27. Introduction to Rates of Corrosion

Chemistry

The rates of corrosion use a subset of the OLI chemistry[46] and is currently only available with the AQ thermodynamic framework.

Neutral Species

H_2O, O_2, CO_2, H_2S, N_2, Cl_2 and all inert gases, SO_2 and NH_3, and organic molecules that do not undergo electrochemical reactions.

Anions

OH^-, Cl^-, Br^-, I^-, HCO_3^-, CO_3^{2-}, HS^-, S^{2-}, SO_4^{2-}, HSO_4^-, NO^{2-}, MoO_4^{2-}, ClO^-, ClO_4^-, Cr(VI) anions, As(III) anions, P(V) anions, W(VI) anions, and Si(IV) anions.

Cations

H^+, alkali metals, alkaline earth metals, Fe(II) cations, Fe(III) cations, Al(III) cations, Cd(II) cations, Sn(II) cations, Zn(II) cations, Pb(II) cations and $NH4^+$.

Calculation types

Single Point

The single point calculation will determine the rates of corrosion at only a single temperature and pressure.

The system may be flowing or static. If the system is flowing, only a single flowrate will be considered. Flowing systems also require the specification of diameter for the pipe or rotating cylinder.

pH Survey

This calculation is analogous to the pH Survey found in other OLI Studio components. The specification requires a titrant acid and base.

[46] These species are subject to change with time, most-likely to increase in number

Temperature Survey

A survey in temperature can be performed. The default range is from 25 to 100 degrees Centigrade. Any range may be used by changing the **Range** option.

The user should consider that some points in the survey may not converge due to phase changes (e.g., boiling off of aqueous liquids).

Composition Survey

A single titrant can be added to the solution and the effects of corrosion determined. The range of the component defaults to 0 to 1 mole with an increment of 0.1 moles. This range can be changed via the **Range** option.

Care should be taken when adding salts that can form hydrates (e.g., $CaCl_2.6H_2O$). When these hydrated salts begin to precipitate from solution, large amounts of water may be complexed with the crystal. The solution may desiccate and non-convergence may be the result.

Pressure Survey

The pressure of solution may be varied. The default range can be changed via the **Range** option.

Care should be taken when working at very low pressures since the solution may inadvertently boil off the liquid and non-convergence may results.

Flow Velocity Survey

In systems that are flowing, the flowrate of the stream can be varied.

Metal Chemistry

The default metal is the generic mild steel (G10100). The user can select from several classes of metals:

Iron/Mild Steels

- Fe (Zone Refined)
- Fe (Pure)
- Fe (ARMCO)
- Carbon Steel A212B
- Carbon Steel A216
- Carbon Steel 1018
- Carbon Steel G10100 (Generic)

300/400 Stainless

- Stainless Steel 304
- Stainless Steel 316
- Alloy 254SMO
- Duplex Stainless 2205

- 13% Cr

Aluminum

- Aluminum 1199 (Pure)
- Aluminum 1100

Nickel Based

- Ni
- Alloy 600
- Alloy 690
- Alloy 825
- Alloy 625
- Alloy C-276
- Alloy C-22

Copper

- Cu
- CuNi 9010
- CuNi 7030

Flow conditions

There are five flow conditions:

- Static Conditions
- Pipe Flow
- Rotating Disk
- Rotating Cylinder

Complete Agitation

Static Conditions

The solution is not flowing in this calculation.

Pipe Flow

The fluid is flowing through a pipe. The pipe diameter and flow velocity must be defined.

The default pipe diameter is **0.1 meters** and the default flow velocity is **2 meters/second**.

Rotating disk

This reproduces a type of experiment that is used quite frequently. A disk is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the disk is specified as well as the revolutions per minute (RPM).

The default diameter is **0.01 meters** and the default RPM is **5000 RPM**.

Rotating Cylinder

This reproduces a type of experiment that is used quite frequently. A cylindrical rotor is rotated to bring fluid to the surface of the electrode in a predictable manner. The diameter of the rotor is specified as well as the revolutions per minute (RPM).

The default diameter is **0.01 meters** and the default RPM is **5000 RPM**.

Complete Agitation

In this calculation, the liquid phase is completely agitated and no mass transfer limitations apply.

Kinetics of general corrosion

Elements of the approach:

- Electrode processes under activation control (Butler-Volmer kinetics)
- Reaction orders according to plausible reaction mechanisms
- Limiting current densities due to diffusion processes and homogeneous reactions in solution
- Effects of adsorption
- A model for the passive current density and the active-passive transition
- Effect of solution species on corrosion in the passive state

Synthesis of the partial processes to obtain a total polarization curve and, hence, corrosion rate

Butler-Volmer kinetics

$$i = i_o \exp [\alpha F (E - E_o) / RT]$$

Exchange current density depends on concentrations of active species:

$$i_o = i^* a_K^k \; a_L^l \; a_M^m \ldots$$

Reaction orders depend on various mechanisms

$$E_0 = E_0^0 + (RT/zF) \Pi a_i^{\nu i}$$

Activities of species that participate in the reaction:

$$a_i \ (i = 1, 2 \ldots)$$

Parameters that result from reaction mechanism:

Electrochemical transfer coefficients Reaction orders with respect to active species.

Parameters that depend only on the metal:

- Exchange current density after factoring out the chemical contribution (i.e., i^*).
- Temperature dependence of i^*, i.e., the activation energy.

Limiting current density due to the diffusion of species X to the interface:

$$i_{lim} = z\, k_m\, F\ \ a_{X,\,bulk}$$

- The mass transfer coefficient km depends on:
- Diffusivity of species X
- Viscosity
- Flow geometry (pipe, rotating cylinder, etc.)
- Flow velocity