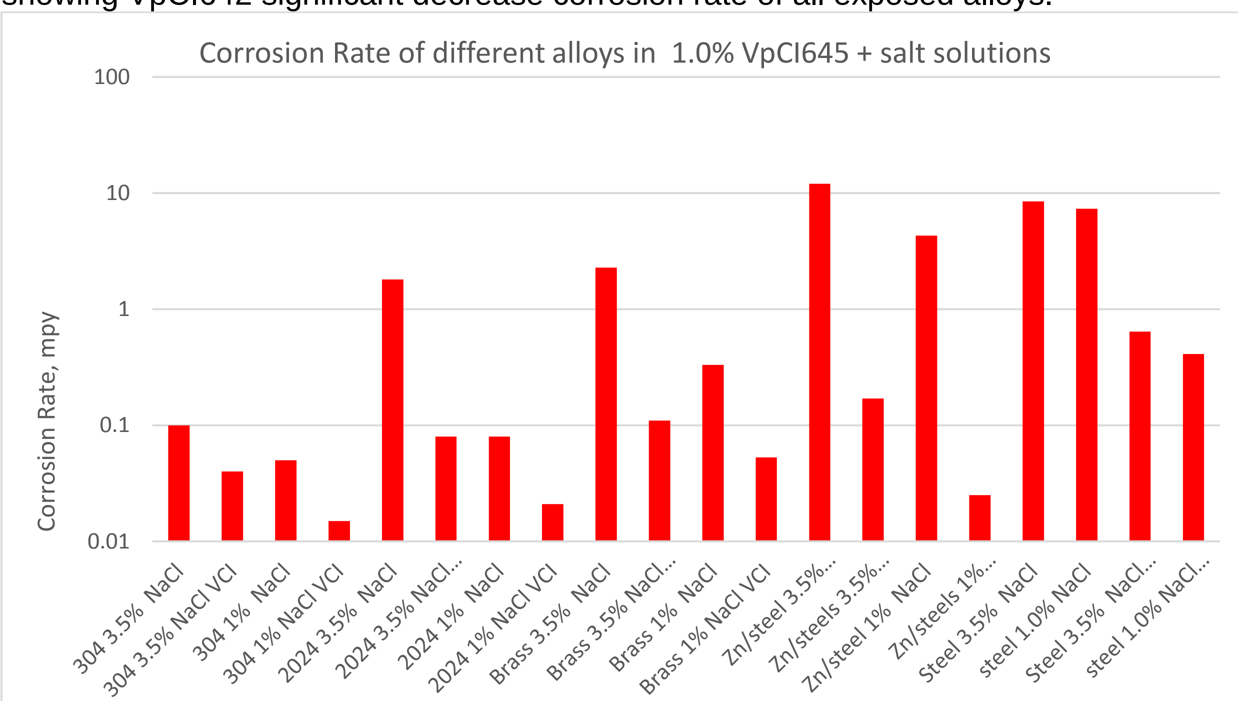


Figure 10: Comparison of corrosion rate of different alloys in different aqueous solutions, showing VpCI645 significant decrease corrosion rate of all exposed alloys.

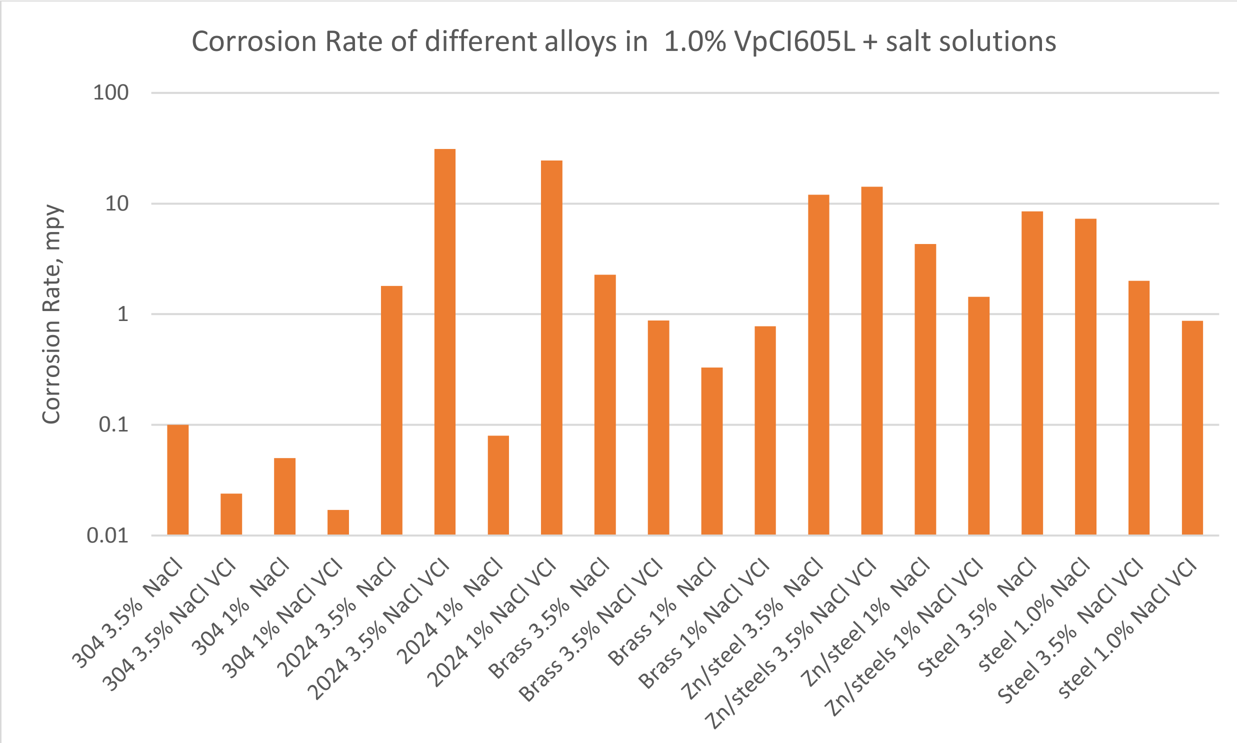


Figure 11: Comparison of corrosion rate of different alloys in different aqueous solutions, showing VpCI605L lowered corrosion rate for ferrous alloy but significantly increase corrosion of Al-alloy, Brass and galvanized steel

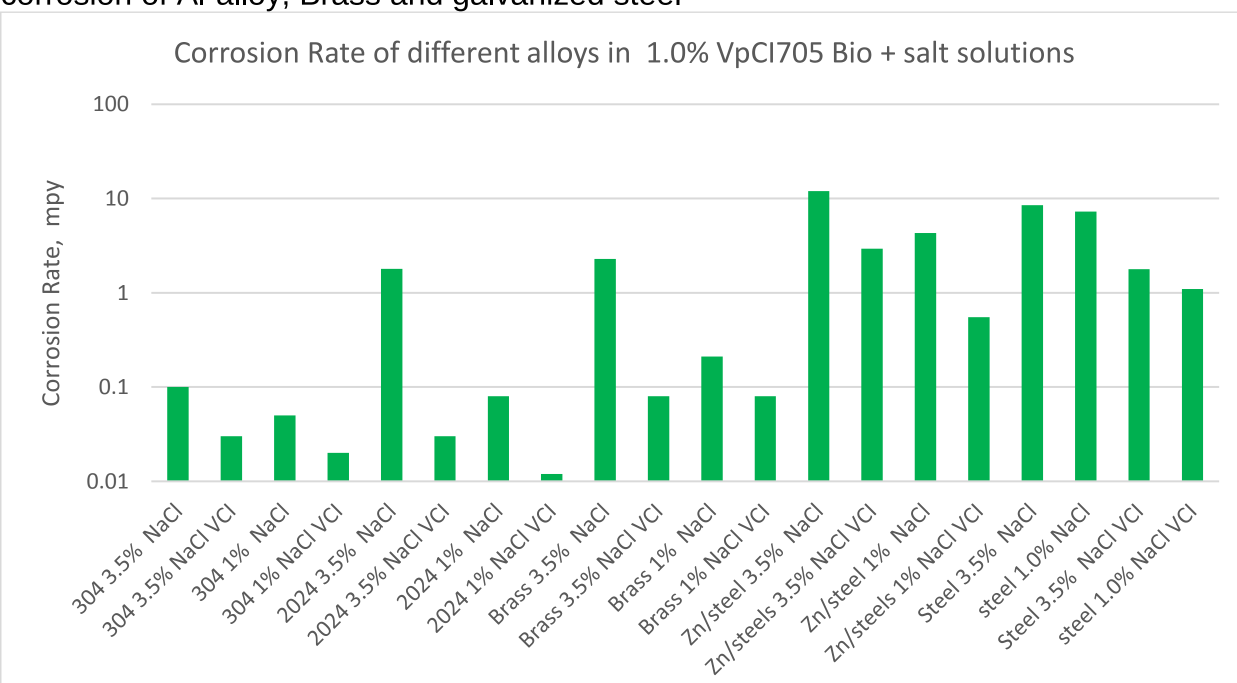


Figure 12: Comparison of corrosion rate of different alloys in different aqueous solutions, showing VpCI705 Bio significant decrease corrosion rate of all exposed alloys, except the galvanized steel.

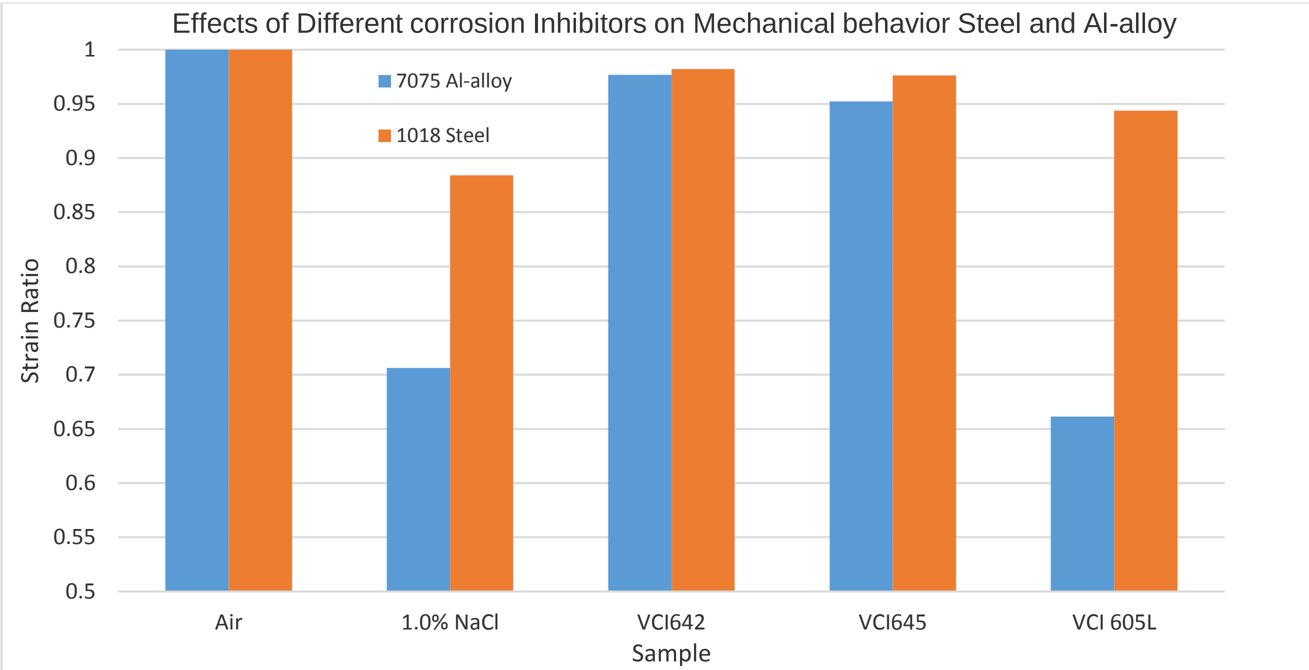


Figure 13: Effects of Different corrosion Inhibitors on Mechanical behavior of UNS G10180 and UNS A97075 Al-alloy. VpCI 605L showed it had adverse effect and increased corrosion damages on Al-alloys mechanical properties.

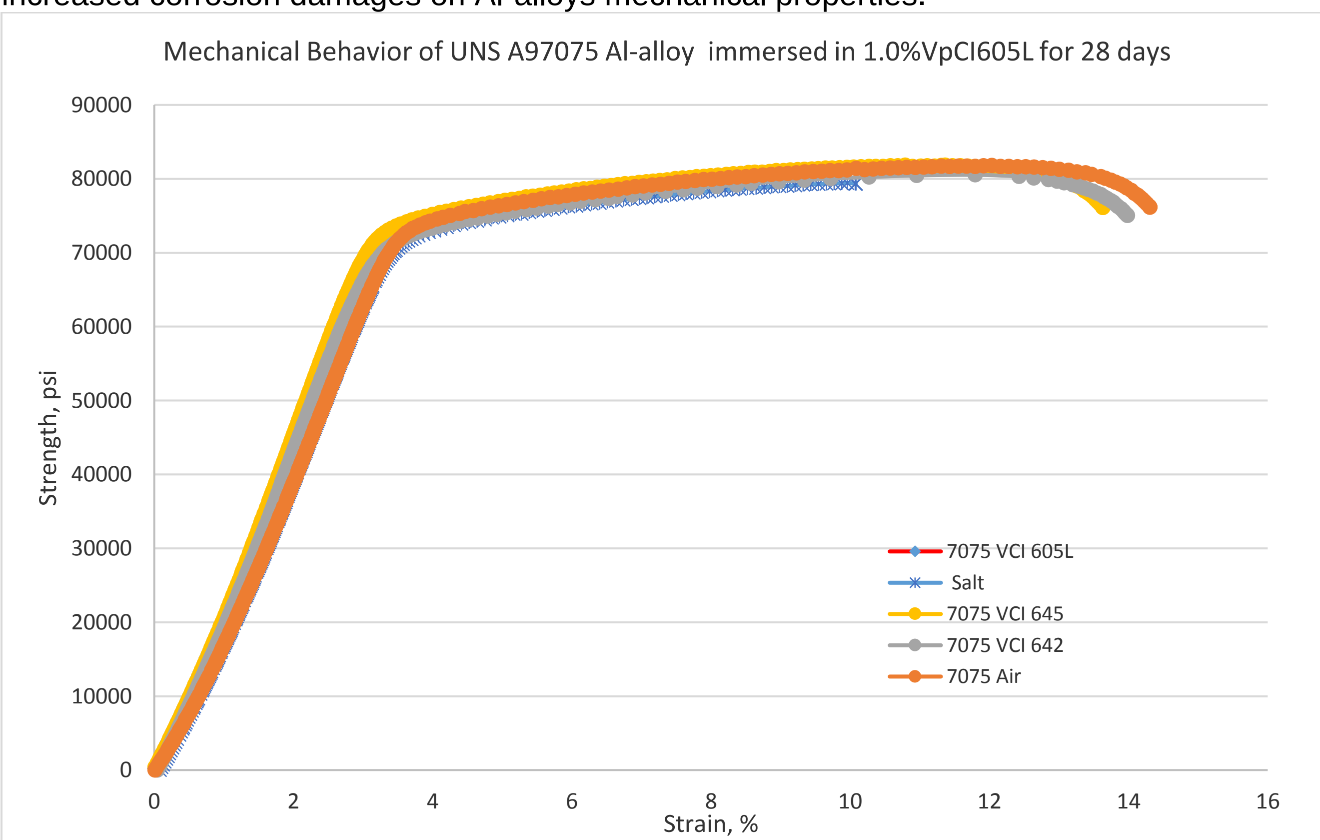
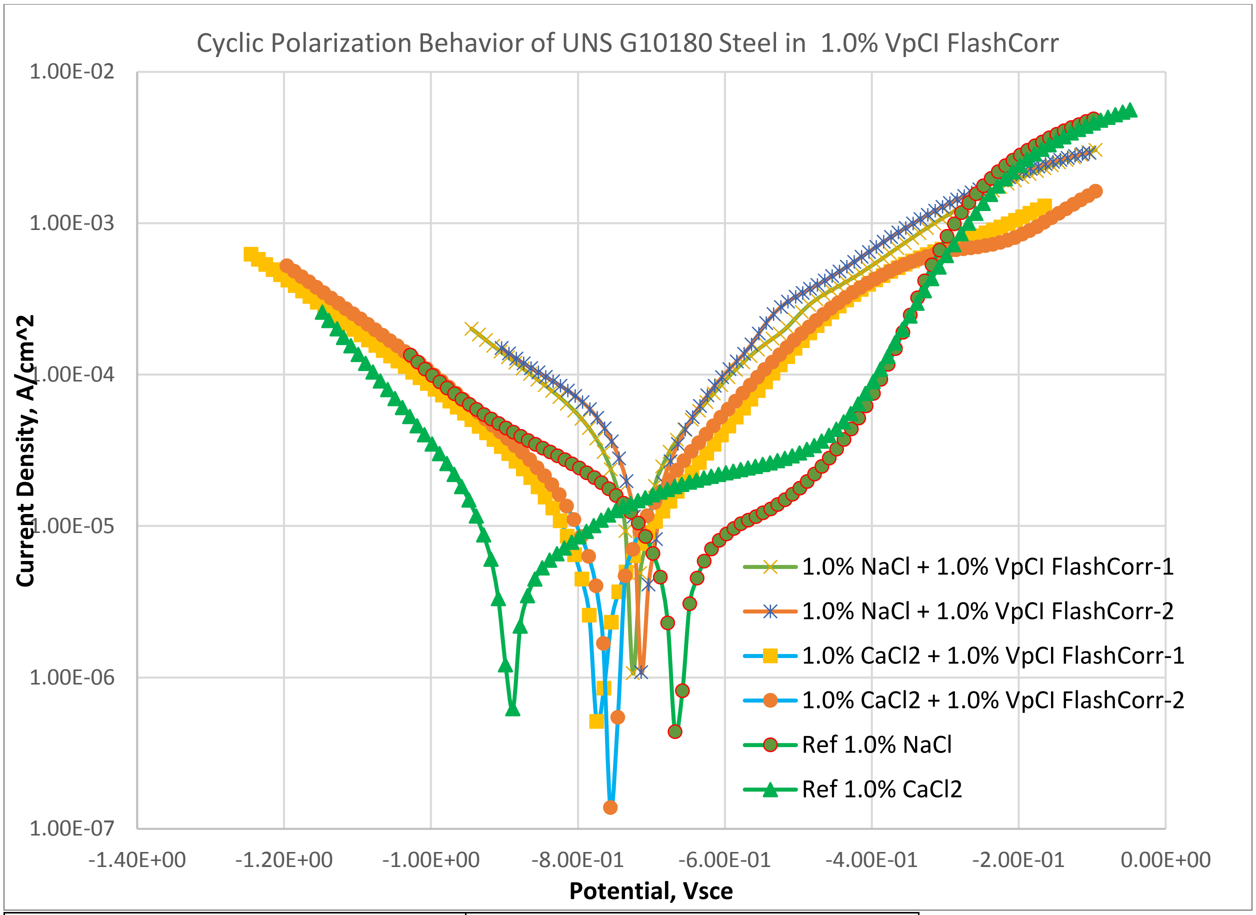


Figure 14: Effects of corrosion Inhibitors on Mechanical behavior of UNS A97075 Al-alloy. VpCI 605L showed it had adverse effect and lower ductility of Al-alloys.



Solution	Corrosion Rate, mpy
1.0% NaCl solution	3.71
1.0% CaCl2 solution	2.06
1.0% NaCl +1.0% VpCI FlashCorr	3.28
1.0% NaCl +1.0% VpCI FlashCorr	2.96
1.0% CaCl2 +1.0% VpCI FlashCorr	1.21
1.0% CaCl2 +1.0% VpCI FlashCorr	1.23

Figure 15: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VpCI FlashCorr Inhibitor at different aqueous solutions. Results showed that this inhibitor is very effective in calcium chloride solution.

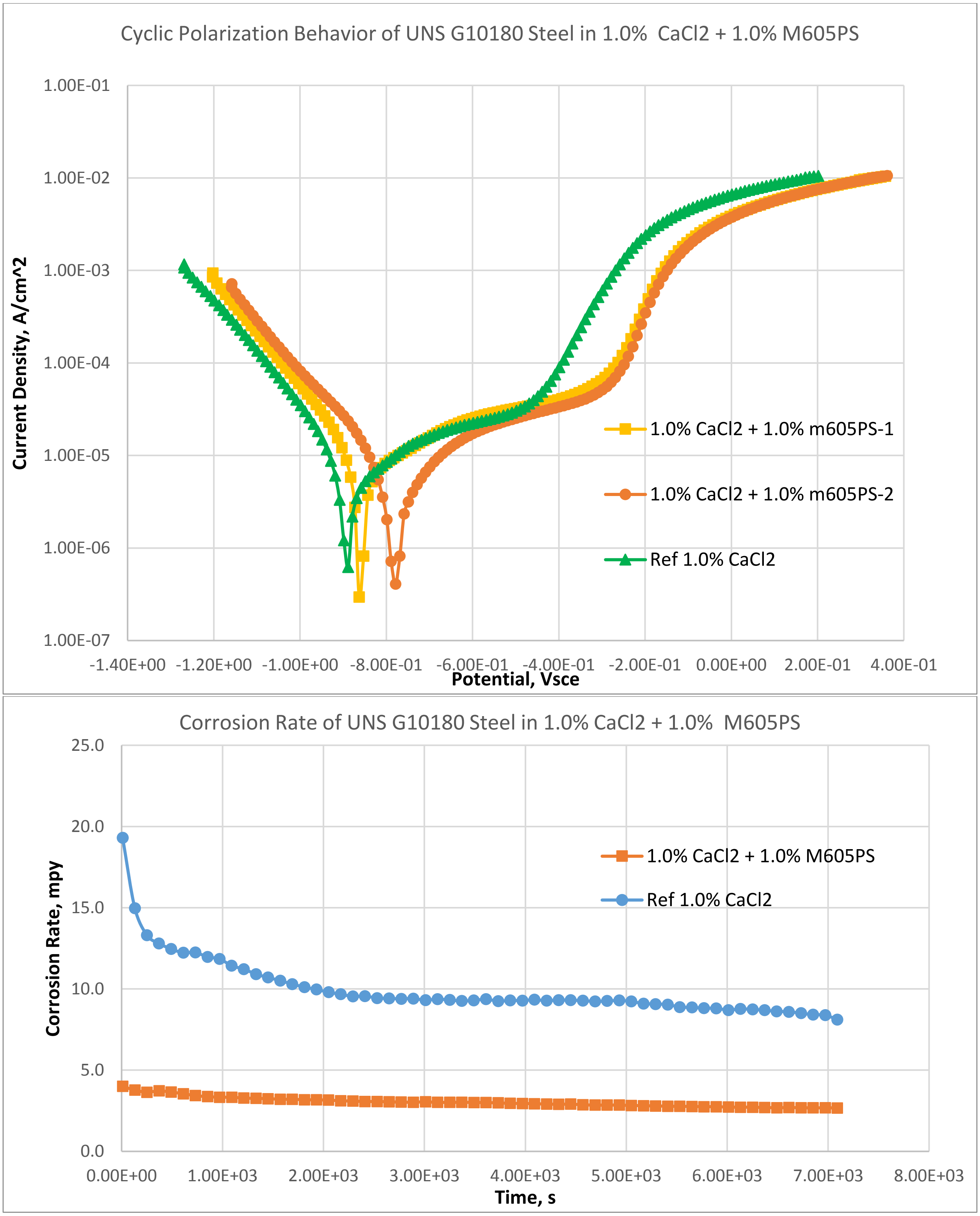
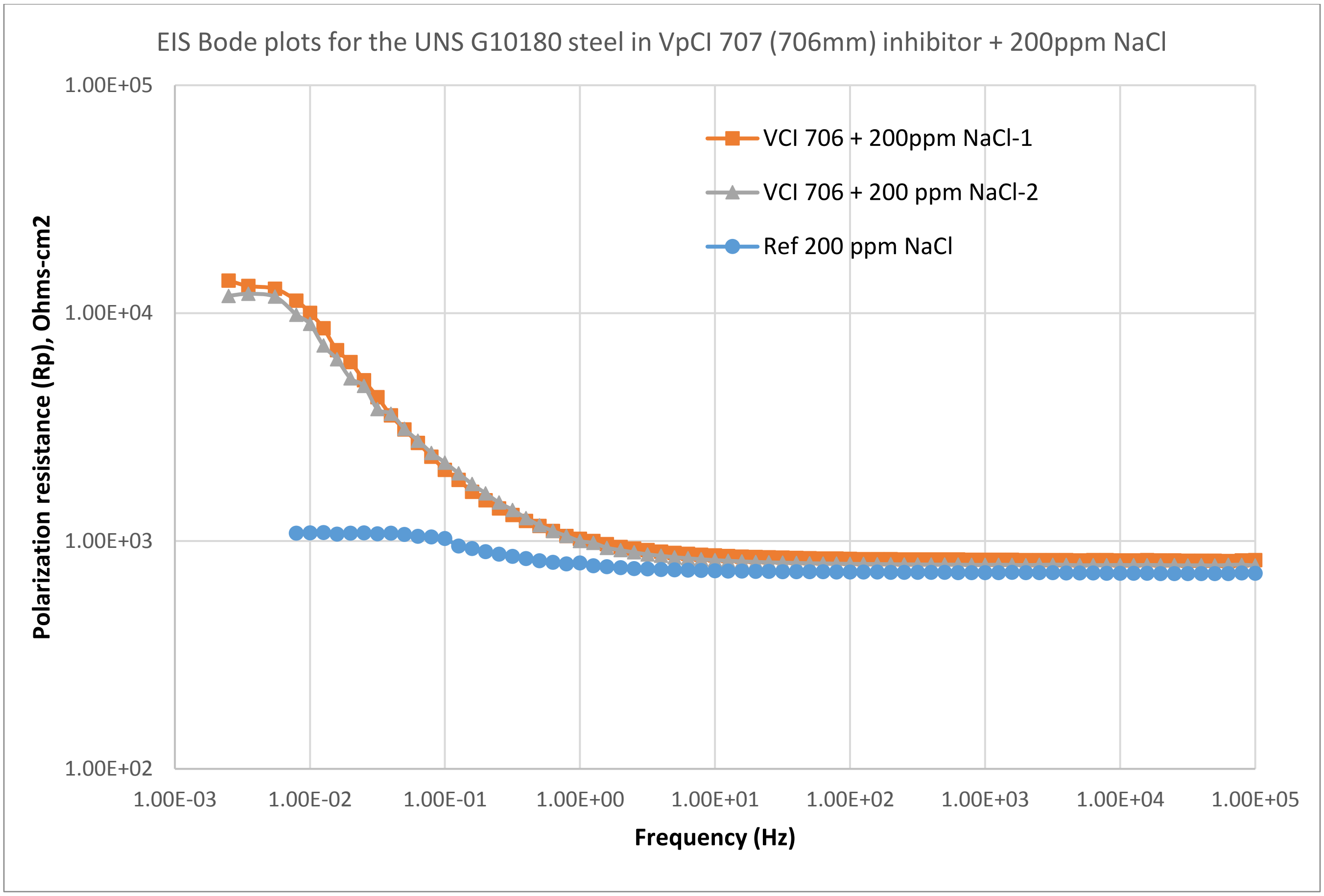
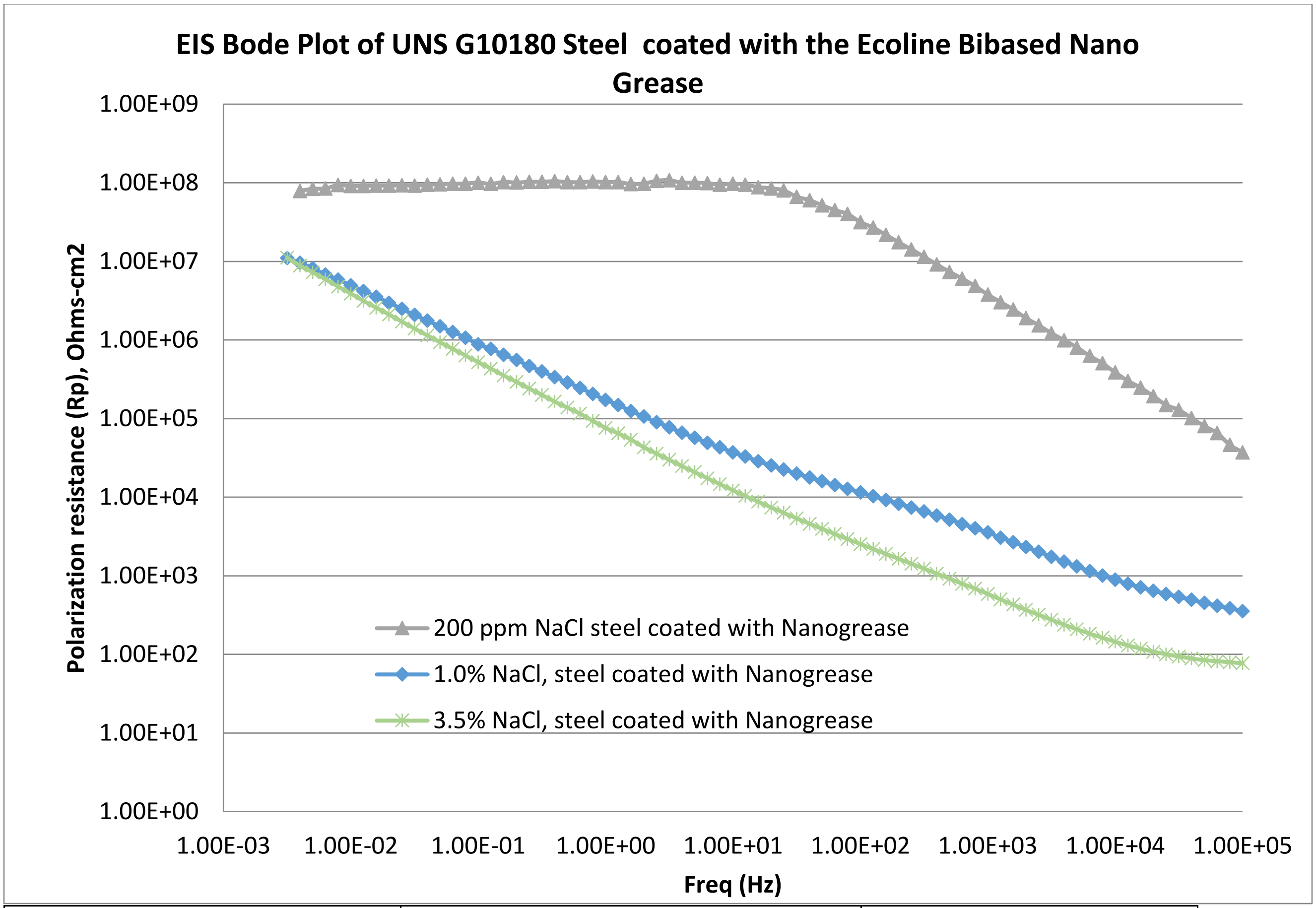


Figure 16: Cyclic Polarization behavior of UNS G10180 steel in 1.0% VpCI 605PS Inhibitor at CaCl2 aqueous solution. Results showed that this inhibitor is very effective in calcium chloride solution.



Solution	Polarization Resistance, ohm.cm^2	Corrosion Rate, mpy
200 ppm NaCl solution	1080	11.07
Salt +1.0% VpCI 707-1	11,200	1.26
Salt +1.0% VpCI 707-2	12,880	1.14

Figure 17: Electrochemical impedance spectroscopy (EIS) behavior of UNS G10180 steel in 1.0% VpCI 707 (706mm) (Fuel additive) Inhibitor in salt aqueous solution. Results showed that this inhibitor is very effective in lower corrosion rate of steel samples.



Solution	Polarization Resistance	Corrosion Rate, mpy
200 ppm NaCl solution	1.03E+8 ohm.cm^2	0.001
1.0% NaCl solution	1.11E+7 ohm.cm^2	0.011
3.5% NaCl solution	8.86E+6 ohm.cm^2	0.013

Figure 18: electrochemical impedance spectroscopy (EIS) behavior of coated UNS G10180 steel with Ecoline Nanogrease Inhibitor in different salt aqueous solution. Results showed that this inhibitor is very effective in lower corrosion rate of steel samples. Coated UNS G10180 steel with Ecoline Nanogrease Inhibitor showed no sign of any corrosion when exposed to salt spray corrosion tests for more than 2,000 hours (ASTM B117).

The Vapor-Inhibiting Ability (VIA) Test Results

The vapor-inhibiting ability (VIA) of various forms of VCI materials for temporary corrosion protection of ferrous metal surfaces were conducted on three VCI-A (Ecoline VpCI-642), VCI-B (VpCI-645) and VCI-C (VpCI 605-L). The VIA corrosion test method provides for standard conditions in a test jar of water-saturated, warm air without the presence of accelerating contaminants. The combination of (1) vapor transport across a gap containing air, water vapor and VCI, and (2) corrosion protection are evaluated in this test

method. The VIA tests consist of four steps of sample conditioning or saturation for 20 hours at 22 ^{o}C, cooling cycle at 2^{o}C, pre-warming at 50^{o}C, followed by three hours at 22 ^{o}C for specimen conditioning. After the last three hour conditioning period, the steel samples were inspected for visible water condensation. Following verification of water condensation on each sample, visual examination of the surface was done and microscopic observation was conducted to determine the corrosion rating for each sample. The corrosion criteria for rating steel specimens consist of grade 0 through grade 4 (Figure 19). To have a valid test, the control sample must have grade 0; samples with no inhibitor received worst grade. The control samples consistently rated a grade 0 for all VIA tests, therefore, validating the test method. Relative humidity and the temperature of each test jar were monitored by (Sensirion) sensors and data logging software.
Samples were visually inspected and their surface conditions were documented after VIA tests were completed. Photography, optical microscopy and SEM/EDAX analysis were conducted using a JEOL JSM-6480LV and Thermo System Seven detector.

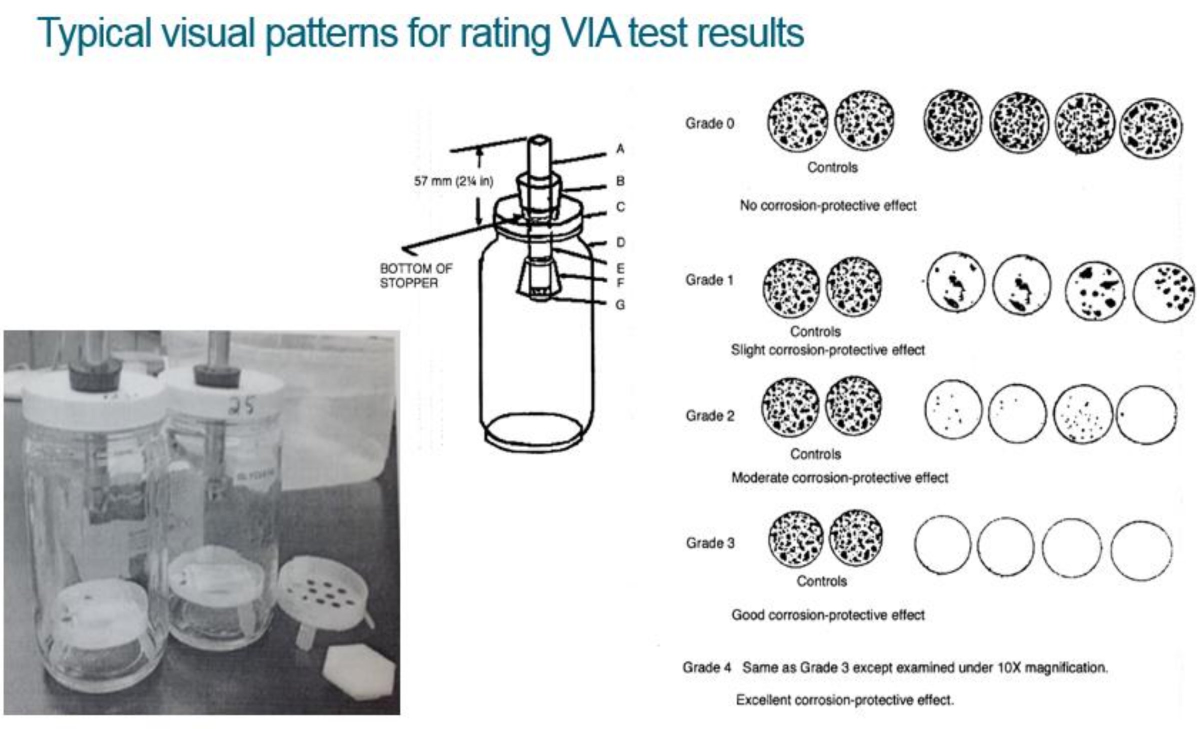


Figure 19: Test setup and rating criteria for the NACE TM 208-2008 Standard Test Method.

The VIA visual observations are shown in Figures 20- 21. The corrosion rating per TM-208 indicated that the control sample had Grade 0, while VpCI-642, VpCI-645 and VpCI-605L rating were Grade 3. Optical micrographs of the surface condition of samples after VIA tests is shown in Figure 20. Figure 21 shows SEM micrographs of the steel sample after VIA tests. The high resolution SEM images show a significant improvement for VCI-642, VCI-645 and VCI-605L with no sign of any pitting corrosion.

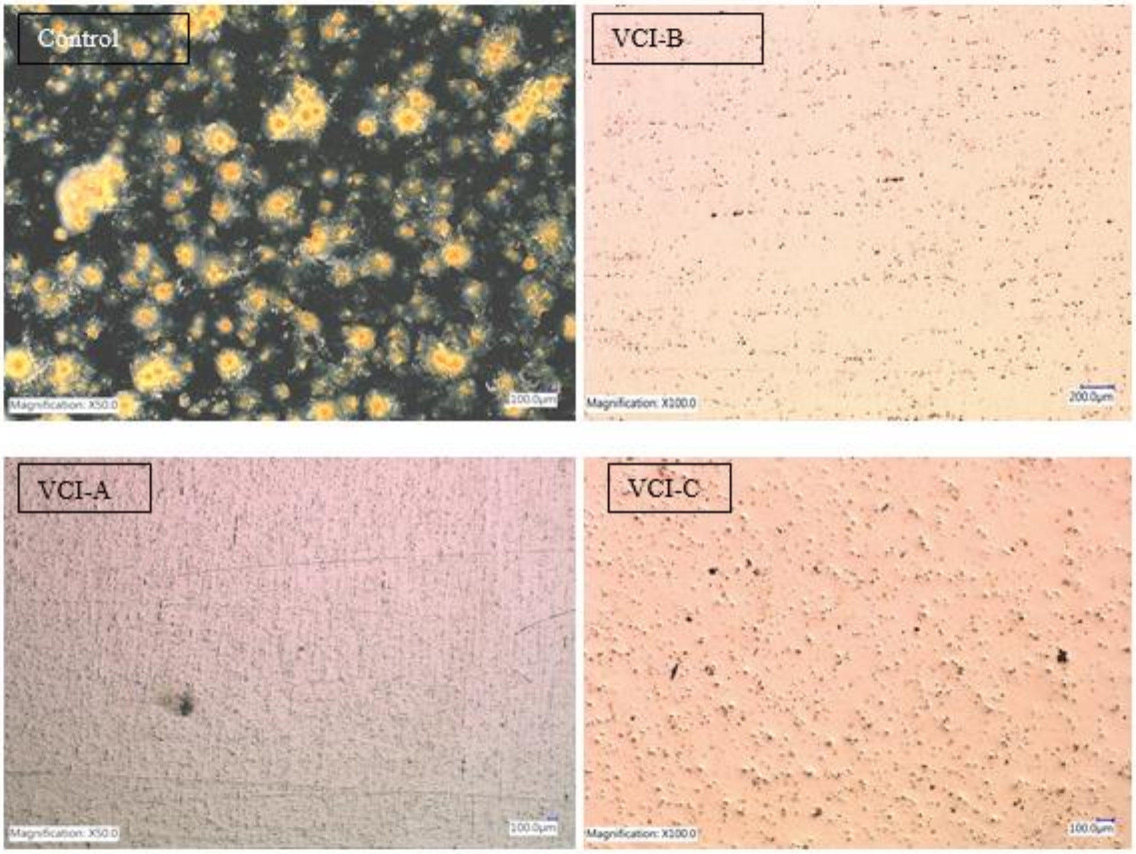


Figure 20: Optical micrographs of the steel sample after VIA tests. These tests showed a significant improvement for VCI A (Ecoline VpCI-642), VCI-B (VpCI-645) and VCI-C (VpCI 605-L) compared with the Control sample. VIA rating is: Control grade 0, VCI-A, VCI-B and VCI-C grade 3

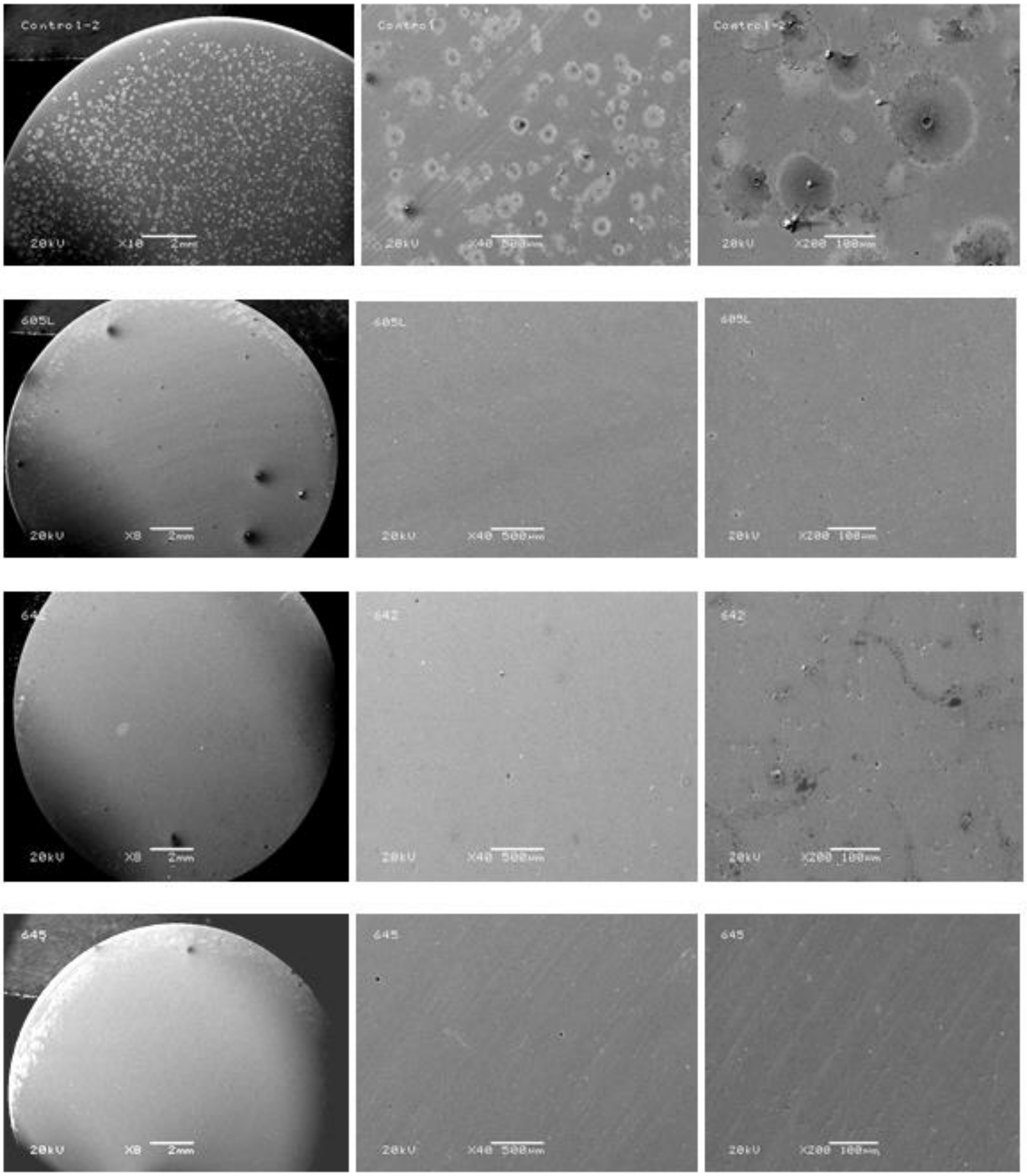


Figure 21: SEM micrographs of steel sample after VIA tests. Superior performance for VpCI-642, VCI-645 and VCI-605L were observed compared with the Control sample.
VIA Rating defined: Control grade 0, while VpCI-642, VpCI-645 and VpCI-605L were rated as grade 3.

Inhibitor Adsorption Mechanism

The adsorption isotherm relationship between surface coverage and temperature for three VpCI-642, VpCI 645 and VpCI 605L inhibitors on the surface of steel is shown in Figure 22. Adsorption energy was roughly -21,520 J/mol for VpCI642 inhibitor, -22,950 J/mol for VpCI645 inhibitor, adsorption energy was roughly -24,970 J/mol for the VpCI 605L inhibitor. This energy range is indicative of a strong physical adsorption to the metal surface. However, it can be seen that interaction of VpCI 605L with the steel surface is higher than other inhibitor, leading to better corrosion protection. XPS depth profiling analysis showed ~ 60-65 nm of adsorbed inhibitor on the exposed samples, indicating that multilayer Brunauer Emmett Teller Model (BET Model) is more realistic adsorption model than the monolayer Langmuir model for this case [12-15]. But for the adhesion energy calculation between inhibitor molecules and metal surface, it is appropriate to use the monolayer Langmuir model.

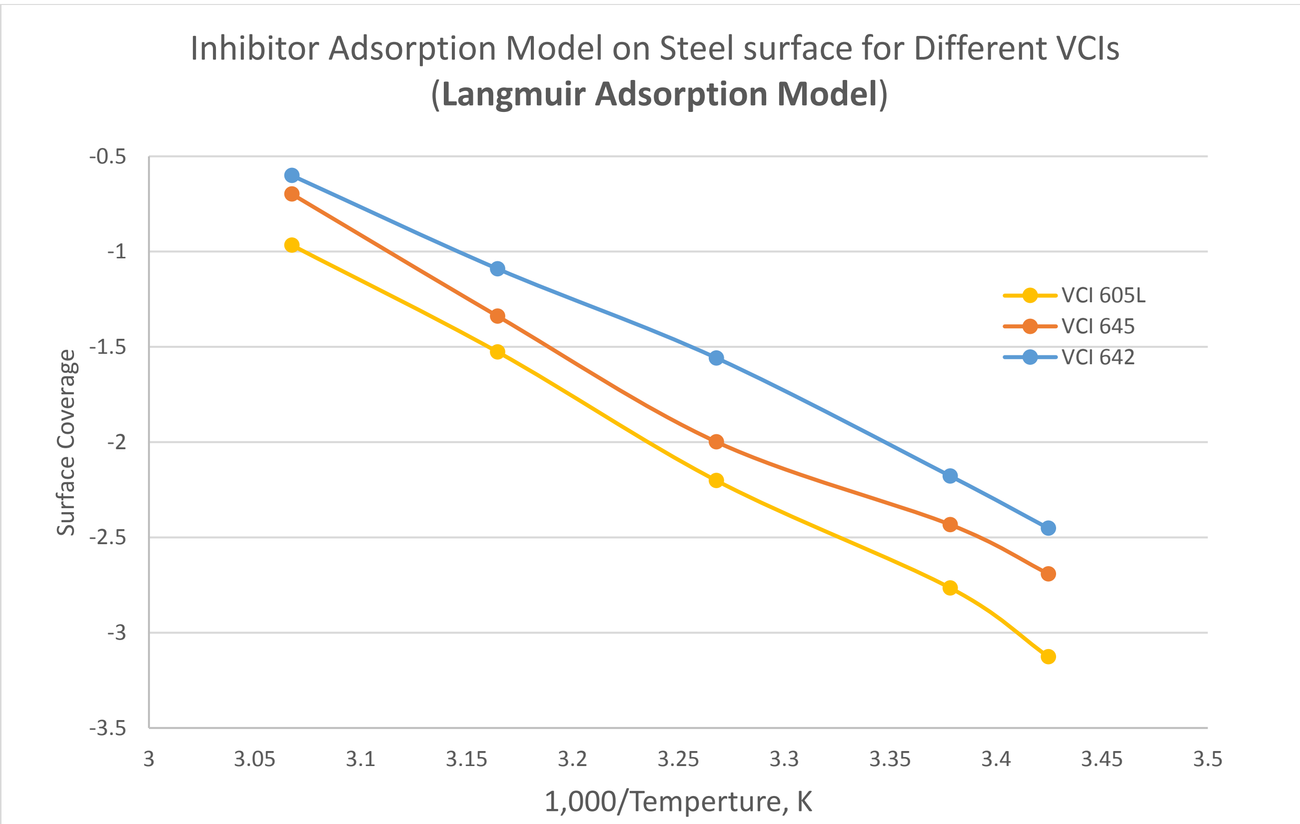


Figure 22: The adsorption isotherm relationship between surface coverage and temperature for different VCI inhibitors on the surface of steel. Adsorption energy was roughly -21,500 and 22,950J/mol for the VCI642 and VCI 645 inhibitors, while, adsorption energy was roughly -24,970 J/mol for VCI 605L size inhibitor.

CONCLUSIONS

This investigation demonstrated that corrosion inhibitor additives can lower the corrosion rate of multi-alloy systems in heavily salt contaminated aqueous solutions. Electrochemical Cyclic polarization showed formation of a stable passive range when these inhibitors were added to environments.

Effectiveness of these corrosion inhibitors is confirmed in various water chemistries including fresh and salt water. Corrosion rate dropped from ~10-12 mpy for salt solution to less than 1.0 mpy (a level of corrosion rate desired for the most of industrial application) when various inhibitors were added. The effectiveness of these inhibitors was remarkable in fresh water (less than 0.4 mpy).

Tensile tests post 28 days immersion did not show any loss in mechanical properties of the exposed samples. Both strength and ductility of the low carbon steel samples were maintained. However, VpCI605L showed adverse effects on mechanical properties of aluminum alloys. Similarly, electrochemical tests showed that VpCI 605L is not compatible with non-ferrous alloys such as aluminum alloys, brass (copper alloys), and galvanized steel (zinc coated), and increased the corrosion rate of these alloys.

Adsorption energy calculations were -21,500 to -24,970 J/mol for these inhibitors, indicating a strong physisorption mechanism for the adhesion of these compound on metallic surfaces.

The vapor-inhibiting ability (VIA) corrosion rating per TM-208 indicated that the control sample had Grade 0, while VpCI-642, VpCI-645 and VpCI-605L ratings were Grade 3. These results confirmed that these inhibitors have a good vapor-inhibiting ability.

VpCI FlashCorr and VpCI 605PS inhibitors were very effective in calcium chloride solution.

Electrochemical impedance spectroscopy (EIS) behavior of coated UNS G10180 steel with Ecoline Biobased Nanogrease results showed that this inhibitor is very effective in lowering the corrosion rate of steel samples. Coated UNS G10180 steel with Ecoline Biobased Nanogrease showed no sign of any corrosion when exposed to salt spray corrosion tests for more than 2,000 hours (ASTM B117). Electrochemical impedance spectroscopy (EIS) of UNS G10180 steel in 1.0% VpCI 707 (fuel additive) inhibitor in salt contaminated solution also showed a high degree of effectiveness in lowering the corrosion rate of steel samples.

This investigation demonstrated that these biobased, environmentally friendly vapor phase corrosion inhibitor additives are very effective. Due to their low toxicity level, any aqueous solutions containing these inhibitor products will satisfy most environmental regulations and be safe for many biological species, allowing safe discharge/drainage according to local specifications.

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Appendix A: Electrochemical data for VpCI642

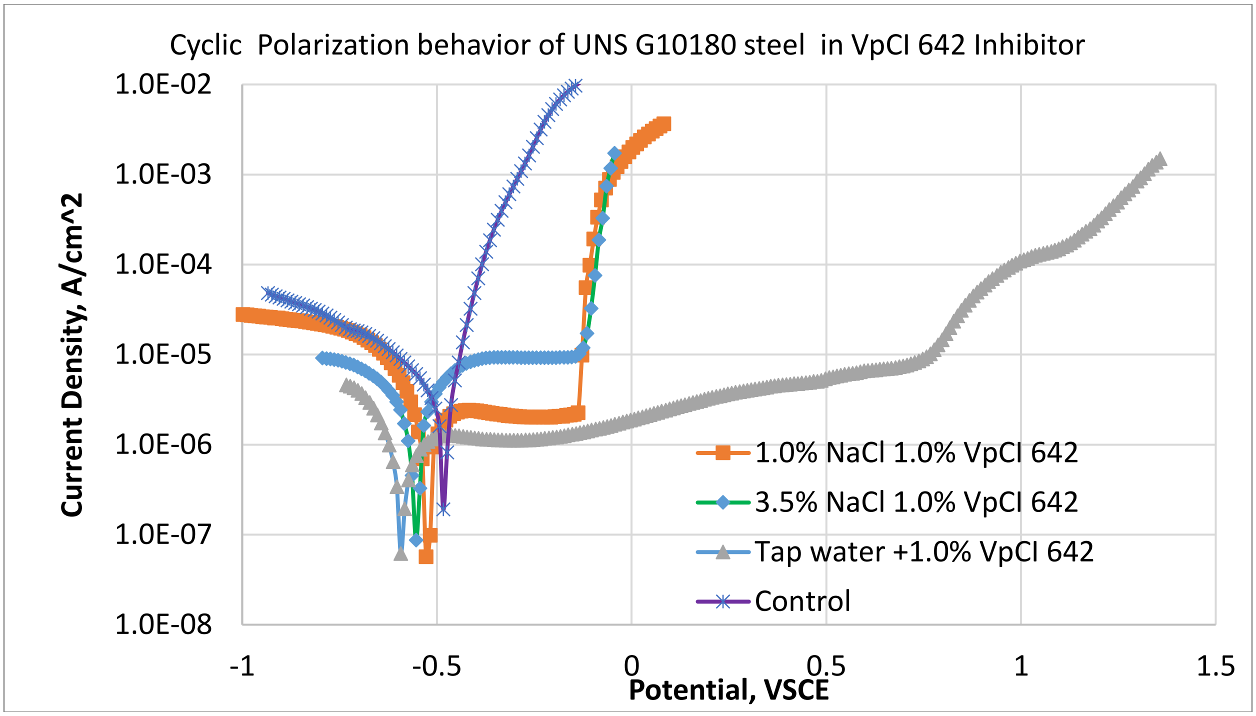


Fig. A-1: CP behavior of VpCI642 for UNS G10180 steel

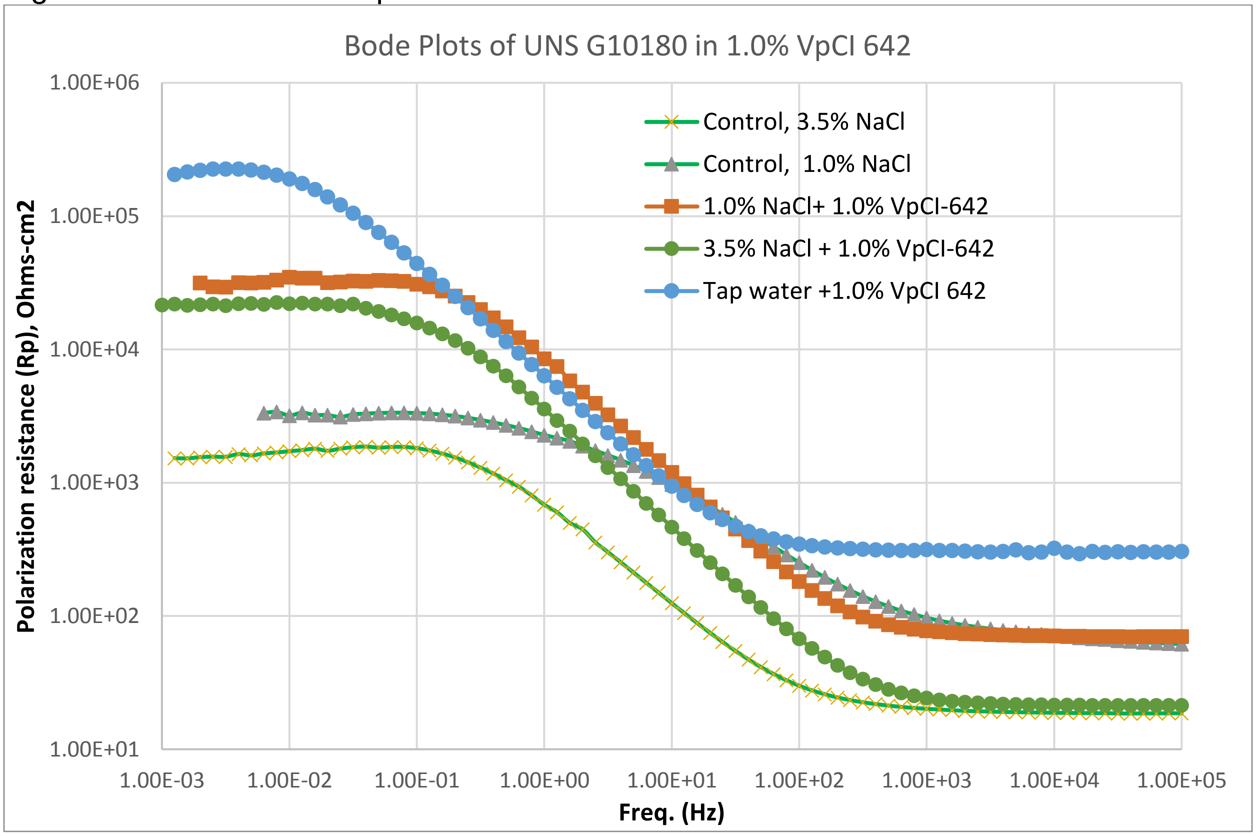


Fig. A-2: EIS behavior of VpCI642 for UNS G10180 steel

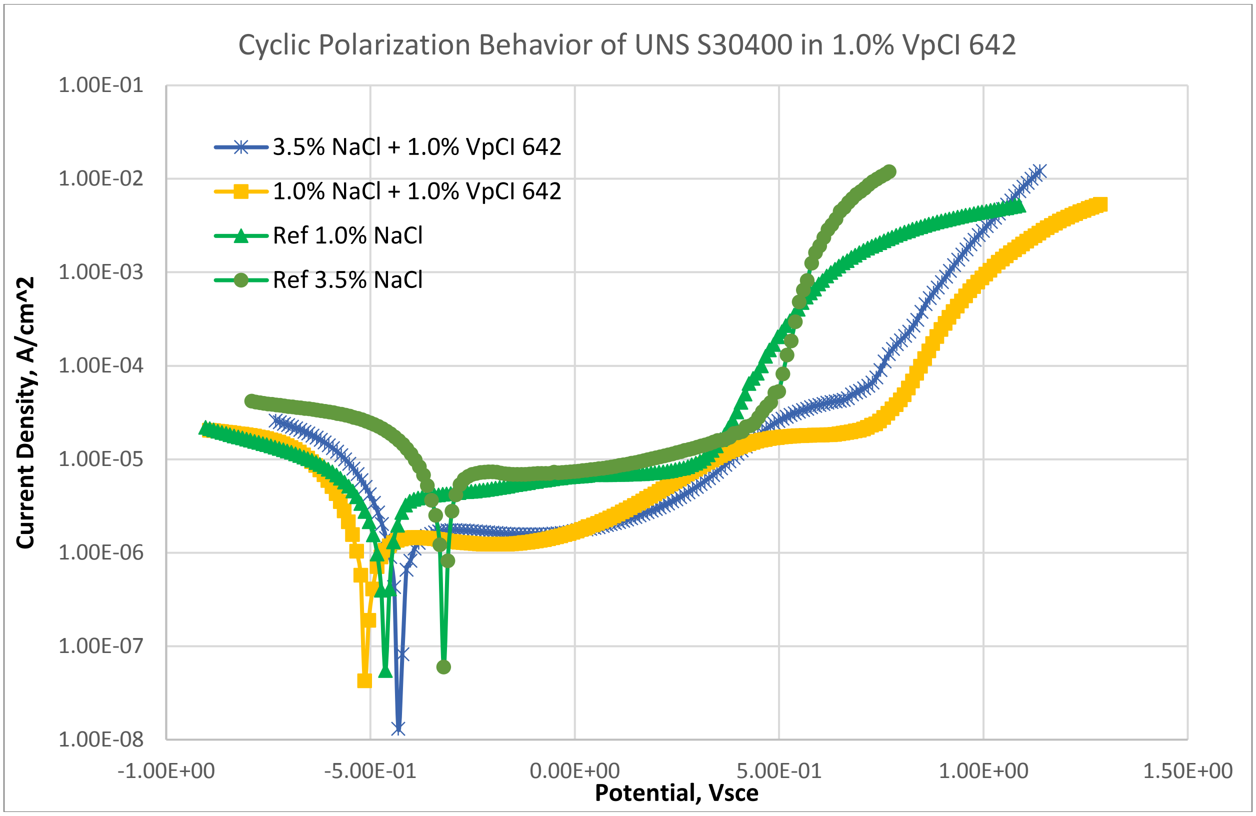


Fig. A-3: CP behavior of VpCI642 for UNS S30400 stainless steel

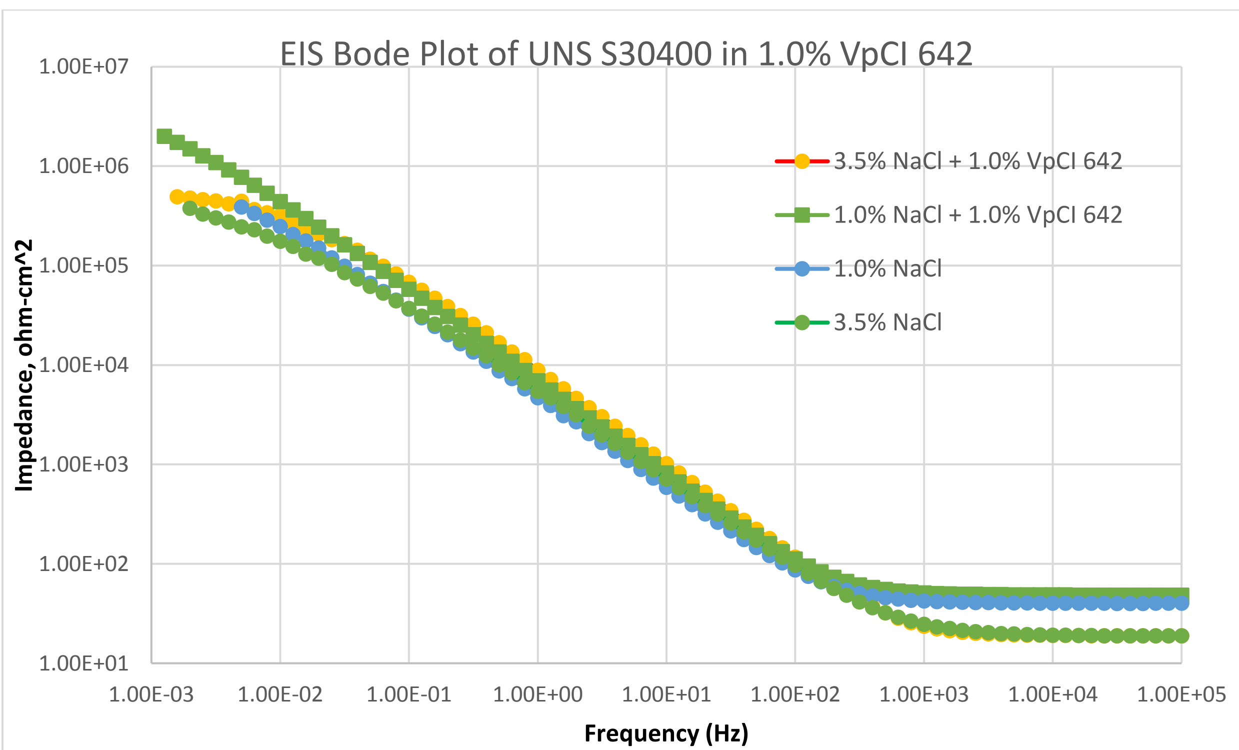


Fig. A-4: EIS behavior of VpCI642 for UNS S30400 stainless steel

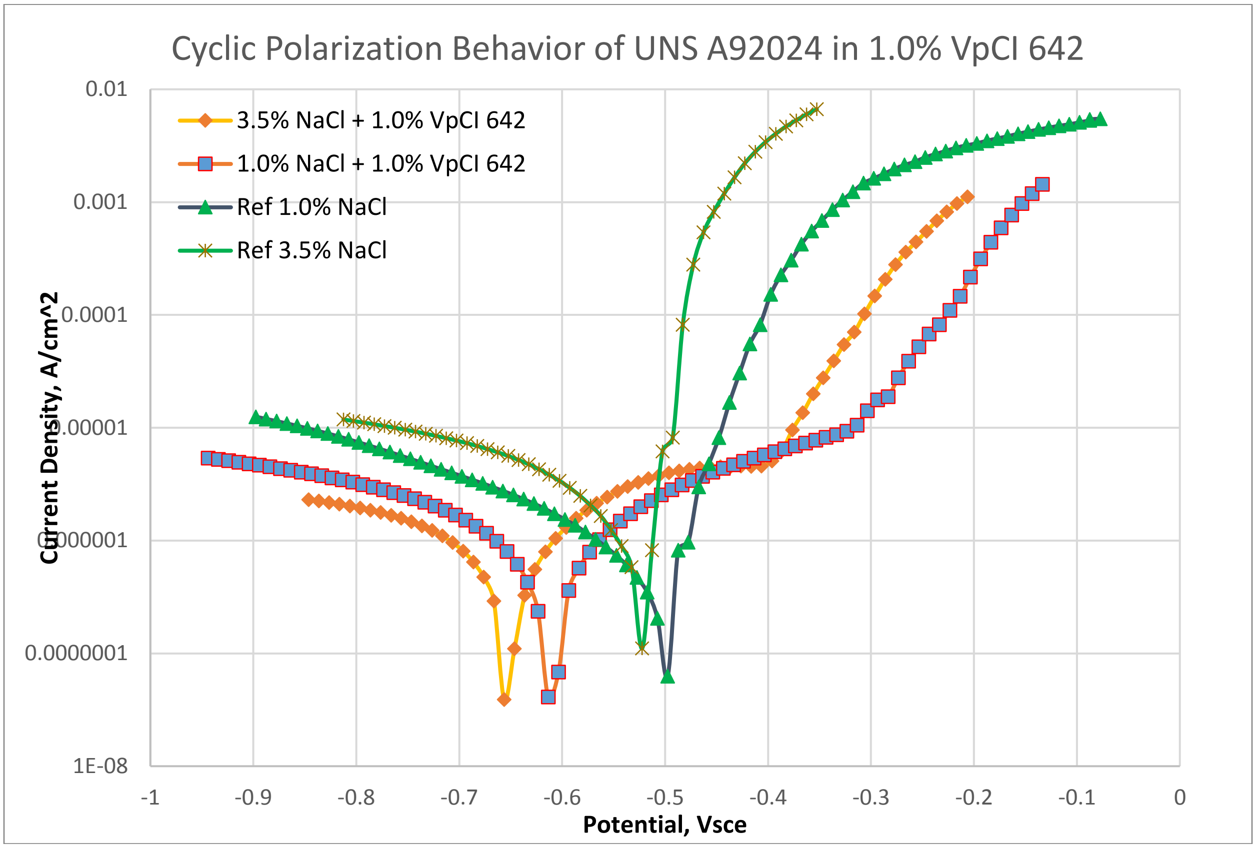


Fig. A-5: CP behavior of VpCI642 for UNS A92024 Al-alloy

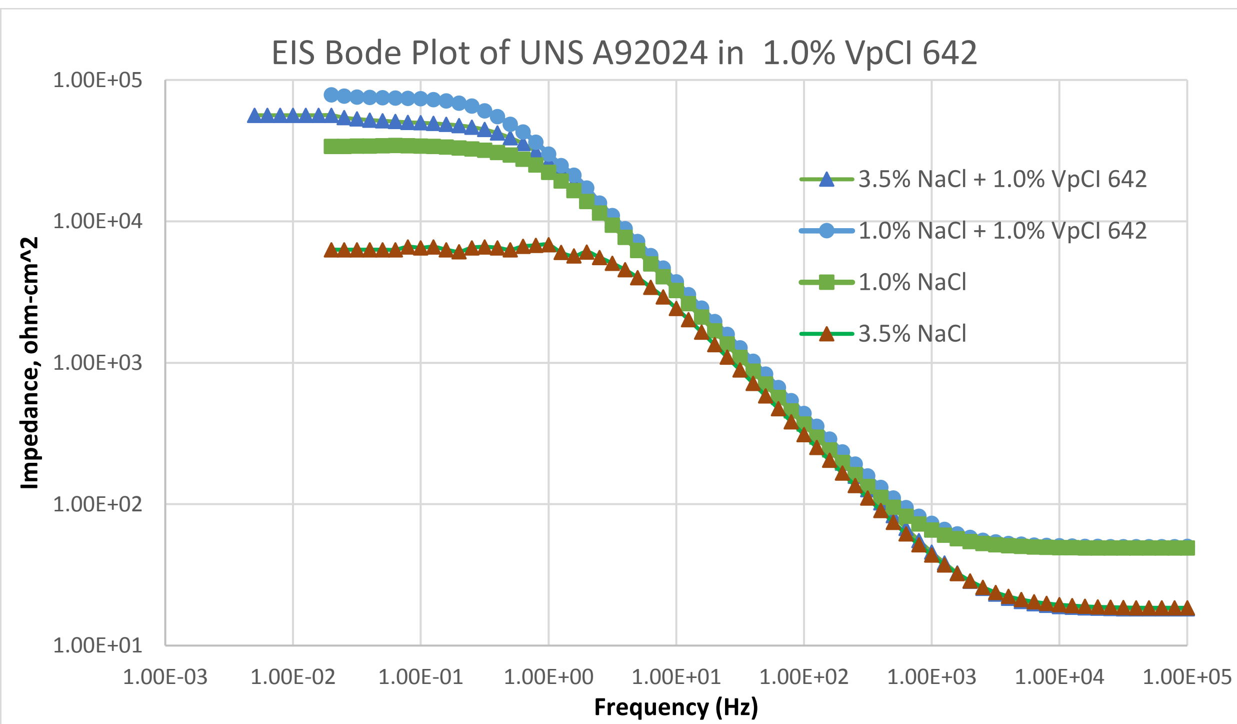


Fig. A-6: EIS behavior of VpCI642 for UNS A92024 Al-alloy

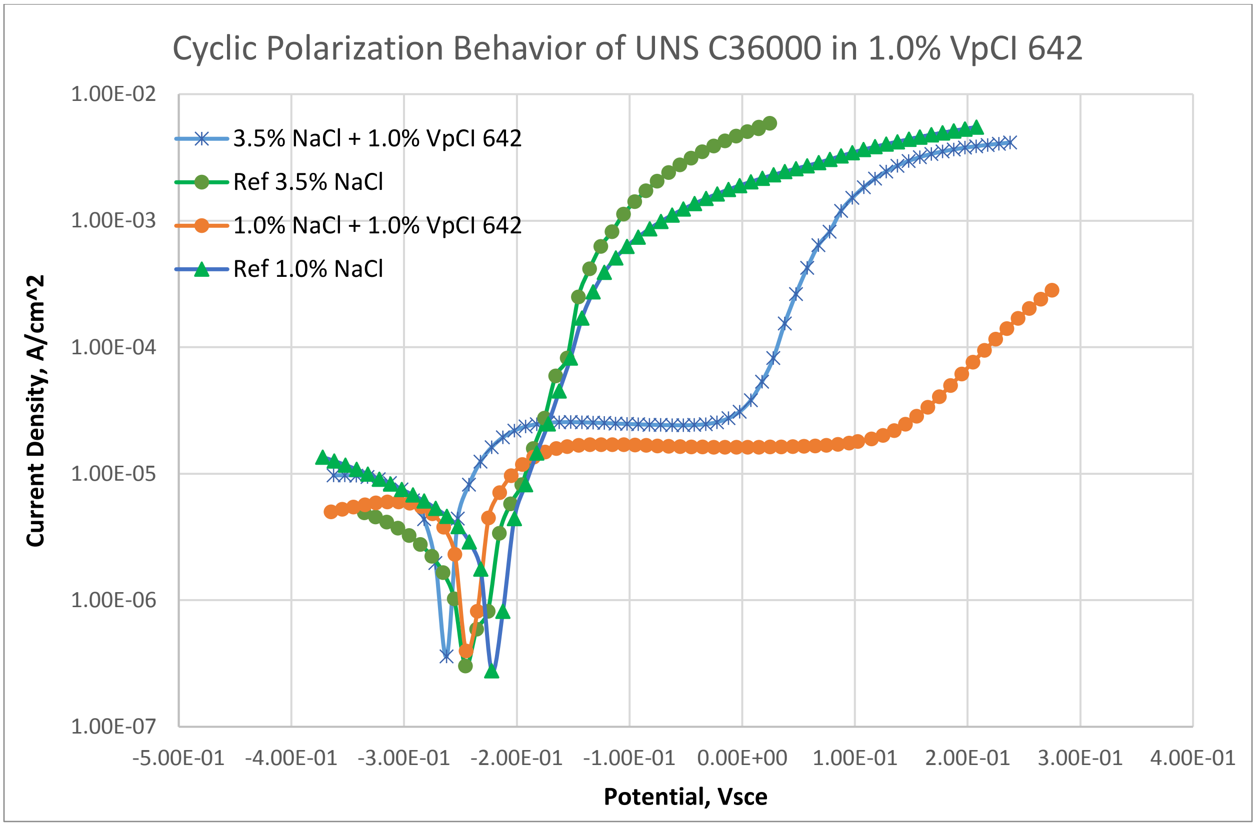


Fig. A-7: CP behavior of VpCI642 for UNS C36000 Brass-alloy

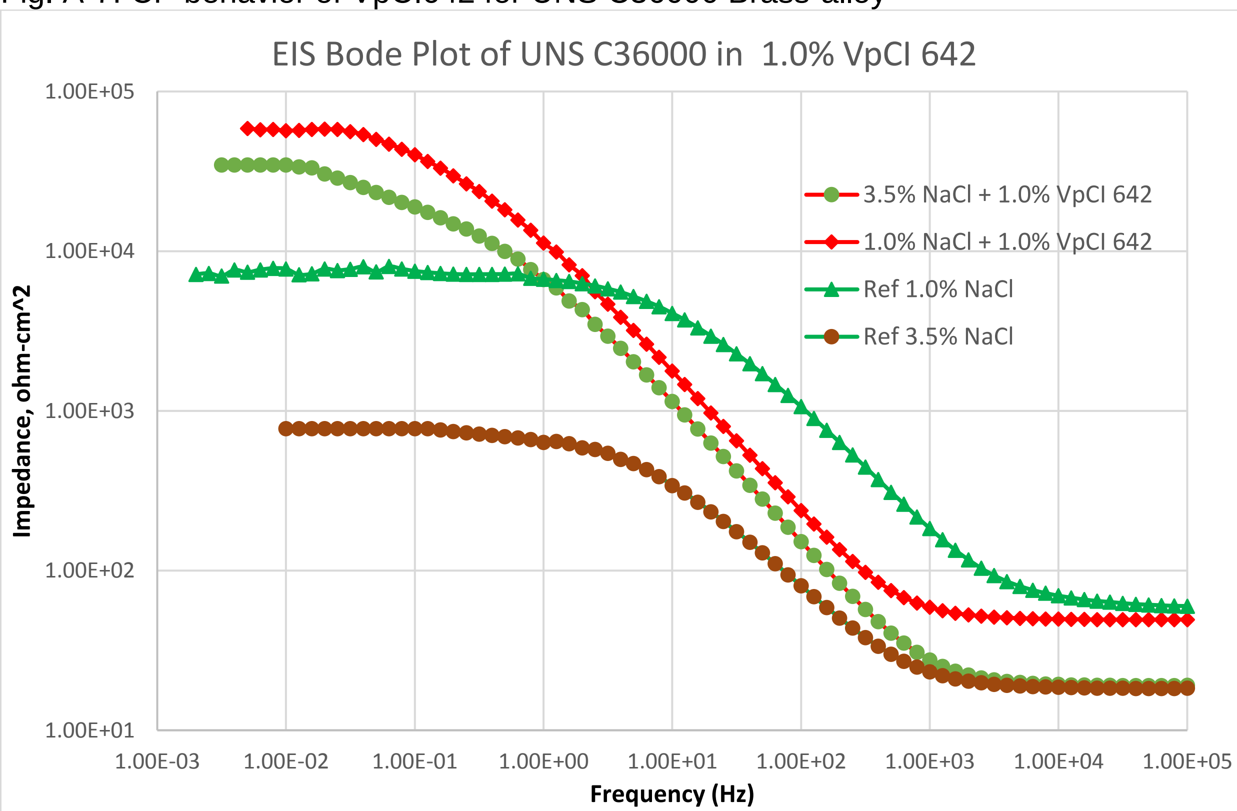


Fig. A-8: EIS behavior of VpCI642 for UNS C36000 Brass-alloy

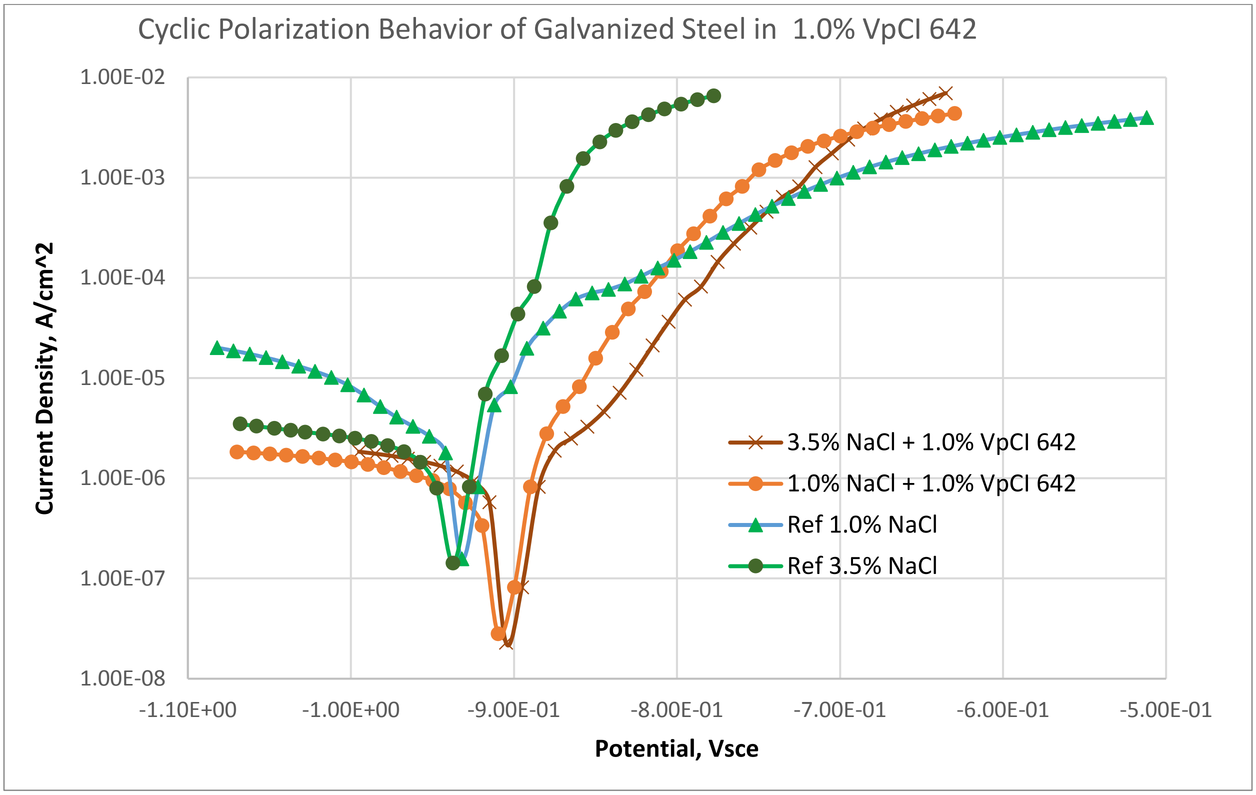


Fig. A-9: CP behavior of VpCI642 for galvanized steel

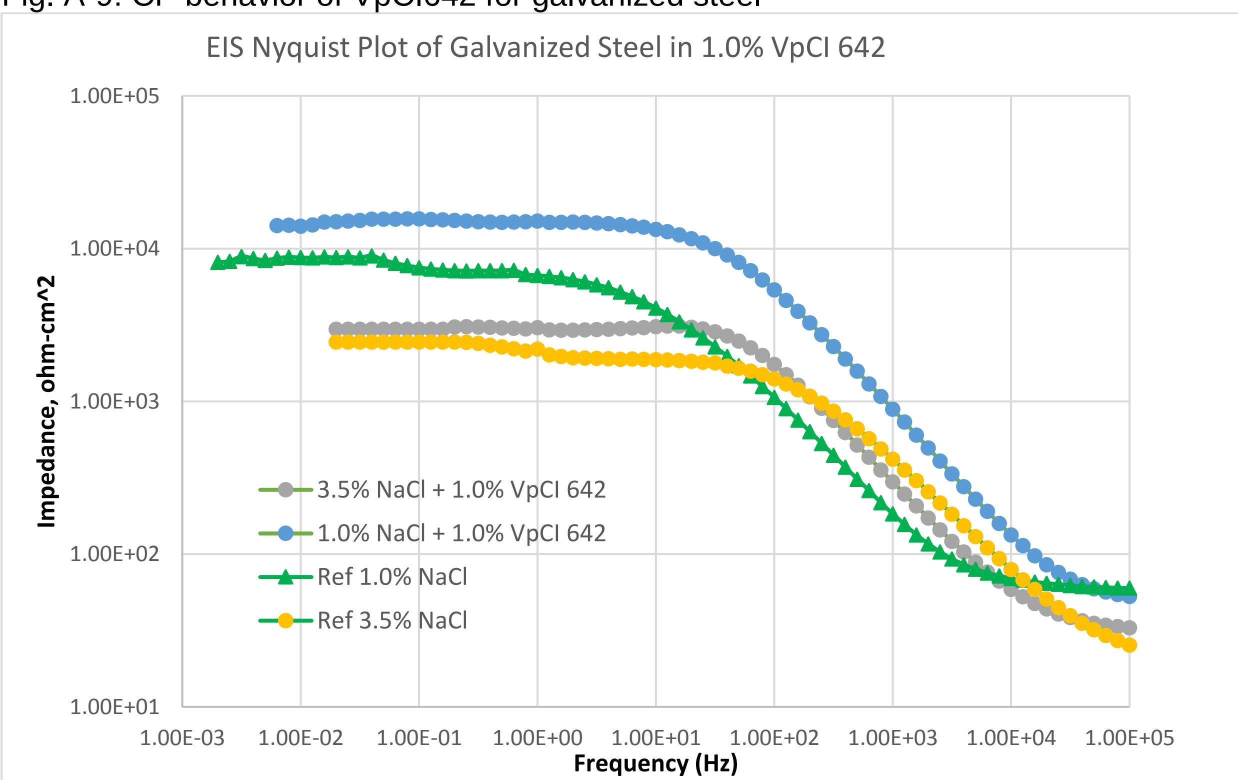


Fig. A-10: EIs behavior of VpCI642 for galvanized steel

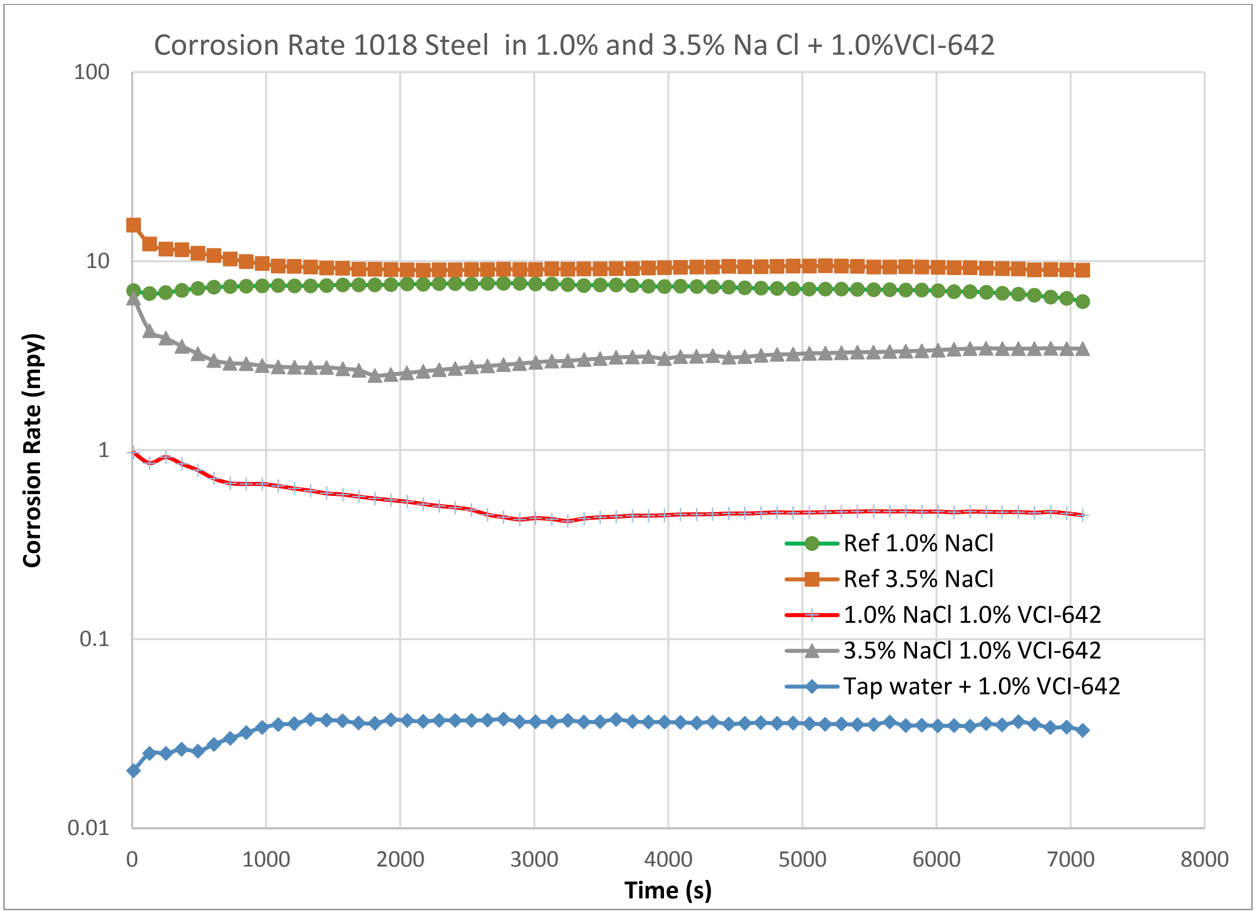


Fig. A-11: Corrosion rate measurements using LPR technique of VpCI642 for UNS G1018 steel.

Appendix B: Electrochemical data for VpCI645

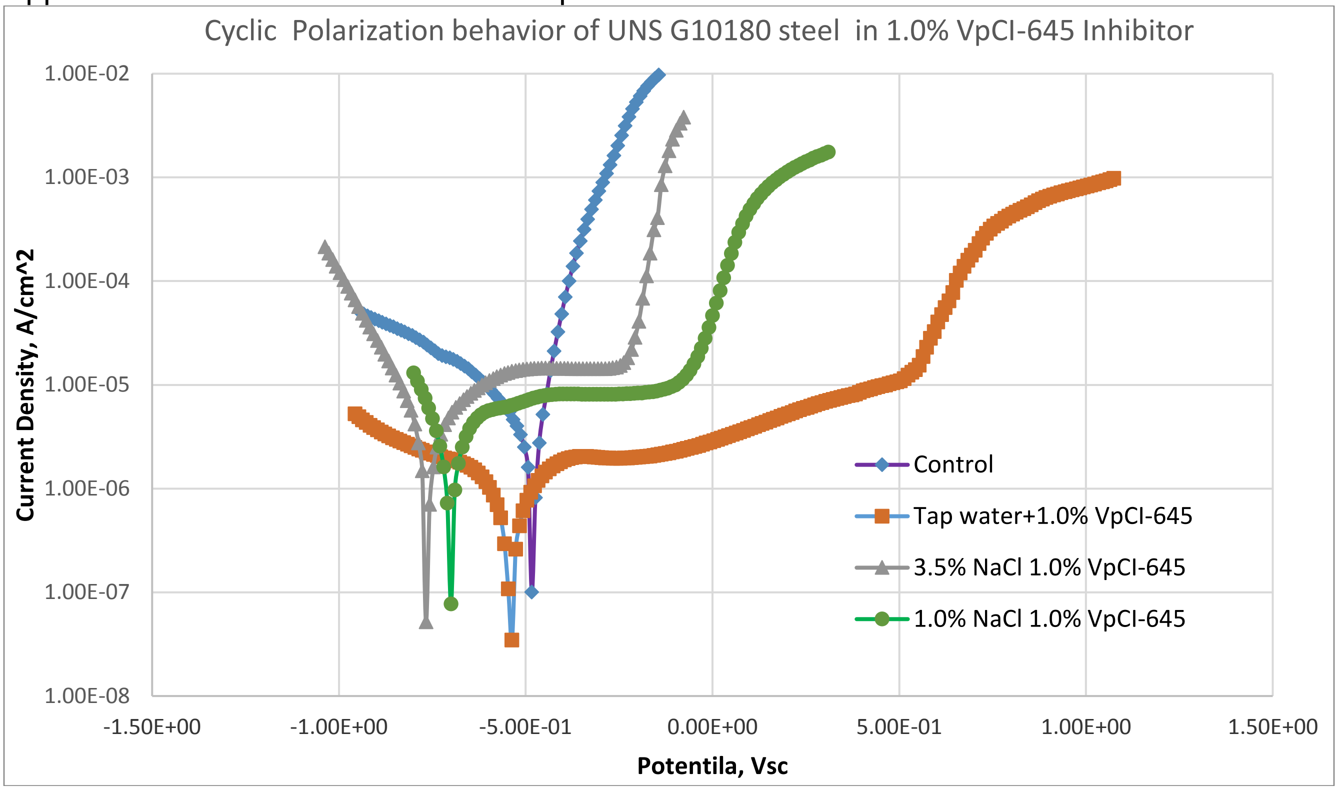


Fig. B-1: CP behavior of VpCI645 for UNS G1018 steel

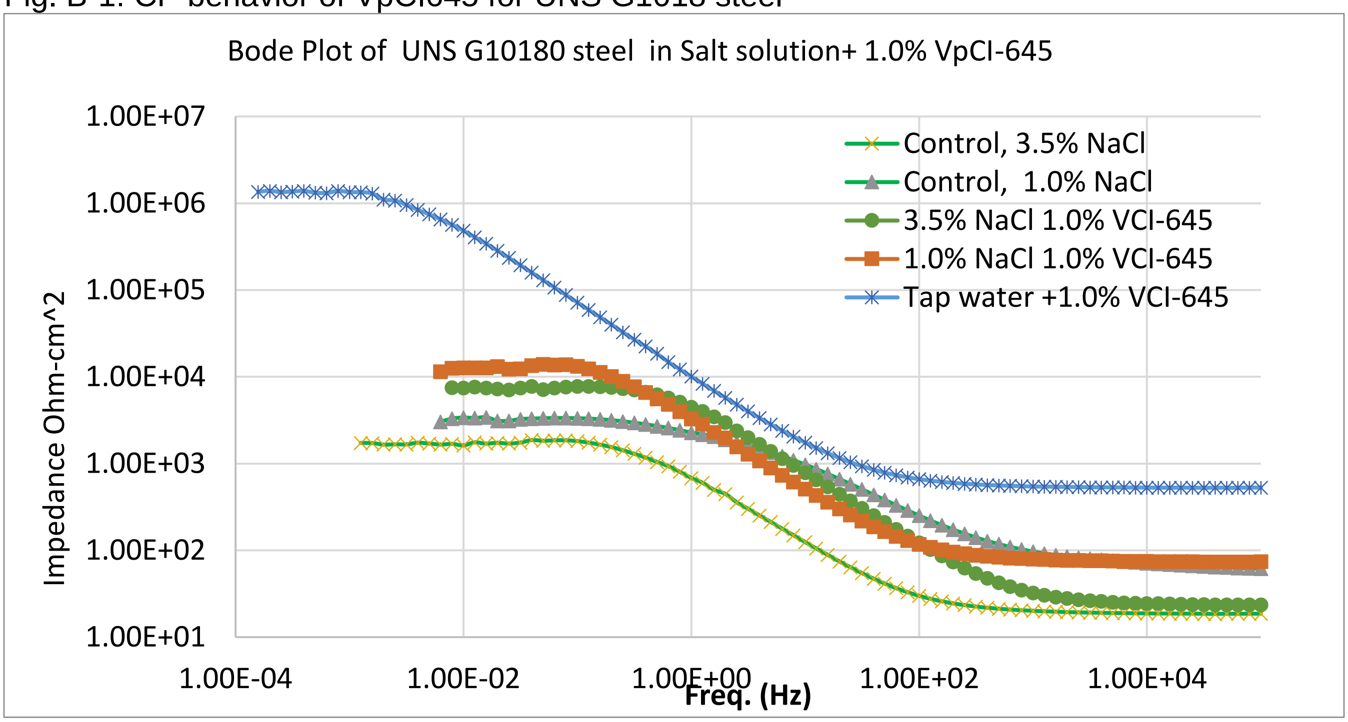


Fig. B-2: EIS behavior of VpCI645 for UNS G1018 steel

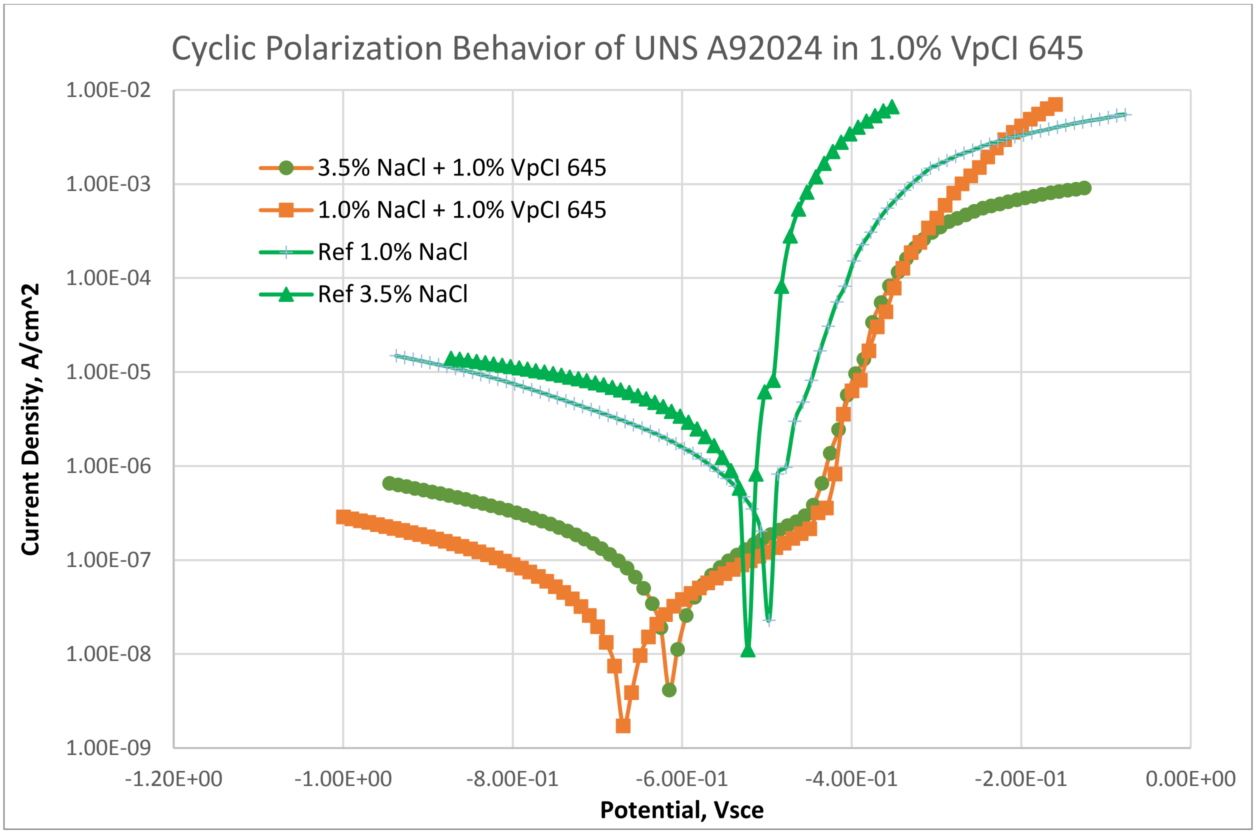


Fig. B-3: CP behavior of VpCI645 for UNS A92024 Al-alloy

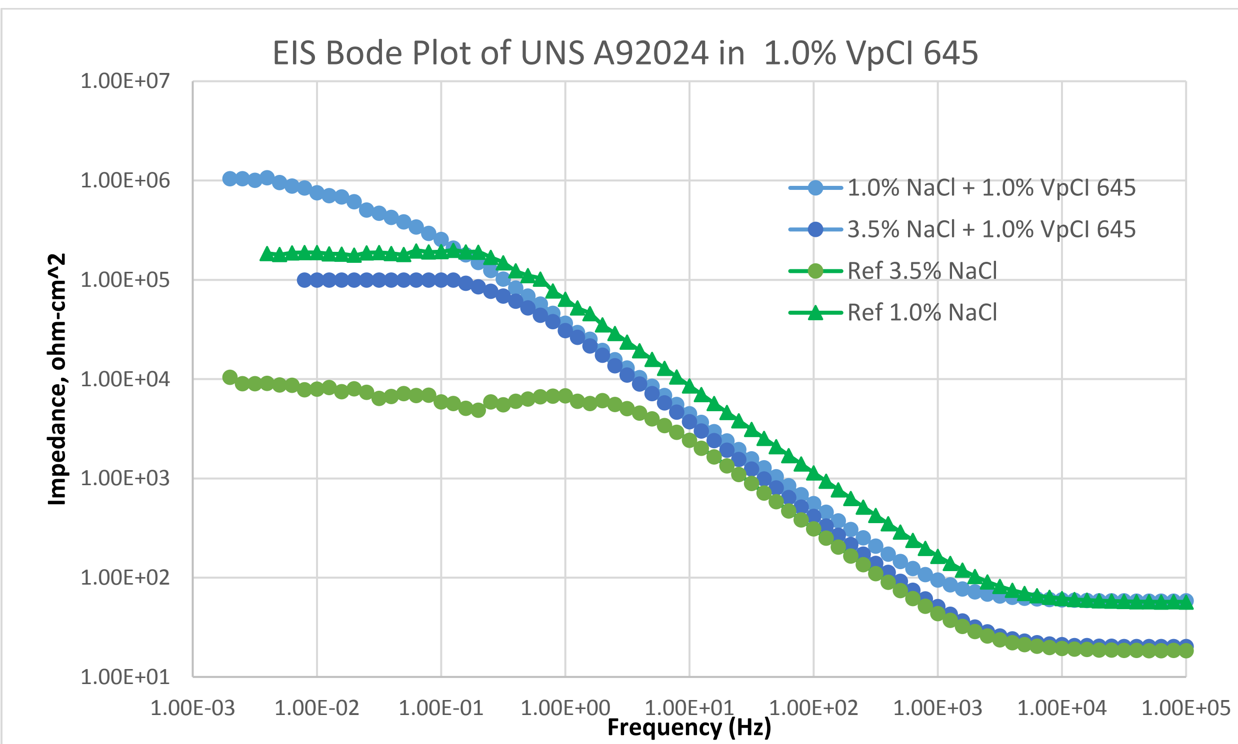


Fig. B-4: EIS behavior of VpCI645 for UNS A92024 Al-alloy

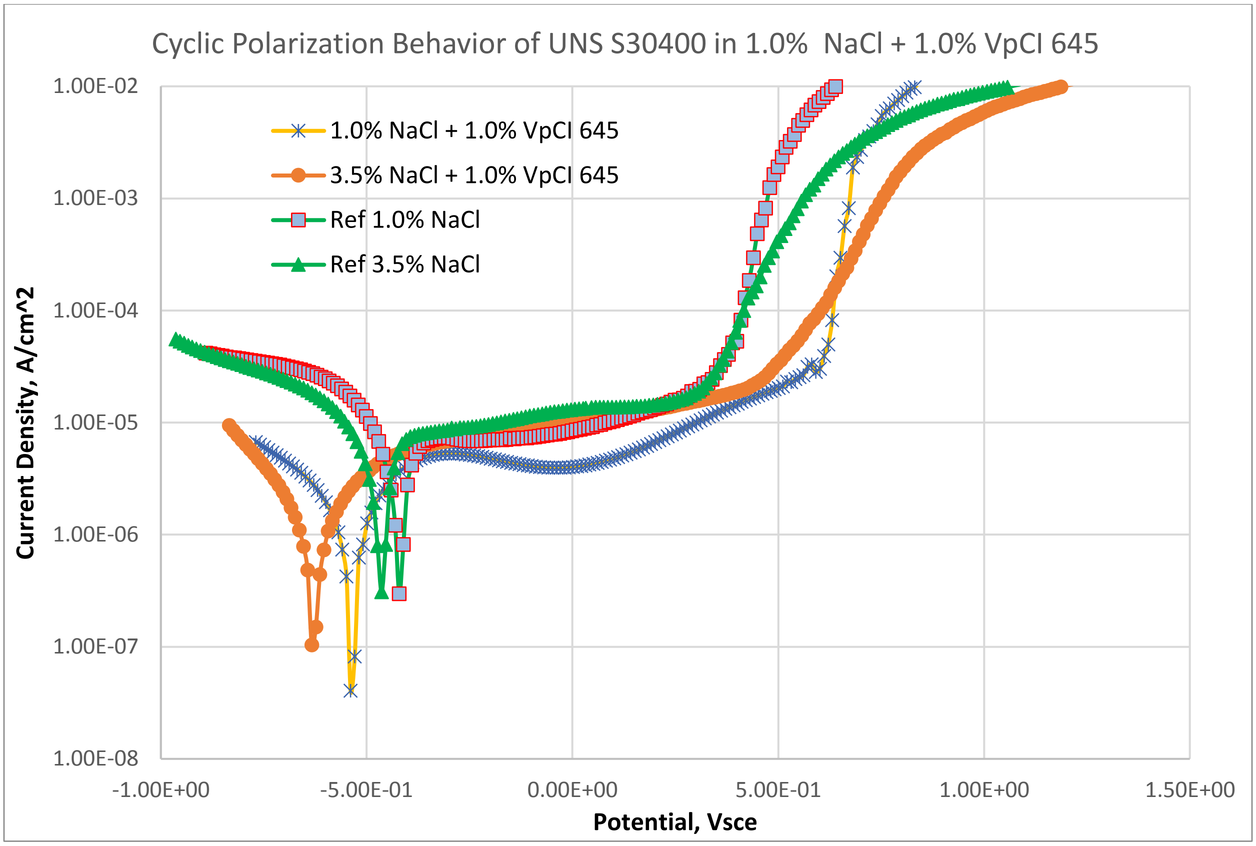


Fig. B-5: CP behavior of VpCI645 for UNS S30400 stainless steel

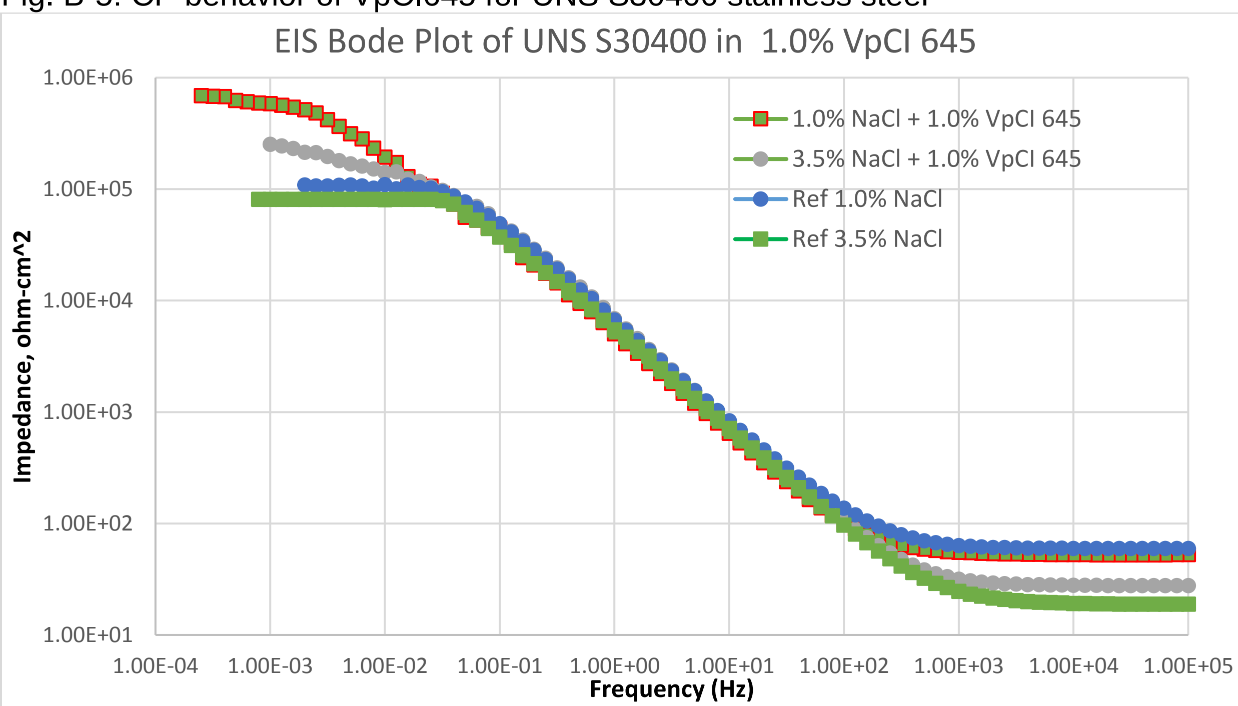


Fig. B-6: EIS behavior of VpCI645 for UNS S30400 stainless steel

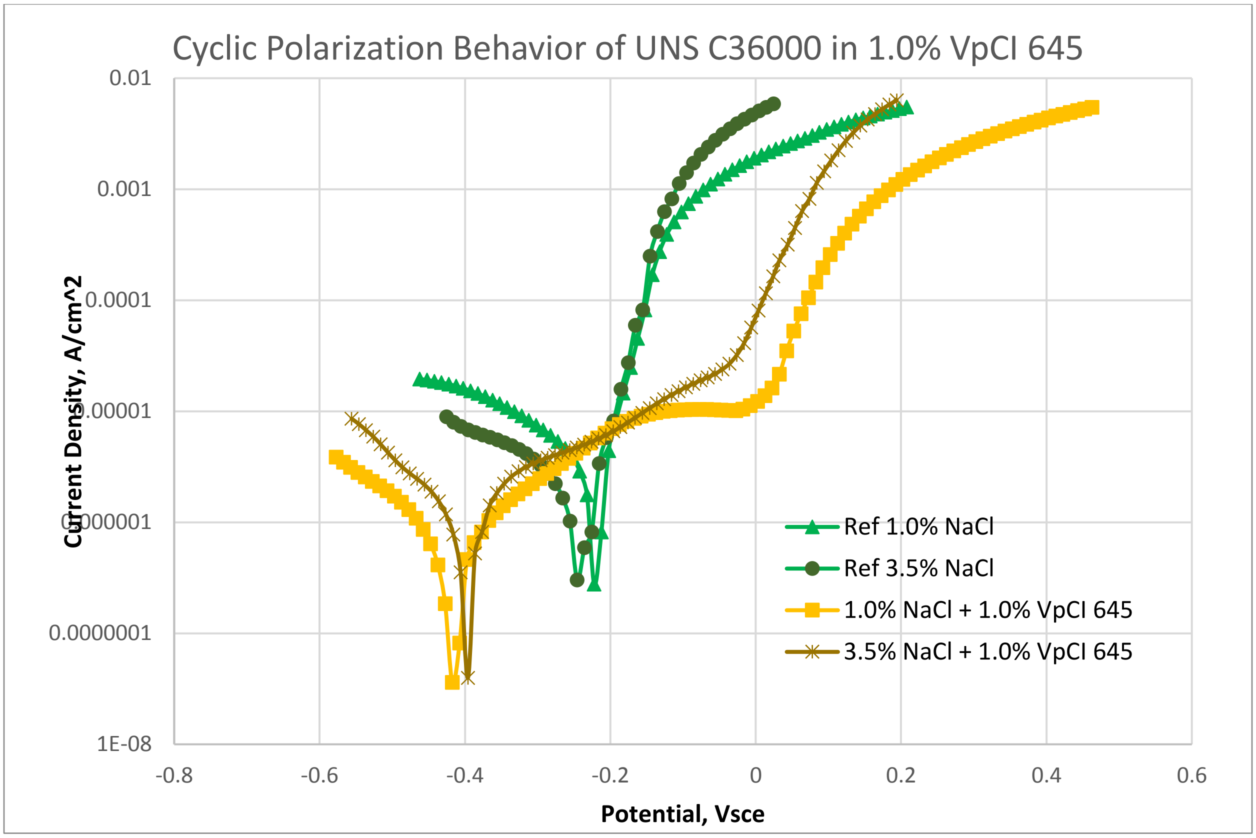


Fig. B-7: CP behavior of VpCI645 for UNS C36000 Brass alloy

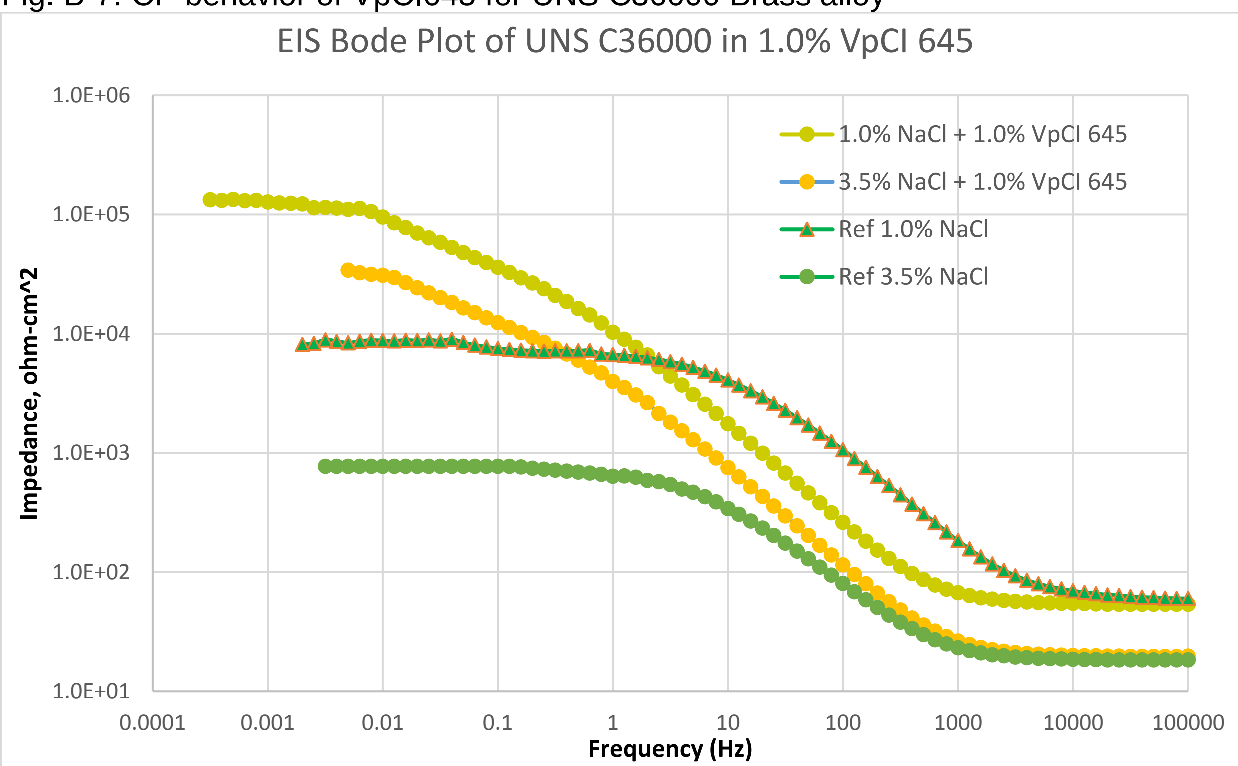


Fig. B-8: EIS behavior of VpCI645 for UNS C36000 Brass alloy

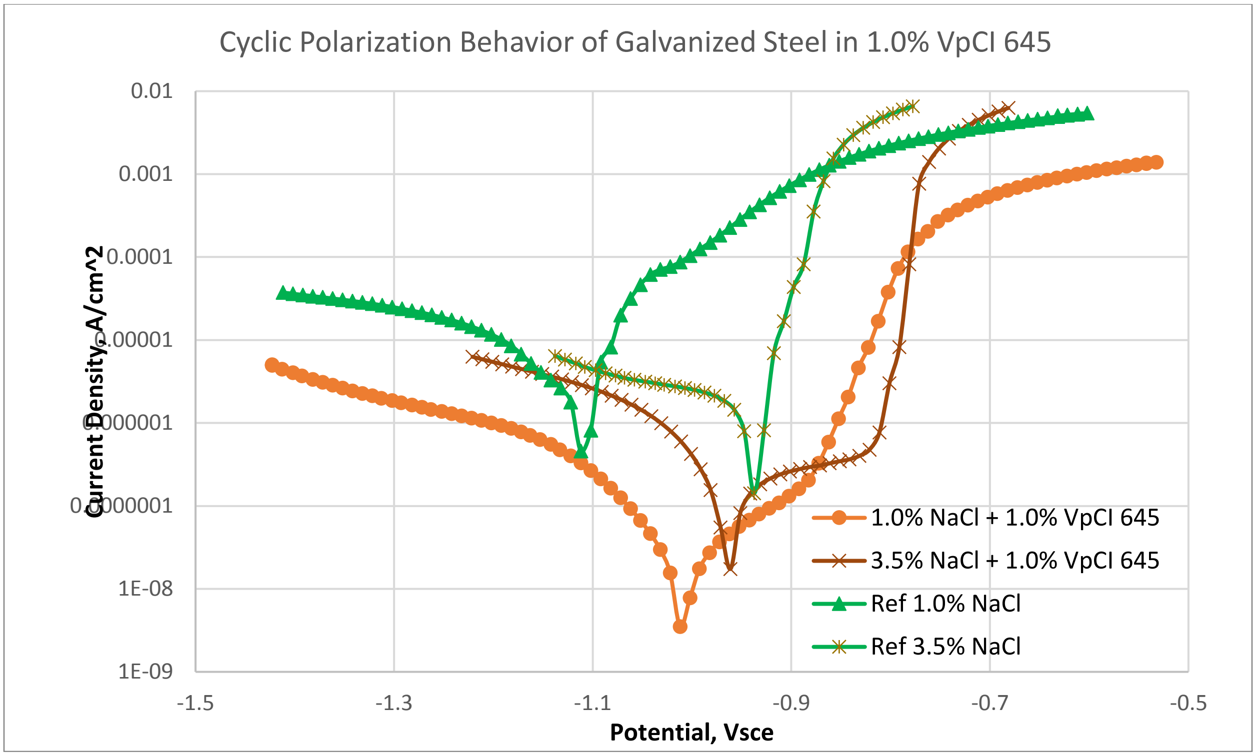


Fig. B-9: CP behavior of VpCI645 for galvanized steel

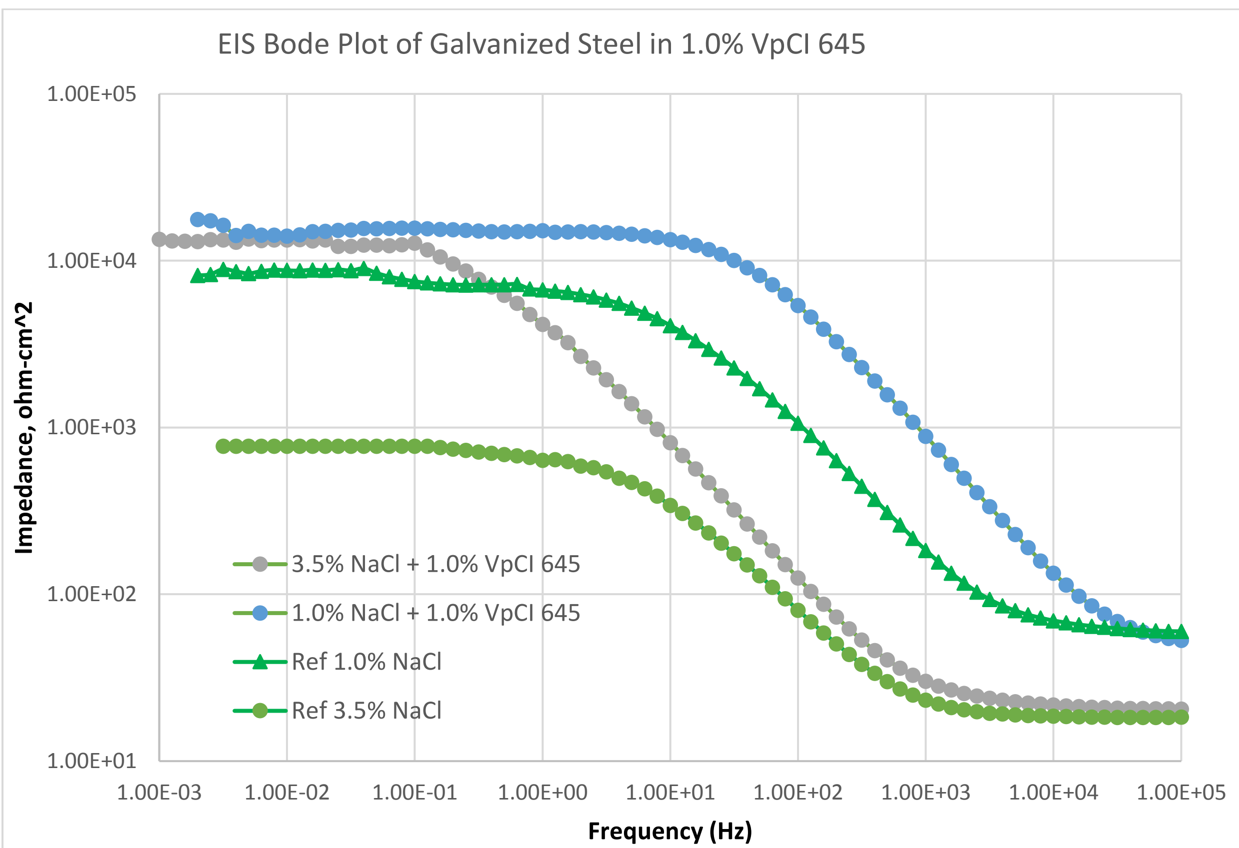


Fig. B-10: EIS behavior of VpCI645 for Galvanized steel

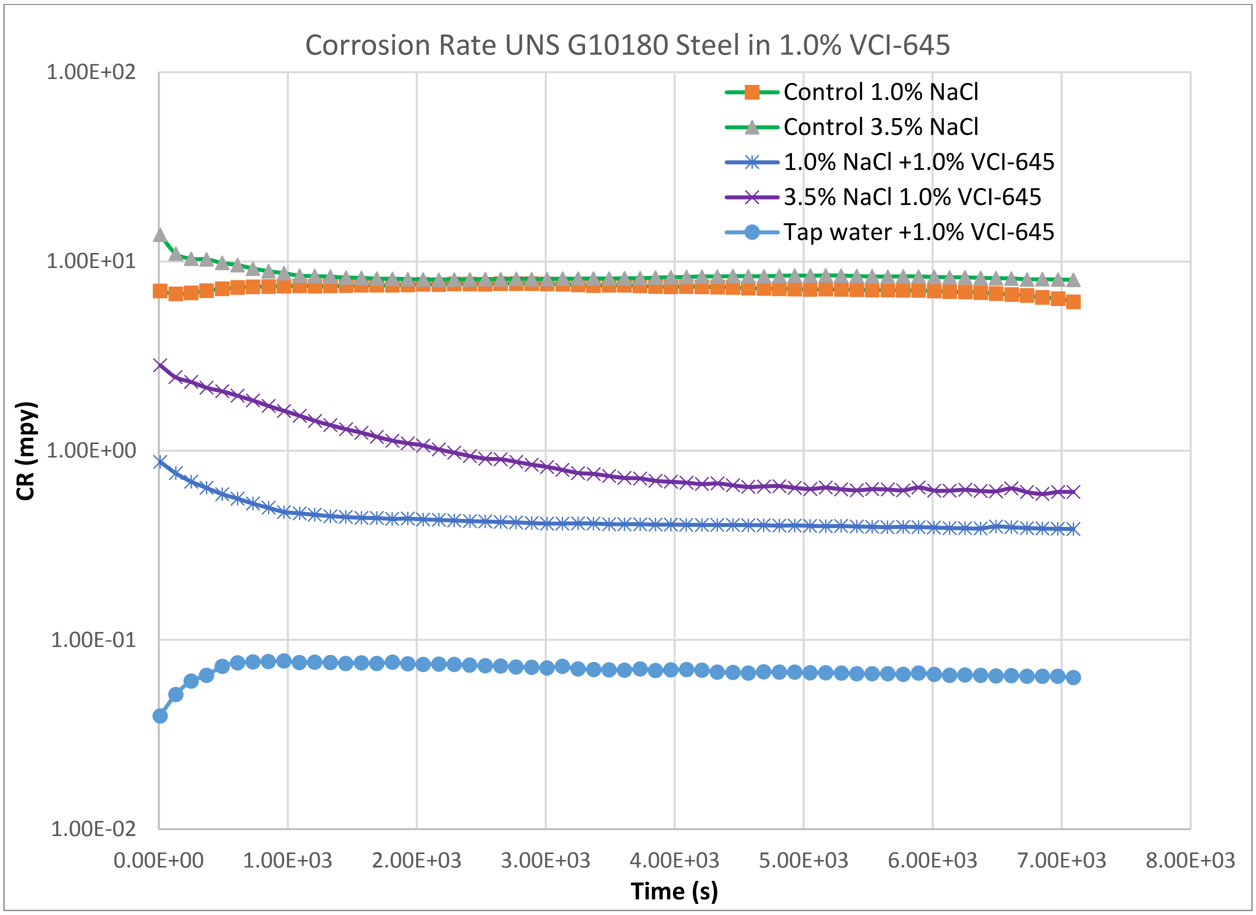


Fig. B-11: Corrosion rate measurements using LPR technique of VpCI645 for UNS G1018 steel.

Appendix C: Electrochemical data for VpCI605L

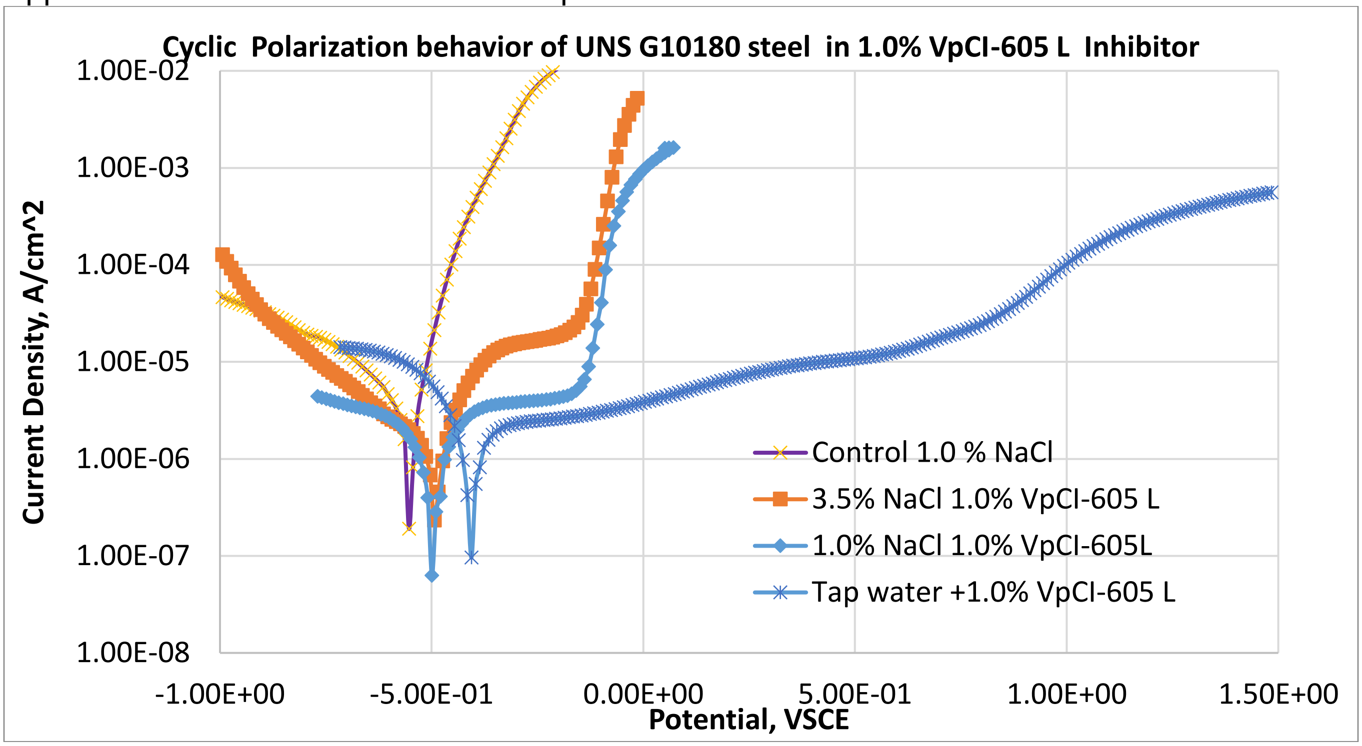


Fig. C-1: CP behavior of VpCI605L for UNS G1018 steel

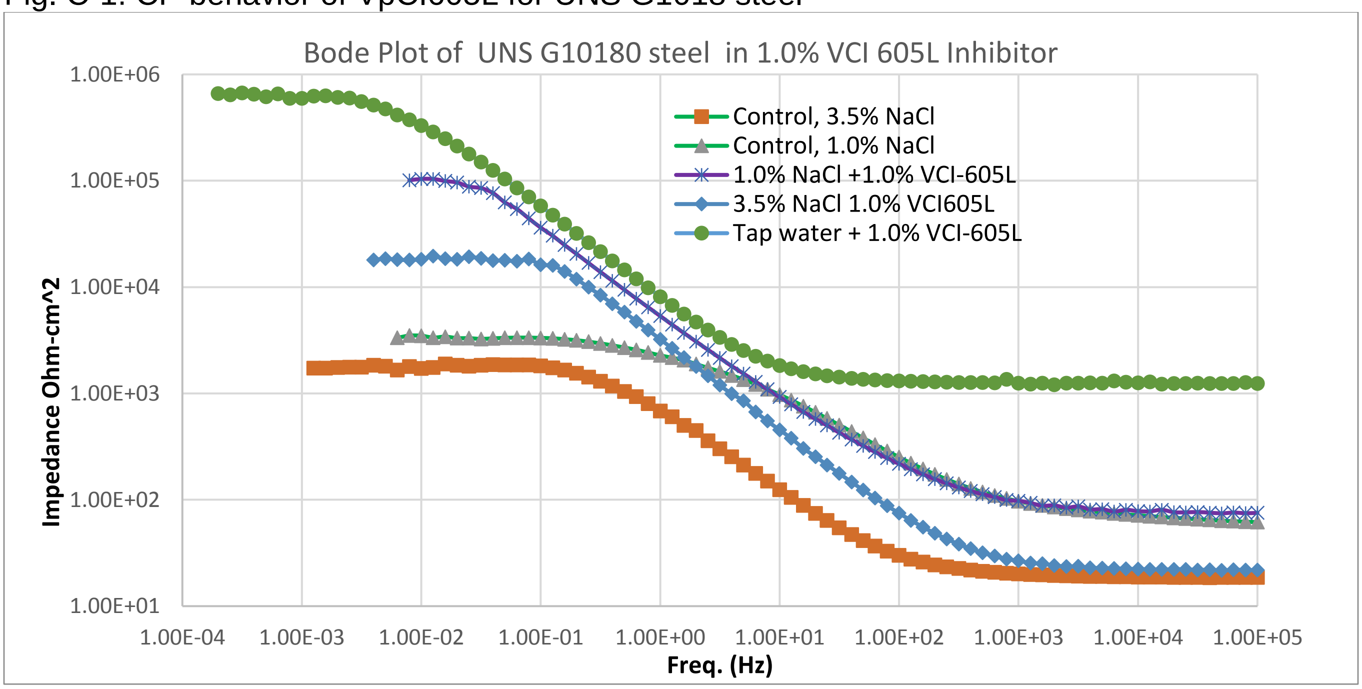


Fig. C-2: EIS behavior of VpCI605L for UNS G1018 steel

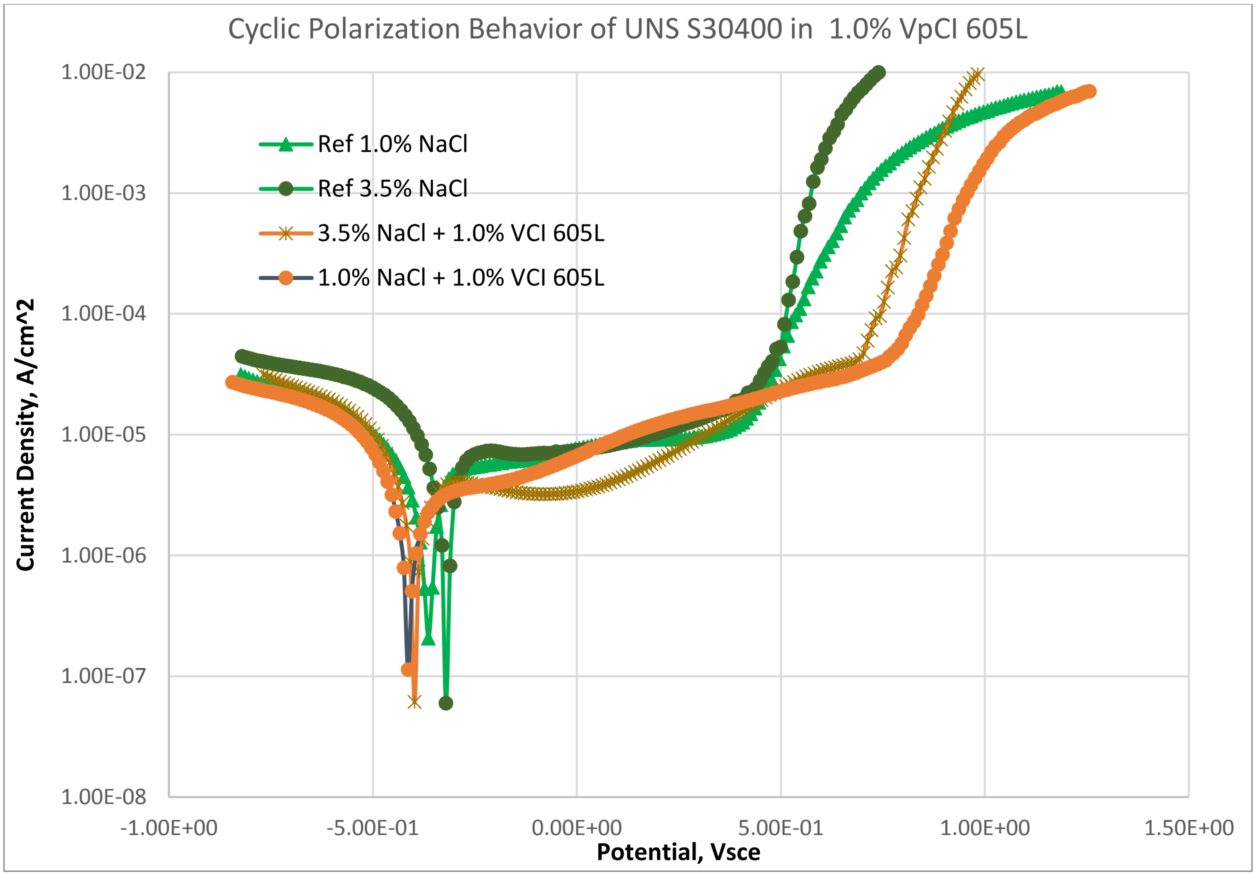


Fig. C-3: CP behavior of VpCI605L for UNS S30400 stainless steel

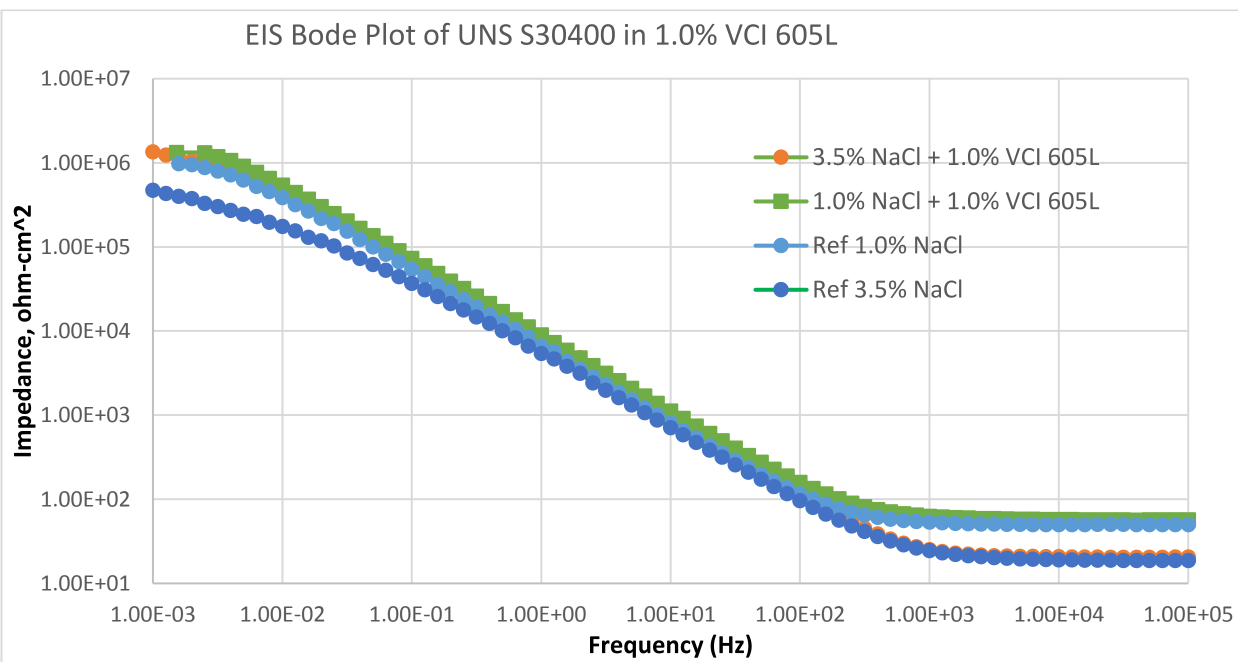


Fig. C-4: EIS behavior of VpCI605L for UNS S30400 stainless steel

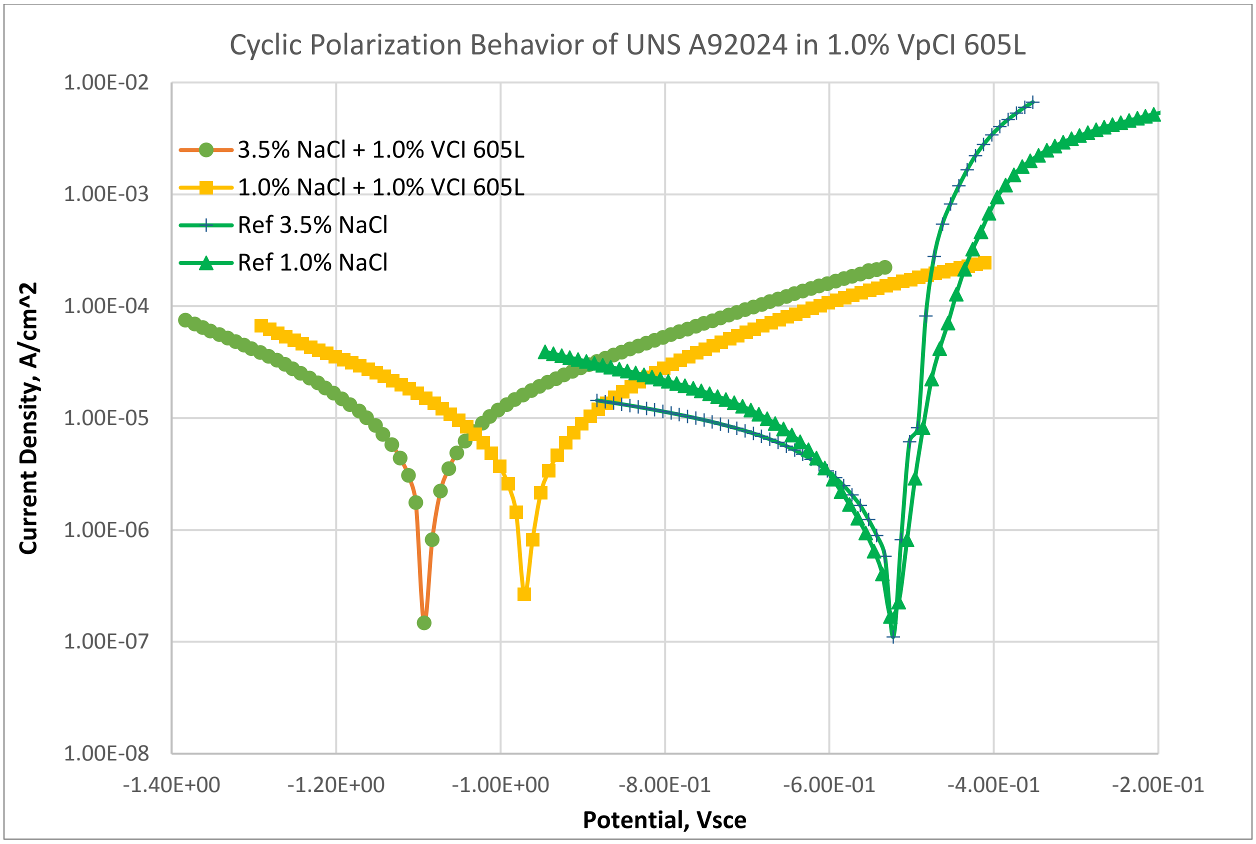


Fig. C-5: CP behavior of VpCI605L for UNS A92024 Al-alloy

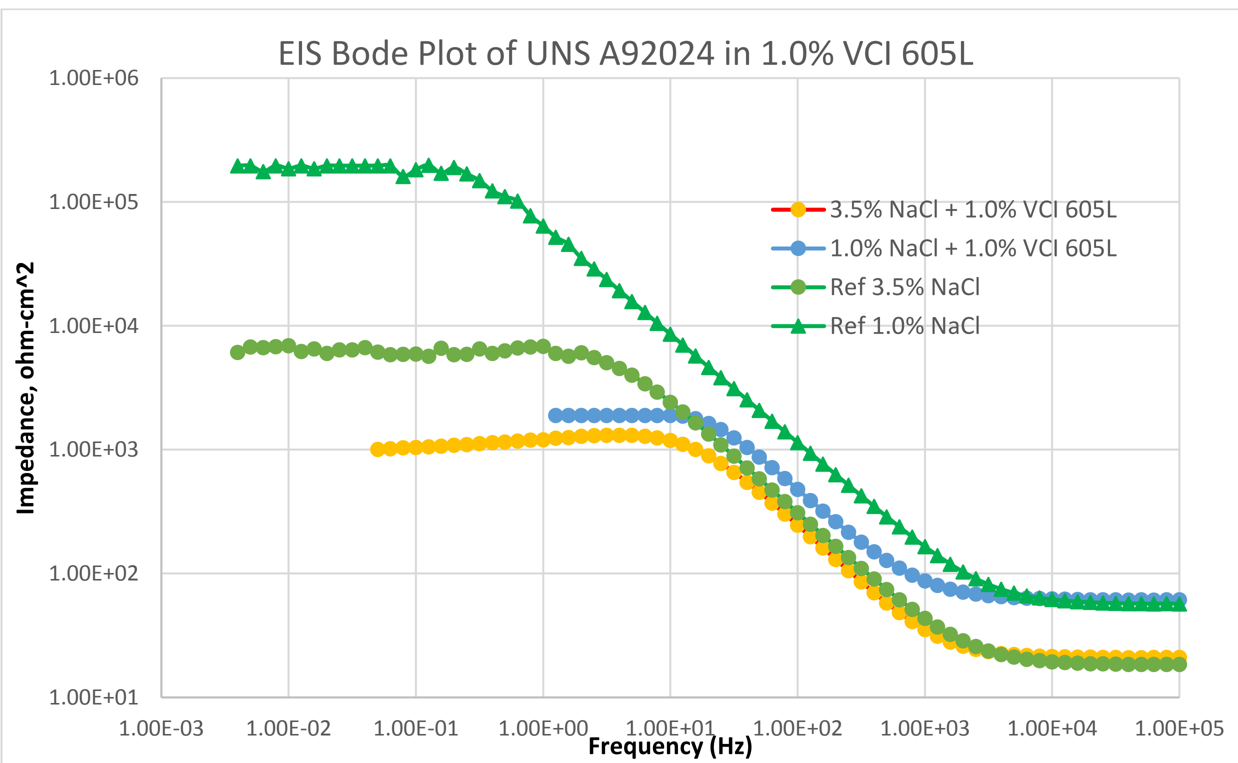


Fig. C-6: EIS behavior of VpCI605L for UNS A92024 Al-alloy

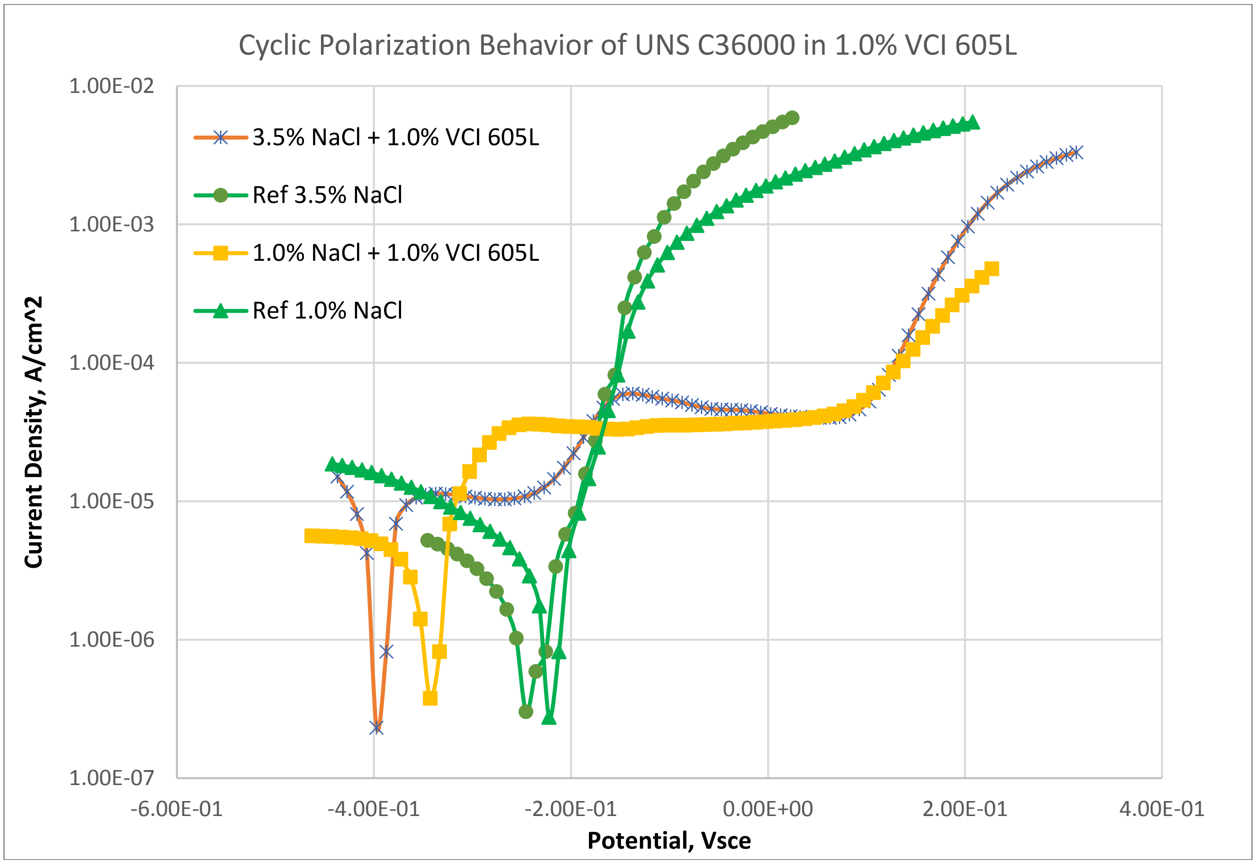


Fig. C-7: CP behavior of VpCI605L for UNS C36000 Brass alloy

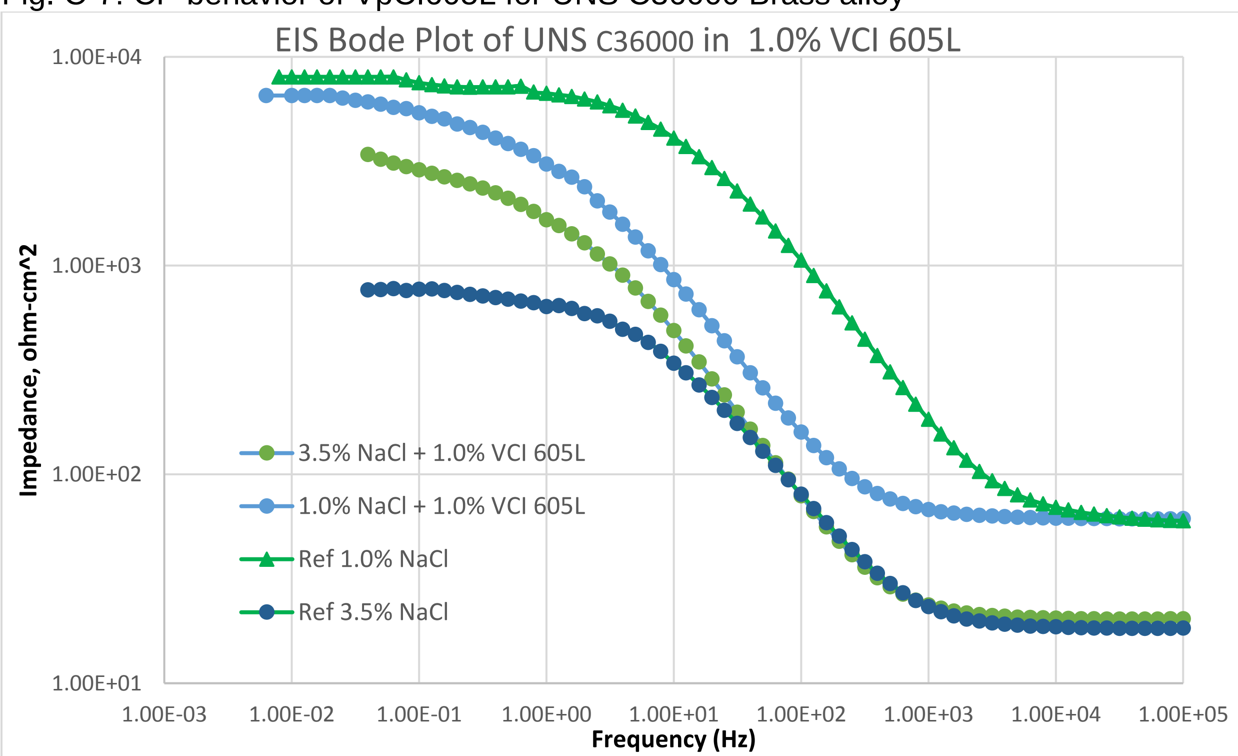


Fig. C-8: EIS behavior of VpCI 605L for UNS C36000 Brass alloy

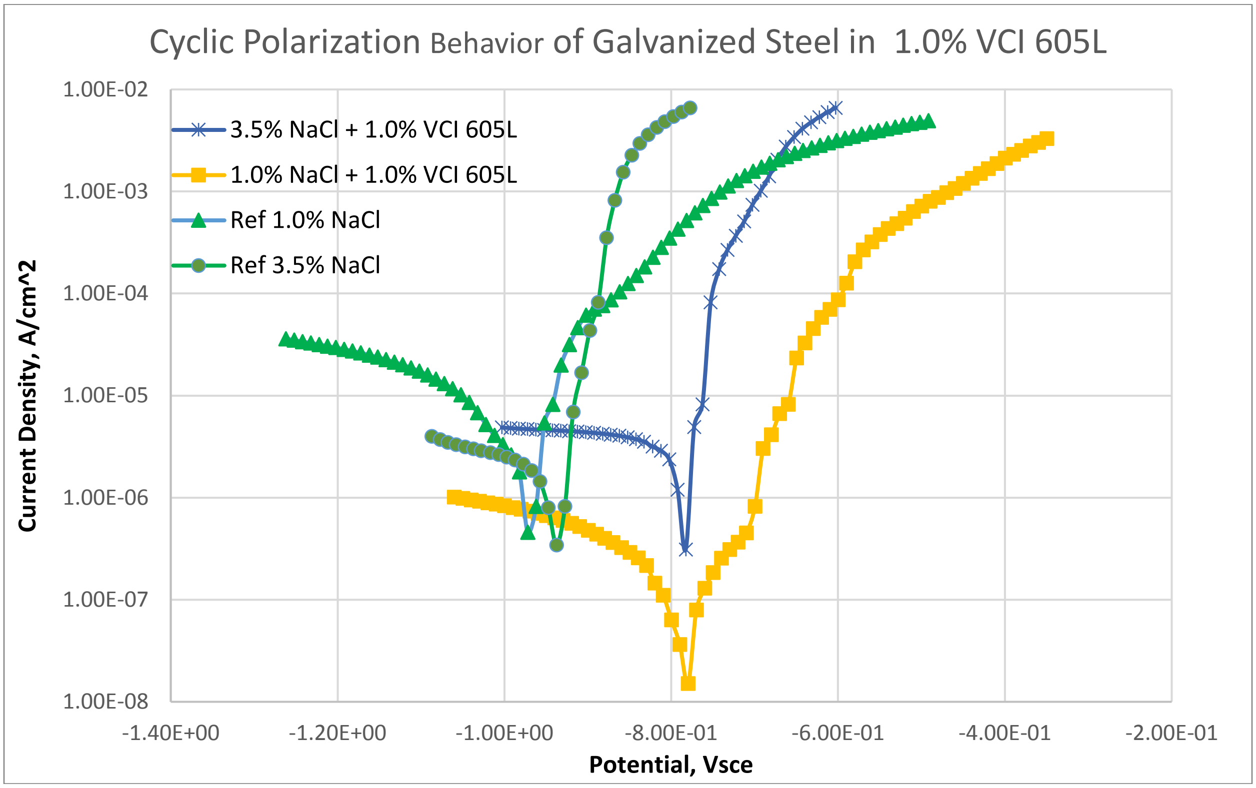


Fig. C-9: CP behavior of VpCI605L for Galvanized steel

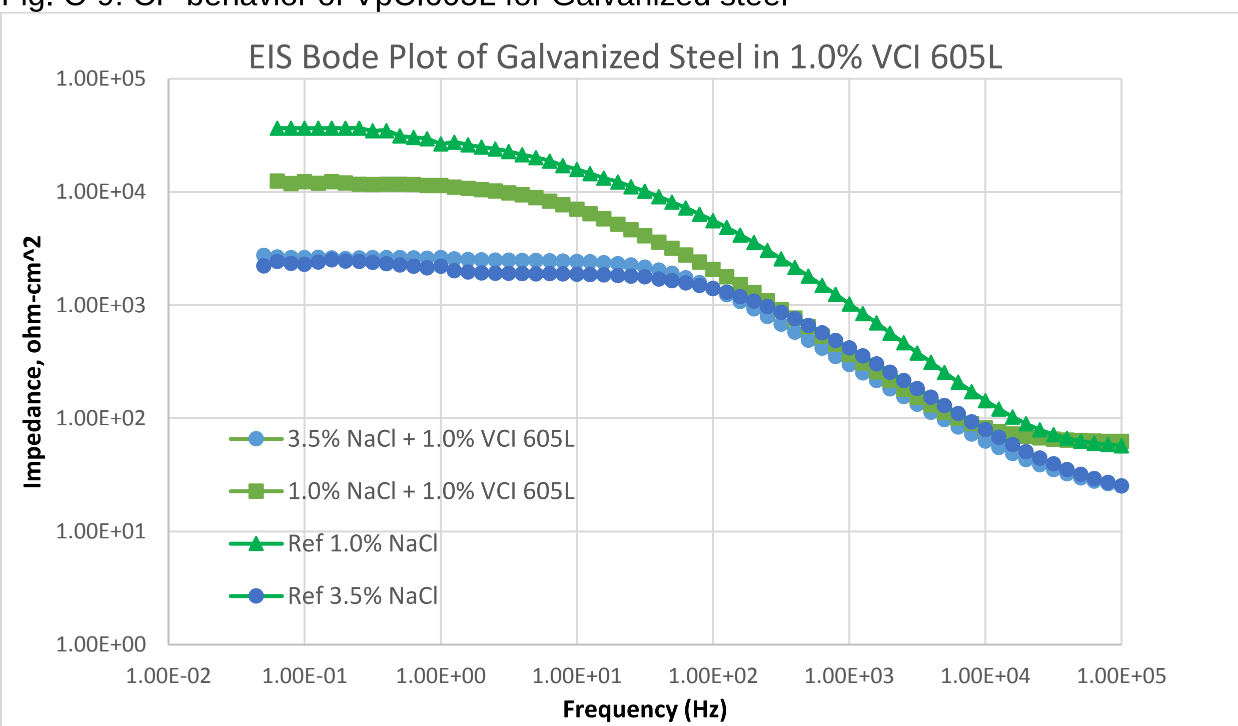


Fig. C-10: EIS behavior of VpCI605L for Galvanized steel

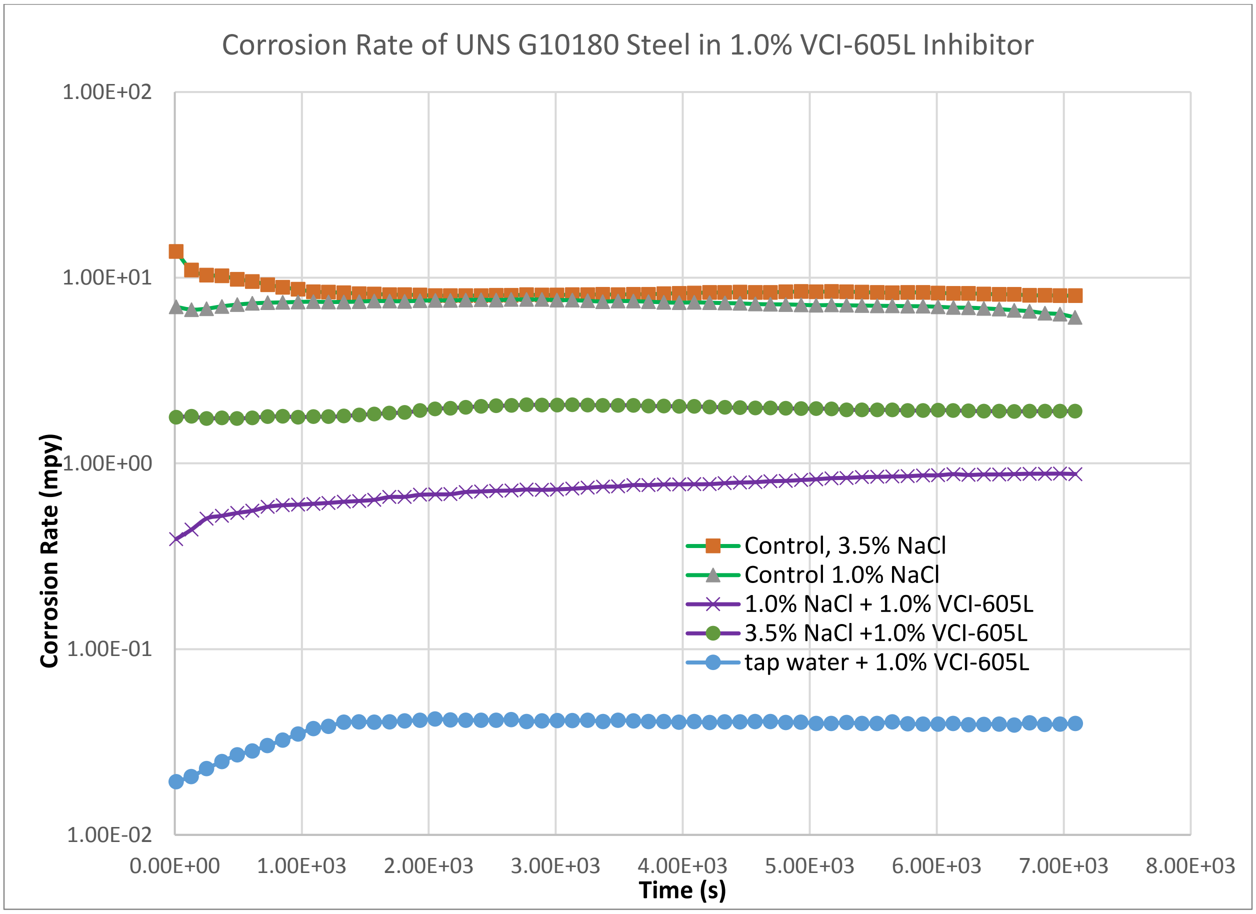
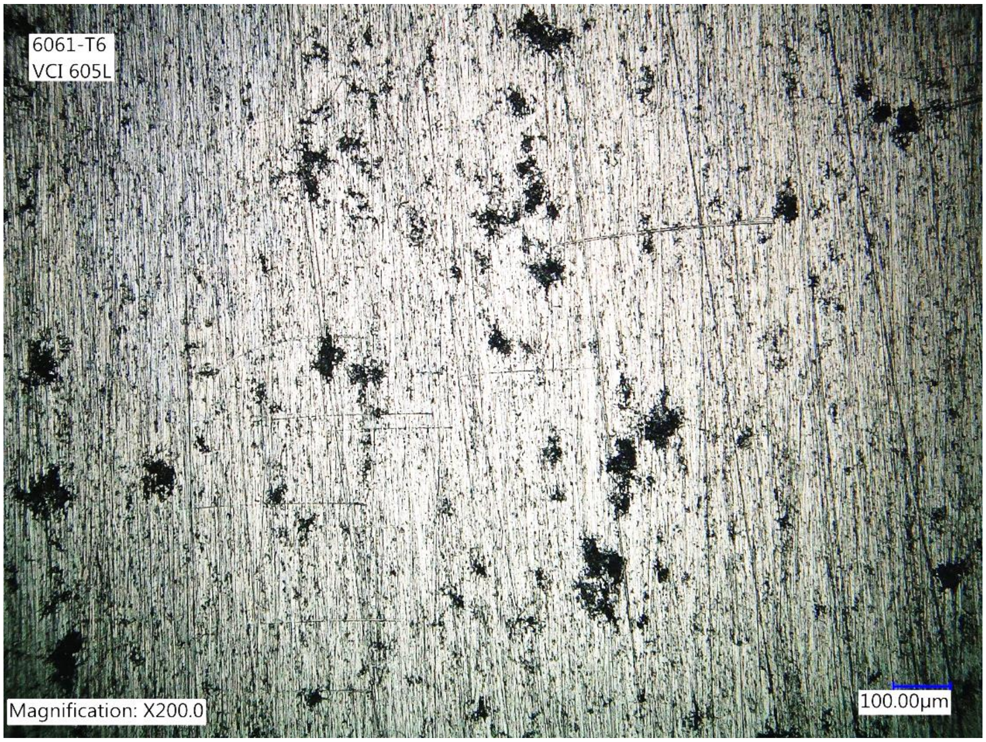


Fig. C-11: Corrosion rate measurements using LPR technique of VpCI 605L for UNS G1018 steel.



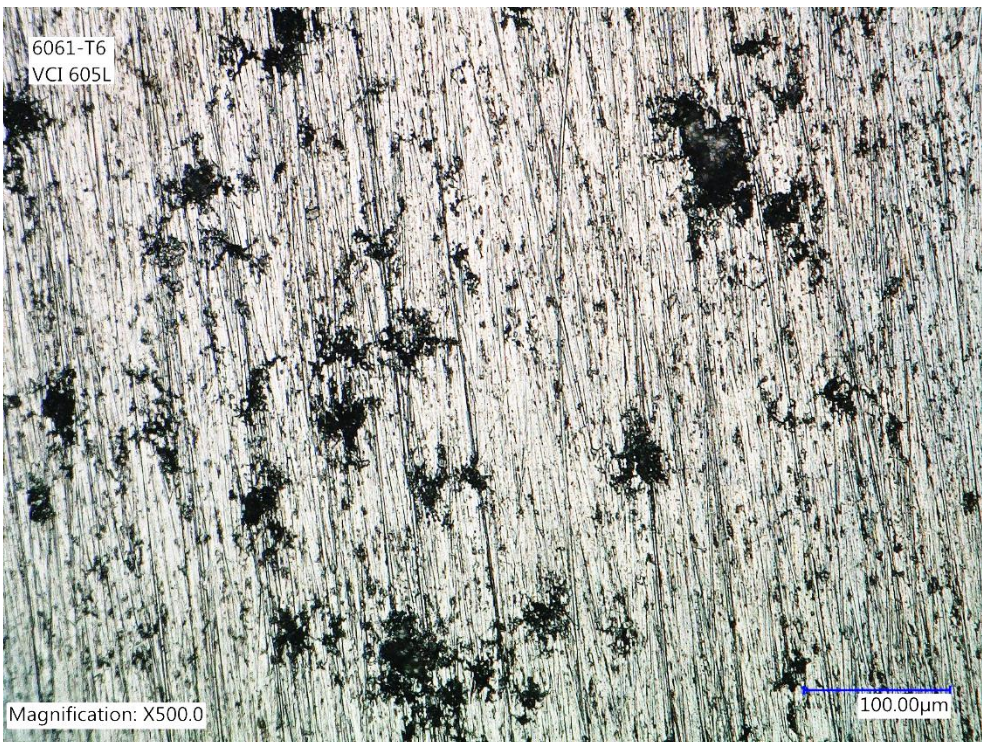


Fig C-12: Optical micrographs of Localized corrosion attacks on 6061-Al-alloy exposed to VpCI 605L

Appendix D: Electrochemical data for VpCI705 Bio

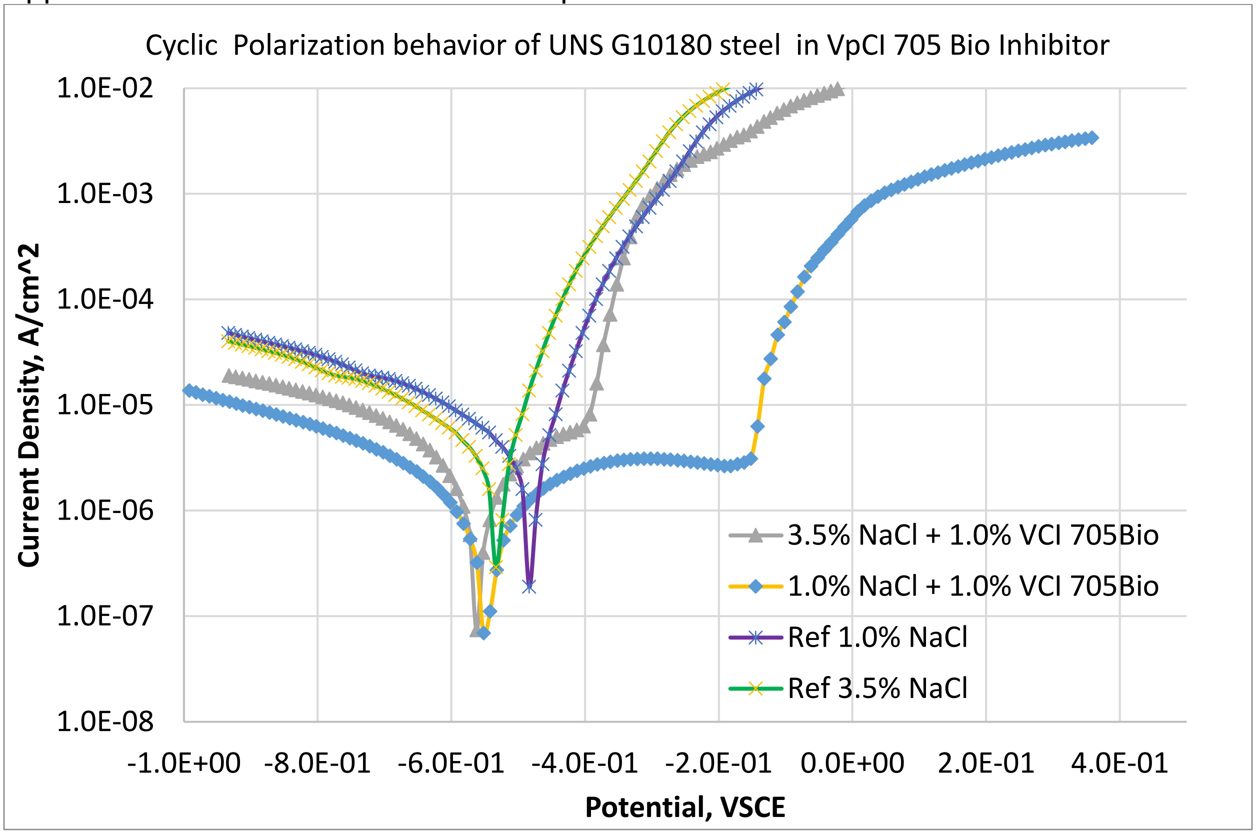


Fig. D-1: CP behavior of VpCI705Bio for UNS G10180 steel

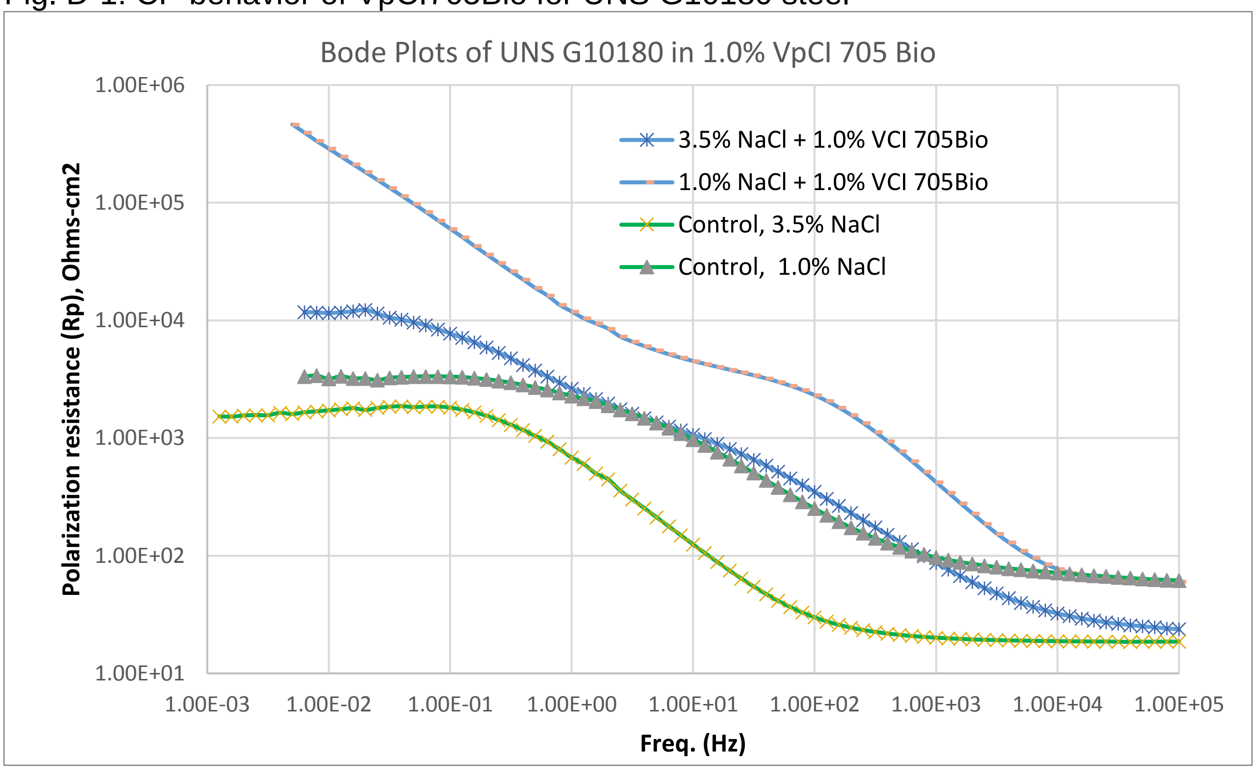


Fig. D-2: EIS behavior of VpCI705Bio for UNS G10180 steel

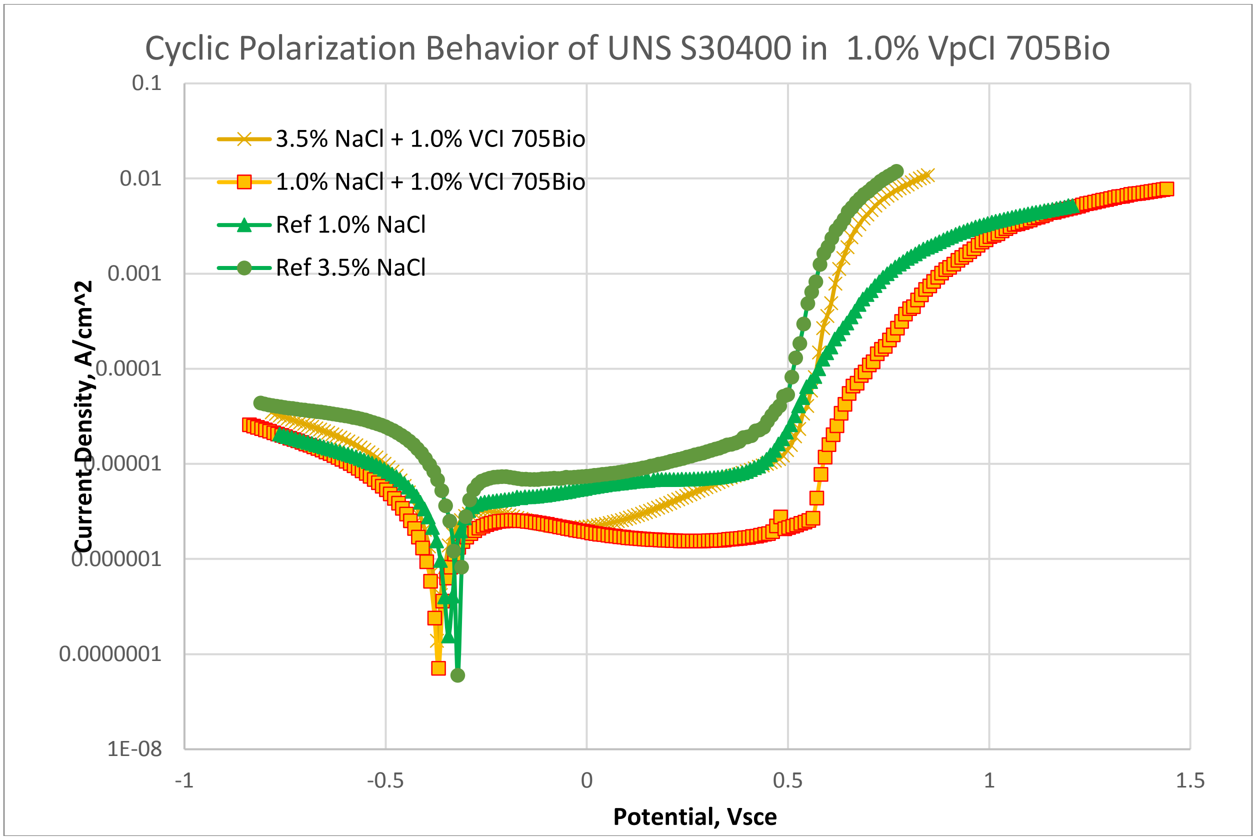


Fig. D-3: CP behavior of VpCI705Bio for UNS S30400 stainless steel

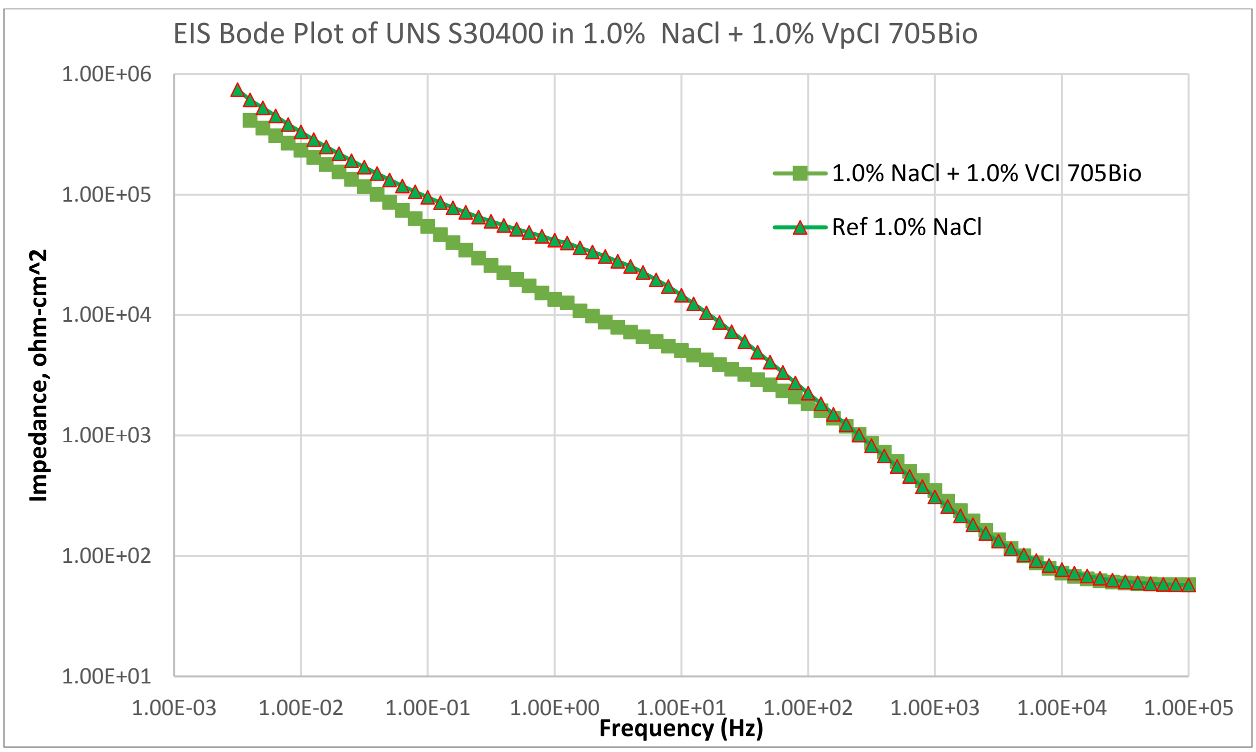


Fig. D-4: EIS behavior of VpCI705Bio for UNS S30400 stainless steel

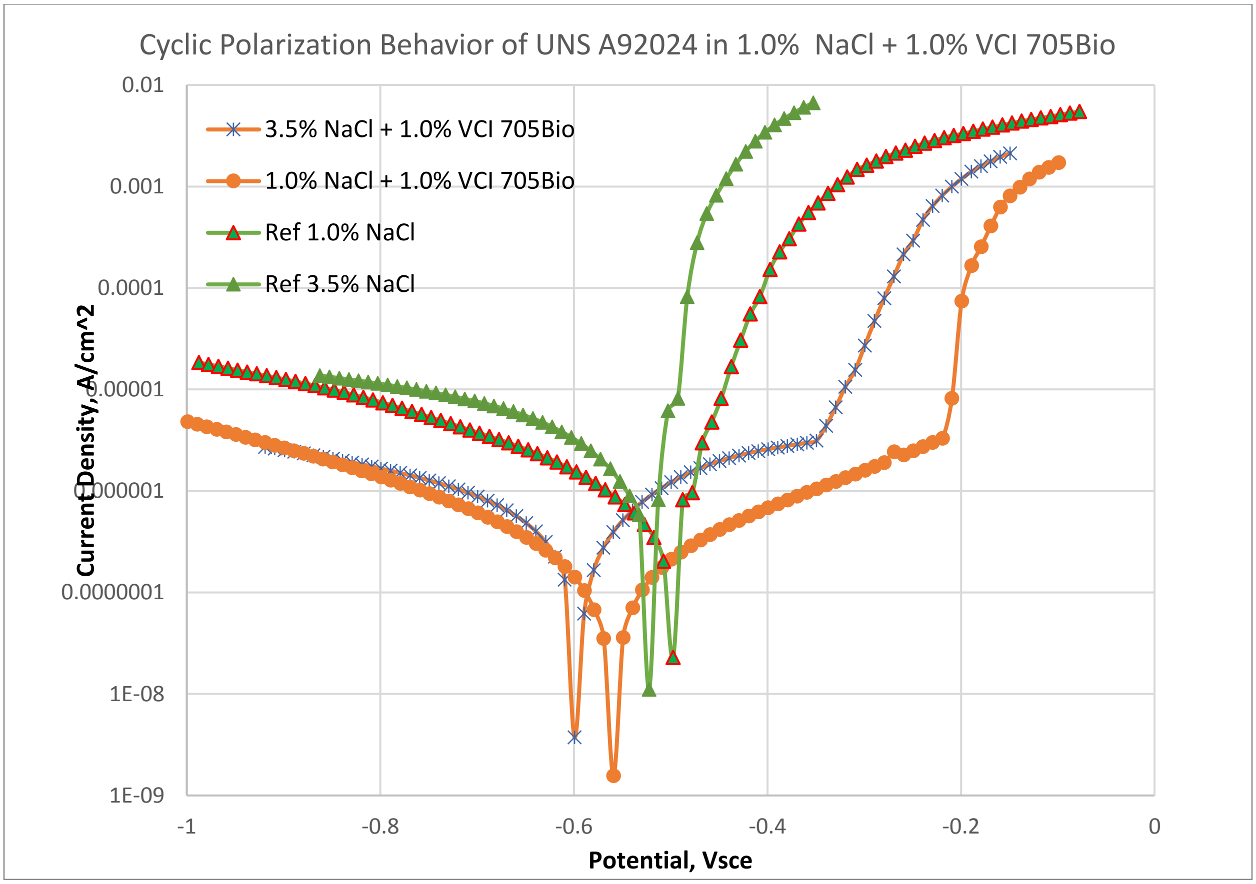


Fig. D-5: CP behavior of VpCI705Bio for UNS A92024 Al-alloy

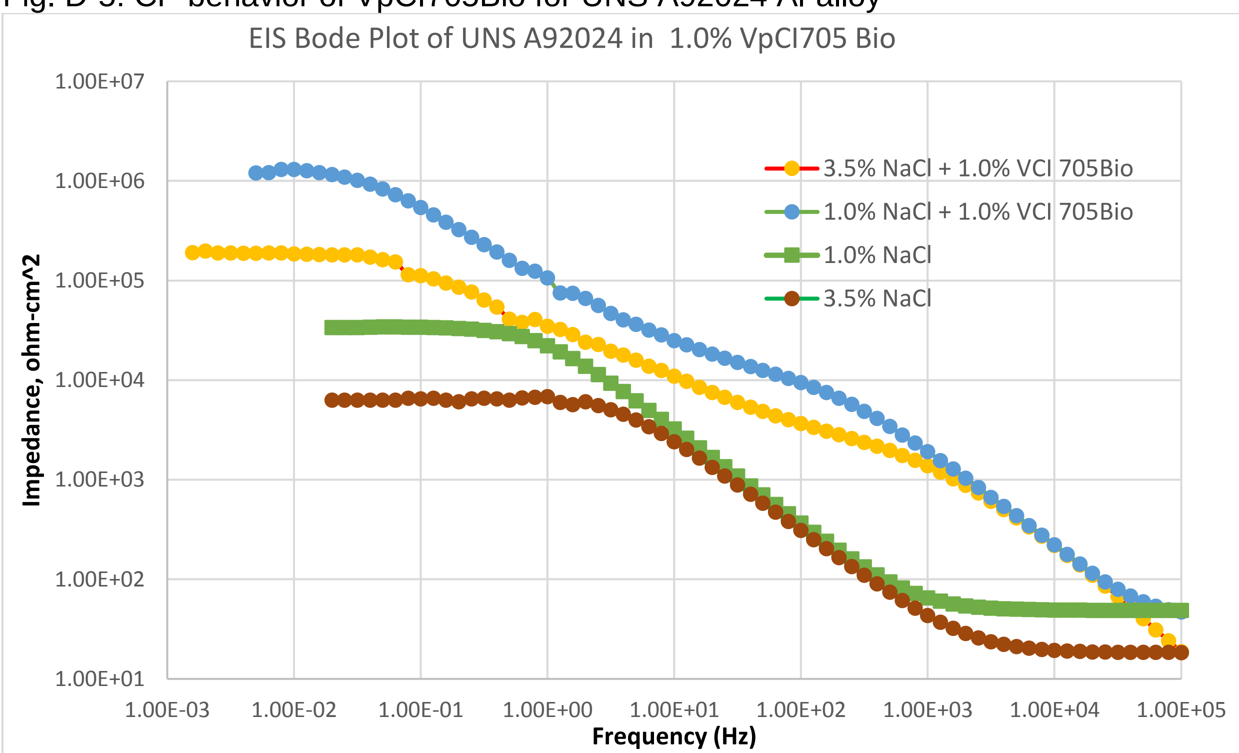


Fig. D-6: EIS behavior of VpCI705Bio for UNS A92024 Al-alloy

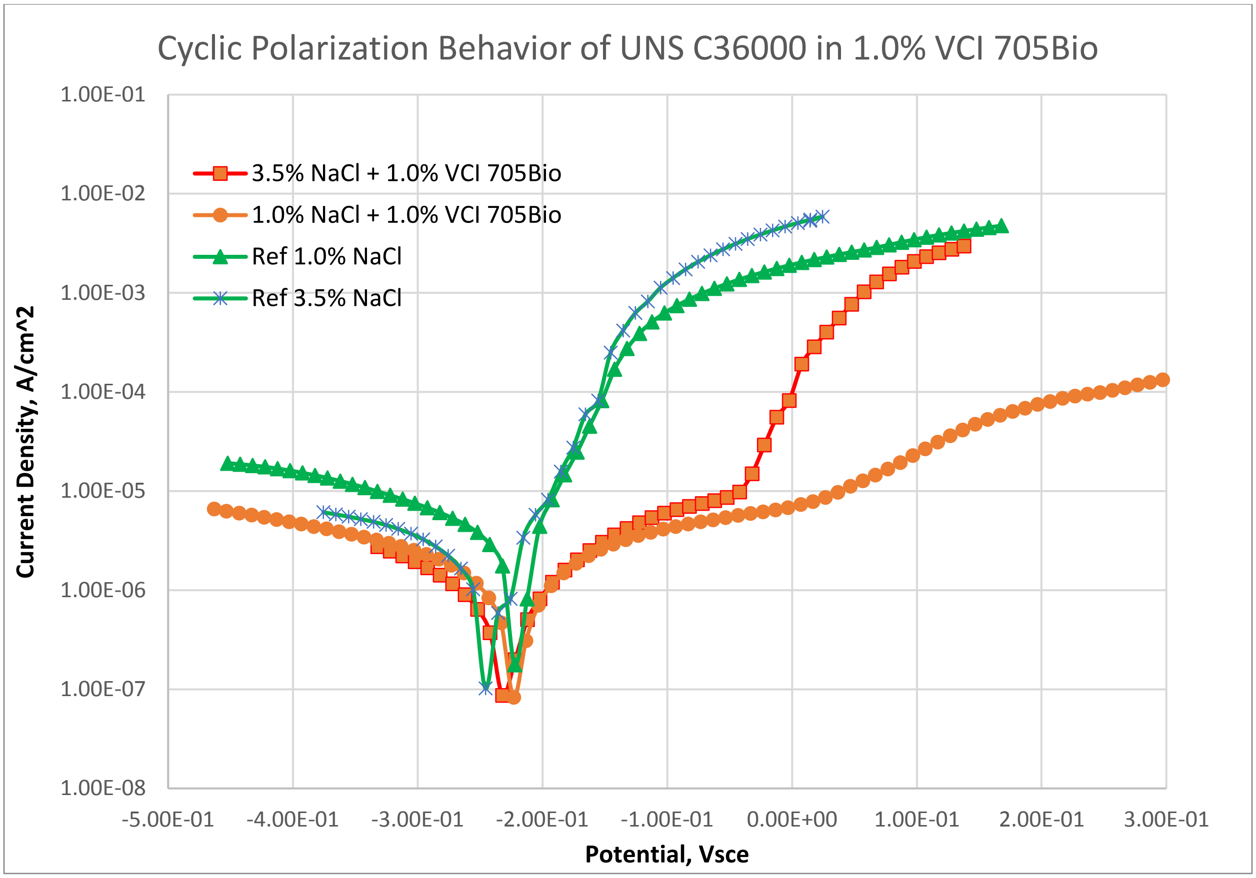


Fig. D-7: CP behavior of VpCI705Bio for UNS C36000 brass alloy

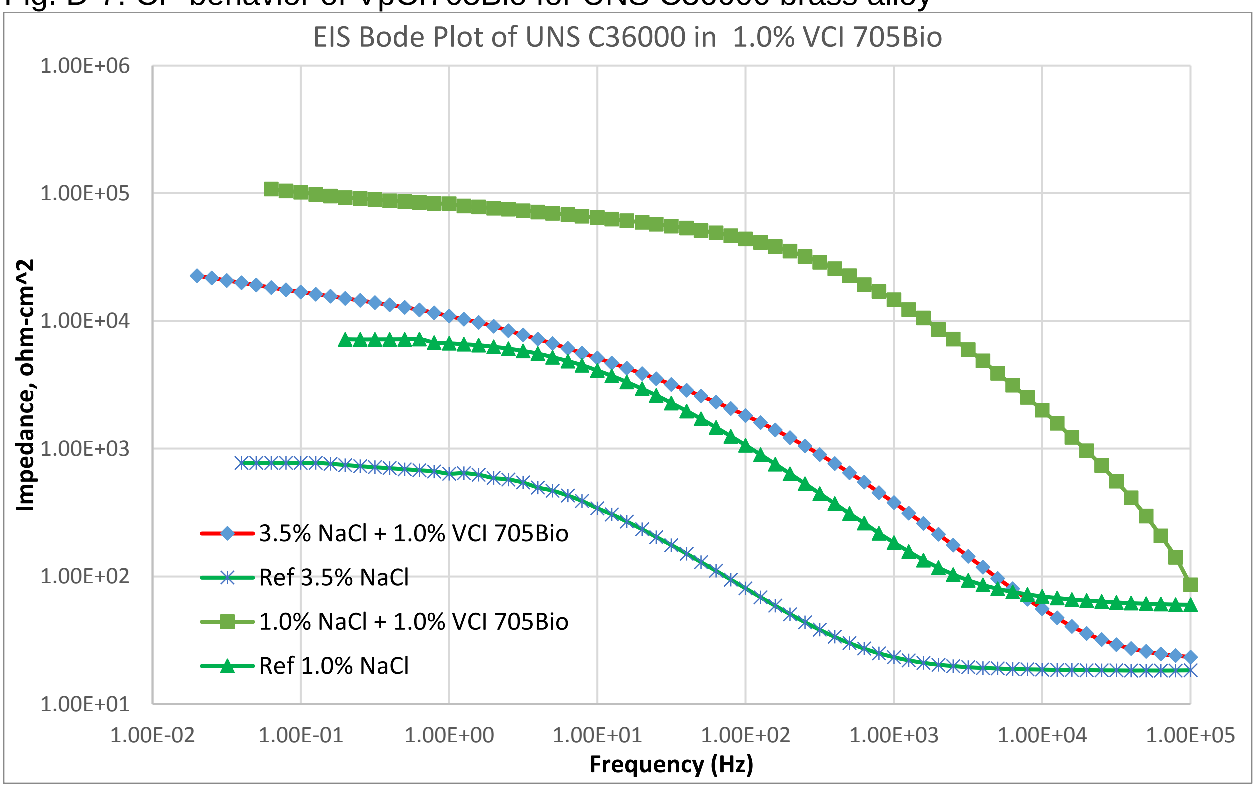


Fig. D-8: EIS behavior of VpCI705Bio for UNS C36000 brass alloy

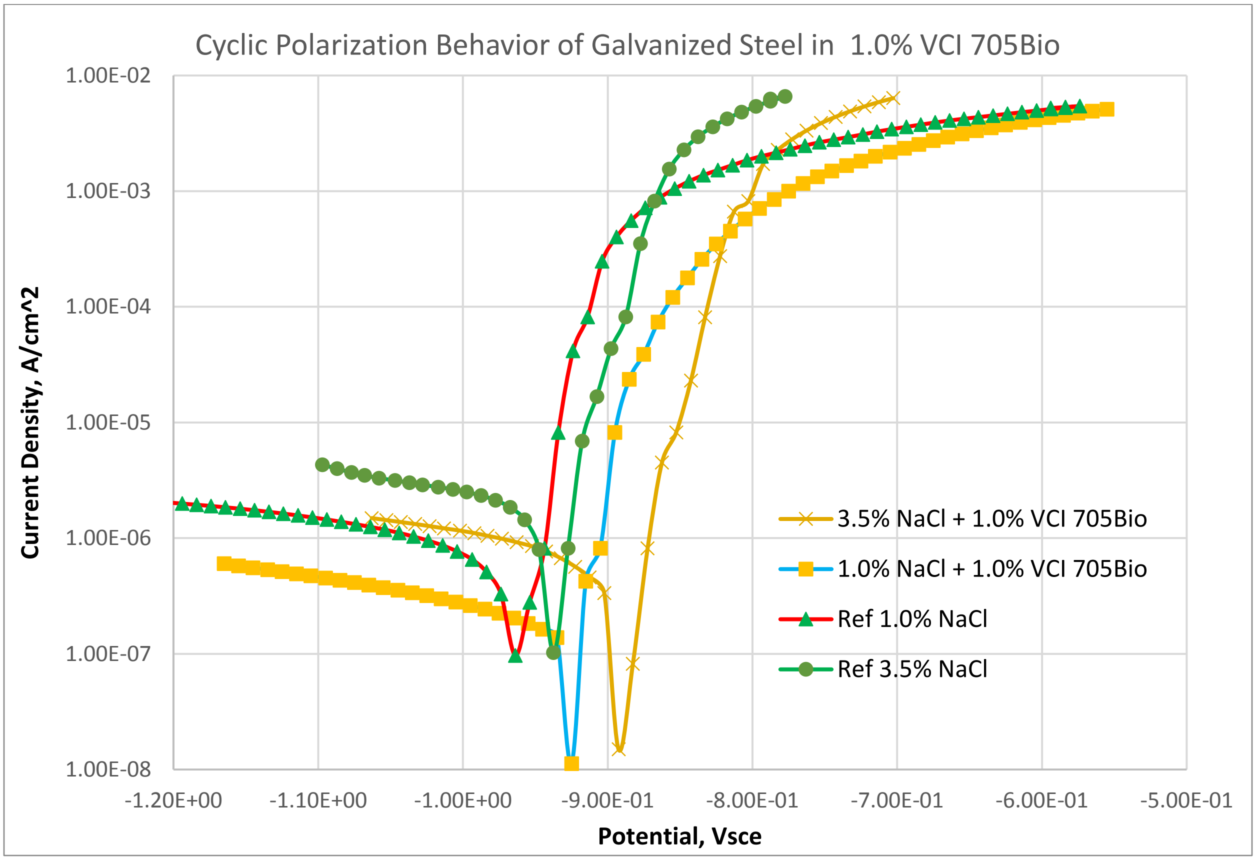


Fig. D-9: CP behavior of VpCI705Bio for Galvanized steel

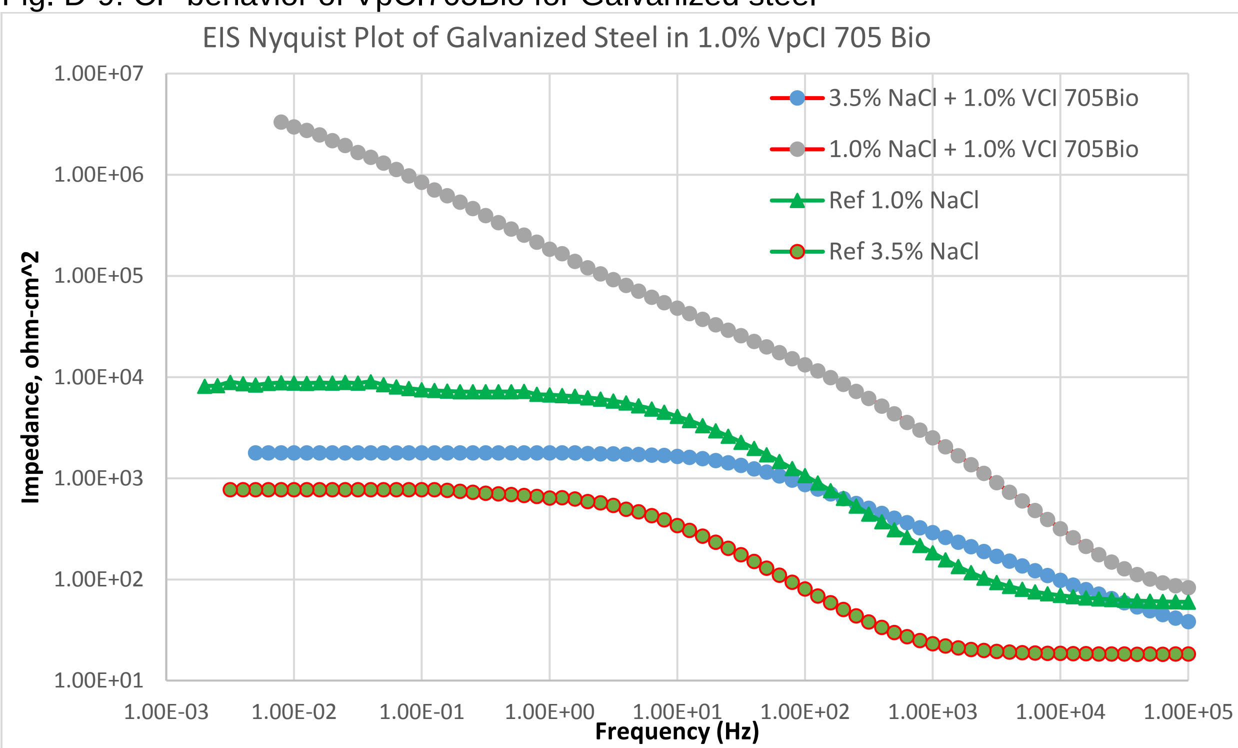


Fig. D-10: EIS behavior of VpCI705Bio for Galvanized steel

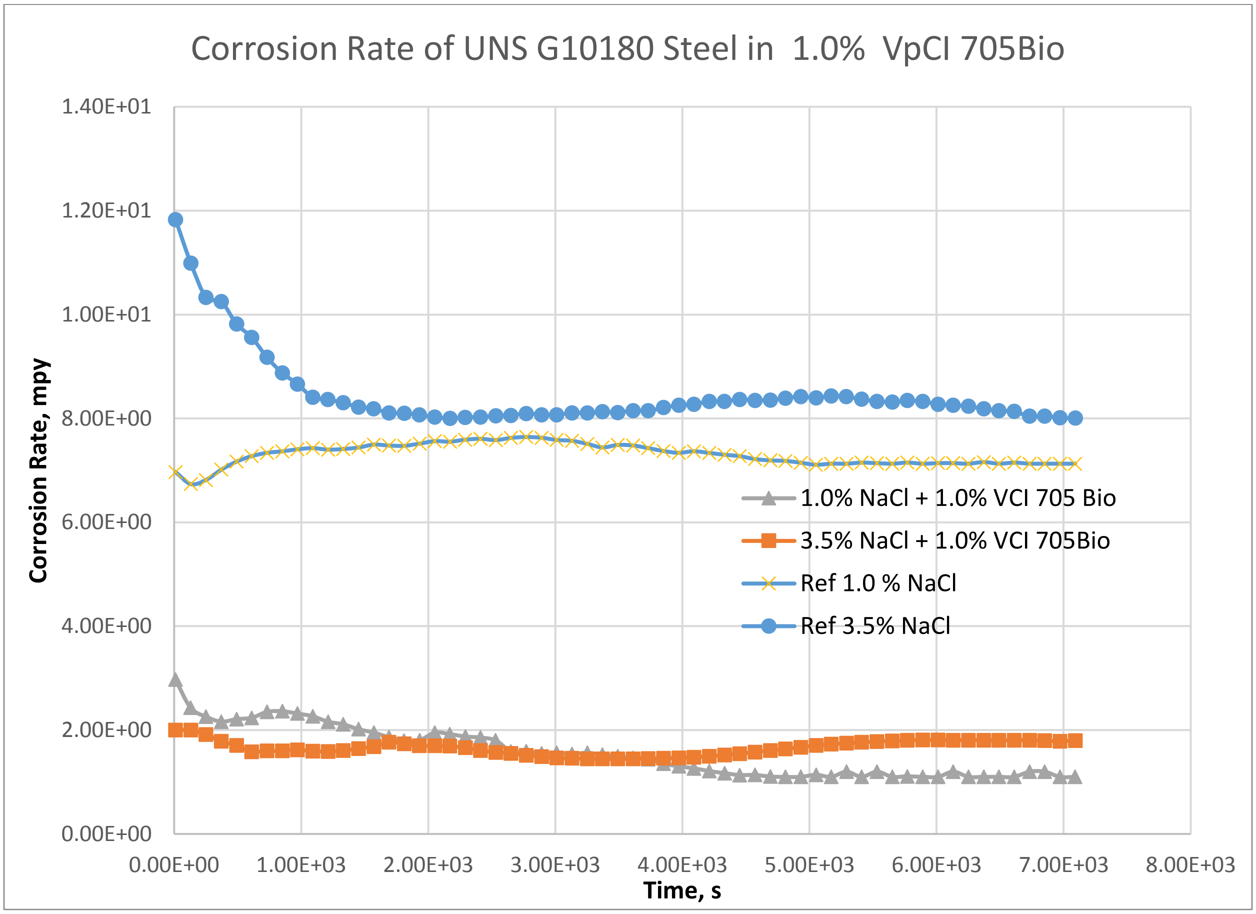


Fig. D-11: Corrosion rate measurements using LPR technique of VpCI 705 Bio for UNS G1018 steel.