



Designation: G 96 – 90 (Reapproved 1996)^{€1}

Standard Guide for On-Line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods)¹

This standard is issued under the fixed designation G 96; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (€) indicates an editorial change since the last revision or reapproval.

€¹ NOTE—Editorial corrections were made throughout in October 1996.

1. Scope

1.1 This guide outlines the procedure for conducting on-line corrosion monitoring of metals in plant equipment under operating conditions by the use of electrical or electrochemical methods. Within the limitations described, these test methods can be used to determine cumulative metal loss or instantaneous corrosion rate, intermittently or on a continuous basis, without removal of the monitoring probes from the plant.

1.2 The following test methods are included: Test Method A for electrical resistance, and Test Method B for polarization resistance.

1.2.1 Test Method A provides information on cumulative metal loss, and corrosion rate is inferred. This test method responds to the remaining metal thickness except as described in Section 5.

1.2.2 Method B is based on electrochemical measurements for determination of instantaneous corrosion rate but may require calibration with other techniques to obtain true corrosion rates. Its primary value is the rapid detection of changes in the corrosion rate that may be indicative of undesirable changes in the process environment.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in 5.6.

2. Referenced Documents

2.1 ASTM Standards:

D 1125 Test Methods for Electrical Conductivity and Resistivity of Water²

G 1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens³

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing³

¹ This guide is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of ASTM Subcommittee G01.12 on In-Plant Corrosion Tests.

Current edition approved March 30, 1990. Published May 1990.

² Annual Book of ASTM Standards, Vol 11.01.

³ Annual Book of ASTM Standards, Vol 03.02.

G 4 Method for Conducting Corrosion Coupon Tests in Plant Equipment³

G 15 Terminology Relating to Corrosion and Corrosion Testing³

G 59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements³

G 102 Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements³

3. Terminology

3.1 *Definitions*—See Terminology G 15 for definitions of terms used in this guide.

4. Summary of Guide

4.1 *Test Method A—Electrical Resistance*—The electrical resistance test method operates on the principle that the electrical resistance of a measuring element (wire, strip, or tube of metal) increases as its cross-sectional area decreases:

$$R = \sigma \frac{l}{A} \quad (1)$$

where:

R = resistance,

σ = resistivity of metal (temperature dependent),

l = length, and

A = cross-section area.

In practice, the resistance ratio between the measuring element exposed to corrosion and the resistance of a similar reference element protected from corrosion is measured, to compensate for resistivity changes due to temperature. Based on the initial cross-sectional area of the measurement element, the cumulative metal loss at the time of reading is determined. Metal loss measurements are taken periodically and manually or automatically recorded against a time base. The slope of the curve of metal loss against time at any point is the correction rate at that point. The more frequently measurements are taken, the better is the resolution of the curve from which the corrosion rate is derived.

4.1.1 The electrical resistance of the metal elements being measured is very low (typically 2 to 10 mΩ). Consequently, special measurement techniques and cables are required to minimize the effect of cable resistance and electrical noise.

4.1.2 Various probe element cross-sectional areas are necessary so that a wide range of corrosion rates can be monitored with acceptable resolution.

4.2 Test Method B—Polarization Resistance:

4.2.1 The polarization resistance test method involves interaction with the electrochemical corrosion mechanism of metals in electrolytes in order to measure the instantaneous corrosion rate. Its particular advantage is its speed of response to corrosion rate upsets. On a corroding electrode subject to certain qualifications (see 12.1), it has been shown that the current density associated with a small polarization of the electrode is directly proportional to the corrosion rate of the electrode.

4.2.2 The polarization resistance equation is derived in Practice G 59. See Practice G 3 for applicable conventions. For small polarization of the electrode (typically ΔE up to 20 mV), the corrosion current density is defined as:

$$i_{corr} = \frac{B}{R_p} \quad (2)$$

where:

B = a combination of the anodic and cathodic Tafel slopes (b_a , b_c), and

R_p = the polarization resistance with dimensions $\text{ohm} \cdot \text{cm}^2$.

$$B = \frac{b_a b_c}{2.303 (b_a + b_c)} \quad (3)$$

4.2.3 The corrosion current density, i_{corr} , can be converted to corrosion rate of the electrode by Faraday's law if the equivalent weight (EW) and density, ρ , of the corroding metal are known (see Practice G 102):

$$\text{corrosion rate} = K_1 \frac{i_{corr}}{\rho} EW \quad (4)$$

where:

K_1 = a constant.

4.2.4 Equivalent weight of an element is the molecular weight divided by the valency of the reaction (that is, the number of electrons involved in the electrochemical reaction).

4.2.5 In order to obtain an alloy equivalent weight that is in proportion with the mass fraction of the elements present and their valence, it must be assumed that the oxidation process is uniform and does not occur selectively; that is, each element of the alloy corrodes as it would if it were the only element present. In some situations these assumptions are not valid.

4.2.6 Effective equivalent weight of an alloy is as follows:

$$\frac{1}{\sum \frac{n_i f_i}{W_i}} \quad (5)$$

where:

f_i = mass fraction of i_{th} element in the alloy,

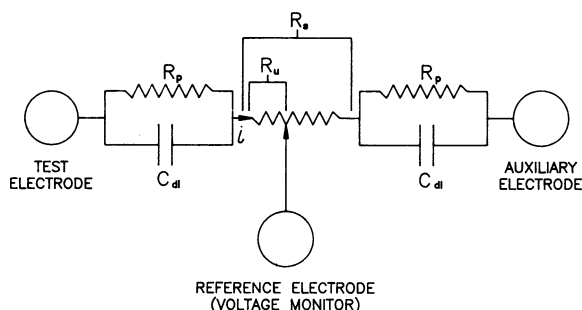
W_i = atomic weight of the i_{th} element in the alloy,

n_i = exhibited valence of the i_{th} element under the conditions of the corrosion process, and

m = number of component elements in the alloy (normally only elements above 1 mass % in the alloy are considered).

Alloy equivalent weights have been calculated for many engineering metals and alloys and are tabulated in Practice G 102.

4.2.7 Fig. 1 represents an equivalent circuit of polarization resistance probe electrodes in a corroding environment. The



NOTE 1— R_s = Solution Resistance ($\text{ohm} \cdot \text{cm}^{-2}$) between test and auxiliary electrodes (increases with electrode spacing and solution resistivity).

R_u = Uncompensated component of solution resistance (between test and reference electrodes) ($\text{ohm} \cdot \text{cm}^{-2}$).

R_p = Polarization Resistance R_p ($\text{ohm} \cdot \text{cm}^2$).

C_{dl} = Double layer capacitance of liquid/metal interface.

i = Corrosion current density.

FIG. 1 Equivalent Circuit of Polarization Resistance Probe

value of the double layer capacitance, C_{dl} , determines the charging time before the current density reaches a constant value, i , when a small potential is applied between the test and auxiliary electrode. In practice, this can vary from a few seconds up to hours. When determining the polarization resistance, R_p , correction or compensation for solution resistance, R_s , is important when R_s becomes significant compared to R_p . Test Methods D 1125 describes test methods for electrical conductivity and resistivity of water.

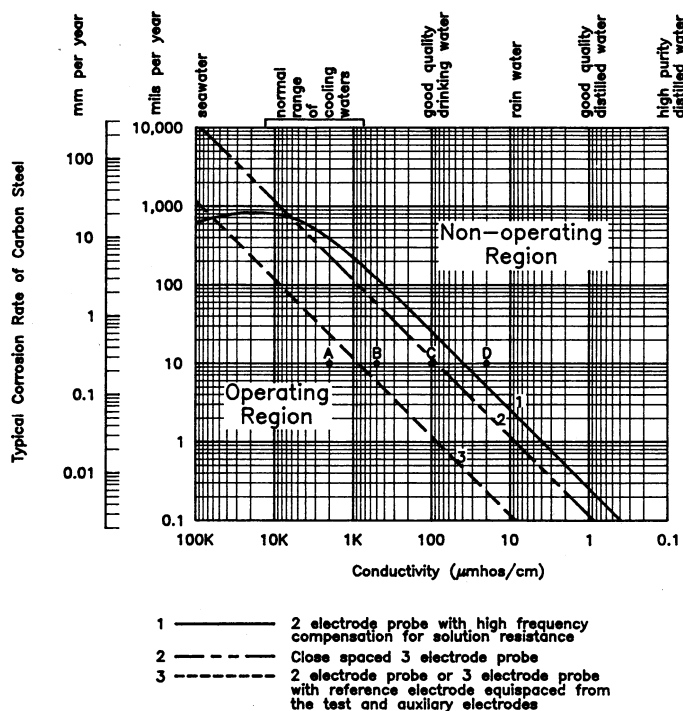
4.2.8 Two-electrode probes, and three-electrode probes with the reference electrode equidistant from the test and auxiliary electrode, do not correct for effects of solution resistance, without special electronic solution resistance compensation. With high to moderate conductivity environments, this effect of solution resistance is not normally significant (see Fig. 2).

4.2.9 Three-electrode probes compensate for the solution resistance, R_s , by varying degrees depending on the position

and proximity of the reference electrode to the test electrode. With a close-spaced reference electrode, the effects of R_s can be reduced up to approximately ten fold. This extends the operating range over which adequate determination of the polarization resistance can be made (see Fig. 2).

4.2.10 A two-electrode probe with electrochemical impedance measurement technique at high frequency short circuits the double layer capacitance, C_{dl} , so that a measurement of solution resistance, R_s , can be made for application as a correction. This also extends the operating range over which adequate determination of polarization resistance can be made (see Fig. 2).

4.2.11 Even with solution resistance compensation, there is a practical limit to the correction (see Fig. 2). At higher solution resistivities the polarization resistance technique cannot be used, but the electrical resistance technique may be used.



NOTE 1—See Appendix X1 for derivation of curves and Table X1.1 for description of points A, B, C and D.

NOTE 2—Operating limits are based on 20 % error in measurement of polarization resistance equivalent circuit (see Fig. 1).

NOTE 3—In the Stern-Geary equations, an empirical value of $B = 27.5$ mV has been used on the ordinate axis of the graph for “typical corrosion rate of carbon steel”.

NOTE 4—Conductivity $\frac{(\mu\text{mhos})}{\text{cm}} = \frac{1\,000\,000}{\text{Resistivity (ohm}\cdot\text{cm)}}$

NOTE 5—Effects of solution resistance are based on a probe geometry with cylindrical test and auxiliary electrodes of 4.75 mm (0.187 in.) diameter, 31.7 mm (1.25 ft) long with their axes spaced 9.53 mm (0.375 in.) apart. Empirical data shows that solution resistance (ohms·cm²) for this geometry = $0.55 \times$ resistivity (ohms·cm²).

NOTE 6—A two-electrode probe, or three-electrode probe with the reference electrode equidistant from the test and auxiliary electrode, includes % of solution resistance between working and auxiliary electrodes in its measurement of R_p .

NOTE 7—A close-space reference electrode on a three electrode probe is assumed to be one that measures 5 % of solution resistance.

NOTE 8—In the method for Curve 1, basic polarization resistance measurement determines $2R_p + R_s$ (see Fig. 1). High frequency measurement short circuits C_{dl} to measure R_s . By subtraction polarization resistance, R_p , is determined. The curve is based on high frequency measurement at 834 Hz with C_{dl} of $40 \mu\text{F}/\text{cm}^2$ on above electrodes and ± 1.5 % accuracy of each of the two measurements.

NOTE 9—Curve 1 is limited at high conductivity to approximately 700 mpy by error due to impedance of C_{dl} at frequency 834 Hz. At low conductivity it is limited by the error in subtraction of two measurements where difference is small and the measurements large.

NOTE 10—Errors increase rapidly beyond the 20 % error line (see Appendix X1, Table X1.1).

FIG. 2 Guidelines on Operating Range for Polarization Resistance