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GALVANIC CORROSION BETWEEN GRAPHITIC ROCK AND GROUND SUPPORT IN UNDERGROUND MINES

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ABSTRACT

Galvanic corrosion between dissimilar materials, such as steel and graphite, leads to safety concerns for many industries, including mining. In this study, researchers from the National Institute for Occupational Safety and Health (NIOSH) analyzed rock samples from two mines in the United States that exhibit electrochemical properties similar to graphite through laboratory measurements to investigate their observed in-situ influence on underground metal support. Uniform corrosion rates of mild steel coupons, inflatable bolt coupons, and friction bolt coupons galvanically coupled to rock samples were obtained using both potentiodynamic polarization and zero resistance ammetry. Increased uniform corrosion rates were witnessed between the coupled rock and steel system, over those of just the steel alone. Surface analysis of the metal samples showed the presence of pitting corrosion, reflective of bolt samples removed from partner mines. Corrosion pitting of ground support structures in contact with graphitic rock in underground mines poses safety concerns for mine workers by increasing the rate of corrosion and decreasing bolt strength over time and will be further investigated for intervention strategies.

INTRODUCTION

Steel rockbolts are used extensively in underground mining to strengthen excavations and provide safe passage of workers and equipment. The combination of high tensile and shear strength and the low cost of mild steel make it an excellent choice to help resist the movement of the rock mass in an excavation. When initially installed, the design strength of a mild steel rockbolt is achieved, and over time it will support the rock mass up to its load-bearing capacity [1]. However, corrosion of steel gradually reduces the load-bearing capacity of a rockbolt and creates safety concerns for the entire ground support system. When the corrosivity of a rock mass is not considered during the design stage, expensive rehabilitation may also be necessary to keep the excavation open for its desired lifespan. Figure 1 shows a rockbolt that has failed pull testing in a partner mine in this study due to advanced corrosion.

Several corrosivity classification methods have been reported by researchers in countries where mining occurs. These tools are useful for site evaluations as they consider atmospheric and groundwater measurements along with rock mass observations to classify the corrosivity of a section [2]. These tools are generally applicable in most mining environments.

However, there are some mine environments where increased corrosion rates are observed due to aggressive minerals present in the host rock. This study investigates the galvanic corrosion of mild steel due to the presence of presumed graphitic minerals contained in host rock collected from two U.S. underground metal mines. Graphite is the stable form of elemental carbon on the earth's surface, and while well-crystalized graphite is rare, materials containing graphitic carbon occur in many deposits. In this study, graphitic host rock samples that surround massive sulfide deposits are analyzed [3].

The increased corrosion rate of steel in contact with graphitic rock, over that of steel alone, is galvanic in nature. When two dissimilar conducting materials are in contact with each other and exposed to an electrolyte, current can flow from one to the other. The direction of the flow can be predicted by the galvanic series. In seawater, graphite is one of the most noble (or cathodic) conductors, while mild steel is less noble, or anodic. Steel undergoes oxidation, protecting graphite, which is ultimately reduced. Since corrosion requires an electrolyte, the extent of the corrosion observed in the field is affected by salinity and wetness. In sections where the host rock is dry, the galvanic corrosion rate is observed to be low, but as the wetness of the rock increases so too increases the observed corrosion rate [4].

Figure 1. Failed corroded rockbolt from a mine in this study.

Most previous research on graphite corrosion relates to the corrosion susceptibility of various metals to composite graphite or carbon fiber materials. These materials are commonly used in the construction, rehabilitation, automotive, and aerospace industries. Miller conducted early electrochemical measurements of the corrosion rate of various metals coupled to graphite-epoxy materials and provides valuable additional data for pure graphite [5]. More recently, other researchers have investigated the galvanic corrosion between certain metals and carbon-fiber-reinforced polymers [6]. There are very few studies of graphite and metals in the rock or soil environment; however, Liu recently investigated the interaction of graphite grounding electrodes and zinc-plated steel grounding straps [7].

EXPERIMENT SETUP

The goals of this study were to: (1) investigate and quantify the influence of high carbon conductive mine rock on the galvanic corrosion rate of mild steels, (2) compare two electrochemical testing methods for estimating corrosion rates of this galvanic system, and (3) investigate if there is a relationship between rock resistivity and corrosion rate. Bulk rock samples were obtained from two northern United States metal mines, referred to as Mine 1 and 2, and these rock samples were cut into rectangular sections with a flat face for testing. An equal-sized copper plate and piece of ultra-low resistivity carbon foam were placed in contact with the rock to create modified "paint cells" and "para-cells" for electrochemical corrosion analysis, as seen in Figures 2 and 3.

Figure 2. Modified paint cells for electrochemical testing.

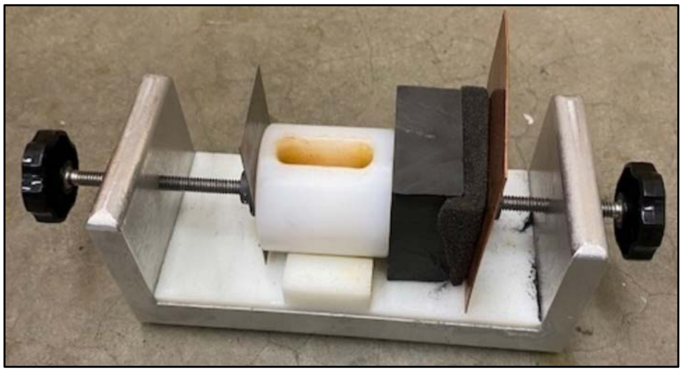

Figure 3. Para-cell for electrochemical testing.

This test setup was used to test 4140 mild carbon steel and sections of uncoated carbon steel friction bolts and inflatable rockbolts.

A 0.1M NaCl solution was used as a standard electrolyte for all testing. This concentration was chosen to approximate the average chloride concentrations present in the affected underground mine areas from which the rock samples were collected. Water samples from both mines were obtained by rubbing de-ionized water into boreholes in the rock body and diluting them to 100 mL. The average chloride concentrations were 1,040 and 11,000 ppm at Mine 1 and 2, respectively. The standard 0.1M NaCl solution falls between these values at roughly 3,500 ppm.

Composition of the rock samples from Mine 1 and 2 were obtained with the use of a portable X-Ray Fluorescent (XRF) analyzer. The device is capable of elemental analysis above element 12 on the periodic table, with all elements below that being reported as a category called "light elements (LE)." Carbon, which is element 6, would be considered a light element and can only be estimated to be a large portion of that category for these samples. A summary of the rock samples can be seen in Table 1 below, with the remaining composition being trace elements.

Table 1. Rock sample composition determined by XRF.

Rock Sample	LE (%)	Ca	Si	S	Al	Fe	Mg
1.1	57.01	20.69	14.60	4.75	1.39	0.08	0
1.2	53.14	20.35	19.62	0.098	2.09	1.25	1.75
1.3	51.27	7.41	32.62	1.02	3.23	0.084	2.99
1.4	53.9	8.27	27.34	2.33	6.04	1.47	0
2.1	48.65	0.05	30.47	0.09	12.13	4.36	1.85
2.2	47.89	0.08	31.16	2.39	11.4	4.02	1.19
2.3	43.52	12.38	14.25	9.64	3.97	13.94	1.49

Linear Polarization Resistance (LPR) Scans

Linear polarization resistance (LPR) scans provide a nondestructive testing method to obtain corrosion rate data. This is achieved by polarizing the material +/- 10 mV around its open circuit potential (OCP), resulting in the material's resistance to polarization being measured. By applying the Stern-Geary equation, an estimated corrosion rate is provided [8]. LPR scans were performed on a potentiostat to obtain a baseline corrosion rate for the selected metals: 4140 mild carbon steel, carbon steel friction bolt, and an inflatable rockbolt.

Potentiodynamic Polarization (PDP) Scans

Potentiodynamic polarization (PDP) scans are destructive tests that sweep across a larger potential range than LPR scans [9]. These scans were performed individually for each rock and metal sample. The corrosion current for a given material can be estimated graphically where the asymptotes of the anodic and cathodic branches intersect, as shown in Figure 4. The location of the corrosion current (I_{corr}) and potential (E_{corr}) are indicated [10].

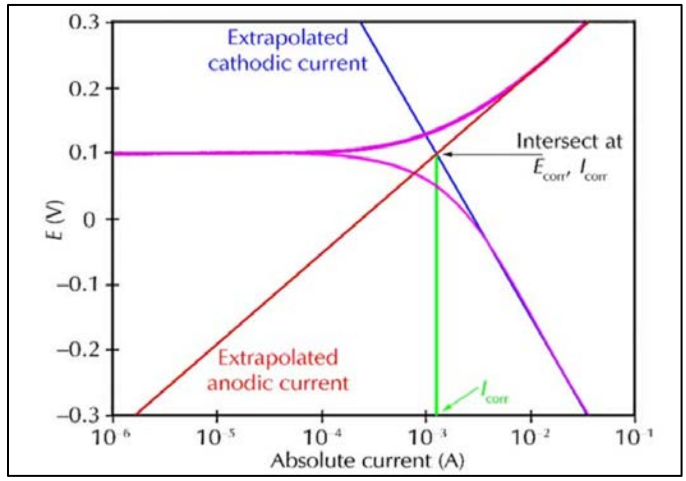

Figure 4. Example PDP scan from Gamry Instruments, Inc. [10].

For a galvanic coupling experiment, PDP scans can be utilized to estimate the corrosion current of the system. Individual scans of the two materials can be graphically overlayed, with I_{corr} and E_{corr} being represented by the intersection of the cathodic branch of one material with the anodic branch of the other. For the rock samples in this study, input parameters were chosen to run the PDP scans primarily for the cathodic reactions. Scans were run similarly to include primarily the anodic reactions for the metal samples. Figure 5 shows a representative overlay for one of the rock and metal sample combinations.

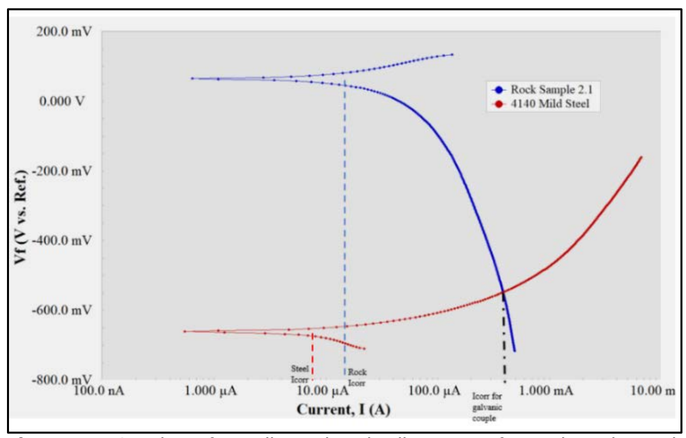

Figure 5. Overlay of anodic and cathodic curves for rock and metal samples.

Gamry Echem Analyst™ software was used to overlay the material scans, allowing for the corrosion currents to be obtained from the curve intersection [11]. The corrosion current was then converted into a corrosion rate using a rearranged version of Faraday's Law below [12].

$$CR\ (mpy) = 0.13 * \frac{icorr * EW}{A * D} \quad (1)$$

Where:

CR = corrosion rate (mpy)
Icorr = corrosion current (µA)
A = sample area (cm^2)

EW = equivalent weight of material
D = density of sample (g/cm^3)

Zero-Resistance Ammetry (ZRA) Scans

Zero-resistance ammeter (ZRA) scans are another method to obtain corrosion current of a galvanic coupling. In ZRA, a voltage is applied to one material, the working electrode, to maintain both materials in the system at the same potential. The applied current of the source is measured and reported [13]. These scans were utilized to obtain the corrosion current for the rock samples galvanically connected to each of the three metals in the experiment, and then the corresponding rate of corrosion was calculated using Equation 1.

Resistivity Measurements

After electrochemical testing concluded, the resistivity of each rock sample was recorded to observe its relationship with corrosion rate. Electrically conductive carbon paste with a known resistivity of 10 Ω*cm was applied to both sides of the rectangular rock samples, and the samples were placed between copper plates. The 4-wire resistance was recorded on a multimeter. This setup can be seen in Figure 6.

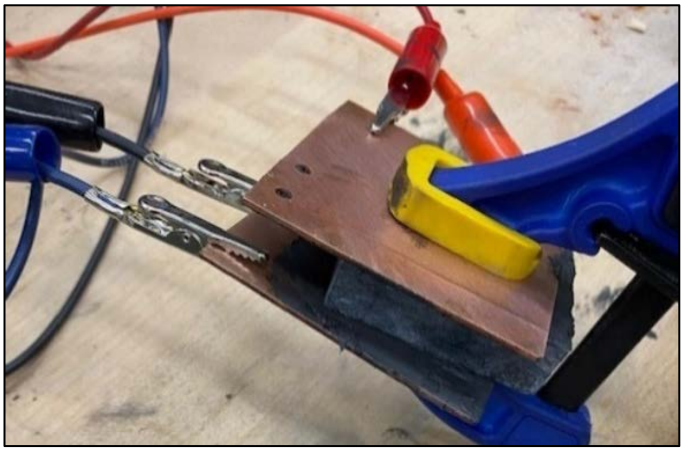

Figure 6. Rock resistivity measurement setup.

The resistivity was then calculated using the following equation:

$$\rho = R\frac{A}{l} \qquad (2)$$

Where:

ρ = Resistivity (Ω*cm)
R = resistance (Ω)
A = cross-sectional area (cm^2)
l = length (cm)

EXPERIMENTAL RESULTS

Corrosion Rate Results

Corrosion rates for 4140 mild carbon steel, sections of carbon steel friction bolts, and inflatable rockbolts from the LPR scans were 5.284, 16.18, and 9.26 mpy, respectfully. Figure A1 in the appendix shows the LPR scan and fit for the 4140 mild steel corrosion rate. The resulting corrosion currents and rates from the PDP scans are listed in Table 2 below.

Table 2. PDP-obtained galvanic corrosion rates for 4140 mild steel, carbon steel friction bolt, and inflatable rockbolt.

	4140 Mild Steel		Friction Bolt		Inflatable Bolt	
Rock Sample	Icorr (μA)	CR (mpy)	Icorr (μA)	CR (mpy)	Icorr (μA)	CR (mpy)
1.1	324	49.8	309	47.5	334	51.3
1.2	309	47.6	300	46.0	328	50.4
1.3	288	44.2	279	42.8	294	45.3
1.4	437	67.2	416	64.0	468	72.0
2.1	385	59.1	363	55.8	417	64.1
2.2	397	61.1	374	57.4	435	66.9
2.3	373	57.4	351	54.0	415	63.8

The I_{corr} values for these scans were obtained from Figure A2 in the appendix.

Results of the ZRA scans and the respective corrosion rates are shown in Table 3.

Table 3. ZRA galvanic corrosion rates for 4140 mild steel, carbon steel friction bolt, and inflatable rockbolt.

	4140 Mild Steel		Friction Bolt		Inflatable Bolt	
Rock Sample	Icorr (μA)	CR (mpy)	Icorr (μA)	CR (mpy)	Icorr (μA)	CR (mpy)
1.1	271	41.6	235	36.1	273	42.0
1.2	296	45.5	399	61.4	195	29.9
1.3	226	34.7	221	33.9	186	28.5
1.4	414	63.7	435	66.8	262	40.3
2.1	302	46.4	278	42.8	232	35.7
2.2	330	50.8	440	67.6	215	33.0
2.3	284	43.7	310	47.7	219	33.7

Figure A3 in the appendix shows a representative ZRA scan for the 4140 mild steel.

Comparison of Corrosion Rate Measurement Methods

The corrosion rates calculated using both PDP and LPR potentiostat methods were subsequently compared to verify the effect that the mine rock had on the metal degradation and to observe the difference in measurement types. The percent difference between the calculated corrosion rates for all three metals based on the two potentiostat testing methods can be seen in Table 4. The 4140 mild steel was used as the baseline reference corrosion rate for these percent difference calculations.

Table 4. Percent difference in corrosion rate between PDP and ZRA scans for the studied metals.

Rock Sample	4140 Mild Steel (%)	Friction Bolt (%)	Inflatable Bolt (%)
1.1	19.7	31.6	22.3
1.2	4.6	25.0	68.3
1.3	27.3	26.2	58.7
1.4	5.50	4.20	78.7
2.1	27.3	30.4	79.8
2.2	20.3	15.0	102.6
2.3	31.3	13.1	89.3
Average	19.4	20.8	71.4

Rock Resistivity Effect on Galvanic Corrosion Rate

Resistivity values for each rock sample were measured and plotted against the corrosion rate of 4140 carbon steel. Figure 7 shows the witnessed relationship amongst the rock used in the test.

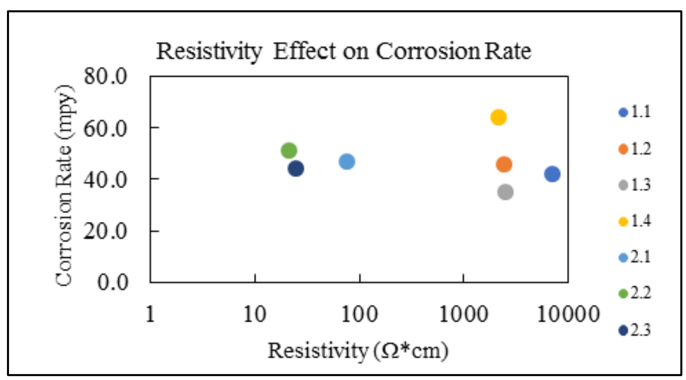

Figure 7. Scatter plot of rock resistivity and the corresponding galvanic system corrosion rate.

DISCUSSION

Effects of Rock Samples on Metal Corrosion Rates

When galvanically coupled to the mine rock samples' electrochemical properties similar to graphite, each of the three metals tested experienced higher corrosion rates. From Table 3, corrosion rates, on average, are approximately 9 times higher for the 4140 mild steel, 3 times higher for the friction bolt, and 3.75 times higher for the inflatable bolt. These results align with the condition of ground support seen in both partner mines, which visibly have much greater corrosion at contact sites of mesh and bolts with the rock.

Comparison of Corrosion Rate Measurement Methods

Both PDP scans and ZRA measurements provided corrosion rates that were higher for the metals galvanically coupled to the rock samples, over the steel samples alone. The calculated corrosion rates were relatively close for both the 4140 mild steel and the friction rockbolt samples, roughly averaging out to a 20% difference as seen in Table 4. Conversely, the inflatable bolt on average was 71% different between the testing methods. This may be attributed to a variance in the passivation behavior of the steel alloy before and during testing.

Though both scans provide relevant data, ZRA is a more robust and convenient way to measure the corrosion current in terms of coupling methodology [5]. For this technique, the potentiostat electrically connects the two materials, while they are also connected through a shared electrolyte, as they would be in a mining environment. ZRA scans can also perform long-term corrosion measurements as an added benefit. The PDP scans provide an interpolated value for corrosion rates, which is useful but is not physically and galvanically linking the materials at the same time. These values are also instantaneous corrosion rates and cannot be continually run over long-time intervals.

While these corrosion measurement methods provide an important starting point in investigating the corrosion rate of metal ground support, field testing is required to further observe and characterize the effects corrosion has had on the level of safety.

Rock Resistivity Effect on Galvanic Corrosion Rate

Rock resistivity was measured on dry rock specimens. From the samples tested, there does not appear to be a strong correlation between the resistivity of the rock and the resulting corrosion rate. The rock samples from both Mine 1 and 2 have much lower resistivity than other typical host rocks encountered underground. Dry rock resistivity below 1 kΩ-cm can be considered “low resistivity.” Typical host dry rock mass resistivity is often in the kilo- or mega-ohm range but is often lower when wet. Figure 7 displays the relation between the resistivity of the rock samples analyzed. Rock samples from Mine 2 had resistivities a magnitude lower than Mine 1; however, corrosion rates fall very close to each other. Despite the weak correlation, it should be noted that low resistivity and high conductivity are important properties of the rock that allow for increased flow of electrons during corrosion reactions.

Through NIOSH’s Managing Ground Support for Long-term Stability project, field and laboratory testing are being performed to develop correlations between corrosion rates and commonly outlined parameters that contribute to the increase in metal degradation. Analysis and documentation of corrosion levels can improve confidence of ground support performance and increase safety at mine sites to keep workers out of areas that need corrosion-related rehab.

CONCLUSIONS

The following conclusions were observed from this electrochemical study:

- Graphitic-behaving mine rock can form a galvanic couple with steel, including steel alloys commonly used for ground support;
- Corrosion rates of 4140 mild carbon steel, sections of carbon steel friction bolts, and inflatable rockbolts are higher in a common electrolyte when galvanically coupled to “graphitic” mine rocks. Corrosion rates were 3–9 times higher the coupling over the metal alone;
- Both PDP and ZRA potentiostat testing methods can provide comparable galvanic corrosion currents; and
- Resistance of graphitic-behaving rocks does not have a strong correlation to the corrosion rate of steel; however, in general low resistance promotes higher corrosion currents and increased electron flow.

Note that these conclusions are based on laboratory studies and provide corrosion estimates that should be confirmed with field testing. The findings in this paper represent general corrosion rates for underground mine support metals, but do not comprehensibly consider all methods of corrosion that could have effects on the support. Future testing should be conducted to relate corrosion rates of ground support in these low-resistance graphitic-behaving rocks to the bolt strength over time to evaluate the capacity and overall safety of the support in corrosive conditions over time. Overall, current and future corrosion studies for NIOSH’s Managing Ground Support for Long-term Stability project are all designed to improve safety for underground mining employees.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DISCLAIMER

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. Mention of any company or product does not constitute endorsement by NIOSH.

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APPENDIX

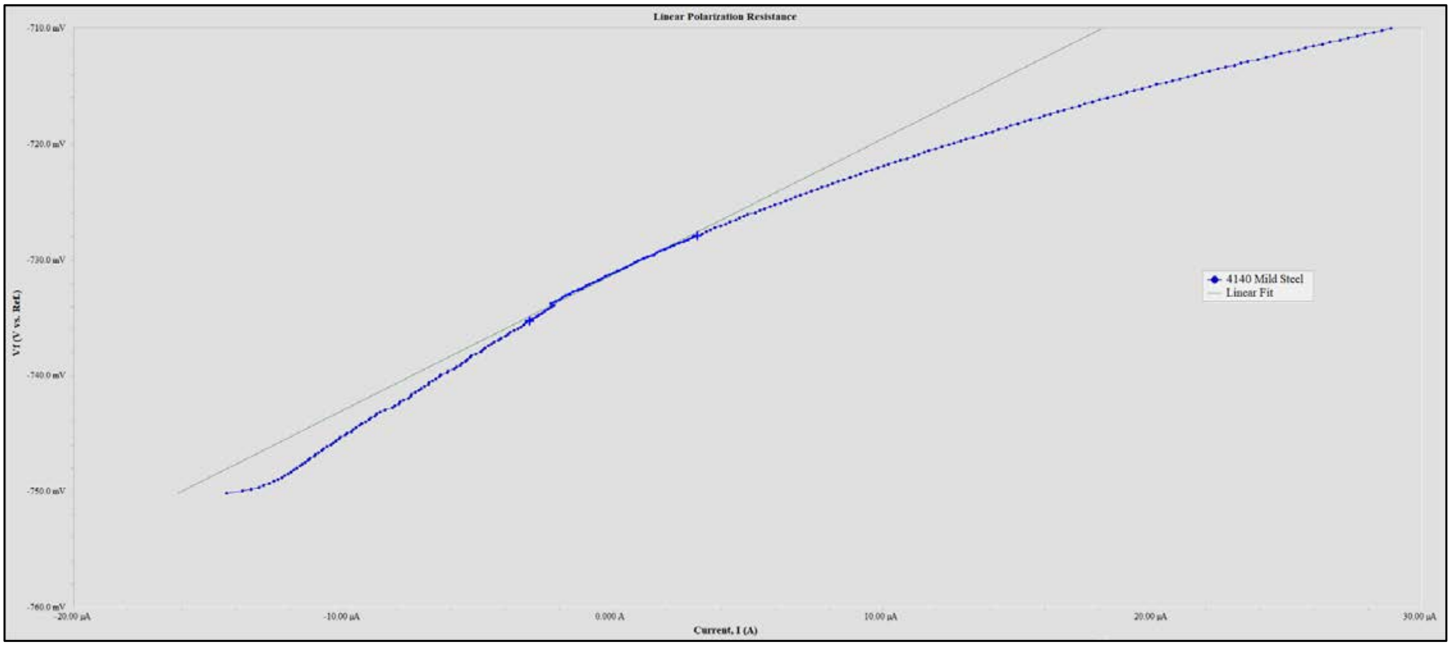

Figure A1. Example LPR scan result and linear fit providing corrosion rate for 4140 mild steel.

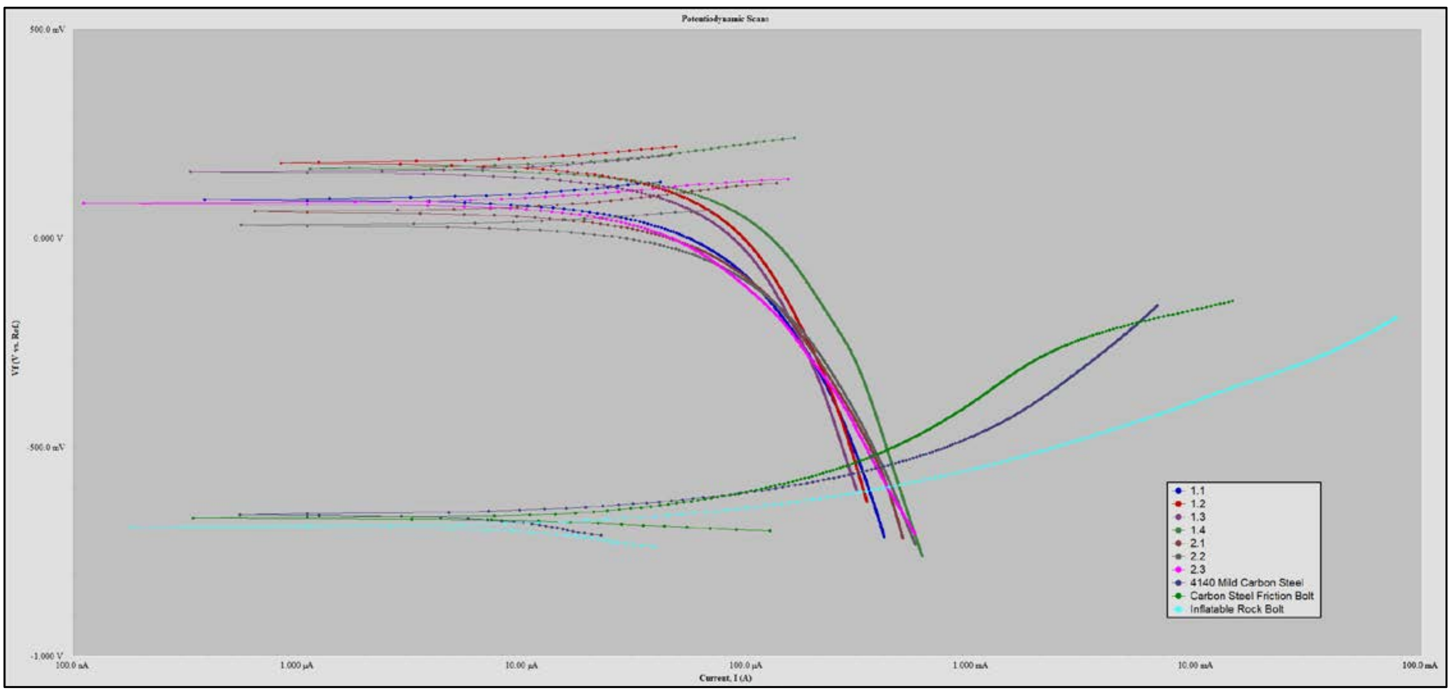

Figure A2. PDP scan results for metal and rock samples. Corrosion current recorded at intersection of metal and rock anodic and cathodic branches, respectively.

APPENDIX (continued)

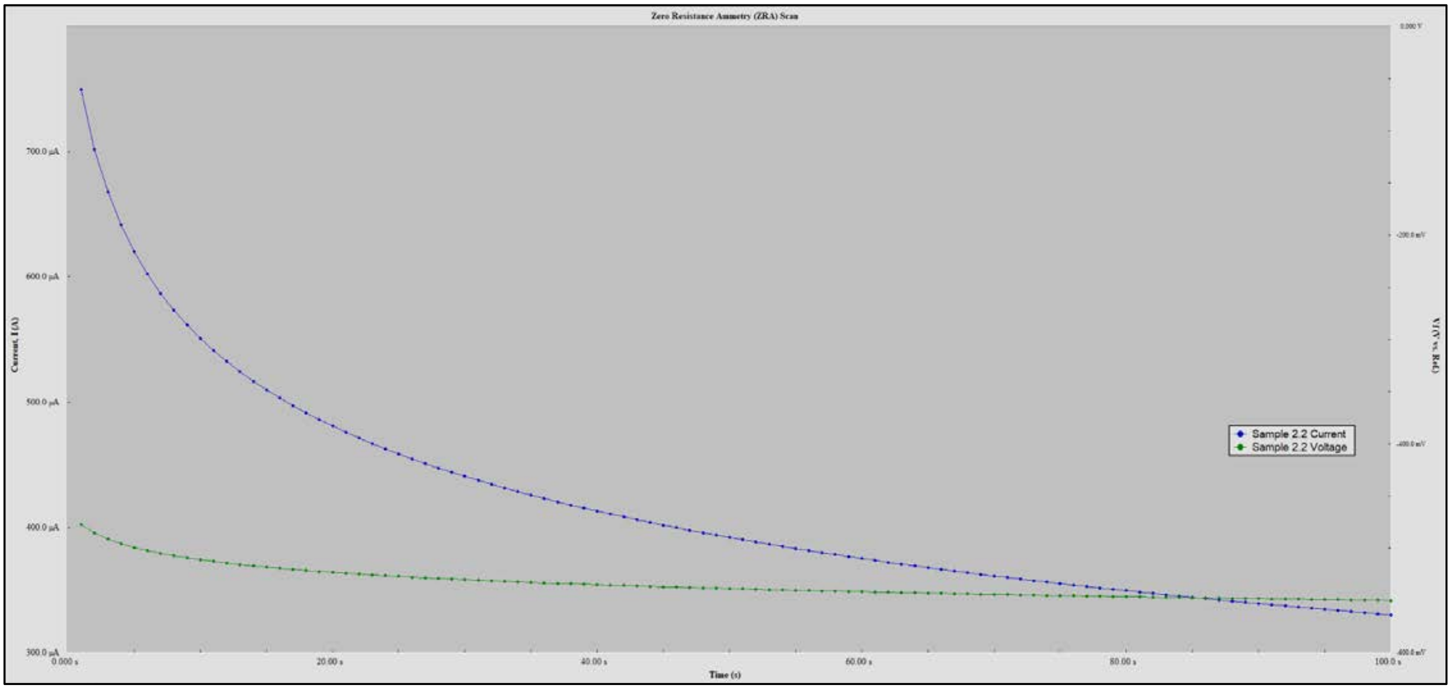

Figure A3. Example ZRA scan for rock sample 2.2 and 4140 mild carbon steel.