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Evaluation of Wear-Corrosion Synergy Through Tribocorrosion Studies

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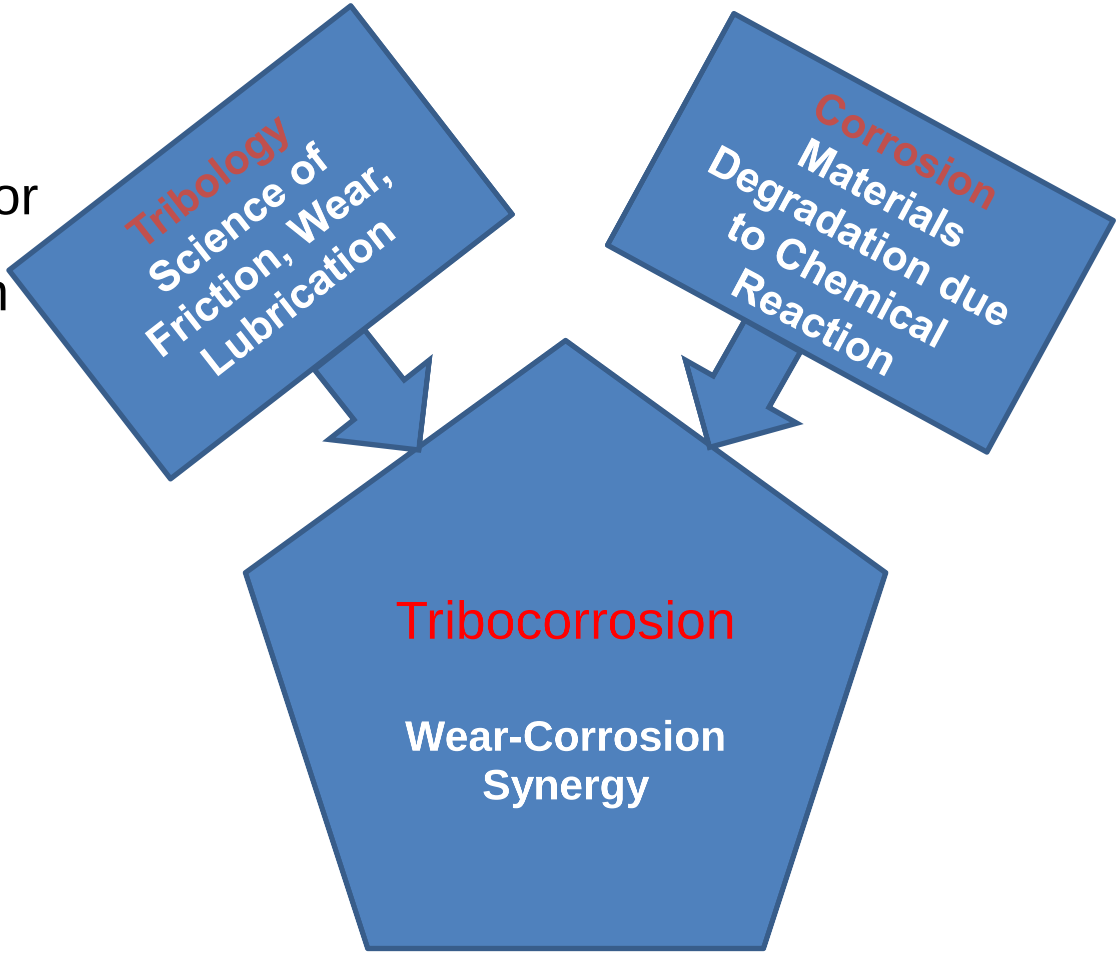
Introduction

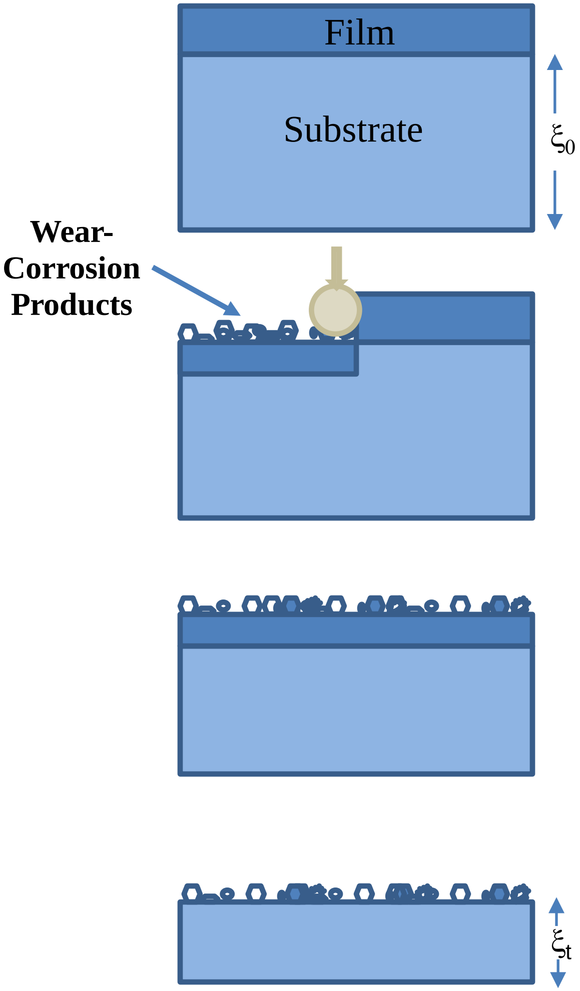
- Tribocorrosion Basics and Applications
- Electrochemical Polarization Methods
- Tribocorrosion Module of CETR-UMT
- Standard Tribocorrosion Test Procedures
- Estimation of Wear-Corrosion Synergy
- Some Test Results Obtained Using CETR-UMT
- Q & A

Tribocorrosion

Tribocorrosion involves mechanical and chemical or electrochemical interaction between bodies in relative motion. Mechanical component: *sliding wear*, *abrasion*, *cavitation damage*, *fretting*, *tribo-oxidation*, *solid particle erosion* etc.



Wear-Corrosion Synergy



An oxide film protects the substrate from corrosion degradation.

Wear removes the film inducing an accelerated corrosion process

Wear-corrosion products enhance the wear

Huge materials loss due to wear-corrosion synergy

Tribocorrosion-Applications

Automotive: *lubricated moving parts or parts subject to tribo-oxidation*

Biomedical: *interaction of biomedical chemicals on implants*

Chemical, Mining and Petrochemical: *degradation of pumps, valves, propellers, heat exchanger tubes, drilling and slurry transportation*

Dental: *evaluation of degradation of arch-wire, dental implants etc.*

Food: *tribocorrosion of food processing equipment*

Marine: *tribocorrosion in sea water*

Lubricant: *Research and Development of novel lubricants*

Semiconductor: *uses tribocorrosion as a beneficial process (CMP)!!!*

Tools for Tribocorrosion Study

Tribocorrosion study requires a Tribometer and an Electrochemical Measurement System

Tribometer:

- Provides controlled mechanical loading and relative motion;
- Measures friction force and normal force
- Yields evolution of coefficient of friction (COF) with time and materials removal rate.

Electrochemical Measurement System:

- Performs voltage and electrical current application and measurement -open-circuit potential (OCP), Electrochemical polarization, Electrochemical impedance etc.
- Yields corrosion potential and current data (E_{corr}, i_{corr}) and materials removal rate due to corrosion.

Tribocorrosion Tests

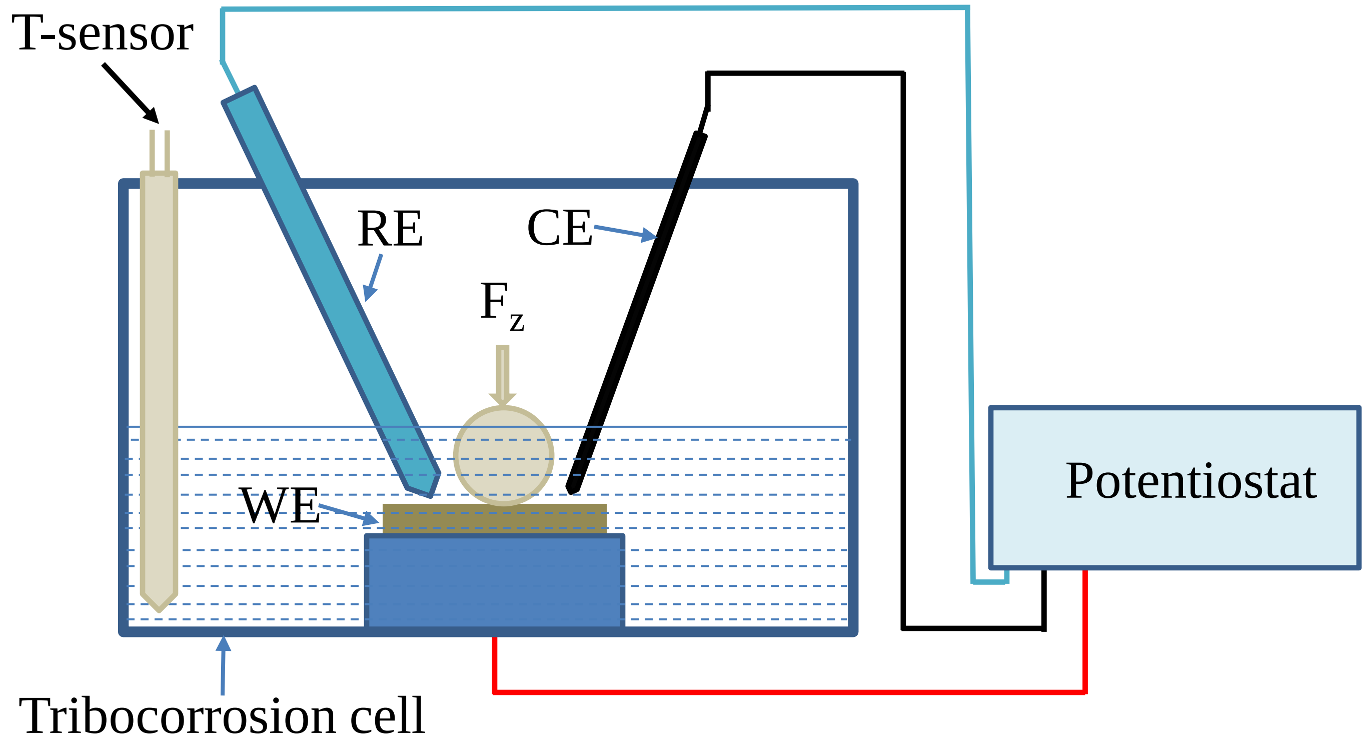
Specimen:

- Bulk or coating of metallic materials (25 mm × 25 mm)
- Chemical solution (acidic, alkaline, oxidants, salt solution, body fluids, ionic lubricants, etc.)

Results:

- Electrochemical Polarization Studies – to evaluate corrosion rate of metals and alloys in chemical environment
- Effect of pH, scan rate, electrolyte concentration, temperature on wear behavior of metallic materials
- Synergistic effect of wear and corrosion

Schematic Tribocorrosion Cell



WE: Working Electrode- metallic specimens;
CE : Counter Electrode (Pt)
RE : Reference Electrode-Ag/AgCl, calomel electrode, etc

Electrochemical Kinetics

Metal dissolution reaction :

$$M \rightarrow M^{z+} + ze^- \qquad \vec{i} \qquad \ldots(1)$$

Metal deposition reaction:

$$M^{z+} + ze^- \rightarrow M \qquad \overleftarrow{i} \qquad \ldots(2)$$

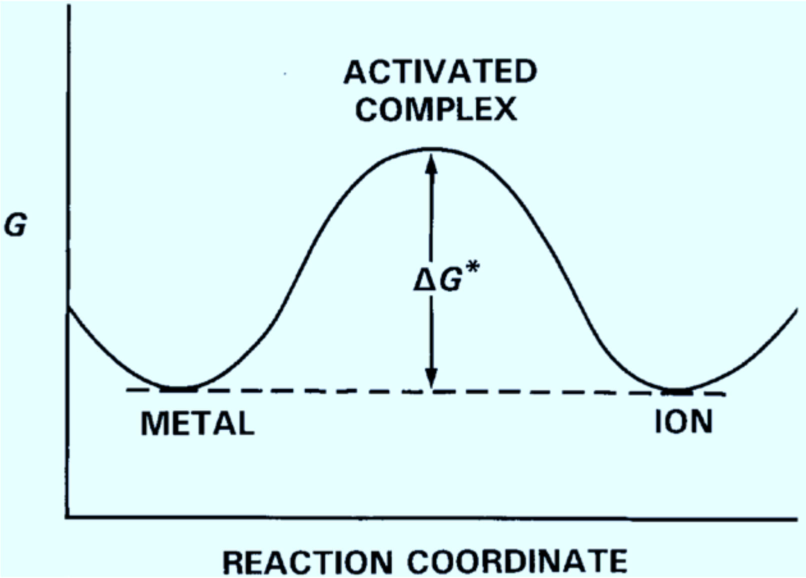
At equilibrium, the magnitude of the partial currents ($\vec{i}$ and $\overleftarrow{i}$) is called the exchange current density (i_0), which is a function of activation free energy (ΔG^*):

$$i_0 = \vec{i} = \overleftarrow{i} = k\ exp\frac{-\Delta G^*}{RT} \qquad \ldots(3)$$

k is a constant, R is the universal gas constant, T is temperature

$$\Delta G^* = -zFE^* \qquad \ldots(4)$$

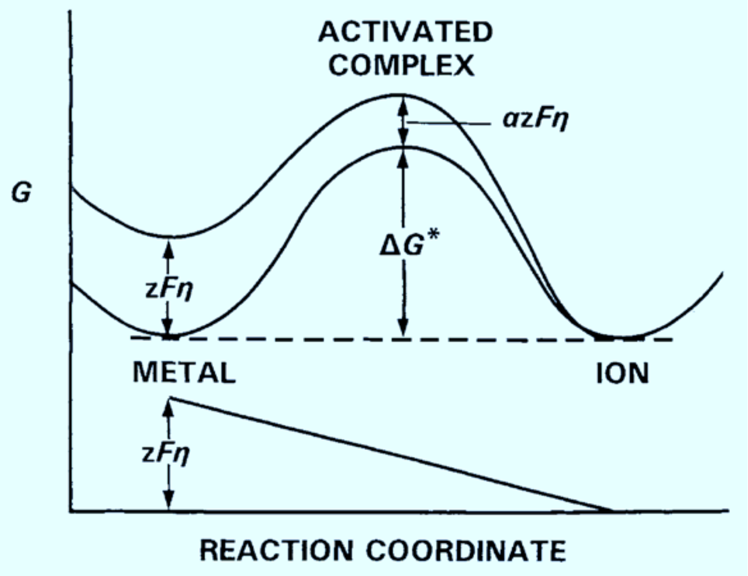
F is Faraday charge (96,490 Coulomb/mol). At equilibrium no net current flows.



Electrochemical Polarization

If the equilibrium at an electrode is disturbed, a net current flows across its surface that shifts the potential. The shift in potential is called the *polarization* and its value is overpotential (η).

Three types of polarization:
(a) *activation*
(b) *concentration*
(c) *resistance*
Activation polarization: anodic when it is +ve; cathodic when –ve.



The free energy profile of an electrode that is subjected to an anodic polarization with an overpotential (η) is shown. It raises the energy of the metal by $zF\eta$ and that of the activated complex by $\alpha zF\eta$, relative to that of the ions, where α is a symmetry factor ($0 < \alpha < 1$) defining the position of the maxima in the energy profile. Therefore,

The activation energy of metal dissolution is decreased to $[\Delta G^* - (1-\alpha)zF\eta]$, and

the activation energy for metal deposition is increased to $[\Delta G^* + \alpha zF\eta]$.

Butler-Volmer Equation

Under anodic polarization condition, metal dissolution current ($\vec{i}$) [eqn (3)] is changed to :

$$\vec{i} = k\ exp\frac{-\{\Delta G^{*} - (1-\alpha)zF\eta\}}{RT} \qquad \ldots(5)$$

$$\vec{i} = k\ exp\frac{-\Delta G^{*}}{RT}.\,exp\frac{(1-\alpha)zF\eta}{RT} \qquad \ldots(6)$$

$$\vec{i} = i_0.\,exp\frac{(1-\alpha)zF\eta}{RT} \qquad \ldots(7)$$

Similarly, deposition current ($\overleftarrow{i}$):

$$\overleftarrow{i} = i_0.\,exp\frac{-\alpha zF\eta}{RT} \qquad \ldots(8)$$

The net anodic (dissolution) current (i_{net}) is obtained by subtracting (8) from (7):

$$i_{net} = \vec{i} - \overleftarrow{i} = i_0.\left[exp\frac{(1-\alpha)zF\eta}{RT} - exp\frac{-\alpha zF\eta}{RT}\right] \qquad \ldots(9)$$

The equation (9) is known as the **Butler-Volmer** equation that relates i_{net} with η.

Tafel Equation

For high-field approximation, when anodic overpotential [$\eta = \eta_{anodic}$] is > 0.1 V, metal deposition reaction is insignificant, and i_{net} from eqn (9) becomes:

$$i_{net} = \vec{i} = i_{anodic} = i_0 . \left[exp \frac{(1-\alpha) zF\eta_{anodic}}{RT} \right] \quad \ldots(10)$$

The equation (10) can be expressed as :

$$\eta_{anodic} = b.log(i_0) + \beta_a.\log(i_{anodic}) \quad \ldots(11)$$

Similarly, for higher cathodic overpotential [$\eta = \eta_{cathodic} < -0.1$ V], metal dissolution reaction is insignificant, and i_{net} from eqn (9) could be expressed as:

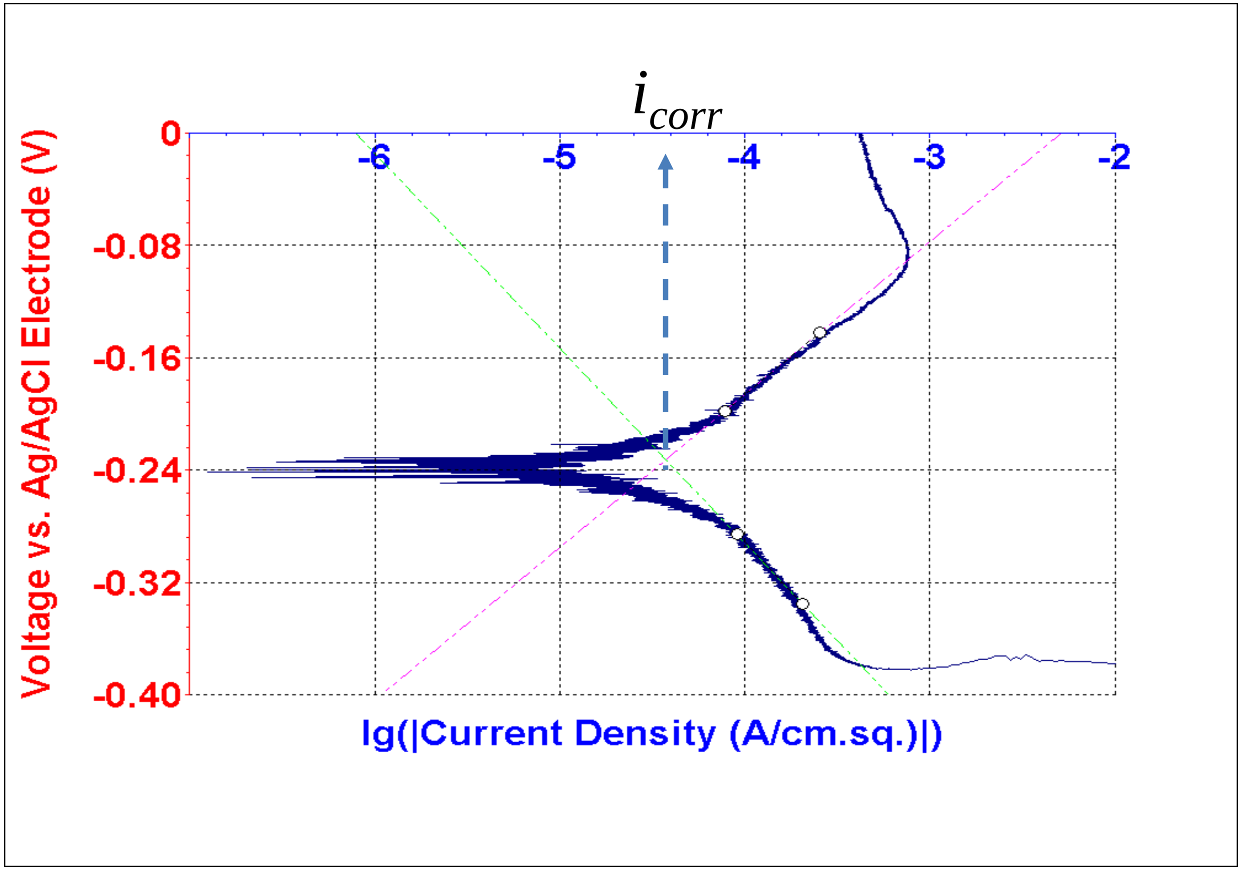
$$\eta_{cathodic} = b.log(i_0) - \beta_c.\log(i_{cathodic}) \quad \ldots(12)$$

Equations (11) and (12) are combined into a single expression and know as Tafel equation:

$$\eta = b.log(i_0) \pm \beta.\log(i) \quad \ldots(13)$$

The symmetry factor α is usually 0.5.

Tafel Extrapolation



Corrosion rate = $k_1 \frac{i_{corr}}{\rho} EW$, where, ρ and EW are the density and the equivalent weight of the metallic specimen, respectively.

CETR-UMT: Tribocorrosion Tester

- Up to 20 N normal load (Fz)-servo controlled-programmable
- Ball or pin-on-Plate wear test up to 30 Hz
- 3-electrode (counter, working, ref.) system
- Potentiostat
- Temperature up to 70 ºC
- **C**orrosion resistant Tribocorrosion cell
- Tests as per ASTM standards

CETR-UMT Tribocorrosion Module

Evaluation of Wear-Corrosion Synergy

ASTM G119

Wear and Corrosion form a Synergistic Couple!

$$T = W_0 + C_0 + S \qquad \text{...(14)}$$

T = Rate of total material loss due to tribocorrosion

W_0 = Rate of mechanical wear in absence of corrosive agent

C_0 = Rate of corrosion in absence of mechanical agent

S = Change in rate of materials loss due to wear-corrosion synergy

Evaluation of Wear-Corrosion Synergy

To obtain Synergy (S), the following tests are performed:

Test 1: Electrochemical polarization to find corrosion potential (E_{corr}) and corrosion current (i_{corr}) to calculate $\mathbf{C_0}$

Test 2: Wear test in corrosive environment; No external potential or electrical current to obtain **T.**

Test 3: Repeat Test 2 to obtain electrochemical corrosion rate in the presence of wear ($\mathbf{C_W}$)

Test 4: Repeat Test 2 with a potential 1V cathodic to E_{corr} to obtain $\mathbf{W_0}$

Evaluation of Wear-Corrosion Synergy

$$T = W_0 + C_0 + S \qquad ...(14)$$

where,

$$S = \Delta C_W + \Delta W_C \qquad ...(15)$$

and

$$\Delta C_W = C_W - C_0 \qquad ...(16)$$

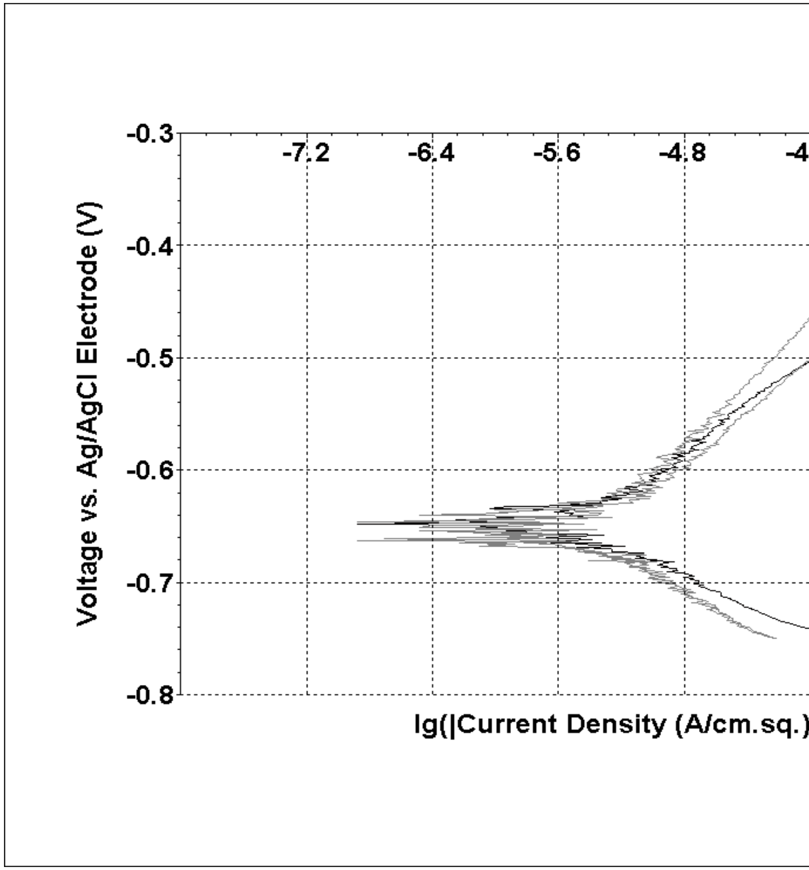
$$\Delta W_C = T - (W_0 + C_W) \qquad ...(17)$$

$$\text{Total Synergism Factor} = \frac{T}{(T-S)} \qquad ...(18)$$

$$\text{Corrosion Augmentation Factor} = \frac{C_W}{C_0} \qquad ...(19)$$

$$\text{Wear Augmentation Factor} = \frac{W_0 + \Delta W_C}{W_0} \qquad ...(20)$$

Electrochemical Corrosion Rate

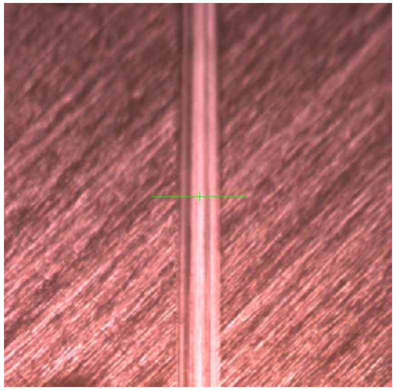


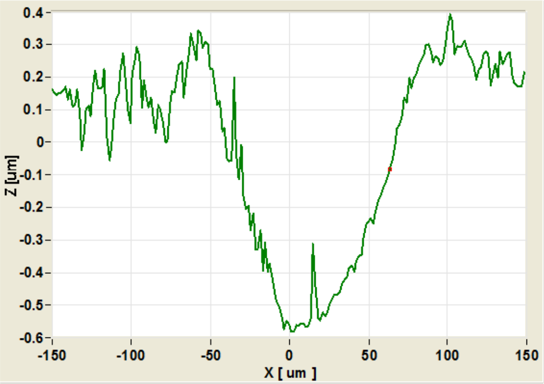
	E_{corr}, mV	I_{corr}, μA/cm2	Corrosion Rate, mm/year
1	-651	4.34	0.042
2	-658	3.93	0.038
3	-647	3.86	0.038

Cast iron in 0.1% NaCl solution

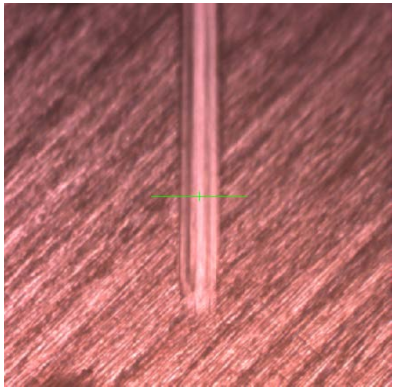
Wear Scar Profile after Tribocorrosion

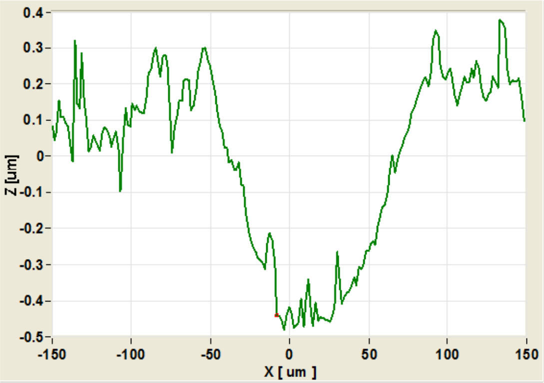
Near the Middle





Near an End





AISI 316 SS in 0.9%NaCl; 900 s with 5 N load with alumina-4.75 mm ϕ ball and reciprocation over 2 mm at 0.4 mm/s.

Wear-Corrosion Synergy Results

Materials Removal Rate of AISI 316 SS in 0.9%NaCl with 5N load, 0.4 mm/s with alumina ball (4.76 mm dia) in mil per year (mpy):

$T = 117.82$; $W_0 = 18.77$;

$C_W = 0.55$; $C_0 = 0.31$

$$\Delta C_W = C_W - C_0 = 0.24;$$

$$\Delta W_C = T - (W_0 + C_W) = 98.50;$$

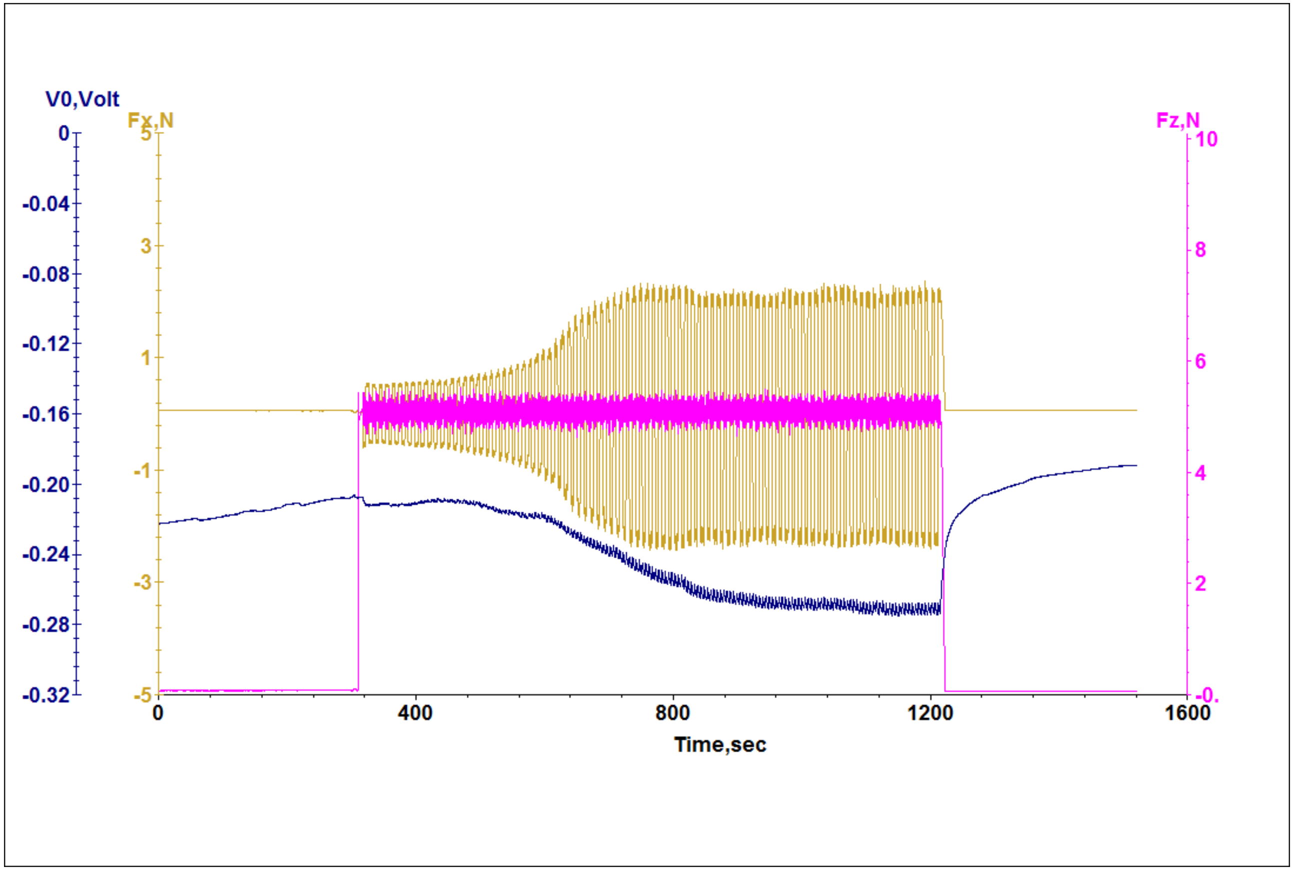
$$S = \Delta C_W + \Delta W_C = 98.74.$$

Total Synergism Factor $= \frac{T}{(T-S)} = 6.18$

Corrosion Augmentation Factor $= \frac{C_W}{C_0} = 1.77$

Wear Augmentation Factor $= \frac{W_0 + \Delta W_C}{W_0} = 6.25$

Tribocorrosion Test: OCP Results

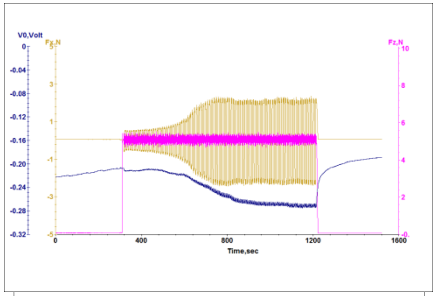


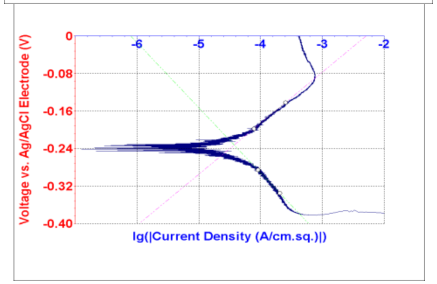
AISI 316 SS in 0.9%NaCl; initial 300 s no load- no movement; next 900 s with 5 N load with alumina-4.76 mm ϕ ball and reciprocation over 2 mm at 0.4 mm/s; Next 300 s load removed and movement stopped.

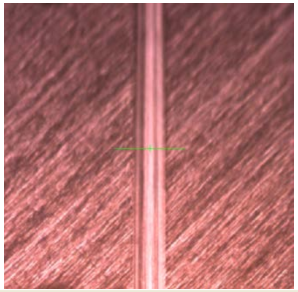
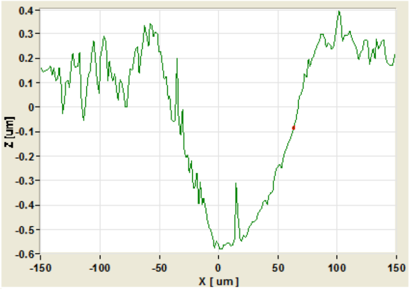
Concluding Remarks

- Tribocorrosion test procedure is important to evaluate metallic materials or solution for their performance under simultaneous wear and corrosion conditions.
- CETR-UMT Test system can evaluate Wear-Corrosion Synergy of an electrochemical system involving chemicals and metallic materials including coatings.







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