

Electrochemical Techniques for Corrosion Measurement



Why Use Electrochemical Techniques for Corrosion Measurement?

- Corrosion is an electrochemical process.
- A broad range of electrochemical techniques have been developed specifically for corrosion measurement.
- Electrochemical techniques are fast.
- Electrochemical techniques are sensitive.
- Nevertheless, there are some Corrosion Engineers who don't use electrochemical techniques...probably because they don't understand them.

Electrochemical Techniques and Corrosion

- Corrosion is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. (*ASTM G 15: Standard Terminology Related to Corrosion.*)

- Corrosion is caused by a redox reaction.



- Fundamentally, corrosion is an electrochemical process, so using electrochemical techniques is obvious.

Electrochemical Techniques are Fast!

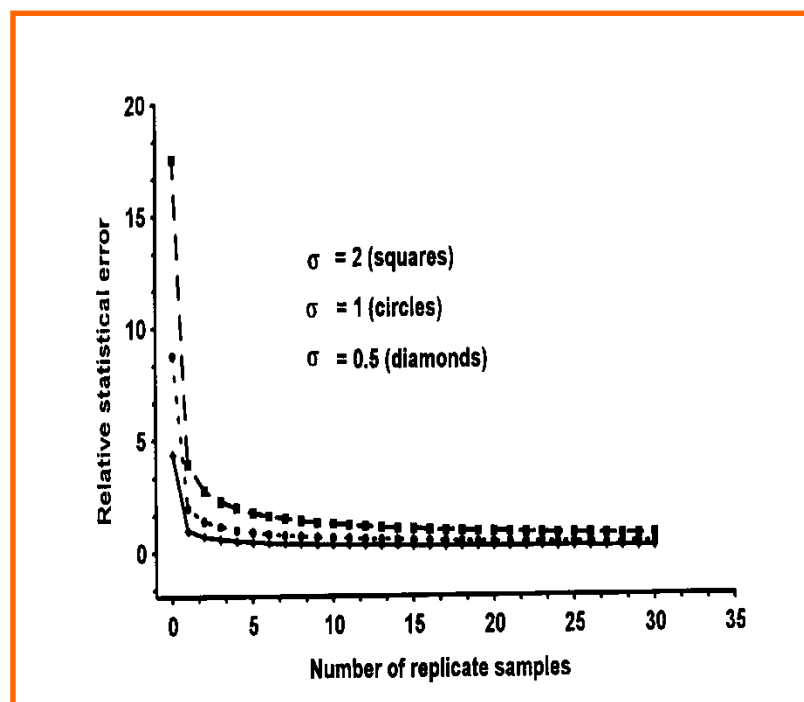
- Corrosion is an inherently slow process. A typical corrosion rate is 10 milli-inches per year (mpy) or 0.254 millimeters per year (mmpy).
- The “best” corrosion tests are weight loss measurements after exposure. However, they are very slow (days, weeks, or months).
- Electrochemical instruments **polarize** the sample to accelerate the corrosion process and make the measurement in minutes or hours. The electrochemical corrosion rate is “instantaneous”.

Electrochemical Techniques Are Sensitive!

- Electrochemical techniques can measure very low corrosion rates.
- A sample with a low corrosion rate will exhibit a low current during the electrochemical experiment. Corrosion scientists may use “corrosion rate” and “current” interchangeably.
- The best measure of a specific potentiostat’s ability to measure low corrosion rates is the lowest current range.

Precision of Electrochemical Corrosion Rate Measurement

- “Corrosion is a messy business!”
-Famous Corrosion Scientist
- Corrosion is a surface process involving a large number of variables that are difficult to understand and/or control.
- A Relative Standard Deviation of 15% is Excellent!
- A minimum of 3 replicates is recommended for corrosion measurements. (“Increase Your Confidence in Corrosion Test Data”, Steve Tait, MATERIALS PERFORMANCE, March 2001)



Comments on the Precision of Electrochemical Corrosion Measurements

- Electrochemical instrumentation is very accurate (<0.5% error)
- High purity Fe polished to a mirror finish gives great results!
- When corrosion occurs, anodic and cathodic events are occurring simultaneously on the surface of the sample.
- The surface of a metal sample is *not* homogeneous. In fact, it may be *very* heterogeneous.
- The anodic and cathodic sites may “turn on” or “turn off” as the local environment changes.
- Electrolyte impurities can also affect the results.
- The corrosion environment is very dynamic and the result is...poor precision



Word to the Corrosion-Wise

- The experts advise corrosion scientists to use as much experimental data as possible to characterize their corrosion system.
- This means that every electrochemical technique should be employed: LPR, Tafel Plots, EIS, EFM (only from Gamry), and maybe even...gasp...Electrochemical Noise!
- It also means that weight loss measurements and solution measurements should be used.

I. The Open Circuit Potential

- The Open Circuit Potential, E_{OC} , is the potential difference between the metal Working Electrode and the Reference Electrode when immersed in the electrolyte.
- E_{OC} is a mixed potential whose value is determined by the potentials of the two or more half-reactions of the electrochemical system, *not* by the potentiostat!
- E_{OC} is where corrosion occurs “in service”. It’s very important!
- E_{OC} is the starting point for virtually all electrochemical corrosion experiments. A stable E_{OC} is taken to indicate that the corroding system has reach a “steady state” and the experiment may begin. This may require minutes to days. If E_{OC} has not stabilized, do not begin the experiment!

II. The Open Circuit Potential

- No measurable current is flowing at E_{OC} .
- An applied voltage that is positive of E_{OC} will accelerate the oxidation (corrosion) reaction. An applied voltage that is negative of E_{OC} will accelerate the reduction reaction of some species in solution.
- The terms " E_{OC} " and " E_{corr} " (corrosion potential) are often used interchangeably. But sometimes " E_{corr} " is used to indicate the zero current point during the experiment.
- The value of the E_{OC} is not particularly useful as a predictive tool.

Electrode Area

- In a corrosion experiment, the area of the electrode must be known precisely.
- Current is always expressed as current density (A/cm^2).
- At a given potential, a large electrode will carry more current than a small electrode.
- Mounting an oddly-shaped sample can be problematic.
- Note that some corrosion experiments (material selection) allow the user to use a sample geometry of his choice. In other cases, the geometry is fixed.

Electrochemical Corrosion Applications

- Quantitative Corrosion Rate Measurements
- Inhibitor Evaluation
- Qualitative Passivity Tendencies
- Pitting and Crevice Corrosion
- Galvanic Corrosion
- Intergranular Corrosion (Sensitization)
- Stress Corrosion Cracking
- Coating Evaluation (EIS)

Mixed Potential Theory

- All electrochemical cells must obey the principle of charge conservation.
- The total rate of oxidation must equal the total rate of reduction.
- Or, the sum of the anodic oxidation currents must equal the sum of the cathodic reduction currents.
- We must have two or more half-reactions.
- Wagner and Traud, 1938

Butler-Volmer Equation

The Butler-Volmer equation describes the relationship between the potential and the current (kinetics) in a mixed potential system.

$$I = I_a + I_c = I_{\text{CORR}}(e^{(2.3(E-E_{\text{oc}})/\beta_a)} - e^{(-2.3(E-E_{\text{oc}})/\beta_c)})$$

Where:

I = cell current (A)

I_{CORR} = corrosion current (A)

E = applied potential (V)

E_{oc} = corrosion potential (V)

β_a = anodic Tafel constant (V/decade)

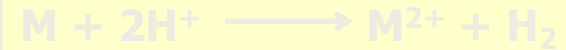
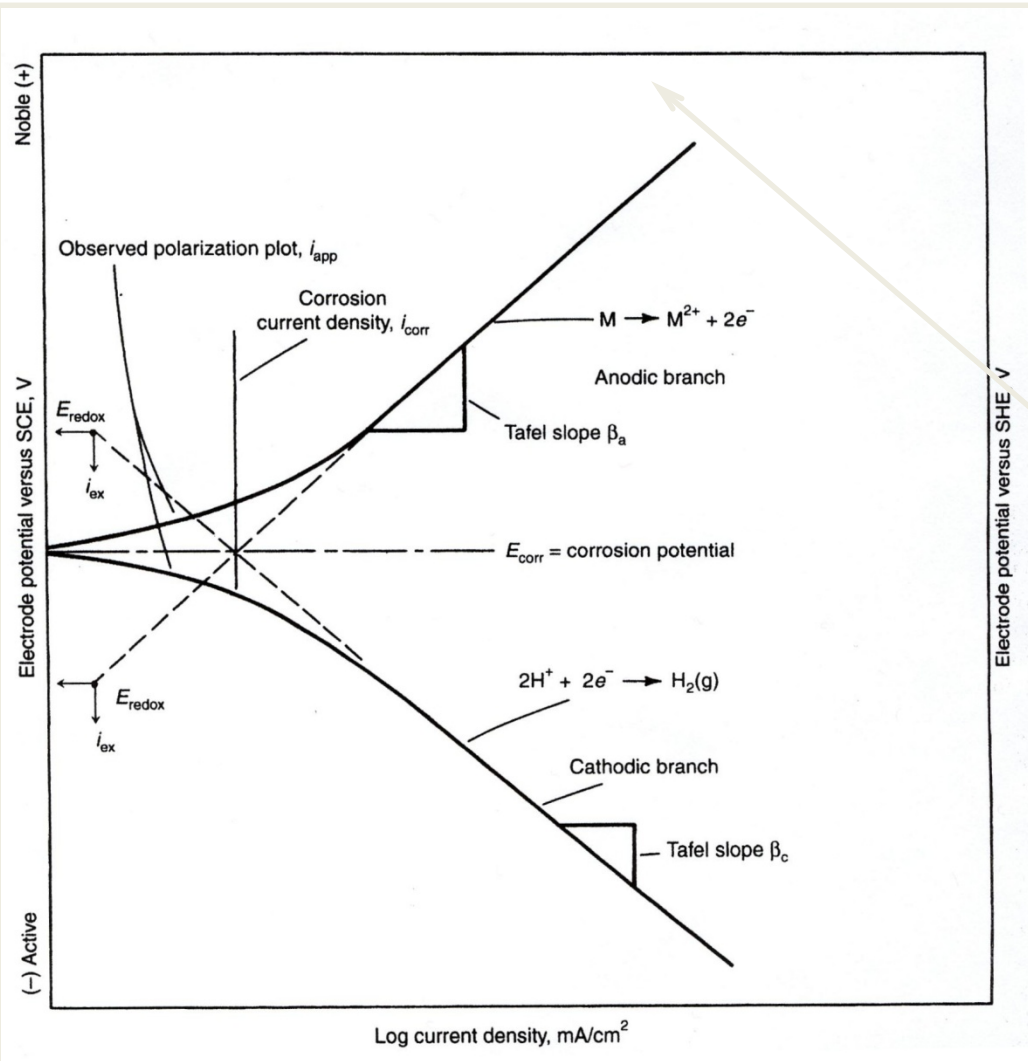
β_c = cathodic Tafel constant (V/decade)



Rate of anodic reaction

Rate of cathodic reaction

Graphical Representation of the Butler-Volmer Relationship between Potential and Current in a Mixed Potential System



An experiment like this is called a "Tafel Plot" and is relatively common in today's corrosion laboratory.

Experimental result from the corrosion measurement system.

J. Scully & R. Kelly, ASM Handbook, Volume 13A, 2003

Butler-Volmer Equation

The Butler-Volmer Equation only holds if:

- The rate is charge-transfer controlled (aka, activation-controlled, electron-transfer controlled). Complicating factors are:
 - Passivity
 - Diffusion-controlled (concentration polarization)
 - Adsorption
- Only one reduction and one oxidation reaction are occurring (first order)
 - Alloys can be complicated
- If the Butler-Volmer equation doesn't hold, then the electrochemical response will not be "classic" and must be interpreted in terms of the chemistry of the system.

Kinetic and Diffusion Considerations

Activation Control

- Activation control is caused by the rate of electron transfer of a faradaic reaction.
- The goal of the electrochemical experiment is to determine this rate.
- Sometimes called “Activation Polarization”

Diffusion Control

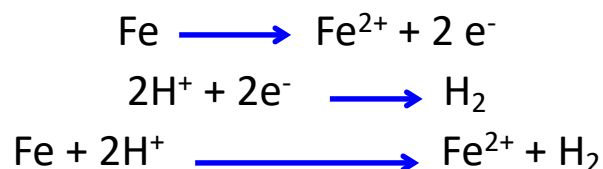
- At high rates of reaction, the double layer is depleted of electroactive species.
- The reaction rate is limited by transport to the electrode surface.
- For corrosion, mass transport is significant primarily for cathodic reduction processes.
- Sometimes called “Concentration Polarization”

Quantitative Corrosion Rate Measurements

- Polarization Resistance and Tafel Curves are experiments designed to measure the rate of uniform corrosion in units of penetration (mmpy or mpy).
- Designed to measure i_{corr} .
- Provides a “snapshot” of the corrosion rate.
- Should be performed when the system has reached “steady state” (stable E_{oc}).

Corrosion Current, I_{corr}

- At E_{OC} , $i_{\text{meas}} = 0$, but we know that corrosion is occurring.



- We need to somehow measure the current due to the anodic or cathodic half-reaction. This current is called the Corrosion Current, I_{CORR} .
- The goal of the Polarization Resistance experiment is to determine the Corrosion Current.
- From the Corrosion Current, we can calculate corrosion rate.
- Don't forget the electrode area! i_{CORR} is usually current (A) and I_{CORR} is usually current density (A/cm^2).

Experimental Procedure for Polarization Resistance

1. Measure E_{OC} and allow to stabilize.
2. Apply initial E that is 10 mV negative of E_{OC} .
3. Scan at a slow scan rate (~ 0.125 mV/s) to a final E that is 10 mV positive of E_{OC} .
4. Measure current, plot E (Y-axis) versus I (X-axis).
5. Measure slope, which has units of resistance ($E/i = R$).
6. Convert R_p to i_{corr}
7. Convert i_{corr} to Corrosion Rate.
8. This procedure works for every corrosion system!

Run a Polarization Resistance Experiment and Measure R_p

Calculation of i_{corr} from R_p

Stern-Geary Equation:

$$R_p = \Delta E / \Delta i = \beta_a \beta_c / 2.3 i_{\text{corr}} (\beta_a + \beta_c)$$

R_p = Slope at the origin of the Polarization Resistance Plot in ohms

i_{corr} = corrosion current, Amperes

β_a, β_c = Tafel Constants from a Tafel Curve, volts/current decade.

This calculation is done automatically in the Gamry Echem Analyst

Calculation of Corrosion Rate from i_{corr}

Faraday's Law

$$Q = nFm/A = it$$

Q = coulombs (A-s/eq), n = number of electrons, F = the Faraday (96,487 coulombs), m = mass (g), A = atomic weight, i = current (A), t = time (s).

Since Equivalent Weight (EW) = A/n ,

Then $m = it(\text{EW})/F$

Corrosion Rate (g/s) = $m/t = i(\text{EW})/F$

Calculation of Corrosion Rate from i_{corr}

From the engineering standpoint, it is convenient to express Corrosion Rate in units of penetration, mpy (milli-inches per year) or mmpy (mm per year).

Divide both sides of the equation by area and density,

$$\text{Corrosion Rate (cm/s)} = i(\text{EW})/FdA$$

i/A = current density (I). After conversion of cm to inches or mm, and seconds to years,

$$\text{Corrosion Rate (mpy)} = 0.13 I_{\text{corr}}(\mu\text{A}/\text{cm}^2)(\text{EW})/d$$

$$\text{Corrosion Rate (mmpy)} = 0.00327 I_{\text{corr}}(\text{EW})/d$$

where I_{corr} is corrosion current density in $\mu\text{A}/\text{cm}^2$.

First, the Good News...Polarization Resistance Works Very Nicely for the Measurement of Corrosion Rates

- Very fast (< 5 minutes).
- In general, plots exhibit good linearity, so data interpretation is easy.
- Potential remains close to E_{OC} , so it is essentially a non-destructive technique and can be used for continuous monitoring for inhibitor evaluation.
- Described in ASTM G 59.

And Now, the Bad News...What Can Go Wrong with Polarization Resistance?

- Unstable E_{oc}
- Complications from alloys containing several electroactive metals (reduction or oxidation of more than one electroactive species)
- Use of a Scan Rate that is too fast (Step Height too high or Sampling Period too short)
- Uncompensated solution resistance
- What's the value of the Tafel Constant(s)!!!

Equivalent Weight of an Alloy

- The Equivalent Weight of an alloy is the reciprocal of the total number of equivalents of all alloying elements (Jones)
- $EW_{\text{alloy}} = 1 / N_{\text{eq}}$
- $N_{\text{eq}} = \sum f_i / (a_i / n_i) = \sum (f_i n / a)$
 f = mass fraction of element i , a = atomic weight, n = # of electrons
- Example: 304 SS is 19% Cr, 9.25% Ni, and 71.75% Fe. Equivalent weight = 25.12
- Question: do all elements in the alloy corrode at the same rate?

Scan Rates in Polarization Resistance

- If the Scan Rate is too high, errors can result due to the capacitance of the Working Electrode. The corrosion rate is usually overestimated.
- The solution? Scan rates are always slow, e.g., 0.125 mV/sec.
- EIS can be used to measure the appropriate scan rate for any system

$$\text{Scan Rate} = \Delta E \cdot \pi \cdot f$$

- At these scan rates, some experiments may take several hours. That's why you have a computer-controlled instrument!

Comments on Current Interrupt iR Compensation

- Current Interrupt for iR Compensation looks straightforward...it's not!
- The corrected curve is typically noisy.
- If $R_p > 5$ kohms, Current Interrupt won't work.
- If R_u is 50% of R_p , it won't work.
- The Interrupt Time can be adjusted by modifying the script, but it's a trial-and-error process.
- Post-experiment compensation may be a better choice in some cases.

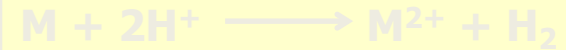
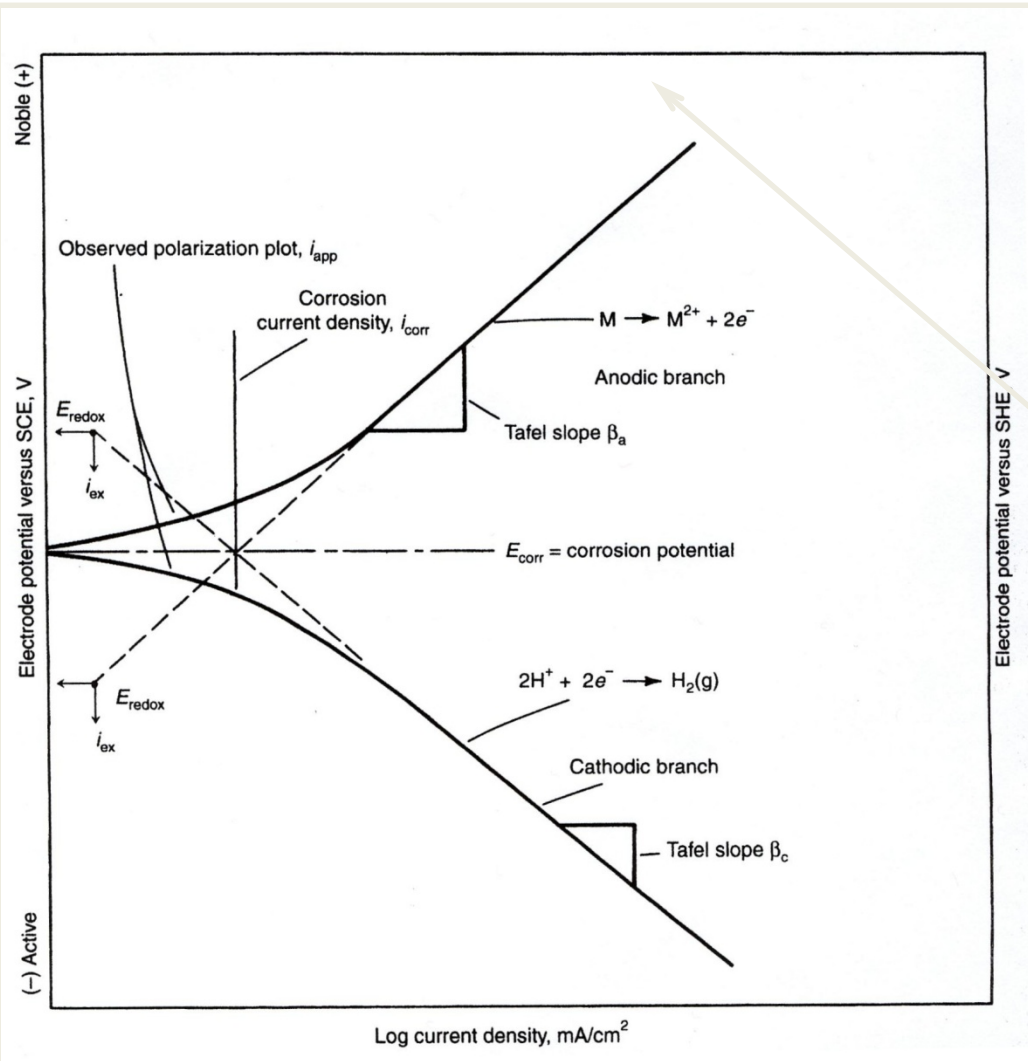
The Problem of Tafel Constants

- For best results in Polarization Resistance, the Tafel Constants are needed.
- Tafel Constants typically vary from 0.12 to 0.50 volts/decade of current.
- β_a is not expected to equal β_c .
- Using 0.12 V/decade as β_a and β_c results in a maximum error of a factor of 2.
- To measure the Tafel Constants, run a Tafel Plot.

Tafel Plot

1. Measure E_{oc} and allow to stabilize.
2. Apply initial E that is 250 mV negative of E_{oc} .
3. Scan at a slow scan rate (0.125 mV/s) to a final E that is 250 mV positive of E_{oc} .
4. Measure current, plot E (Y-axis) versus $\log I$ (X-axis).

Graphical Representation of the Butler-Volmer Relationship between Potential and Current in a Mixed Potential System



An experiment like this is called a "Tafel Plot" and is relatively common in today's corrosion laboratory.

Experimental result from the corrosion measurement system.

J. Scully & R. Kelly, ASM Handbook, Volume 13A, 2003

Corrosion Rates from Tafel Plots

- Tafel Constants are not an issue.
- Insufficient linear region is a major problem.
- Given a choice, trust the cathodic Tafel Plot, not the anodic Tafel Plot.

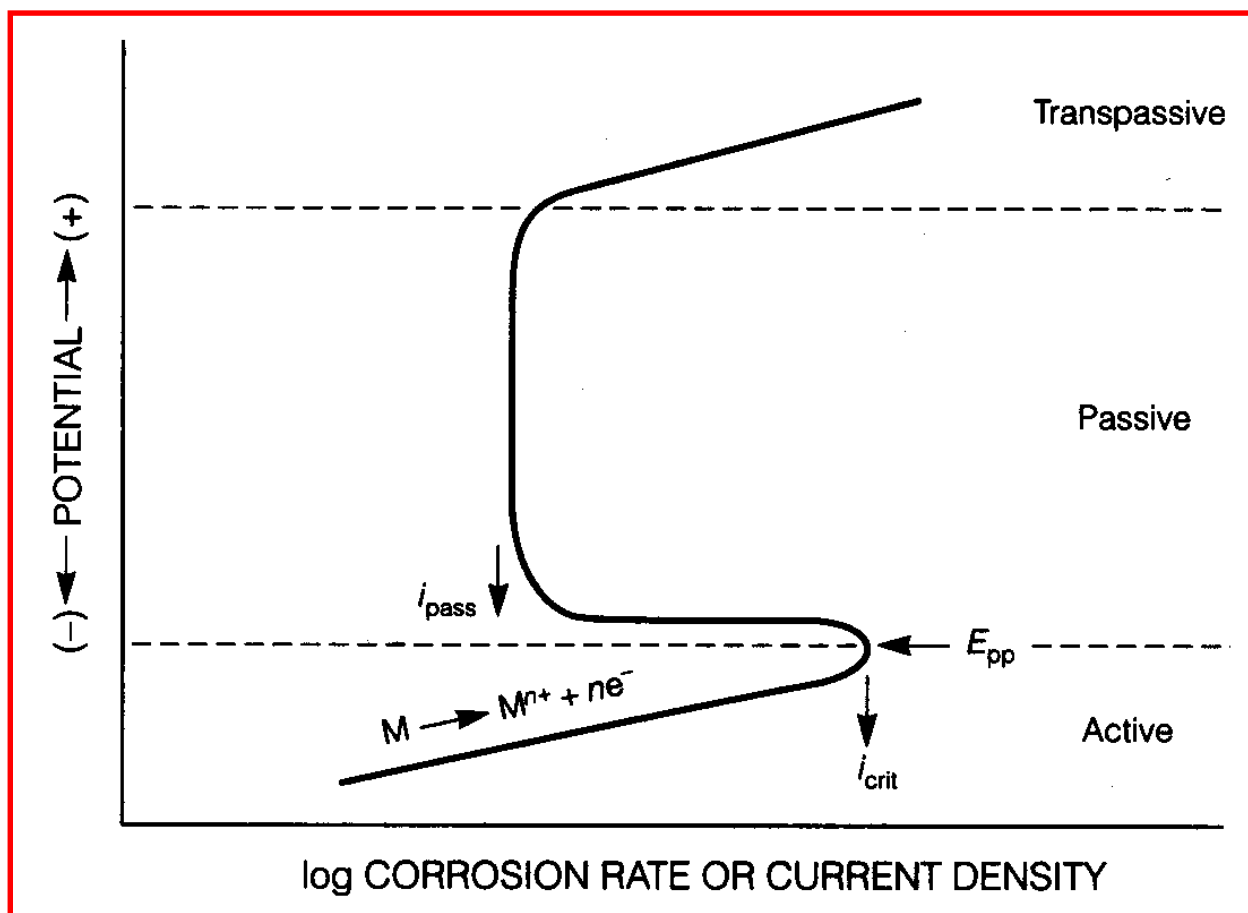
Potentiodynamic Polarization

- Potentiodynamic Plots (ASTM G 5) are controlled potential tests that allow qualitative observations on the corrosion behavior of the sample.
- A wide voltage range is scanned (1-2 V).
- The passivation characteristics of the sample can be determined.

Potentiodynamic Polarization

1. Measure E_{oc} and allow to stabilize.
2. Apply initial E that is 10 mV negative of E_{oc} .
3. Scan at a slow scan rate to a final E that is 1-1.5 V positive of E_{oc} .
4. Measure current, plot E (Y-axis) versus $\log I$ (X-axis)
5. Observe qualitative features that indicate passivity or stability.

Schematic Active-Passive Polarization Behavior

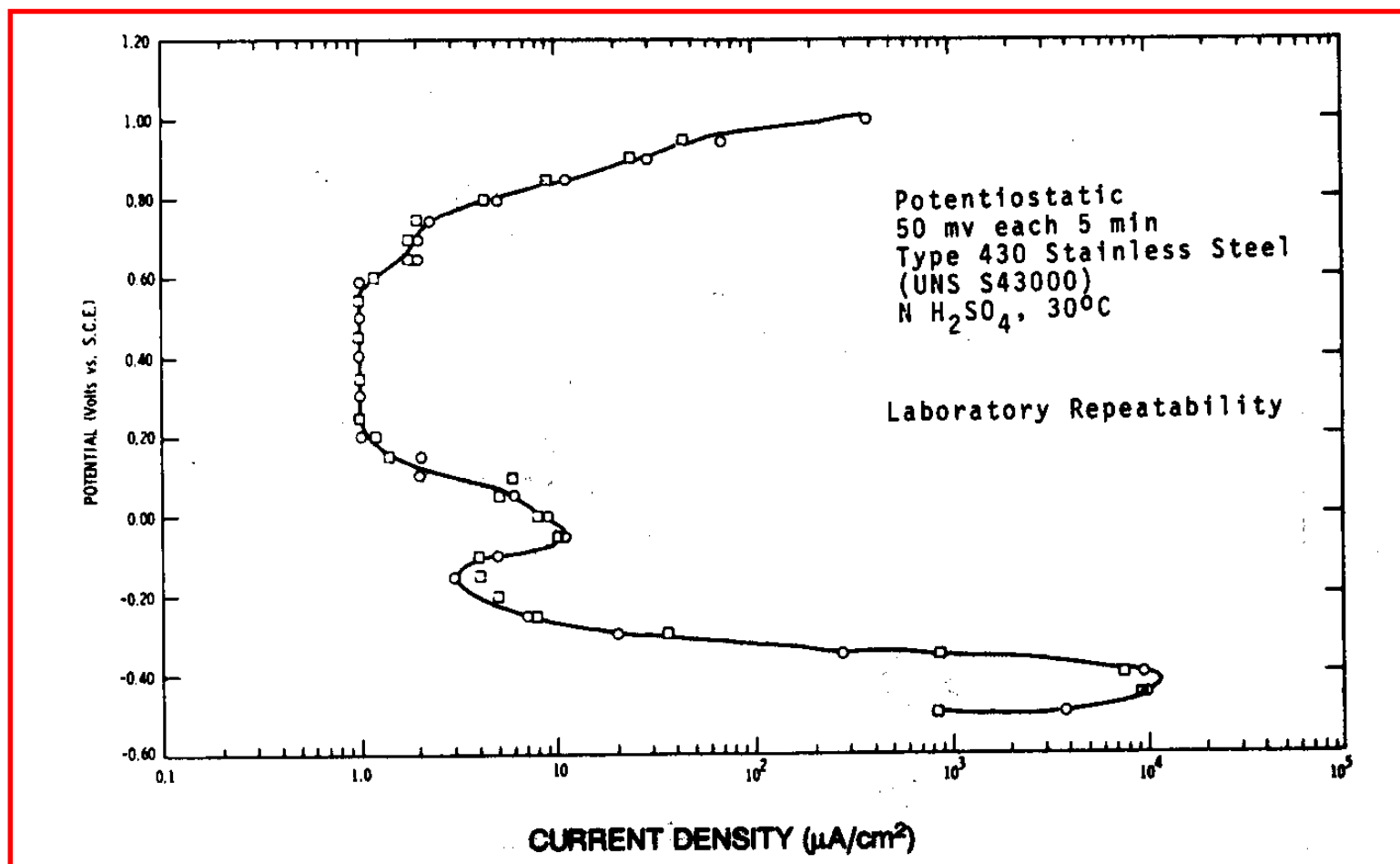


E_{pp} = Primary Passivation Potential

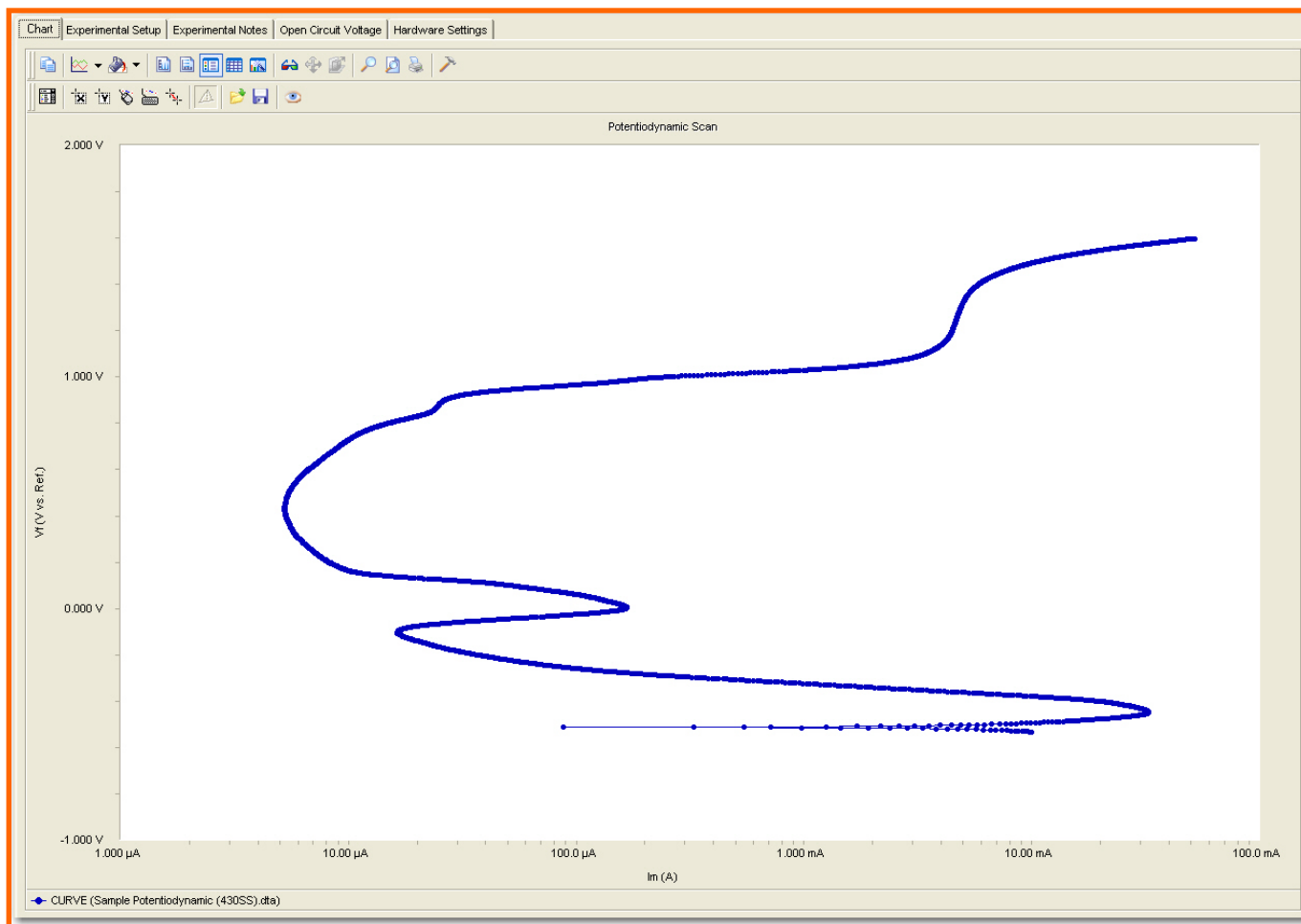
I_{crit} = Critical Current Density

I_{pass} = Passive Current Density

Potentiodynamic Polarization Curve of 430 SS in 1N H₂SO₄ from ASTM G 5*



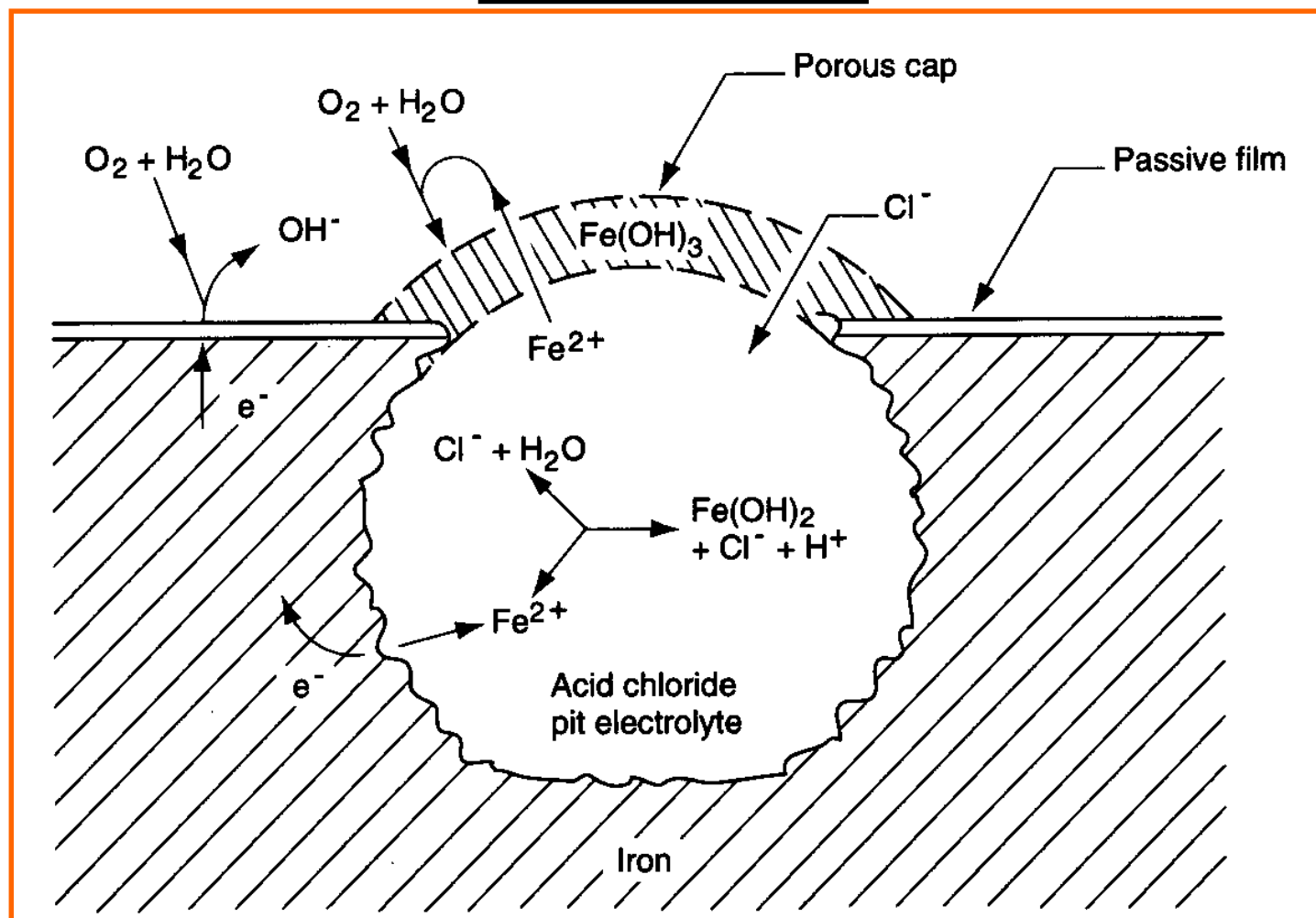
430 SS in 1 N H₂SO₄ on a Gamry System



Pitting and Crevice Corrosion

- Pitting and crevice corrosion is a very aggressive form of corrosion that is *localized* to a small area.
- Crevice corrosion is dependent on crevice geometry and dimensions.
- Localized corrosion results from a failure of the passive film...or any film (oilfield)!
- Chloride ion is the most common pitting agent.
- Pitting is probably the industry's most critical problem.
- It is not possible to measure a pitting rate! You can only say that one material is better/worse than another.

Chemical Processes in an Actively Growing Pit in Iron in NaCl



Electrochemical Tests for Pitting

- Cyclic Polarization (ASTM G 61)
- Cyclic Polarization for Medical Implants (F 2129)
- Critical Pitting Potential (ASTM F 746)
- THE Technique (ASTM G 78)
- Critical Pitting Temperature (ASTM G 150)
- These standards are on your CD.

Cyclic Polarization Experiment for Pitting Evaluation

- Described in ASTM G 61 and ASTM F 2129 for medical implants...a very important standard.
- Measure Eoc
- Scan positively until the onset of pitting is observed, signaled by a rapid increase in the current.
- At a specified current density, reverse the scan direction and scan back to Eoc.

Cyclic Polarization Plot

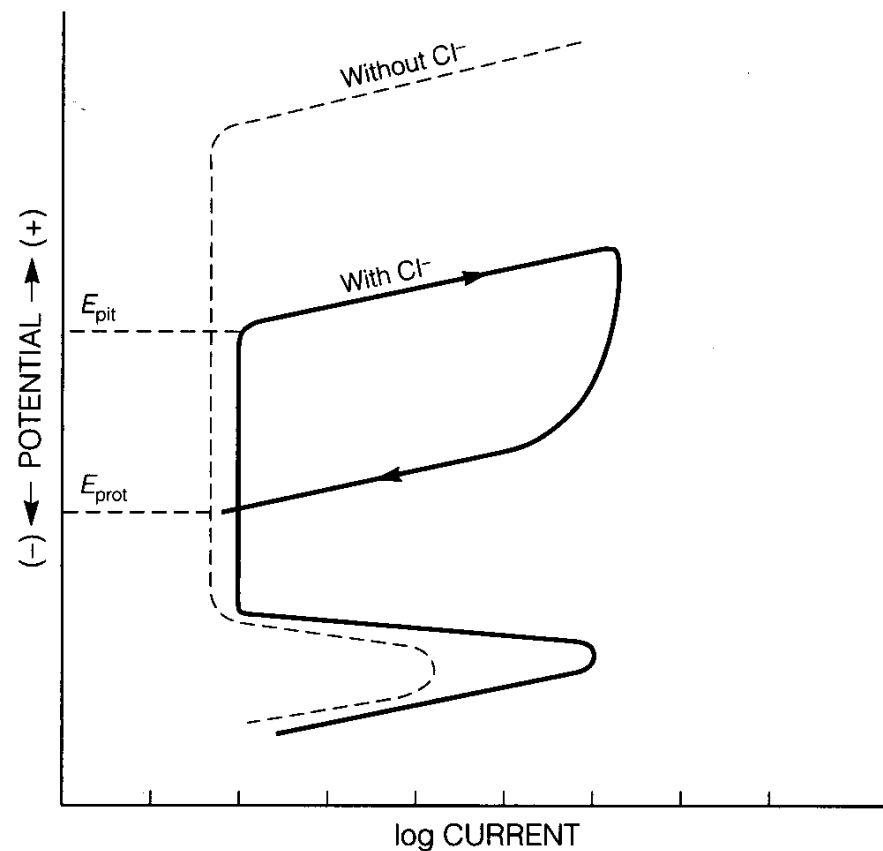
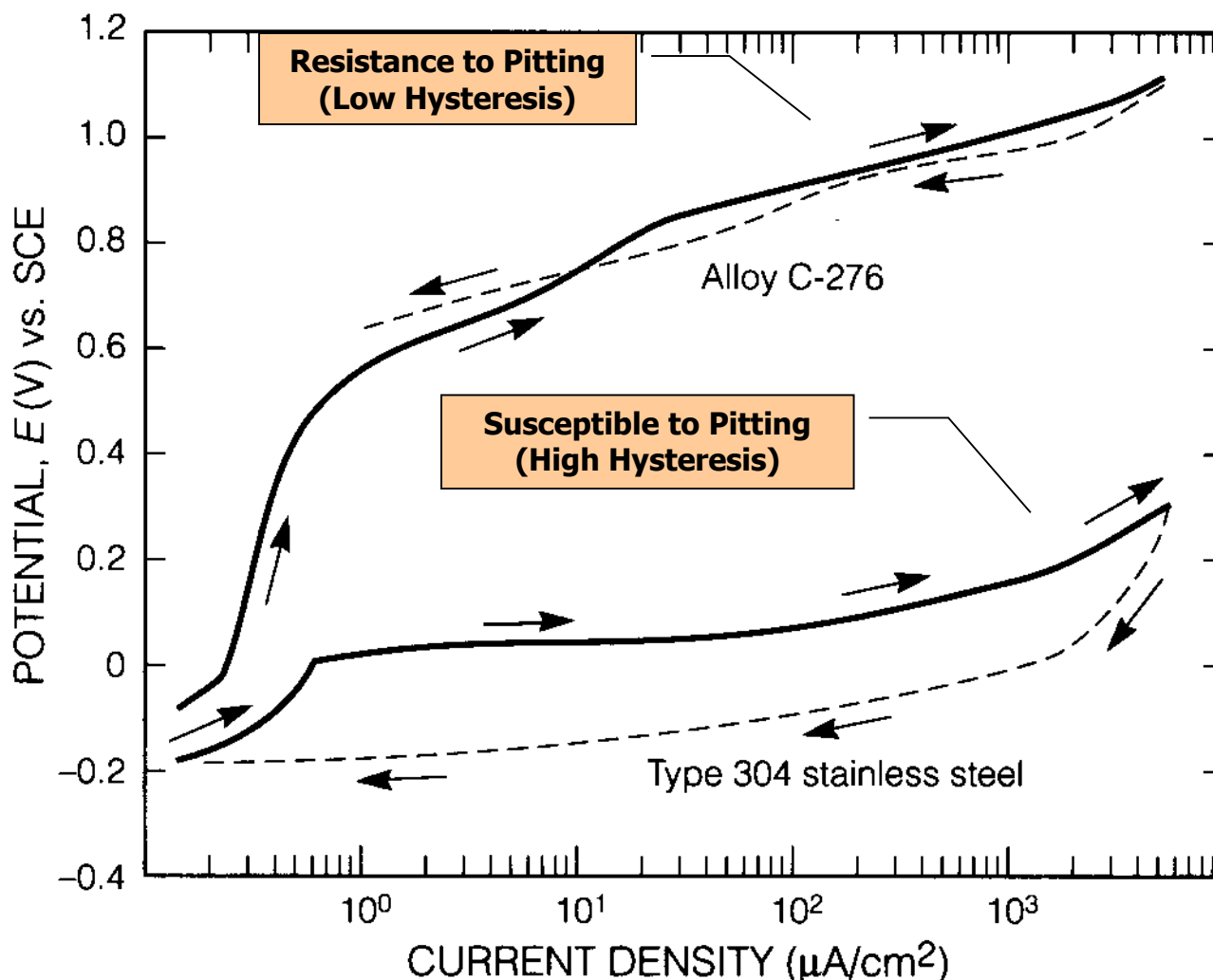


FIGURE 7.19 Cyclic polarization to give pitting, E_{pit} , and protection, E_{prot} , potentials (schematic).

Interpretation of Cyclic Polarization Plots

- The Pitting Potential (E_{pit}) is the potential at which pits are initiated.
- The Protection Potential (E_{prot}) is the potential at which the pits are re-passivated.
- Pits start to grow above E_{pit} and can continue to grow above E_{prot} .
- The most resistant material has the highest (most positive) E_{pit} and E_{prot} .
- It is not possible to quantitatively measure a pitting rate.

Cyclic Polarization Results



Critical Pitting Potential Technique

- The CPP Technique first steps into the anodic region to initiate pits, then steps “back” to re-passivate the pits. When the pits fails to re-passivate, that is the Critical Pitting Potential.
- Described in ASTM F 746 for “Pitting Corrosion of Metallic Surgical Implant Materials.”
- Gamry includes CPP in the DC105 Corrosion Techniques Software.

THE Technique

- Combination potentiostatic/galvanostatic technique to measure the repassivation of pits.
- Long test...over 12 hours.
- Developed at Lawrence Livermore National Labs for evaluation of Alloy 22 for Yucca Mountain Nuclear Depository.
- Originally proposed by Japanese researchers.
- A Gamry exclusive.

Critical Pitting Temperature

- Described in ASTM G 150.
- Start the CPT test by exposing the sample to 1M NaCl at 0° C.
- Polarize the sample at +700 mV vs. SCE (above the Pitting Potential).
- Ramp the temperature at 1°C/min, while monitoring the current.
- The CPT is defined as the temperature at which the current exceeds 100 $\mu\text{A}/\text{cm}^2$.

CPT Experimental Profile

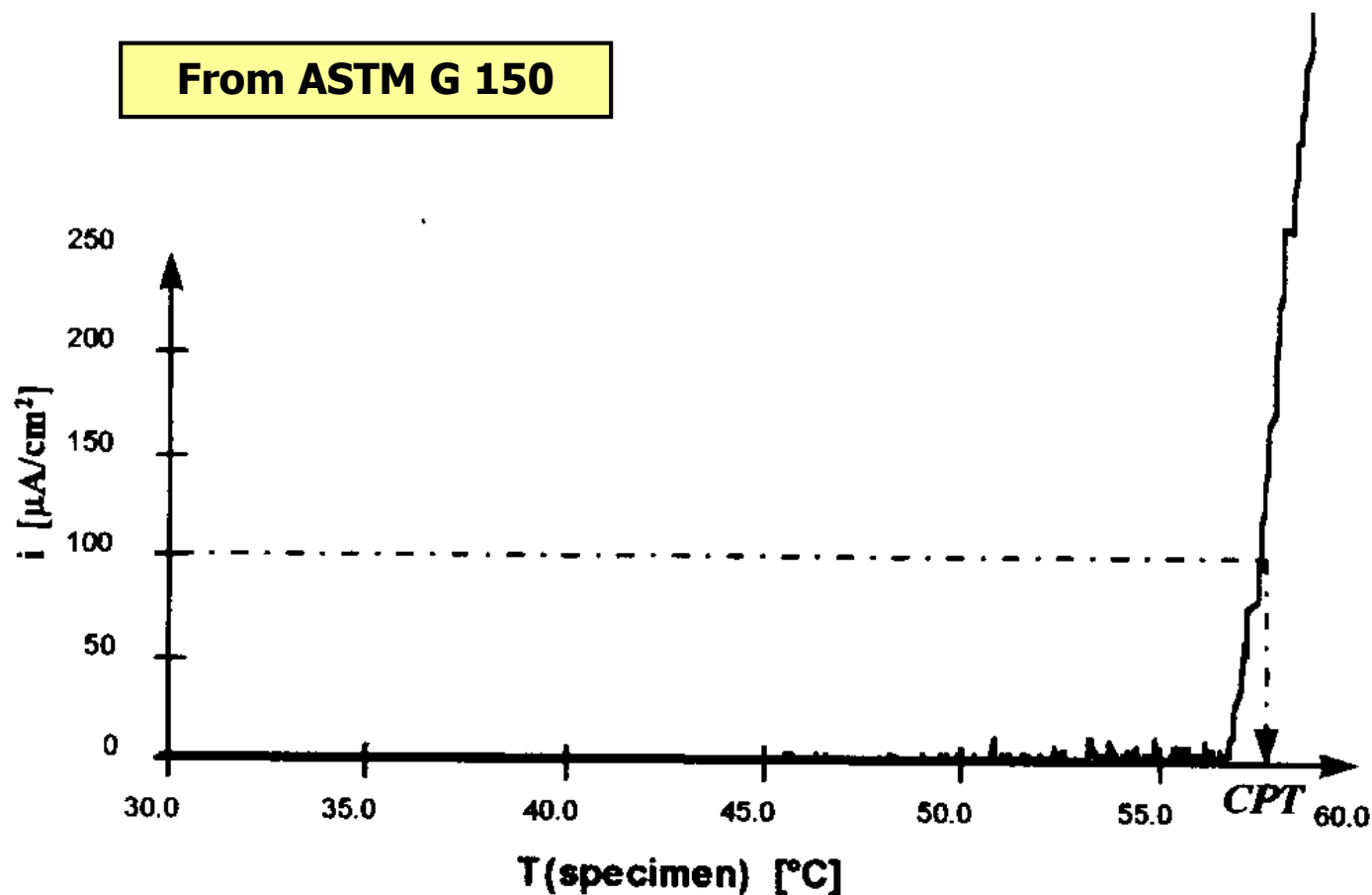


FIG. 1 Determination of CPT

Galvanic Corrosion

- Galvanic corrosion occurs when two dissimilar metals are connected electrically while both are immersed in an electrolyte.
- Only one of the two metals corrodes.
- The behavior of a metal in a galvanic couple depends upon its place in the Galvanic Series.

Galvanic Series in Seawater

The more active metal becomes the anode in the galvanic couple. The noble metal is the cathode.

The Galvanic Series is dependent upon the electrolyte.

Cathodic (noble)
↑
platinum
gold
graphite
titanium
silver
zirconium
AISI Type 316, 317 stainless steels (passive)
AISI Type 304 stainless steel (passive)
AISI Type 430 stainless steel (passive)
nickel (passive)
copper-nickel (70-30)
bronzes
copper
brasses
nickel (active)
naval brass
tin
lead
AISI Type 316, 317 stainless steels (active)
AISI Type 304 stainless steel (active)
cast iron
steel or iron
aluminum alloy 2024
cadmium
aluminum alloy 1100
zinc
magnesium and magnesium alloys
↑
Anodic (active)

Electrochemical Galvanic Corrosion Testing

- Galvanic corrosion currents are measured with a Zero Resistance Ammeter.
- Relative areas of the anode and cathode are very important. A small anode is BAD!
- Polarization curves can be used to predict galvanic corrosion behavior.

References for Electrochemical Corrosion Testing

- Principles and Prevention of Corrosion, Denny A. Jones, Prentice-Hall, Upper Saddle River, NJ 07458 (1996). ISBN 0-13-359993-0.

An excellent textbook covering all types of corrosion and corrosion testing.

- DC Electrochemical Test Methods, N. Thompson and J. Payer, NACE International, 1998, ISBN 1-877914-63-0.

An excellent tutorial that is highly recommended.

- "Polarization Resistance Method for Determination of Instantaneous Corrosion Rates", J. R. Scully, CORROSION, 56, 19-218 (2000).

An excellent up-to-date review of Polarization Resistance.

- Electrochemical Techniques in Corrosion Engineering, 1986, NACE International
36 papers. Covers the basics of the various electrochemical techniques and a wide variety of papers on the application of these techniques. Includes impedance spectroscopy.
- Corrosion Testing and Evaluation, STP 1000, Edited by R. Baboian and S. W. Dean., ASTM, 1989, ISBN 0-8031-1406-0.

30 papers covering electrochemical and non-electrochemical corrosion testing.

- An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists, 1994, W. Stephen Tait, PairODocs Publications, 2048 Saint Clair St., Racine, WI 53402-4764. E-mail: pairodocs@execpc.com.

Very basic discussion of DC and AC electrochemical techniques.