# Environmental Degradation Fundamentals

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# Outline

- Thermodynamics of Corrosion: Pourbaix Diagrams

- Corrosion Kinetics

  - Polarization Diagrams

  - Corrosion Rate and Corrosion Potential

  - Passivation

- Design Implications

# Thermodynamics

# Corrosion Cell Schematic
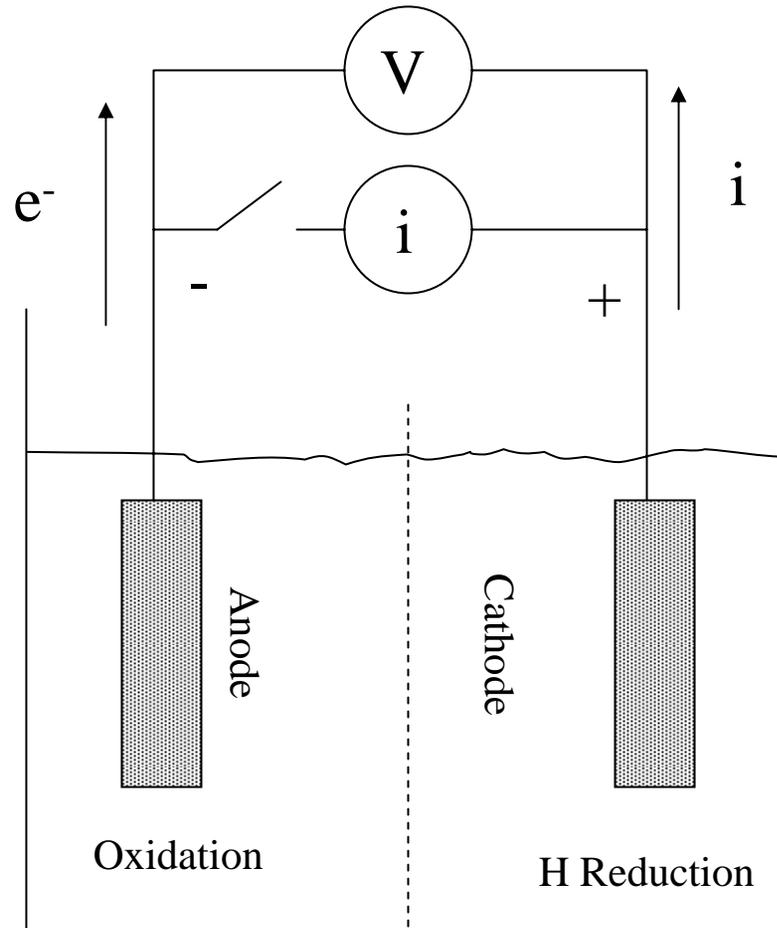
# Standard Cell
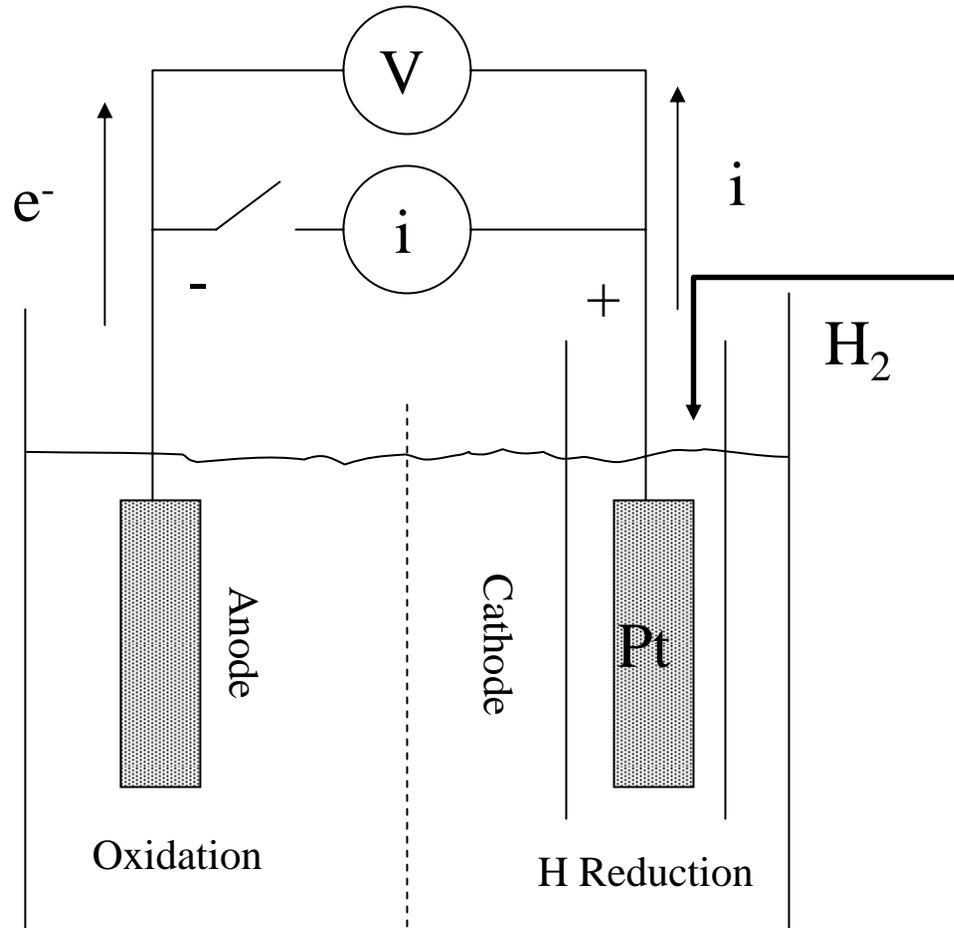


Standard Conditions
- 1 Atm
- pH = 0
- Unit Activity
- 25°C
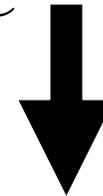
Standard Potential ($E_0$)
$$E_{0, H} = 0$$

Table of Standard Potentials for various Electrode
Reactions removed due to copyright restrictions.

Data referenced to Latimer, W. *Oxidation
Potentials*. Prentice-Hall, 1952.

# Schematic of Corrosion Reactions



Metal (M)

M$^{2+}$

H$^+$

H$^+$

e$^-$

H$^+$

H$_2$

H$^+$

e$^-$

H$^+$

H$^+$

H$^+$

Figure by MIT OCW.

$$M + H_2O \rightarrow M^{z+}_{aq} + ze^-$$

$$M + nH_2O \rightarrow MO^{n-}_n + 2nH^+ + ne^-$$

$$M + H_2O \rightarrow MO + 2H_2O + 2e^-$$

$$M^{z+}_{aq} + H_2O \rightarrow MO + H^+$$

$$2H^+ + 2e^- \rightarrow H_2$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
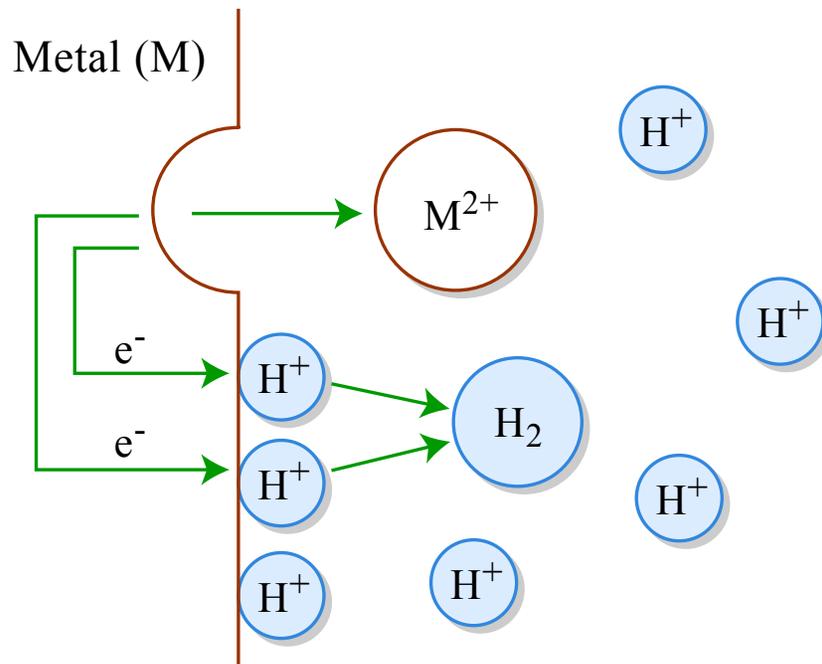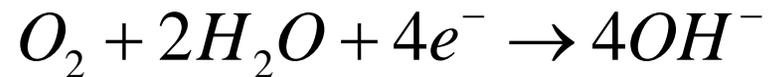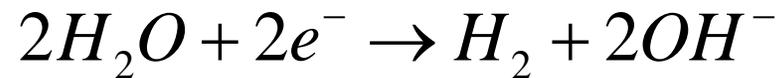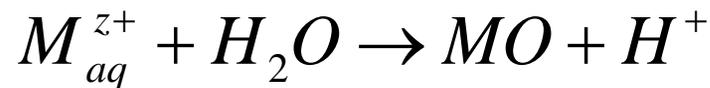
# Basic Relationships

$$lL + mM + ... \rightarrow qQ + rR + ...$$

$$\Delta G = (qG_Q + rG_R + ..) - (lG_L + mG_m + ..)$$

$$Anode(\text{Oxidation})$$

$$M \rightarrow M^{+ne^-} + ne^-$$

$$Cathode(\text{Reduction})$$

$$M^{ne^-} + ne^- \rightarrow M$$

$$2H^+ + 2e^- \rightarrow H_2(g)$$

- G = Free Energy (J/mol)
- n = # Equivalents Involved (# electrons)

7
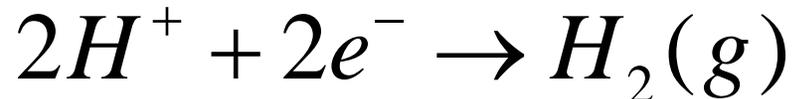
# Key Relationships

$$\Delta G = -nFE$$

$$E = E_0 - \frac{RT}{nF} \ln \frac{(Activity_{\text{Products}})}{(Activity_{\text{Reactants}})}$$

$$pH = -\log [H^+]$$

- G = Free Energy (J/mol)
- n = # Equivalents Involved (# electrons)
- F = Faraday's Constant (96,500 J/eq)
- E = Potential (V)
- $E_o$ = "Standard" Potential (V), Potential @ 25°C, Unit Activity, pH = 0
- R = Gas Constant (Appropriate Units)
- Activity = ~ Concentration (mol/l) for Dilute Solutions
  (Activity Coefficient X Concentration for Concentrated Solutions

# Pourbaix Diagram: Fe-H$_2$O @ 25°C

Figure removed due to copyright restrictions.

# Pourbaix Diagram: Cr-H$_2$O @ 25°C

Figure removed due to copyright restrictions.

# Pourbaix Diagram: Ni-H$_2$O @25°C

Figure removed due to copyright restrictions.

# Pourbaix Diagram: Ti-H$_2$O @ 25°C

Figure removed due to copyright restrictions.

# Fe-Cr-Ni System @ 25°C

# Combined Fe-Cr-Ni @ 25°C
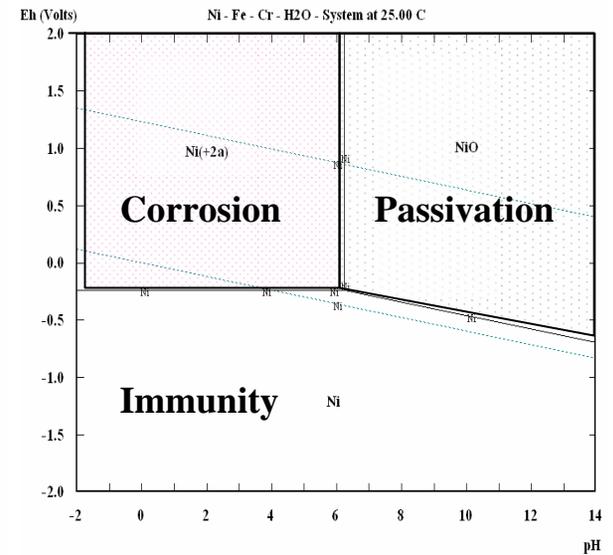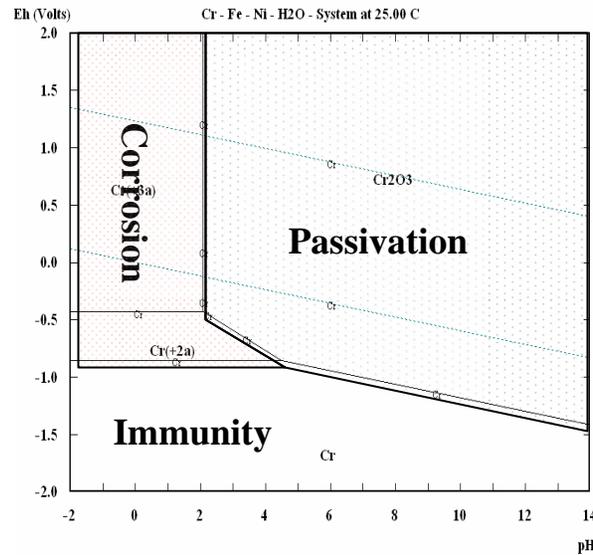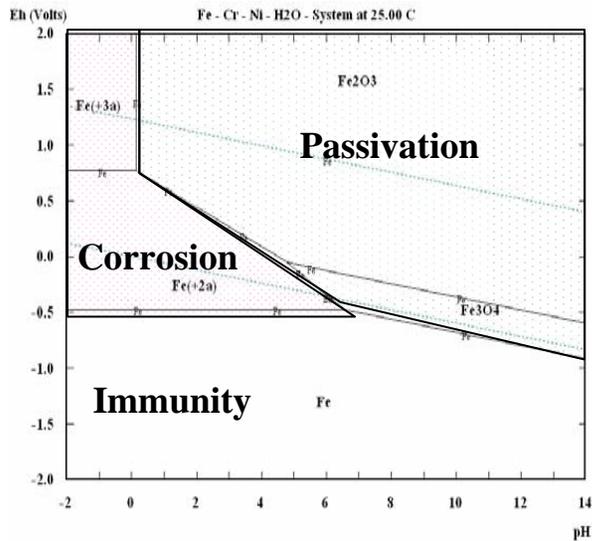


Fe - Cr - Ni - H2O - System at 25.00 C
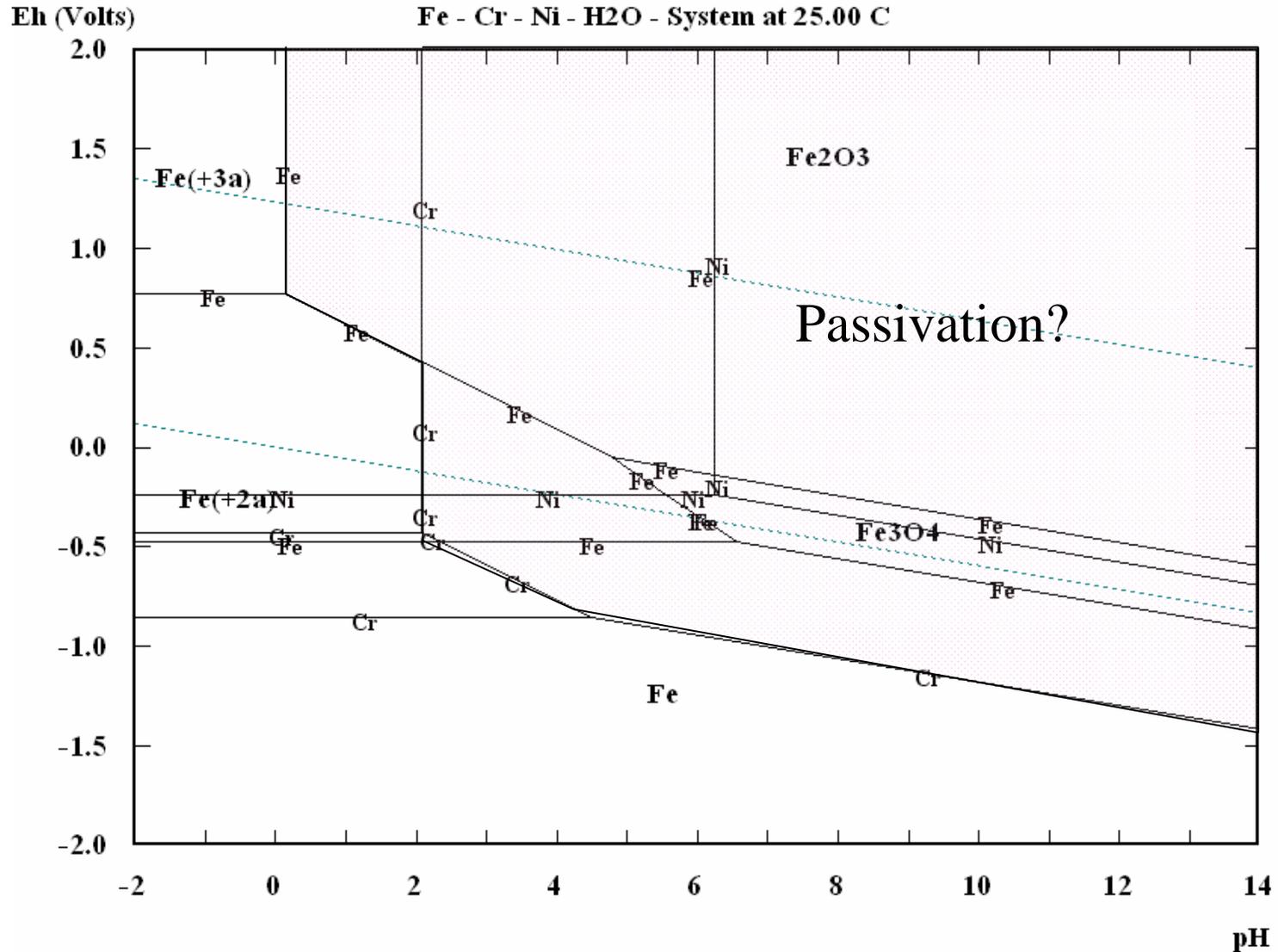
# **Kinetics**

# Schematic "Evans" Diagram



$(+)$

Potential, E (v) vs. SHE

$(-)$

$E_{R, Cath.}$

$E_{Corr}$

$E_{R, Anode}$

$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \rightarrow H_2$

$\beta_{Cathode}$

$\eta_{Cathodic}$

$M \rightarrow M^{n+} + ne^-$

$\beta_{Anode}$

$\eta_{Anodic}$

$M^{n+} + ne^- \rightarrow M$

$i_{0, Anode.}$     $i_{0, Cath.}$     $i_{Corrosion}$

Current Density (A/cm$^2$)

16
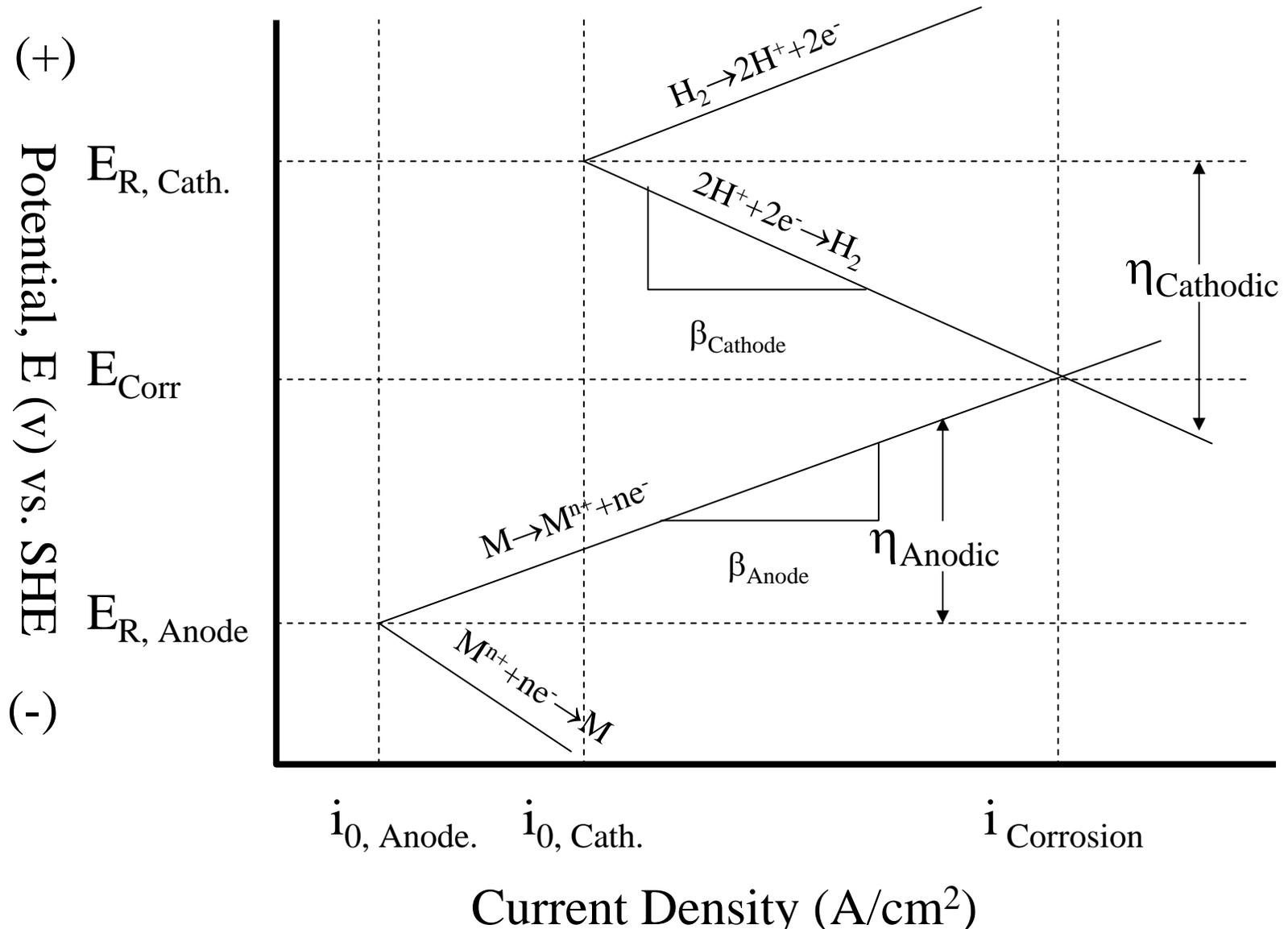
# Schematic of Passive Behavior (Anode)



(+)

Potential, E(v) vs. SHE

(-)

$E_{Passive}$

Transpassive

Passive

$i_L$

$M \rightarrow M^{n+} + ne^-$

Active

$i_{Passive}$

$i_{Critical}$

Current Density (log), (A/cm$^2$)
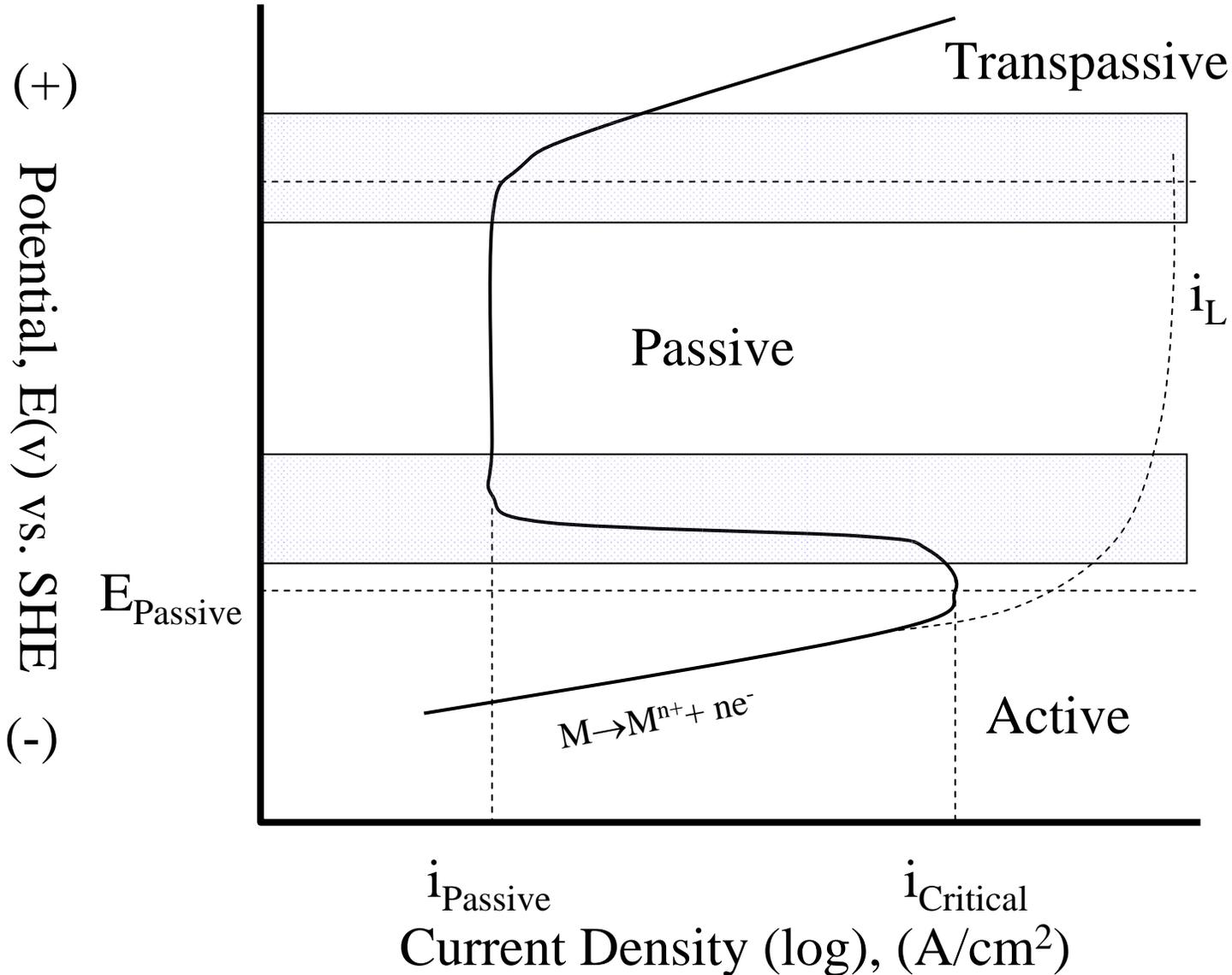
## Schematic of Anodic & Cathodic Interactions-Interplay



(+)

Potential, E(v) vs. SHE

(-)

$i_{o, \text{Noble Cathode}}$

Noble Cathode

$E_{\text{Corr, Passive}}$

Reduction Reaction

Flow, T

Active Cathode

$i_{l, C1}$   $i_{l, C2}$   $i_{l, C3}$   $i_{l, C4}$

$E_{\text{Passive}}$

$E_{\text{Corr, Active}}$

$M \rightarrow M^{n+} + ne^-$

$i_{\text{Passive}}$   $i_{\text{Critical}}$   $i_{L, \text{Anode}}$

Current Density (log), (A/cm$^2$)

18
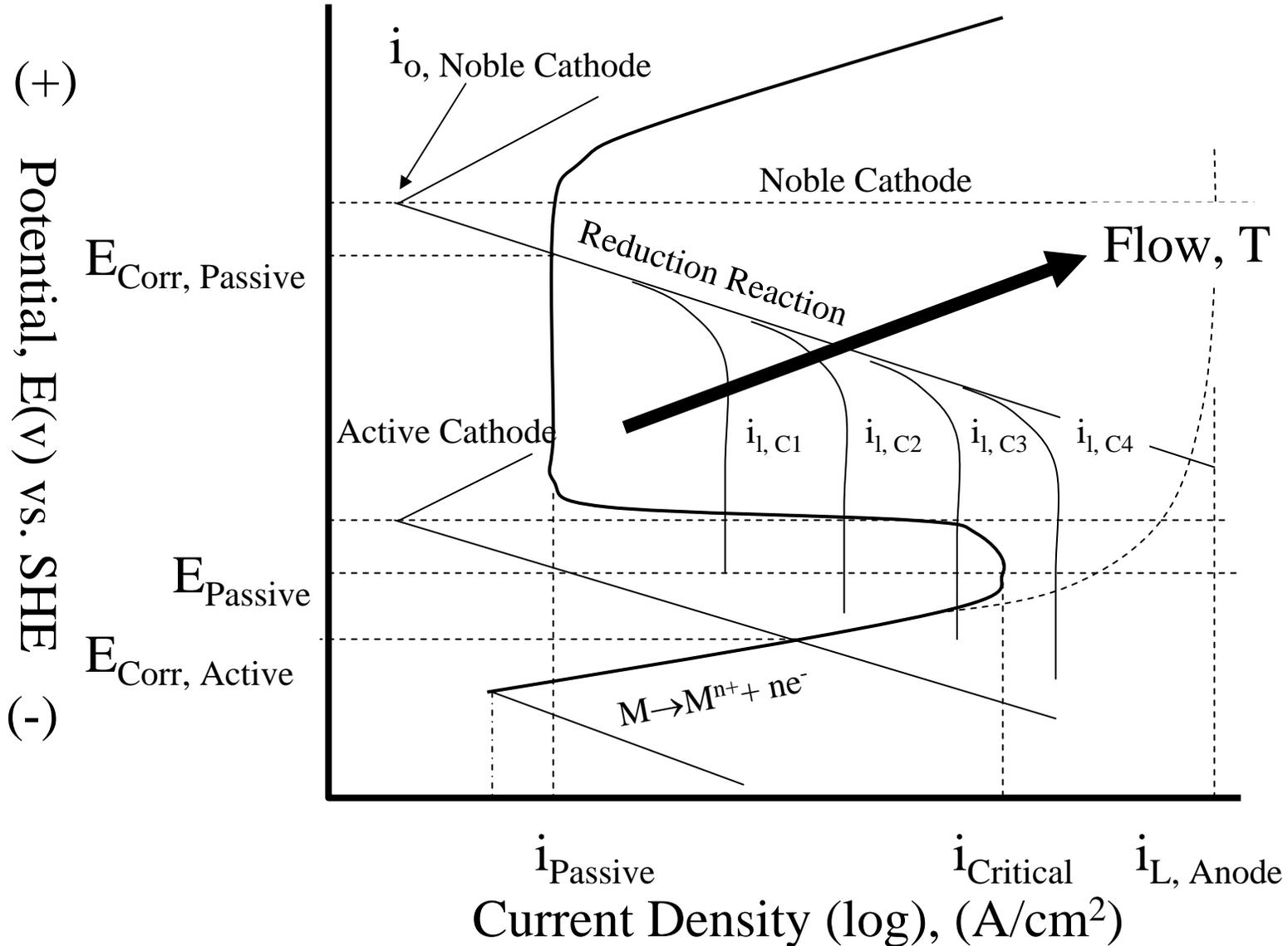
# Key Kinetics Relationships

$$\eta = \beta \log \frac{i}{i_0}$$

$$\eta = -\frac{RT}{nF} \ln \frac{i_L}{i_L - i}$$

$$i_L = \frac{DnF}{\delta t} c$$

$$D = D_0 e^{-\frac{Q}{RT}}$$

- $\beta$ = "Tafel" Slope
- $i$ = Current density
- $i_o$ = Exchange Current Density (A/cm$^2$)
- R = Gas Constant (appropriate units)
- n = # Equivalents (electrons) transferred
- F = Faraday's Constant (96,500 C/eq)
- $\eta$ = Overvoltage (V)
- D = Diffusion Coefficient (cm$^2$/sec)
- $D_o$ = Constant
- Q = Activation Energy (Units consistent with R)
- T = Temperature (°K)
- c = Concentration (M)
- $\delta$ = transference #
- t = Surface Layer (in solution) Thickness (cm)

# Key Variables

- Temperature
  - 15°C ~ 2X in Rates
- Concentrations
  - M, Hydrogen, Oxygen, Contaminants
- Flow Velocity
- Potential (Dominated by $O_2$ Concentration)
- Compositions (Microstructure)
- Stress
- Radiation Dose, Dose rate, Radiation Type

# The Role of Electrochemical Processes in Environmental Degradation

# OBSERVATIONS

- From an electrochemical point of view all structural materials are composites.

- Electrochemical differences can result in accelerated electrochemical reactions.

- If these reactions occur environmentally assisted attack may be promoted.

- In these situations both anodic and cathodic processes must be considered.

**PASSIVATING CRACK FLANKS**

**ANODIC OR CATHODIC PRECIPITATES**

**REGION I CRACK TIP/METAL INTERFACE**

**REGION II METAL**

**MASS TRANSFER**

**REGION III CRACK ENCLAVE**

**LOCAL DEPLETIONIN INTERFACE REGION**

**DIFFUSION OF METAL OR IMPURITY ATOMS TO GRAIN BOUNDARY**

**PRECIPITATE AT TIP/METAL INTERFACE**

**MASS TRANSFER**

**GRAIN BOUNDARY**

**IMPURITY SEGREGATION**

**MAJOR ELEMENT DEPLETION**

**BARE SURFACE**

**METAL DISSOLUTION**

**HYDROGEN REDUCTION**

**PRECIPITATE/MATRIX CELL**

# Model For EAC Process

# IMPORTANT PHENOMENA IN REGION 1

- Creation of fresh metal by crack propagation.

- Galvanic coupling between matrix and precipitates.

- Metal dissolution and other anodic reactions.

- Hydrogen reduction or other cathodic reactions.

- Mass transfer to or from the crack enclave due to diffusion, convection or ion migration.

- Crack extension, by mechanical or chemical or electrochemical means.

- Hydrogen assisted crack growth.

# IMPORTANT PHENOMENA IN REGION II

- Precipitation at grain boundaries.

- Minor/major element segregation.

- Near grain boundary element depletion or accumulation.

- Development of plastic zone due to crack propagation.

# IMPORTANT PHENOMENA IN REGION III

- Mass transfer into and out of the crack by diffusion, convection and ion migration.

- Oxygen reduction on passive or active crack walls.

# ENVIRONMENT ASSISTED CRACKING MECHANISMS

- Stress Corrosion Cracking

- Hydrogen Embrittlement

- Intergranular Attack

- Corrosion Fatigue

# KEY VARIABLES

- Grain Boundary Morphology.

- Electrochemical Activity of the Grain Boundary.

- Fresh Metal Exposure Rate.

- Reaction Kinetics.

   Film formation rate

   Corrosion currents

- Galvanic Couples Between Grain Boundary Phases.

- Crack Tip pH.

- Crack Tip Potential in Relation to Reversible Hydrogen Potential

# TYPICAL PHASES

Gamma Prime ($Ni_3(Al,Ti)$)

Gamma Double Prime ($Ni_3Nb$)

Eta  ($Ni_3Ti$)

Laves ($Fe_2Ti...$)

MC Carbides

$M_7C_3$ Carbides

$M_{23}C_6$ Carbides

MnS Inclusions

Oxide Inclusions

Delta ($Ni_3Nb$)

# IMPORTANT PHASE CHARACTERISTICS

- Is it anodic or cathodic with respect to other phases or matrix?

- Does it exhibit active or passive behavior?

- What are the kinetics of passivation?

- Corrosion current density?

- Exchange current density?

- Solubility of metal ions?

# Design Implications

# Materials Selection Considerations

- **Applicability**
- **Suitability**
- **Fabricability**
- **Availability**
- **Economics**
- **Compromise**

# General Material Failure Modes

**1. Overload**

**2. Creep Rupture**

**3. Fatigue**

**4. Brittle Fracture**

**5. Wastage**

**6. Environmentally Enhanced**

# Environmentally Enhanced Failure Modes

1. **General Corrosion**

2. **Localized Corrosion**

   **Galvanic**

   **Pitting**

   **Crevice Corrosion**

   **Stress Corrosion Cracking**

   **Hydrogen Embrittlement**

   **Corrosion Fatigue**

   **Intergranular Attack**

   **Erosion-Corrosion**

   **Creep-Fatigue Interaction**

# Key Point

- **Big Difference Between General & Localized Corrosion**
  - **General Corrosion**
    - **Predictable**
    - **Slow (Normally)**
  - **Localized Corrosion**
    - **"Unpredictable"**
    - **Potentially Very Rapid**
    - **Can be Multi-Phenomena (Pitting leading to Crack Initiation)**
  - **Significant Design Implications**

# How Do Things "Fail" (Sometimes)

- Crack Initiation
  - Often Multiple Sites (Pitting)
  - Defects "Become" Cracks
    - Respond to Stress
- Multiple Cracks Link Up
  - Higher Driving Force (K) for "Linked System
- "Main" Crack Propagates to Failure

$$K = f(a, \sigma, geometry)$$

$$\frac{da}{dn} = C(\Delta K)^n$$

$$\frac{da}{dt} = \exp\left[-\frac{Q_g}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]\alpha(K - K_{th})^\beta$$

$$K \to K_C \to Unstable$$

# Crack "History"



Crack Length (a)

$a_0$

Unacceptable NDE Sensitivity

"Adequate" NDE Sensitivity ??

Ideal NDE Sensitivity

**Unstable Crack Growth (Exceed $K_{Crit}$)**

Time
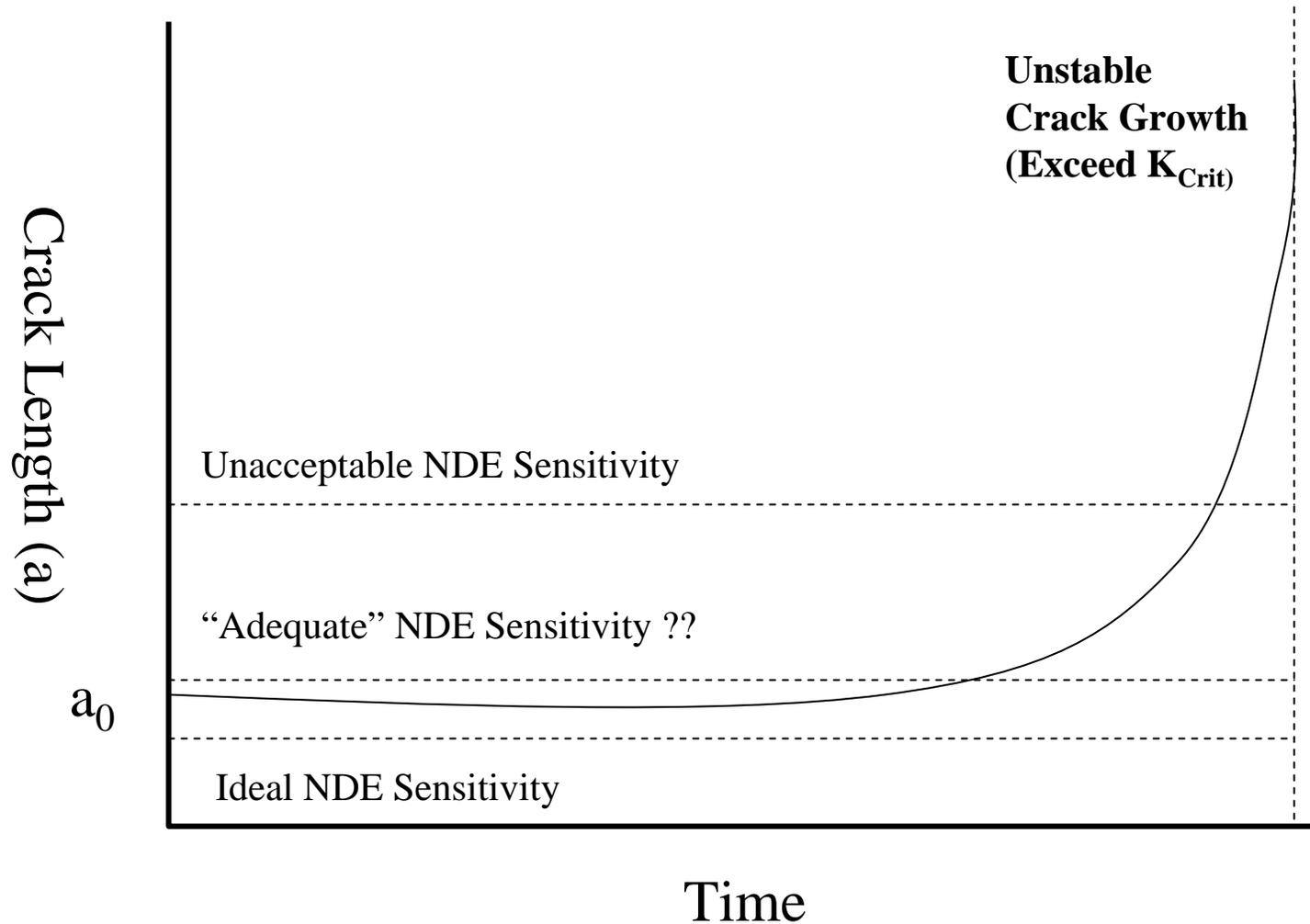
# Indian Point R2C5 Crack

Photos removed due to copyright restrictions.

# General Design "Rules"

1. **Avoid Stress/ Stress Concentrations**
2. **Avoid Galvanic Couples**
3. **Avoid Sharp Bends of Velocity Changes in Piping Systems**
4. **Design Tanks for Complete Draining**
5. **To Weld or Not to Weld?**
6. **Design to Exclude Air**
7. **Avoid Heterogeneity**
8. **Design for Replacement**