**SANDIA NATIONAL LABORATORIES**  
**WASTE ISOLATION PILOT PLANT**

**AP-189**  
**Revision 0**

**Analysis Plan for Determination of Iron/Lead Corrosion Rates by Electrochemical Tests Under TP 06-02**

**Task 4.4.2.2.1**

**Effective Date:** May 17, 2021

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1 **Introduction and Objectives**

1.1 Introduction

A series of corrosion experiments have been conducted under Test Plan TP 06-02 Rev. 3 (Sisk-Scott & Icenhower, 2016b). In addition to Single-Pass Flow-Through (SPFT) and static corrosion experiments, electrochemical methods (i.e. Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization (PDP)) were proposed to assess the state of the coupon surface under WIPP-relevant conditions. Collected EIS measurements were summarized in the FY20 milestone report (Zhang, 2020).

Previously, Analysis Plan (AP) AP-159 Rev. 0 (Roselle, 2011) and AP-175 Rev. 0 (Sisk-Scott & Icenhower, 2016a) were developed for the determination of corrosion rates, gas generation rates and corrosion products from corrosion experiments performed. The purpose of this AP is to describe the calculations needed to determine corrosion rates for steel and lead from EIS and PDP measurements at WIPP-relevant conditions. As of Compliance Recertification Application 2019 (CRA-2019) (Day, 2019; U.S. DOE, 2019), WIPP-relevant conditions are: ionic strengths ranging from 5.7 m to 9.1 m (mol/kg-H2O), pH values ranging from 4.6 to 11.8, fugacities of CO2 ($f_{CO2}$) ranging from 0 to 2.74×10^{-3} atm, and concentrations of Total Inorganic Carbon (TIC) ($C_{TIC}$) ranging from 0 to 8.69×10^{-4} M (mol/L-solution), temperature at 27 °C, and pressures ranging from 0.1 to 18 MPa. The corrosion rates from EIS and PDP measurements and from other experiments (e.g., SPFT, static) will be compared and used for the determination of gas generation rates from the corrosion of steel and lead in the WIPP Performance Assessment (PA) calculations. The electrochemical method could obtain corrosion rates and their dependence on factors such as brine type, concentration, temperature, etc. in less time than methods like SPFT or static corrosion.

1.2 Objective

The objective of this AP is to determine steel and lead corrosion rates from electrochemical measurements (EIS and PDP) performed on steel and lead coupons under WIPP-relevant conditions per this TP-directed corrosion studies. The corrosion rates by this AP will be used to determine gas generation rates in PA calculation for compliance decision analysis per NP 9-1, Analyses.

2 **Approach**

2.1 General Procedure

Electrochemical methods (such as EIS and PDP) can be used to measure the corrosion rate of metals in high salinity brines. The key parameters are electrochemical potential relative to a reference electrode, the surface reaction rate (current), and the resistance to passing charge through the interface. Electrochemical tests are performed in order to broaden the scope of ongoing iron corrosion tests. These tests will provide a deeper insight into corrosion mechanisms by allowing for the measurement of a corrosion rate at an instantaneous point in time (Gateman et al., 2019; Groysman, 2010). The corrosion rate can be determined from the corrosion current density measured by the electrochemical method.
A Gamry electrochemical cell was utilized to satisfy the desired experimental conditions (SP 12-40, *Calibration and Use of the Gamry Interface 1010E Potentiostat/Galvanostat*). As shown in Figure 1, a 3-electrode technique was implemented for measuring corrosion rates: reference electrode (saturated calomel electrode through a bridge tube filled with the testing brine solution), counter electrode (platinum wires), and working electrode (C1018 steel or lead coupon).

EIS tests were run every few hours (e.g., 2-4 hours) for a certain period of time in each test depending on the stability of the corrosion experiments. Polarization resistance, $R_p$, can be determined from the EIS measurements. At the end of the EIS tests, one PDP test was conducted to determine the Tafel slope of both anodic and cathodic reactions for calculating the corrosion rates. The following provides a guideline to obtain the corrosion rate by EIS and PDP measurements.

### 2.2 Determination of the Polarization Resistance, $R_p$

![Figure 1. Electrochemical cell setup with an electric heating jacket. It is equipped with reference electrode (saturated calomel electrode through a bridge tube filled with a testing brine solution), counter electrode (platinum wires), and working electrode (C1018 coupon).](image)
Figure 2a shows EIS spectra (Bode phase angle and magnitude) from an electrochemical test as an example. The polarization resistance, $R_p$, is obtained by fitting the EIS data to an appropriate model based on the tested material (metal) and its environment (e.g., brine solution). The polarization resistance ($R_p$) and solution resistance ($R_s$) can be determined by fitting the EIS spectra to the Randles model (Figure 2b) provided by Gamry’s Echem Analyst (Gamry-Instruments, 2011). As shown in Figure 2a, the real axis value at the low frequency intercept is the sum of the polarization resistance and the solution resistance ($R_p + R_s$) while the value at the high frequency intercept is the solution resistance. The Randles circuit is a simple model for initial analysis, other models (such as Constant Phase Element (CPE)) will be also tried to fit to the same EIS data and $R_p$ will be selected from the model that gives a better fitting.

2.3 Determination of The Stern-Geary Coefficient, $B$

Generally, in a PDP test, a potentiostat is used to control the potential of the working electrode, scanning between a fixed start and final potential. For an anodic PDP scan, the start potential is slightly cathodic of Open Circuit Potential (OCP) and the final potential is sufficiently anodic of the open circuit to capture the electrochemical regions of interest. For a cathodic PDP scan, the start potential is slightly anodic of OCP and the final potential is sufficiently cathodic of the open circuit to capture the electrochemical region of interest (e.g., Oxygen Reduction Reaction (ORR) dominated region, ORR limiting current density, and Hydrogen Evolution Reaction (HER). As a PDP is generally destructive (i.e., irreversible changes are made to the metal surface) a separate sample should be used for each anodic and cathodic polarization curve. In the Gamry electrochemical cell (Figure 1), this PDP test is generally performed in a DC corrosion experiment by specifying small initial and final potentials (reference to OCP) where the potential is started and scanned from low to high (i.e. from cathodic to anodic) to obtain the potentiodynamic polarization, as shown in Figure 3. In order to permit acquiring valid anodic and cathodic Tafel slopes from a single sample, the voltage perturbation from open circuit was kept small; specifically, it was varied from about -0.5 V below to +0.5 V above the steady state OCP. Once the PDP test is completed, a plot of potential vs. current density (at logarithmic scale) is generated and fitted to obtain the Tafel slope of anodic and cathodic reactions. The Stern-Geary coefficient, $B$, can be determined from the anodic and cathodic Tafel slopes, and is used in calculating the corrosion current density (Kelly et al., 2003).

Figure 3 shows an example of a PDP test and its Tafel fitting. When slopes of the anodic and cathodic reactions are obtained, the Stern-Geary coefficient in V/decade can be calculated by the following equation:
Figure 3. Tafel extrapolation from a potentiodynamic polarization (PDP) test when open circuit potential, scanning from cathodic to anodic is applied to the coupons. Tafel slope of anodic reaction ($\beta_a$) and of cathodic reaction ($\beta_c$) are obtained for the determining corrosion rate from EIS tests. Tafel coefficients are determined by linearly fitting cathodic and anodic curves in the PDP test using the software package Echem Analyst™ (Gamry Instruments, 2011). The corrosion potential and current in the PDP test under the applied potential can be also extracted.

2.4 Calculation of the Corrosion Rates

The corrosion current density ($i_{corr}$) can be determined by the $R_p$ and $B$ from EIS and PDP tests, respectively:

$$i_{corr} = \frac{B}{R_p}$$  \hspace{1cm} (2)

where

- $i_{corr}$ – Corrosion current density, A/cm²
- $B$ – Stern-Geary coefficient, V/decade
- $R_p$ – Polarization resistance, Ohm·cm²

Once the corrosion current density $i_{corr}$, in µA/cm², is calculated using Equation (2), it can be converted into the corrosion rate, in µm/year, using the following equation:

$$r = \frac{315,360 \times F_w}{nF \rho} \times i_{corr}$$  \hspace{1cm} (3)

where

- $r$ – Corrosion rate, µm/year
- $\rho$ – Density of tested material, g/cm³ (7.87 g/cm³ coupon C1018 or 11.34 g/cm³ for lead at room temperature)
\( F_w \) – Formula weight of testing material, g/mol (55.85 g/mol for C1018 or 207.20 g/mol for lead)

\( n \) – Mole of electrons for anodic reaction (n=2 for Fe or Pb, assuming ferrous/lead ions dominant)

\( F \) – Faraday constant, 96485.33 C/mol

\( i_{corr} \) – Corrosion current density, \( \mu A/cm^2 \)

This equation gives a conversion factor of 11.6 (i.e. 1 \( \mu A/cm^2 \) = 
\[ \frac{315,360 \times 55.85}{(2 \times 96485.33 \times 7.87)} = 11.6 \ \mu m/year \]) for the tested material steel C1018 and 29.9 for lead.

3 Tasks

3.1 Task 1 – Determination of Corrosion Rates

The objective of this AP is to determine iron and lead corrosion rates by electrochemical (EIS and PDP) measurements at WIPP-relevant conditions. At the conclusion of the corrosion experiments conducted in an electrochemical cell, all EIS and PDP experimental data are processed and analyzed by the software Gamry Echem Analyst™ (Version 7.07) for corrosion rates. All acquired data (raw data) and analysis results (e.g., polarization resistances, Tafel constants at each condition) will be attached and documented in a milestone report and/or an Analysis Report (AR).

Current TP 06-02 Rev. 3 states that electrochemical method could be used to study iron/lead corrosion but does not provide details on electrochemical methods. A new revision of TP 06-02 (Rev. 4) will be prepared to include the electrochemical methods (EIS and PDP) and specify brine solutions and test conditions. Additional EIS and PDP tests are continuing in brine solutions such as NaCl, MgCl₂, SGWB, GWB, and ERDA-6 with and without sulfide at the proposed temperatures 50, 70, and 90 °C. This AP can be used to analyze all EIS and PDP data from these tests. The following table identifies the individuals who will perform the tasks, task deliverables and expected completion date for subtasks of this AP.

**Table 1.** A list of subtasks, task description, deliverable, owner, and expected completion date

<table>
<thead>
<tr>
<th>Subtask</th>
<th>Task Description/Deliverable</th>
<th>Individual to Perform Task</th>
<th>Expected Completion Date</th>
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<td>1.1</td>
<td>Analysis of EIS and PDP measurements for iron corrosion in brines (NaCl, MgCl₂, SGWB, GWB, and ERDA-6) at 50, 70, 90 °C</td>
<td>L. Zhang</td>
<td>December 2023</td>
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<td>1.2</td>
<td>Analysis of EIS and PDP measurements for iron corrosion in brines (NaCl, MgCl₂, SGWB, GWB, and ERDA-6) with sulfide at 50, 70, 90 °C</td>
<td>L. Zhang</td>
<td>December 2024</td>
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<tr>
<td>1.3</td>
<td>Analysis of EIS and PDP measurements for lead corrosion in brines (NaCl, MgCl₂, SGWB, GWB, and ERDA-6) at 50, 70, 90 °C</td>
<td>L. Zhang</td>
<td>December 2024</td>
</tr>
<tr>
<td>1.4</td>
<td>Analysis of EIS and PDP measurements for lead corrosion in brines (NaCl, MgCl₂, SGWB, GWB, and ERDA-6) with sulfide at 50, 70, 90 °C</td>
<td>L. Zhang</td>
<td>December 2024</td>
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3.2 Task 2 – Application of Results

The corrosion rates from the EIS and PDP measurements will be compared with those from other methods (mass loss, surface retraction, chemical analysis, and corrosion product characterization) analyzed by AP-159 Rev. 0 and AP-175 Rev. 0 and used to formulate new gas generation parameters for the WIPP PA calculations. The comparison of corrosion rates in μm/year by the electrochemical (EIS and PDP) method to those from other methods will be conducted for the same coupon materials at the same or similar conditions when each of subtasks in Section 3.1 is completed. The individuals, task deliverables and expected completion date for this task 2 will be similar to task 1.

4 Software List

Echem Analyst™ Version 7.07 (Gamry-Instruments, 2011) is Gamry’s dedicated data-analysis program, the companion to Gamry’s data-acquisition program called Framework™ (Gamry-Instruments, 2018). Data files generated by experiments in Gamry Framework then can be analyzed in Echem Analyst™. Included in Echem Analyst™ are procedures to perform circuit modeling and other analyses with EIS data, as well as procedures to perform Tafel extrapolation on PDP data. A guide to using Echem Analyst™ is readily available (Gamry-Instruments, 2011). Other commercial, off-the-shelf spreadsheet programs, such as Microsoft Excel, will also be used for data manipulation and plotting.

5 Special Considerations

No special considerations have been identified.

6 Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed when conducting these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, Qualification and Training. Analyses will be performed and documented in accordance with the requirements of NP 9-1, Analyses and NP 20-2, Scientific Notebooks. All software used will meet the requirements of NP 19-1, Software Requirements. The analyses will be reviewed following NP 6-1, Document Review Process. All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, Records.

For all procedures listed in this document, the most current revision of the document will be used for data analysis.

7 References


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