**Corrocal—A computer program for corrosion current density determinations from polarisation experiments**

R Rengesh Siva, R Prabhakar & V S Murafidharan*
Central Electrochemical Research Institute, Karaikudi, India

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One area in which computers find use is in the calculation of Corrosion current density and rate calculations. To calculate electrochemical parameters such as anodic and cathodic Tafel slopes, corrosion current density and polarisation resistance, a software has been developed using C++ language. The software would process data obtained either from a galvanostatic experiment or potentiostatic experiment. The potentials are given in millivolts and the current as microamperes as input. The developed software would find: a) Corrosion currents by anodic and cathodic Tafel line extrapolations, b) corrosion rates expressed as mpy, c) Cathodic and Anodic Tafel Slopes, d) Corrosion currents by Stern-Geary method, e) Corrosion currents by Barnett’s method, f) Corrosion currents by Oldham and Mansfield’s method. Details of the Corrocal and its applications to various systems are presented.

Implementing computers is an organisational necessity today, especially for those scientists who have set their sights on global researches. Computers in scenario hasn’t happened yet, the day isn’t far especially for the applications in the tedious and repetitive field of Electrochemistry and Corrosion\(^1\). An earlier program calculated corrosion rates from sets of data such as (i) resistance data probe, (ii) weight loss coupon, (iii) ion count and (iv) linear polarization resistance method. Another similar short program calculated corrosion rates and electrochemical parameters from polarisation data\(^2\) from a variety of corroding systems. The “BETACRUNCH” program eliminated the cumbersome and often inaccurate, linear polarisation and Tafel extrapolation techniques. Another program analysed the polarisation data in the vicinity of the corrosion potential\(^3\) and used the Gauss-Newton method to generate a new set of parameter estimates and the process was repeated until the nonlinear residual error failed to change by more than a present value. Mansfield\(^4\) developed "CORFIT" which analysed the polarisation resistance in the Pre-Tafel region. Since it only requires the determination of a polarisation curve and resulted in the values of all corrosion parameters with their errors.

The above mentioned and similar programs were written in "ancient" languages and not compatible to the present day computers. Hence a software has been developed to process current and potential data obtained either from galvanostatic or potentiostatic measurements to determine kinetic and mechanistic parameters using C++ language.

**Theory**

Wagner and Traud\(^5\) proposed the concept of mixed potential theory which postulated that the net corrosion reaction is the result of two or more partial electrochemical reactions which are in principle independent of each other. The interaction between oxidation and reduction reactions occurring on corroding metals can be described on the basis of the mixed potential theory using the relationships between current and potential\(^6\).\(^7\).

For the pair of electrochemical reactions,

\[ R_1 \leftrightarrow OX_1 + Z_1e \]  
\[ OX_2 + Z_2e \leftrightarrow R_2 \]

which occur concurrently, the relationship between current \(I\) and potential \(\varepsilon\) can be written as,

\[ I_1 = I_{10} + I_{1e} = I_{10} [\exp((\varepsilon - \varepsilon_{01})/b') - \exp((\varepsilon - \varepsilon_{01})/b)] \]  
\[ I_2 = I_{20} + I_{2e} = I_{20} [\exp((\varepsilon - \varepsilon_{02})/b') - \exp((\varepsilon - \varepsilon_{02})/b)] \]

The above equations have a characteristic reversible potential \(\varepsilon_{0}\) and an exchange current density \(I_{0}\). The constants depend on the reaction mechanism. The

\*For Correspondence: (Email: varagur@yahoo.com)
partial currents \( I_{fa} \) and \( I_{fc} \) relate to the forward and backward reaction rates while \( I_{2a} \) and \( I_{2c} \) relate to Eq. (2).

At corrosion potential \( E_{corr} \), the external current, \( I=0 \),

\[
I_{fa}(E_{corr}) = I_{2a} \quad (E_{corr}) = I_{corr} \quad \ldots (5)
\]

Where \( I_{corr} \) is the corrosion current.

\[
I_{corr} = I_{a1} \exp((E_{corr} - E_{a1})/b'_{1a}) = I_{a2} \exp((-E_{corr} - E_{a2})/b'_{2a}) \quad \ldots (6)
\]

\[
I = I_{corr} [\exp((E-E_{corr})/b'_{1a})-\exp(-(E-E_{corr})/b'_{2a})] \quad \ldots (7)
\]

Differentiation of the above equation w.r.t \( E \) gives \( \delta I/\delta E \)

\[
\delta I/\delta E_{corr} = I_{corr} (1/b'_{1a} + 1/b'_{2a}) \quad \ldots (9)
\]

The Eq. (9) shows that the \( I_{corr} \) can be calculated from

- the measured slope of a \( I-E \) plot at \( E_{corr} \) provided the
  constants \( b'_{1a} \) and \( b'_{2a} \) are known. Since these
  constants are related to the \( b_a \) and \( b_c \) by

\[
b_a = 2.303 b'_{1a} = 5e / 5 \log I_{a1} \quad \ldots (10)
\]

\[
b_c = 2.303 b'_{1c} = 5e / 5 \log I_{c2} \quad \ldots (11)
\]

\[
(\delta I/\delta E)_{corr} = I_{corr} (2.303 (b_a + b_c) / b_a b_c) \quad \ldots (12)
\]

This "polarisation conductance" is directly

- proportional to \( I_{corr} \), Bonhoeffer and Jena\(^{11}\) and
  Stern\(^{12,13}\) preferred \( (\delta I/\delta E) \) and christened the term
  polarisation resistance \( R_p \).

Therefore, \( I_{corr} = B / R_p \) \quad \ldots (13)

The constant \( B \) has to be determined in an independent experiment or by

- graphical technique or computer analysis\(^{14}\). It was pointed in the
  original discussion of the Stern-Geary method\(^{15}\), \( \Delta E/\Delta I = R'_p \)
depends heavily on the judgement which an investigator uses to determine the extent of the linear polarisation curve. In order to assess the potential region within which a polarisation curve is "linear within a given error", the error was calculated.

The maximum error in potential was described as

\[
e = b(2.303 \times 0.48) \log I/I_{corr} \quad \ldots (14)
\]

for \( b_a = b_c = b \).

Barnatt\(^{16}\) in his "linear corrosion kinetics" predicted a range of linearity up to 60mV within the error. He also proposed a three-point method for the study of electrode reaction mechanisms. Three potentiostatic pulses \( \Delta E_1, 2\Delta E_1 \) and \( -2\Delta E_1, -2\Delta E_1 \) and \( 2\Delta E \) are applied. The resulting currents are measured and substituted in a system of simple equations from which the corrosion current density and the Tafel slopes are obtained. Oldham and Mansfield (loc. cit) described a graphical method, which does not require a prior knowledge of the Tafel slopes. It involved the measurements in the vicinity of \( E_{corr} \), changes in the test metal surface due to the measurement process are avoided.

**Program**

The program to process data is written in C++ language\(^{17}\). Fig. 1 presents the flow chart.

The program would display

- \( E-I \) curves
- \( E - \log I \) curves
- Over Potential – \( \log I \) curves

and also determine

- Corrosion currents by Anodic and Cathodic Tafel Line Extrapolations
- Corrosion rates expressed as mpy.
- Anodic and Cathodic Tafel Slopes
- Corrosion currents by Stern – Geary Method
- Corrosion currents by Barnatt’s Three-point Method.
- Corrosion currents by Oldham and Mansfeld Method.

**Example 1**

**Polarisation Data on the corrosion of Carbon Steel in 1.0 N Sulphuric Acid**\(^{18}\)

<table>
<thead>
<tr>
<th>Voltage,mV</th>
<th>Current,microAmps</th>
</tr>
</thead>
<tbody>
<tr>
<td>-515</td>
<td>200</td>
</tr>
<tr>
<td>-520</td>
<td>800</td>
</tr>
<tr>
<td>-525</td>
<td>1000</td>
</tr>
</tbody>
</table>
Figs 2, 3 and 4 present the potential-current, potential-log current and overpotential-log current curves for Carbon Steel in 1.0 N sulphuric acid solution respectively.

**Fig. 1**—Flowchart for Corrosion Program.

**Fig. 2**—Potential-Current curves for the corrosion of Carbon Steel in 1N Sulphuric Acid.

**Fig. 3**—Potential-log Current curves for the corrosion of Carbon Steel in 1N Sulphuric Acid.

**Fig. 4**—Over Potential-log Current curves for the corrosion of Carbon Steel in 1N Sulphuric Acid.
The results are displayed as shown below:

Anodic Tafel Slope (40-80mv) = 30.298212
Anodic Tafel Slope (80-125mv) = 42.409309
Cathodic Tafel Slope (40-80mv) = -41.703735
Cathodic Tafel Slope (80-125mv) = -45.970024

\[ I_{corr}(40-80\text{mv}) = 763.600952 \text{ micro Amps} \]
\[ I_{corr}(80-125\text{mv}) = 422.435993 \text{ micro Amps} \]

Cathodic corrosion rate(40-80mv) = 142.652988 mpy
Cathodic corrosion rate(80-125mv) = 580.844434 mpy
Anodic corrosion rate(40-80mv) = 346.812606 mpy
Anodic corrosion rate(80-125mv) = 853.560409 mpy

**STERN-GEARY METHOD**

<table>
<thead>
<tr>
<th>Charge Transfer Resistance</th>
<th>20.581085 ohms</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_{corr} )</td>
<td>2.340349 micro amps</td>
</tr>
</tbody>
</table>

**BARNATT-THREE POINT-TECHNIQUE**

\[ I_{corr} = 3014.159668 \text{ micro Amps} \]

Anodic Tafel Slope = 163.33168 mpy
Cathodic Tafel Slope = 22.088314 mpy

**OLDHAM MANSFELD TECHNIQUE**

\( I_{corr} = 2.903709 \text{ micro amps} \)

**Example 2**

Polarisation data on the corrosion of 90/10 cupronickel alloy in 0.05M sodium chloride solutions

<table>
<thead>
<tr>
<th>Voltage (mV)</th>
<th>Current (microAmps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-70</td>
<td>3330</td>
</tr>
<tr>
<td>-60</td>
<td>3040</td>
</tr>
<tr>
<td>-50</td>
<td>2760</td>
</tr>
<tr>
<td>-40</td>
<td>2490</td>
</tr>
<tr>
<td>-30</td>
<td>2230</td>
</tr>
<tr>
<td>-20</td>
<td>1940</td>
</tr>
<tr>
<td>-10</td>
<td>1640</td>
</tr>
<tr>
<td>0</td>
<td>1400</td>
</tr>
<tr>
<td>10</td>
<td>1120</td>
</tr>
<tr>
<td>20</td>
<td>860</td>
</tr>
<tr>
<td>30</td>
<td>600</td>
</tr>
<tr>
<td>40</td>
<td>330</td>
</tr>
<tr>
<td>50</td>
<td>110</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>70</td>
<td>150</td>
</tr>
<tr>
<td>80</td>
<td>350</td>
</tr>
</tbody>
</table>

Figs 5, 6 and 7 present the potential-current, potential-
Log Current and OverPotential-Log Current curves for 90/10 cupronickel in 0.05 M sodium chloride solutions respectively.

**Discussions**

Tables 1 and 2 present the comparison of the values obtained from Corrocal and the reported values for the corrosion of carbon steel in 1.0 N sulphuric acid.
Fig. 5—Potential-Current curves for the corrosion of 90/10 Cupronickel Alloy in 0.05M Sodium chloride solutions.

Fig. 6—Potential-log Current curves for the corrosion of 90/10 Cupronickel Alloy in 0.05M Sodium chloride solutions.

Tables 3 and 4 present the comparison of the values obtained from Corrocal and the reported values for the corrosion of 90/10 cupronickel in 0.5M sodium chloride solutions.

Sources of Errors:

It was found that in deriving Eq. (3):

(a) The Charge Transfer kinetics can be adequately described with the Butler-Volmer equation.

(b) The adsorption of any species on the surface is potential dependent.

(c) The reactions are under kinetic control and the effect of mass transport is negligible.

(d) The double layer effect of electrode kinetics is negligible.

(e) The uncompensated solution resistance between the metal and the reference electrode is negligible.

(f) The rate of the reverse reactions of the anodic and cathodic partial reactions is negligible.

(g) Only one cathodic reaction and only one anodic reaction take place during the corrosion process.

(h) The corrosion is "Uniform" over the whole surface of the specimen, i.e., the anodic and cathodic current densities are uniform and equal and can be calculated on the basis of the full surface area of the specimen.

(i) The products of the anodic reaction are soluble in the solution at least to the extent that no product film forms on the surface.

(j) The system is time invariant i.e., all system parameters are constant with time of measurement.

Error sources and the calculation methods

Error of the measurement occurs whenever one of the simplifying assumptions is not justified. The errors defined as 

\[ 100 \frac{|t_{\text{meas}} - t_{\text{true}}|}{t_{\text{true}}} \] 

are
generally a function of several parameters characterizing both the corroding system and the measuring technique. The simulation is typically carried out for a practical range of all parameters. The three-point technique is typically evaluated with several data sets in the polarisation range of ±30 mV. The curve fitting technique is typically evaluated with 61 points in the range of ±30 mV.

Of the four electrochemical techniques discussed, the errors of the Tafel Plot technique have been the least evaluated. Consequently, it is difficult to compare this technique to the others. The errors of the polarization resistance technique have been very thoroughly and quantitatively evaluated and the reported errors are the smallest among the four techniques for all categories. The errors of the three-point technique are generally somewhat larger than those of the polarization technique. The errors in curve fitting technique have been reported to be approximately the same as those of the three-point technique. In contrast to the polarization resistance technique numerical values for the appropriate correction terms are not needed, since they can be treated as unknowns in the curve fitting.

### Table 2—Comparison of the values obtained by the linear polarisation obtained—Corrocal and the earlier reported values

<table>
<thead>
<tr>
<th>Method</th>
<th>Corrocal</th>
<th>Reported value/ calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stern – Geary</td>
<td>2.34</td>
<td>3</td>
</tr>
<tr>
<td>Barnatt’s method</td>
<td>3014</td>
<td></td>
</tr>
<tr>
<td>Oldham &amp; Mansfield</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3—Comparison of the values obtained by the Tafel extrapolation obtained—Corrocal and the earlier reported values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Corrocal</th>
<th>Reported value/ calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion current density (anodic)</td>
<td>580</td>
<td>500</td>
</tr>
<tr>
<td>Corrosion current density (cathodic)</td>
<td>879</td>
<td>500</td>
</tr>
<tr>
<td>Anodic Tafel slope</td>
<td>62 &amp; 93</td>
<td>60</td>
</tr>
<tr>
<td>Cathodic Tafel slope</td>
<td>42 &amp; 100</td>
<td>40</td>
</tr>
</tbody>
</table>

### Table 4—Comparison of the values obtained by the linear polarisation obtained—Corrocal and the earlier reported values

<table>
<thead>
<tr>
<th>Method</th>
<th>Corrocal</th>
<th>Reported value/ calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stern – Geary</td>
<td>1032</td>
<td>500</td>
</tr>
<tr>
<td>Barnatt’s method</td>
<td>1145</td>
<td></td>
</tr>
<tr>
<td>Oldham &amp; Mansfield</td>
<td>3.08</td>
<td></td>
</tr>
</tbody>
</table>

### References