ASTM G102

Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements
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1. Scope

1.1 This practice is intended to provide guidance in converting the results of electrochemical measurements to rates of uniform corrosion. Calculation methods for converting corrosion current density values to either mass loss rates or average penetration rates are given for most engineering alloys. In addition, some guidelines for converting polarization resistance values to corrosion rates are provided.

2. Referenced Documents

2.1 ASTM Standards:
D 2776 Test Methods for Corrosivity of Water in the Absence of Heat Transfer (Electrical Methods)
G 5 Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
G 59 Practice for Conducting Potentiodynamic Polarization Resistance Measurements

3. Significance and Use

3.1 Electrochemical corrosion rate measurements often provide results in terms of electrical current. Although the conversion of these current values into mass loss rates or penetration rates is based on Faraday's Law, the calculations can be complicated for alloys and metals with elements having multiple valence values. This practice is intended to provide guidance in calculating mass loss and penetration rates for such alloys. Some typical values of equivalent weights for a variety of metals and alloys are provided.

3.2 Electrochemical corrosion rate measurements may provide results in terms of electrical resistance. The conversion of these results to either mass loss or penetration rates requires additional electrochemical information. Some approaches for estimating this information are given.

3.3 Use of this practice will aid in producing more consistent corrosion rate data from electrochemical results. This will make results from different studies more comparable and minimize calculation errors that may occur in transforming electrochemical results to corrosion rate values.

4. Corrosion Current Density

4.1 Corrosion current values may be obtained from galvanic cells and polarization measurements, including Tafel extrapolations or polarization resistance measurements. (See Reference Test Method G 5 and Practice G 59 for examples.) The first step is to convert the measured or estimated current value to current density. This is accomplished by dividing the total current by the geometric area of the electrode exposed to the solution. It is assumed that the current distributes uniformly across the area used in this calculation. In the case of galvanic couples, the exposed area of the anodic specimen should be used. This calculation may be expressed as follows:

\[ i_{\text{cor}} = \frac{i_{\text{an}}}{A} \]  

where:
\( i_{\text{cor}} \) = corrosion current density, \( \mu \text{A/cm}^2 \),
\( I_{\text{an}} \) = total anodic current, \( \mu \text{A} \), and
\( A \) = exposed specimen area, \( \text{cm}^2 \).

Other units may be used in this calculation. In some computerized polarization equipment, this calculation is made automatically after the specimen area is programmed into the computer. A sample calculation is given in Appendix X1.

4.2 Equivalent Weight—Equivalent weight, EW, may be thought of as the mass of metal in grams that will be oxidized by the passage of one Faraday (96 489 ± 2 C (amp-sec)) of electric charge.

Note 1—The value of EW is not dependent on the unit system chosen and so may be considered dimensionless.

For pure elements, the equivalent weight is given by:

\[ EW = \frac{W}{n} \]  

where:
\( W \) = the atomic weight of the element, and
\( n \) = the number of electrons required to oxidize an atom of the element in the corrosion process, that is, the valence of the element.

4.3 For alloys, the equivalent weight is more complex. It is usually assumed that the process of oxidation is uniform and does not occur selectively to any component of the alloy. If this is not true, then the calculation approach will need to be adjusted to reflect the observed mechanism. In addition, some rationale must be adopted for assigning values of \( n \) to
the elements in the alloy because many elements exhibit
more than one valence value.

4.4 To calculate the alloy equivalent weight, the following
approach may be used. Consider a unit mass of alloy
oxidized. The electron equivalent for 1 g of an alloy, \( Q \), is then:

\[
Q = \sum \frac{n_i f_i}{W_i}
\]  

(3)

where:

- \( f_i \) = the mass fraction of the \( i \)th element in the alloy,
- \( W_i \) = the atomic weight of the \( i \)th element in the alloy, and
- \( n_i \) = the valence of the \( i \)th element of the alloy.

Therefore, the alloy equivalent weight, \( EW \), is the reciprocal of
this quantity:

\[
EW = \frac{1}{\sum \frac{n_i f_i}{W_i}}
\]  

(4)

Normally only elements above 1 mass percent in the alloy
are included in the calculation. In cases where the actual
analysis of an alloy is not available, it is conventional to use
the mid-range of the composition specification for each
element, unless a better basis is available. A sample calculation
is given in Appendix X2 (1).4

4.5 Valence assignments for elements that exhibit multiple
valences can create uncertainty. It is best if an indepen-
dent technique can be used to establish the proper valence
for each alloying element. Sometimes it is possible to analyze
the corrosion products and use those results to establish the
proper valence. Another approach is to measure or estimate
the electrode potential of the corroding surface. Equilibrium
diagrams showing regions of stability of various phases as a
function of potential and pH may be created from thermo-
dynamic data. These diagrams are known as Potential-pH
(Pourbaix) diagrams and have been published by several
authors (2, 3). The appropriate diagrams for the various
alloying elements can be consulted to estimate the stable
valence of each element at the temperature, potential, and
pH of the contacting electrolyte that existed during the test.

Note 2—Some of the older publications used inaccurate thermody-
namic data to construct the diagrams and consequently they are in error.

4.6 Some typical values of EW for a variety of metals and
alloys are given in Table 1.

4.7 Calculation of Corrosion Rate—Faraday's Law can be
used to calculate the corrosion rate, either in terms of
penetration rate (CR) or mass loss rate (MR) (4):

\[
CR = K_1 \frac{i_{cor}}{\rho} \cdot EW
\]  

(5)

\[
MR = K_2 \frac{i_{cor}}{\rho} \cdot EW
\]  

(6)

where:

- CR is given in mm/yr, \( i_{cor} \) in \( \mu A/cm^2 \),
- \( K_1 = 3.27 \times 10^{-3} \), mm g/\( \mu A \) cm yr (Note 3),
- \( K_2 = 8.954 \times 10^{-3} \), g cm\(^2\)/\( \mu A \) m\(^2\) d (Note 3).

Note 3—EW is considered dimensionless in these calculations.

Other values for \( K_1 \) and \( K_2 \) for different unit systems are
given in Table 2.

4.8 Errors that may arise from this procedure are dis-

cussed below.

4.8.1 Assignment of incorrect valence values may cause
serious errors (5).

4.8.2 The calculation of penetration or mass loss from
electrochemical measurements, as described in this standard,
assumes that uniform corrosion is occurring. In cases where
non-uniform corrosion processes are occurring, the use of
these methods may result in a substantial underestimation of
the true values.

4.8.3 Alloys that include large quantities of metalloids or
oxidized materials may not be able to be treated by the above
procedure.

4.8.4 Corrosion rates calculated by the method above
where abrasion or erosion is a significant contributor to the
metal loss process may yield significant underestimation of
the metal loss rate.

5. Polarization Resistance

5.1 Polarization resistance values may be approximated
from either potentiodynamic measurements near the cor-
rosion potential (see Practice G 59) or stepwise potentiostatic
polarization using a single small potential step, \( \Delta E \), usually
either 10 mV or -10 mV, (see Test Method D 2776). Values of
\( \pm 5 \) and \( \pm 20 \) mV are also commonly used. In this case, the
specimen current, \( \Delta I \), is measured after steady state occurs,
and \( \Delta E/\Delta I \) is calculated. Potentiodynamic measurements
yield curves of \( I \) versus \( E \) and the reciprocal of the slope of the
curve (dE/dI) at the corrosion potential is measured. In
most programmable potentiodynamic polarization equip-
ment, the current is converted to current density automati-
cally and the resulting plot is of \( i \) versus \( E \). In this case, the
polarization resistance is given by \( \Delta E/\Delta I \) at the corrosion
potential and 5.2 is not applicable.

5.2 It is necessary to multiply the dE/dI or \( \Delta E/\Delta I \) value
calculated above by the exposed specimen geometric area

to obtain the polarization resistance. This is equivalent to the
calculation shown in 4.1 for current density.

5.3 The Stern-Geary constant \( B \) must be estimated or
calculated to convert polarization resistance values to cor-
rosion current density (6, 8).

5.3.1 Calculate Stern-Geary constants from known Tafel
slopes where both cathodic and anodic reactions are activa-
tion controlled, that is, there are distinct linear regions near
the corrosion potential on an \( E \log i \) plot:

\[
B = \frac{ba \cdot bc}{2.303 (ba + bc)}
\]  

(7)

where:

- \( ba \) = slope of the anodic Tafel reaction, when plotted on
  base 10 logarithmic paper in V/decade,
- \( bc \) = slope of the cathodic Tafel reaction when plotted on
  base 10 logarithmic paper in V/decade, and
- \( B \) = Stern-Geary constant, V.

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4 The boldface numbers in parentheses refer to the list of references at the end of
this standard.
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5.3.2 In cases where one of the reactions is purely diffusion controlled, the Stern-Geary constant may be calculated:

\[ B = \frac{b}{2.303} \]  

(8)

where:

- \( b \) = the activation controlled Tafel slope in V/decade.

It should be noted in this case that the corrosion current density will be equal to the diffusion limited current density. A sample calculation is given in Appendix X4.

Cases where both activation and diffusion effects are similar in magnitude are known as mixed control. The reaction under mixed control will have an apparently larger \( b \) value than predicted for an activation control, and a plot of \( E \) versus log \( I \) will tend to curve to an asymptote parallel to the potential axis. The estimation of a \( B \) value for situations involving mixed control requires more information in general and is beyond the scope of this standard. In general, Eqs 7 and 8 may be used, and the corrosion rate calculated by these two approximations may be used as lower and upper limits of the true rate.

5.3.3 It is possible to estimate \( b_{an} \) and \( b_{cl} \) from the deviation from linearity of polarization curves in the 20–50 mV region around the corrosion potential. Several approaches have been proposed based on analyses of electrode kinetic models. See Refs (9–11) for more information.

5.3.4 In cases where the reaction mechanism is known in detail, the Tafel slopes may be estimated from the rate controlling step in the mechanism of the reaction. In general, Tafel slopes are given by (12):
\[ b = \frac{KRT}{nF} \]  

(9)

where:
- \( K \) = a constant,
- \( R \) = the perfect gas constant,
- \( T \) = the absolute temperature,
- \( n \) = the number of electrons involved in the reaction step, and
- \( F \) = Faraday’s constant.

At 25°C, \( \frac{RT}{2.303 F} \) is 59.2 mV/decade. For simple one-electron reactions, \( K \) is usually found to be 2.0.

5.3.5 In cases where the Tafel slopes cannot be obtained from any of the methods described above, it may be necessary to determine the Stern-Geary constant experimentally by measuring mass loss and polarization resistance values.

5.4 The corrosion current density may be calculated from the polarization resistance and the Stern-Geary constant as follows:

\[ i_{cor} = \frac{B}{R_p} \]  

(10)

The corrosion rate may then be calculated from the corrosion current, as described in Section 4. A sample calculation is given in Appendix X5.

5.5 There are several sources of errors in polarization resistance measurements:

5.5.1 Solution resistivity effects increase the apparent polarization resistance, whether measured by the potentiostatic or potentiodynamic methods (13). The effect of solution resistivity is a function of the cell geometry, but the following expression may be used to approximate its magnitude.

\[ R_p = R_a - \rho l \]  

(11)

where:
- \( R_a \) = the apparent polarization resistance, ohm cm²,
- \( \rho \) = the electrolyte resistivity in ohm cm,
- \( l \) = the distance between the specimen electrode and the Luggin probe tip, or the reference electrode in cm, and
- \( R_p \) = the true polarization resistance in ohm cm².

Significant solution resistivity effects cause the corrosion rate to be underestimated. A sample calculation is given in Appendix X6.

5.5.2 Potentiodynamic techniques introduce an additional error from capacitative charging effects. In this case, the magnitude of the error is proportional to scan rate. The error is illustrated by Eq (12):

\[ I_{total} = I_f + c \frac{dV}{dt} \]  

(12)

where:
- \( I_{total} \) = the cell current,
- \( I_f \) = the Faradaic current associated with anodic and cathodic processes,
- \( c \) = the electrode capacitance, and
- \( dV/dt \) = the scan rate.

The capacitance charging effect will cause the calculated polarization resistance to be in error. Generally, this error is small with modest scan rates (14).

5.5.3 Corroding electrodes may be the site for other electrochemical reactions. In cases where the corrosion potential is within 50 to 100 mV of the reversible potential of the corroding electrode, the electrochemical reactions will occur simultaneously on the electrode surface. This will cause either the anodic or cathodic \( b \) value to appear smaller than the corrosion reaction above. Consequently, the Stern-Geary constant \( B \) will be inflated and the predicted corrosion current will be overestimated (15). In this case, the concentration of the corroding electrode ions is generally of the same magnitude or higher than other ions participating in the corrosion process in the electrolyte surrounding the electrode. Other redox couples that do not necessarily participate in the corrosion reaction may have similar effects. This is especially true for metals exhibiting passive behavior.

6. Keywords

6.1 corrosion current; corrosion rate; electrochemical; equivalent weight; polarization resistance; Tafel slopes

APPENDIXES

(Nonmandatory Information)

X1. SAMPLE CALCULATION—CORROSION CURRENT DENSITY

X1.1 Data:
X1.1.1 Corrosion Current—27.0 μA.
X1.1.2 Specimen Size—round anode area exposed.
X1.1.3 Diameter—1.30 cm.
X1.2 Calculation—See Eq (1) in text:

\[ i_{cor} = \frac{27.0}{(1.30)^2 \pi} = \frac{27.0}{1.32} = 20.3 \text{ μA/cm}^2 \]

X2. SAMPLE CALCULATION—ALLOY EQUIVALENT WEIGHT

X2.1 Data:
X2.1.1 Alloy—UNS S31600, actual composition not available.
X2.1.2 Corrosion Potential—300 mV versus SCE in sulfuric acid.
X2.2 Assumptions:
REFERENCES


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