

**CENTER FOR NUCLEAR WASTE
REGULATORY ANALYSES**

TECHNICAL OPERATING PROCEDURE

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Title

PROCEDURE FOR CONDUCTING AND VERIFYING POTENTIODYNAMIC POLARIZATION TESTS

EFFECTIVITY AND APPROVAL

Revision 0 of this procedure became effective on 4-20-90. This procedure consists of the pages and changes listed below.

<u>Page No.</u>	<u>Change</u>	<u>Date Effective</u>
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Supersedes Procedure No. None

Approvals

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Quality Assurance by <i>Robert D. Brient</i> Robert D. Brient	Date <u>4/20/90</u>	Cognizant Director <i>Allen R. Whiting</i> Allen R. Whiting	Date <u>4/20/90</u>

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PROCEDURES FOR CONDUCTING AND VERIFYING POTENTIODYNAMIC POLARIZATION TESTS

1. PURPOSE

The purpose of the document is to provide procedures for conducting a potentiodynamic polarization scan and for verifying the accuracy and reproducibility of potentiodynamic measurements. This procedure establishes controls required by CQAM Section 3, "Scientific Investigations and Analysis Control."

2. SCOPE

This document describes two types of tests:

1. Verification test: This is performed as prescribed in ASTM G-5 on 430 stainless steel in a solution of 1.0N sulfuric acid. The resulting current-voltage curve is compared to the band of curves given in the ASTM standard. The purpose of this test is to ensure that the electrochemical system, including potentiostat, data acquisition system, and the cell are functioning properly. Hence, this is more than an electronic calibration of the individual instruments such as potentiostat.

2. Data Collection tests: This pertains to all other tests performed to collect data on the electrochemical polarization behavior of a given material in a given electrolyte at any temperature.

3. Applicable Documents

- (1) ASTM Designation G5 - "Standard Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"
- (2) ASTM Designation G15 - "Standard Definitions of Terms Relating to Corrosion and Corrosion Testing"
- (3) ASTM Designation G3 - "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Test"

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- (4) ASTM Designation G61 - "Standard Practice for Conducting Cyclic Polarization Measurements for Localized Corrosion"
- (5) CNWRA Technical Operating Procedure 003-01 - (latest revision), for preparing electrochemical/corrosion test specimens.

4. RESPONSIBILITY

- 4.1 The cognizant Element Manager shall be responsible for the development and maintenance of this procedure.
- 4.2 The cognizant Principal Investigator shall be responsible for the implementation of this procedure.
- 4.3 Personnel performing tests described in this procedure are responsible for complying with its requirements.

5. APPARATUS

5.1 Test Cell

A polarization test cell such as described in ASTM G5 is required. Other polarization cell designs may be equally suitable provided the cell has a capacity of approximately 1 liter and has suitable ports to permit the introduction of working electrode (test sample), counter electrode, a salt bridge (Luggin probe with PARC-Vycor tip, or equivalent), gas inlet and gas outlet through a water trap, and a thermometer (or other temperature sensing device such as a thermister or thermocouple). The tip of the salt bridge shall be movable so that it can be brought in close proximity to the working electrode. A suitable heating device such as a mantle heater or a constant temperature bath is also required.

5.2 Working Electrodes

Verification Test:

Standard AISI Type 430 stainless steel samples obtained from ASTM Headquarters shall be used for the verification test. These are cylindrical specimens made from a single heat of metal.

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Data Collection Tests:

For conducting potentiodynamic tests on samples other than the ASTM sample, samples shall be machined according to the practice described in CNWRA TOP-003-01. If a sample of sufficient thickness is not available, a flat sample as described in ASTM G-61 may be used. The type of sample used shall be noted in reporting the results. Samples may be polished to any finish desired. Usually, they are polished to a 600-grit finish with silicon carbide paper.

5.3 Working Electrode Electrical connection

To make electrical connection to the sample, cylindrical specimens shall be mounted on a suitable holder as described in ASTM G5. Flat samples shall be mounted in a suitable holder as described in ASTM G61. In cases where mounting in such holders is not suitable due to concerns with crevice corrosion in the mounted interface, alternate electrical connections may be made provided galvanic contact with the electrical connector is avoided. Such methods may involve spot welding a wire of the same material to the tip of the sample and ensuring that the spot welded area is not immersed in the solution.

5.4 Counter Electrode

Counter electrodes normally will be made of platinum, the surface of which may be platinized to increase the surface area. The detailed procedure for platinizing the platinum electrode is given in ASTM G-5, and is essentially an electrolytic deposition of platinum from a platinum chloride solution. High-density graphite rods may also be used as counter electrodes. The total surface area of the counter electrode that is immersed in the test solution shall be at least twice that of the immersed surface area of the working electrode.

5.5 Reference Electrode

A Saturated Calomel Reference Electrode (SCE) shall be used in the verification test as described in ASTM G5. Reference electrodes should have a controlled leakage rate on the order of 3 to 8 micro liter/hr.

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Normal precautions shall be taken to maintain the reference electrodes in good condition. They shall be stored with the tips immersed in a saturated KCl solution when they are not in use. Potentials of the reference electrodes shall be checked against an unused electrode before and after each test to ensure that they remain accurate. For such measurements, a high impedance voltmeter/electrometer is essential. An example of such an electrometer is Keithley Model 602 electrometer (a detailed procedure for measuring the potential difference using this instrument is given at the back of the instrument box). Reference electrode potentials shall not differ from each other by more than 5 millivolts.

In potentiodynamic tests conducted in systems other than that described ASTM G5 test, the reference electrode may be chosen to match the test needs. For example, Silver/Silver Chloride electrode may be chosen for tests involving temperatures higher than about 70 deg. C.

5.6 Reagents

The 1.0N sulfuric acid used as the test solution in the ASTM G5 test shall be prepared with 27.2 mL of reagent grade (98%) sulfuric acid diluted with high purity (17-18 Mohms) water to 1 liter total solution volume. High-purity hydrogen is recommended as the purge gas although high-purity argon is also acceptable.

Saturated KCl for reference electrode storage is made by dissolving potassium chloride salt in nanopure water.

Reagent grade acetone shall be used to degrease the specimen.

20% nitric acid is made from reagent grade, 70% nitric acid by dilution with high purity water.

5.7 Instrumentation

Potentiostats meeting the general requirements outlined in ASTM G5 shall be used. Voltage scans shall be performed by using a programmable voltage scan generator or by means of a digital computer and appropriate software. Separate instruments or instruments integral to the potentiostat may

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be used to measure and monitor the test parameters. The instruments shall be periodically calibrated.

6. EXPERIMENTAL PROCEDURE

6.1 Verification Test:

The verification test shall be conducted in accordance with the detailed procedure given in ASTM G5. The current-vs-potential data shall be acquired and plotted directly on an X-Y recorder, or stored on a computer disk for later retrieval and display or printed as a hardcopy.

The verification test shall be conducted periodically on all potentiostats at the beginning and end of a set of potentiodynamic experiments. The frequency of the verification test will be dictated by the number of potentiodynamic experiments that are in progress.

6.2 Data Collection Tests:

The general procedure for conducting a potentiodynamic polarization test consists of increasing the potential in steps or by continuous scanning of the potential and recording the resulting current flow. The data is plotted as a graph of logarithm of current density (total current divided by the working electrode area) vs. applied potential.

In all the tests conducted, the pertinent experimental information shall be recorded in Scientific Notebooks. A hard copy of the plot of current-vs-potential shall be placed in a file that is identified appropriately. If the test was performed under computer control, a printout of the data points shall also be included in the file. All computer files shall be backed-up with a copy and kept in the same file. The test results at the end of a sequence of experiments to be determined by the Principal Investigator shall be recorded in the Scientific Notebooks and signed by the person conducting the test and countersigned by the cognizant Principal Investigator.

The procedure for conducting these tests follows, in general, the procedure given in ASTM G-5. However, the details of the

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variations from the ASTM procedure shall be recorded as discussed in the following sections.

6.2.1 Initial Conditions

The starting conditions may depend on the specific purpose of the test. In some cases, the samples may be pre-passivated by immersing them in a 20% (by wt.) HNO_3 solution for 24 hours at room temperature. The sample then is rinsed in high purity water, acetone and then dried before introducing the sample into the test solution. In some cases, pre-passivation is necessary to obviate crevice corrosion at the mounted surface. In this case, the rest of the surfaces may be mechanically polished, cleaned and then put in test solution. The starting conditions such as gas purging time before introducing the sample, open-circuit potential, time at open-circuit potential, the starting potential (if different from open-circuit potential), time at starting potential, and any cathodic conditioning given shall be recorded. The specimen surface preparation shall also be recorded. It is also recommended that the open-circuit potential of the counter electrode be recorded at the start and end of test.

6.2.2 Scanning

The scan rate in a continuous scan test or potential steps and time increments in a stepwise test shall be recorded. Generally, the potentiodynamic curves are scanned in one direction of increasing potential (anodic scan). However, the scan direction must be recorded if performed otherwise.

6.2.3 Information To Be Recorded

The conventions applicable to electrochemical measurements and the terms used shall follow those given in ASTM G-3.

In addition to the data that can be gathered from the generated curve, the following information shall be recorded for each test:

1. Time (t_i) at corrosion (open-circuit) potential
2. Corrosion potential at the start of the test (before t_i)
3. Potential of the counter electrode at the start of the test (before t_i)

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4. Conditioning potential (If applicable)
5. Conditioning time (If applicable)

6. Prepassivation treatment (If applicable)
7. Specimen condition (rolled, annealed etc)
8. Temperature at the start of the test
9. pH of the solution at the start of the test
10. Purge gas used (If applicable)
11. Scan rate
12. Temperature at the end of the test
13. pH at the end of the test
14. Visual observation of the sample including the crevice at the mounting surface.

7. RECORDS

The files containing the test data and the Scientific Notebooks are controlled as records in-process in accordance with CQAM Section 17. These shall be maintained in project files until completion of the project activities at which time they will be compiled in to a project data package, and processed as QA records as specified by CQAM Section 17.