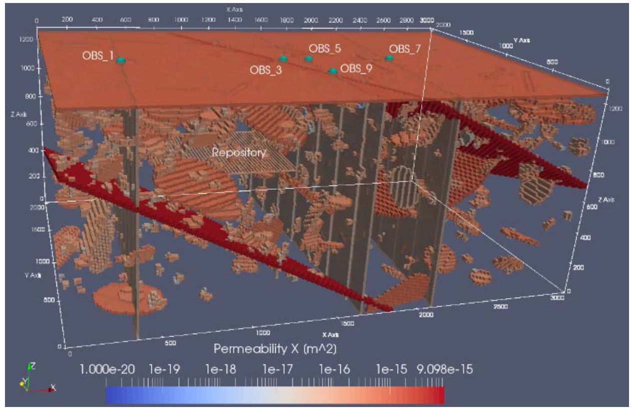

Fuel Matrix Degradation Modeling and Electrochemical Testing

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U.S. NWTRB Meeting

May 22, 2024

Knoxville, Tennessee

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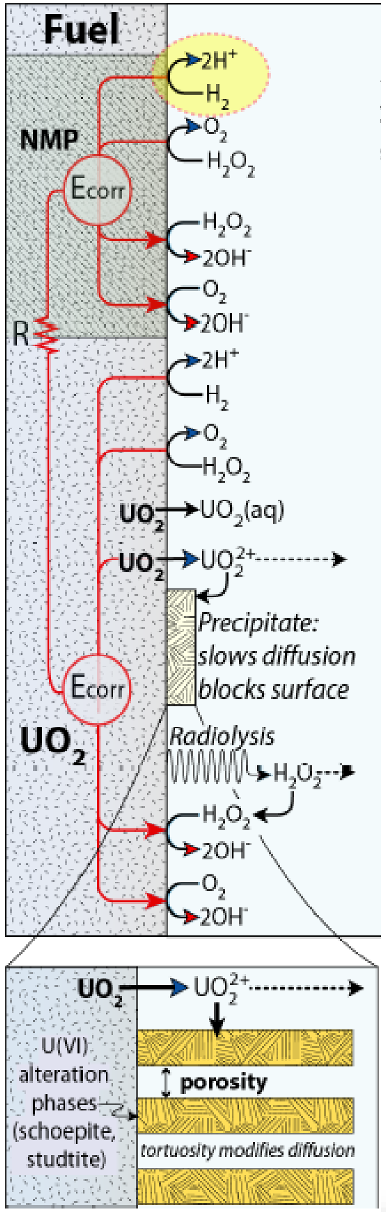
Spent Fuel and Waste Science and Technology (SFWST)

Outline

- **Part 1 – FMD Modeling**
  - Fuel matrix degradation (FMD) models in repository reference cases
  - Surrogate models of the FMD process model

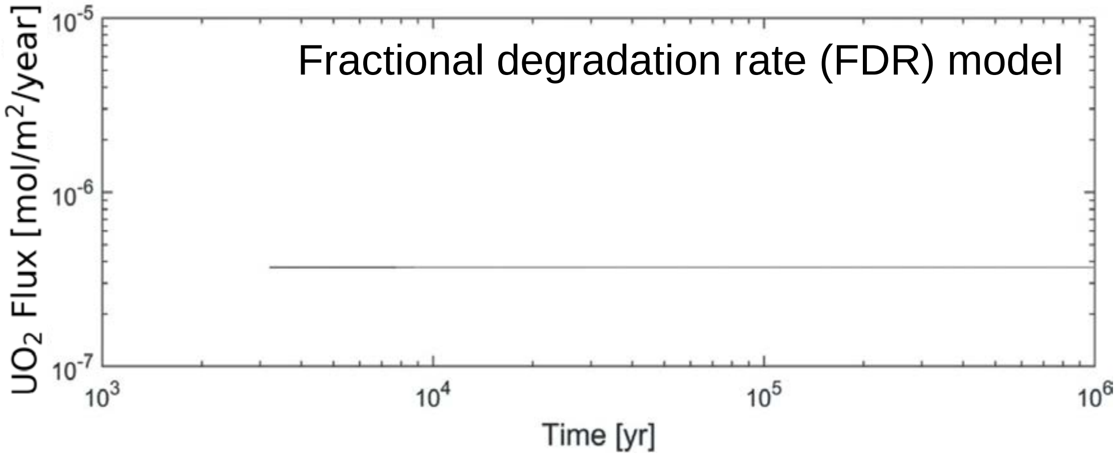
- **Part 2 – Electrochemical Testing**
  - Electrochemical corrosion testing of simulated spent fuel (SIMFUEL)

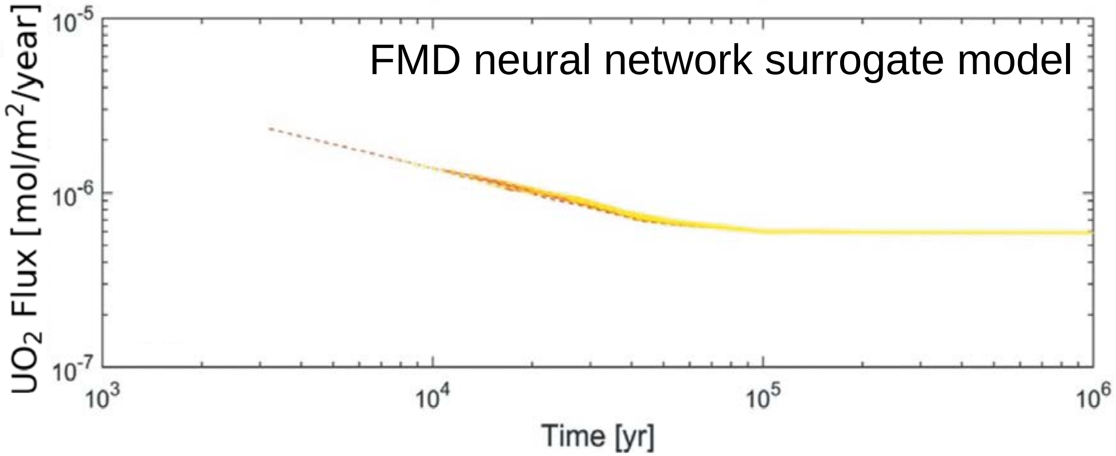


(Jerden et al. 2017)

Fuel Matrix Degradation in Repository Reference Cases

- **Two general approaches used in GDSA reference cases**
  - Fractional degradation rate (FDR) model
    - Fixed rate: ~10^{-6} to 10^{-8} per year
      - E.g., SKB (2006)
  - Fuel matrix degradation (FMD) surrogate models
    - Variable rate
    - Emulate FMD process model
      - Neural network surrogate
      - K nearest neighbors surrogate
    - Tested in
      - GDSA shale reference case (right)
      - GDSA crystalline reference case (Swiler et al. 2022)





Both approaches demonstrated for 2,000 failed 4-PWR waste packages in a shale repository simulation (Debusschere et al. 2023)

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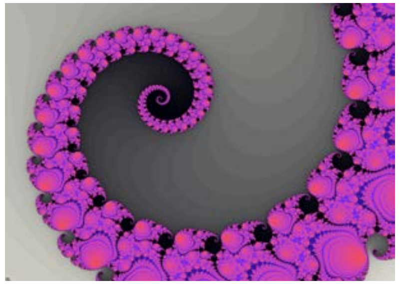
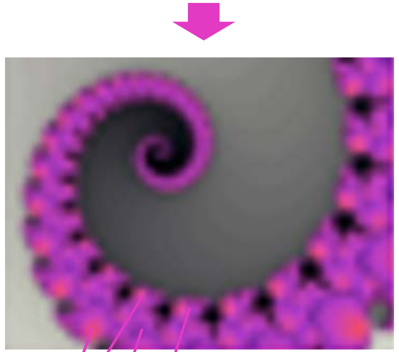
FMD Surrogate Models

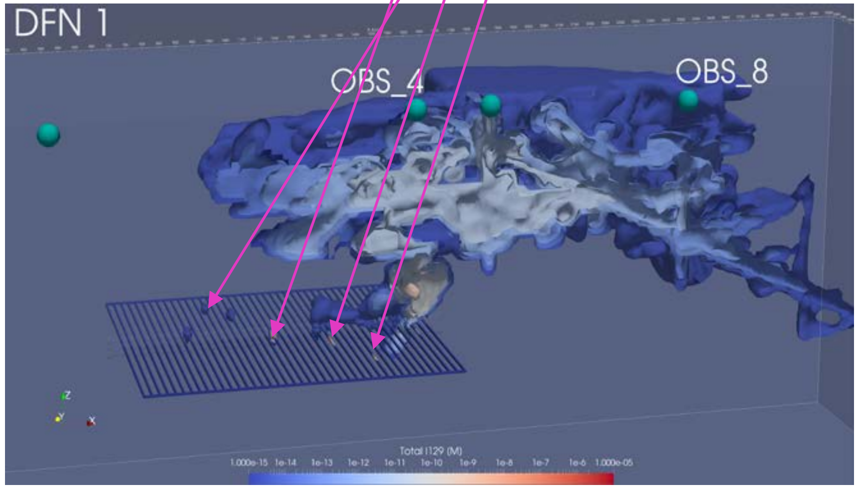
- **Repository performance can be highly sensitive to fuel degradation rates**
- **Fuel degradation rates**
  - Sensitive to
    - Temperature
    - Dose rate (radiolysis)
    - H_2, O_2, Fe^{2+}, CO_3^{2-} concentrations
  - Change over repository lifetime
- **FMD process model**
  - Too expensive for repository simulations
- **FMD surrogate models**
  - Rapidly emulate the FMD process model
  - Emulation can be verified by comparing against process model calculations



Process model



Surrogate model
1,000s of times faster computationally



Performance assessment (PA) model

Mariner et al. 2020

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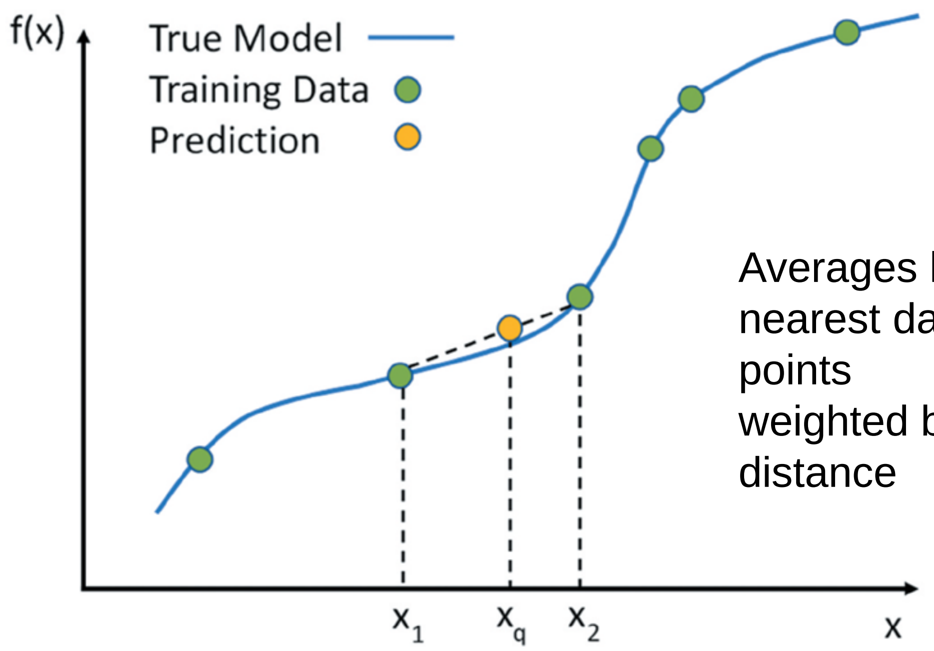
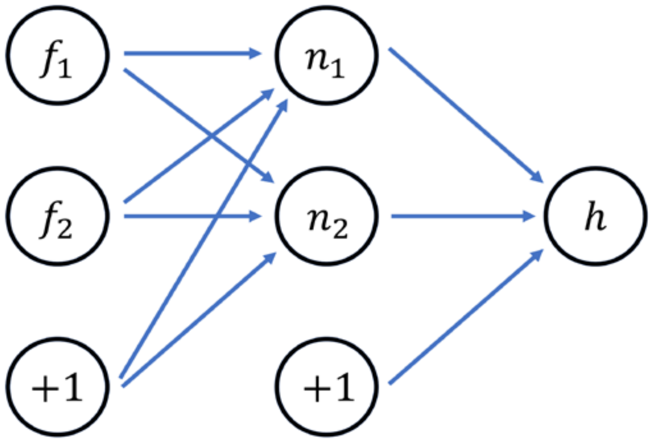
Surrogate Model Approaches

k Nearest Neighbors Regression (kNNr)



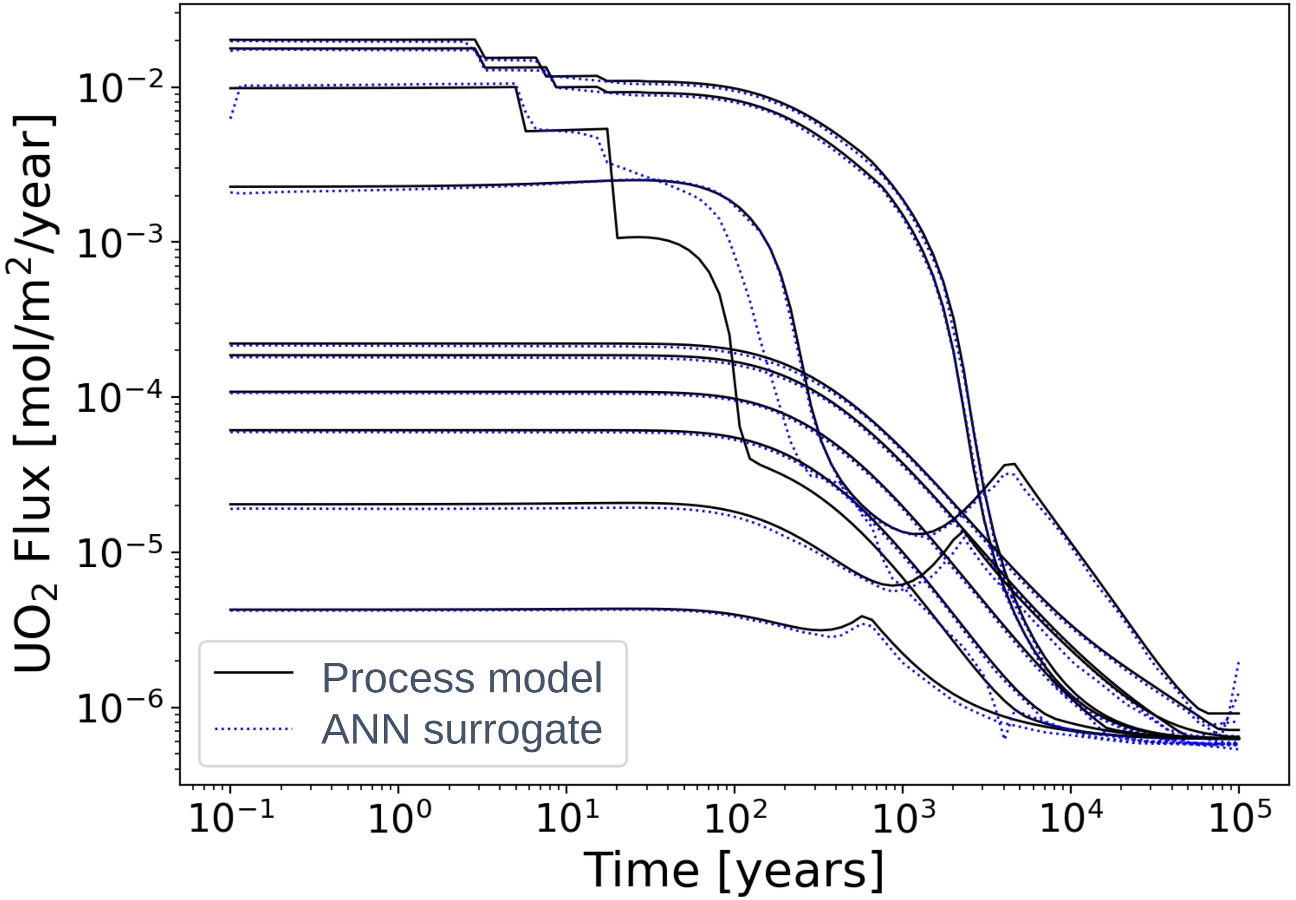
Averages k nearest data points weighted by distance

Artificial Neural Network (ANN)



Single layer feed-forward **neural network** with 2 input features and 2 neurons in the hidden layer

Surrogate Comparison



Input Ranges for Training and Testing

Input Features	Range
Initial Temp. (K)	300 – 400
Fuel Burnup (GWd/MTHM)	40 – 65
Env CO_3^{2-} Conc (mol/m^3)*	10^{-3} – 2×10^{-2}
Env O_2 Conc (mol/m^3)*	10^{-7} – 10^{-5}
Env Fe^{2+} Conc (mol/m^3)*	10^{-3} – 10^{-2}
Env H_2 Conc (mol/m^3)*	10^{-5} – 2×10^{-2}

* Log-uniform sampling distribution

Comparison to FMD Process Model

Error Metric	kNNr	ANN
Normalized Mean Square Error	0.11	0.12
Mean Absolute Percentage Error	29%	14%

Mariner et al. 2023

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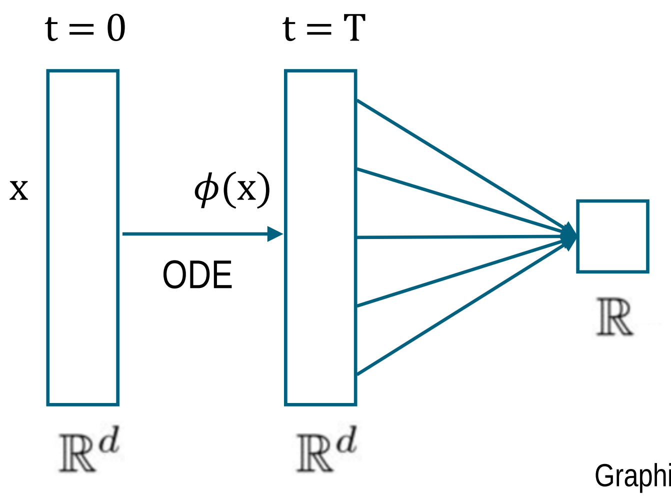
Future Improvements

- **Ability to handle changes in chemical conditions over time**
- **Exploring a Neural Ordinary Differential Equations (nODE) surrogate approach**
- **Calculation of surrogate error (compared to FMD process model) for a repository reference case simulation**

Neural Ordinary Differential Equations (nODE)



Fits a neural network to the **time-derivative** of process model data

Graphic modified from Dupont et al. (2019)

Electrochemical corrosion testing of simulated spent fuel (SIMFUEL)

Rationale for electrochemical model and testing

- The Fuel Matrix Degradation Model (FMDM) was developed as an electrochemical model because the dominant pathway for radionuclide release from the UO_2 matrix fraction of Commercial Spent Nuclear Fuel (CSNF) is an electrochemical process: the oxidation of $U^{IV}O_{2(s)}$ to soluble U(VI) species

$$UO_{2(s)} \rightarrow UO_2^{2+} + 2e^-$$

- Electrochemical corrosion tests using simulated spent fuel (SIMFUEL) electrodes address knowledge gaps on factors affecting UO_2 matrix dissolution kinetics in a breached geologic repository:
  - Fuel chemistry
  - Galvanic coupling to cladding
  - Environmental conditions (e.g., H_2, pH, CO_3^{2-}, Eh, Br^-, and temperature)

Rationale for electrochemical testing using simulated spent fuel (SIMFUEL)

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- Use of simulated spent fuel (SIMFUEL) provides composition control and excludes beta and gamma radiation fields to represent aged fuel in repository
  - Fuel Matrix Degradation Model assumes fuel has aged prior to waste package breach such that only long-lived alpha emitting fission products remain

- Controlled electrochemical experiments are designed to elucidate mechanisms, e.g.,:
  - Catalytic protection by noble metal fission product particles in contact with UO_2 matrix
  - Galvanic protection by noble metal fission product particles in contact with the UO_2 matrix

- Model predictions are validated and parameters calculated from short-term electrochemical measurements

Electrochemical testing using simulated spent fuel (SIMFUEL)

- Single variables are systematically controlled in electrochemical tests to quantify their effects on measured electrochemical parameters for FMDM validation
  - Noble metal content
  - Dissolved H_2 concentration
  - Total carbonate concentration
  - Temperature
  - Oxidant concentration (produced due to alpha radiolysis)
- Results from electrochemical tests may indicate need to include additional parameters and processes not currently included in FMDM
  - Noble metal alloy composition
  - Fuel composition and compositional changes over time
  - pH
  - Catalytic poisons (Br^-)
  - Galvanic coupling between UO_2 matrix and noble metals and UO_2 matrix and waste package alloys

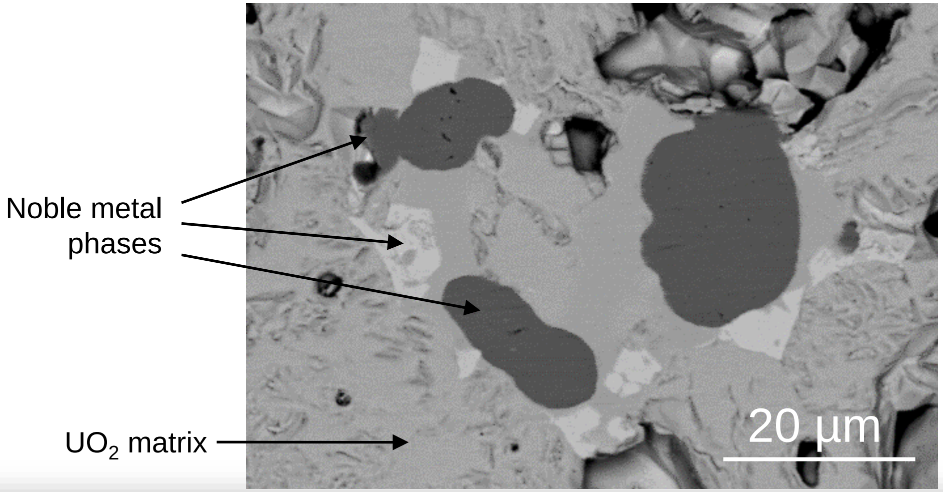
SIMFUEL synthesis and electrode fabrication

- SIMFUEL compositions include UO_2, lanthanide oxides, and different amounts of noble metal surrogate fission products to quantify the effects of noble metals[1]

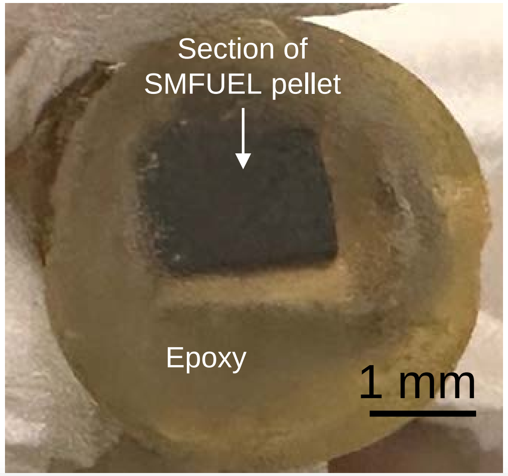
SIMFUEL material	UO_2-N	UO_2-L	UO_2-M	UO_2-H
Noble metal concentration (wt %)	0	0.6	1.7	2.9

Sintered SIMFUEL pellet

Backscattered electron micrograph of polished UO_2-H surface



SIMFUEL electrode



[1] Based on Lucuta, P. G., Verall, R. A., Matzke, H., and Palmer, B. J. **1991**. “Microstructural Features of SIMFUEL - Simulated High-Burnup UO_2-Based Nuclear Fuel.” *Journal of Nuclear Materials* 178: 48–60.

Electrochemical parameters in FMDM

- FMDM includes 11 half reactions that occur on the fuel surface and calculates the corrosion potential (E_{CORR}) and current densities (i) of each half reaction such that the net current at the fuel surface is zero

$$\text{At } E_{CORR},\ \sum i_{anodic} + \sum i_{cathodic} = 0$$

- UO_2 dissolution rate is calculated from the sum of current densities of 3 surface reactions
- Parameter values needed for half reaction current density equations can be determined from electrochemical measurements (FMDM currently uses placeholder values for some reactions)

Current density equation in FMDM for half reaction x

$$i_x = n_x F \sigma \boldsymbol{k_x} [C]^a e^{\left[\frac{\alpha_x F}{RT}(E_{CORR} - E_{0,x})\right]}$$

Fraction of fuel surface area containing sites where reaction occurs (σ)

Concentration of chemical reactant at fuel surface ($[C]$)

Determined from electrochemical measurements (i_x)

Rate constant parameter (k_x)

Determined from electrochemical measurements (E_{CORR})

Electrochemical methods

- Electrochemical tests use SIMFUEL as the working electrode in the standard three electrode system
- Method provides control of solution pH, chemistry, and temperature
- Determining the effect of one variable under known conditions involves multiple measurements

Electrochemical measurements

- Open circuit potential (OCP) measurements
- Potentiodynamic (PD) scans
- Potentiostatic (PS) tests

SIMFUEL surface characterization

- Electrochemical impedance spectroscopy (EIS)
- Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDS) analysis

Solution composition

- Inductively coupled plasma mass spectrometry (ICP-MS) for dissolved metal concentration

Electrochemical methods and results

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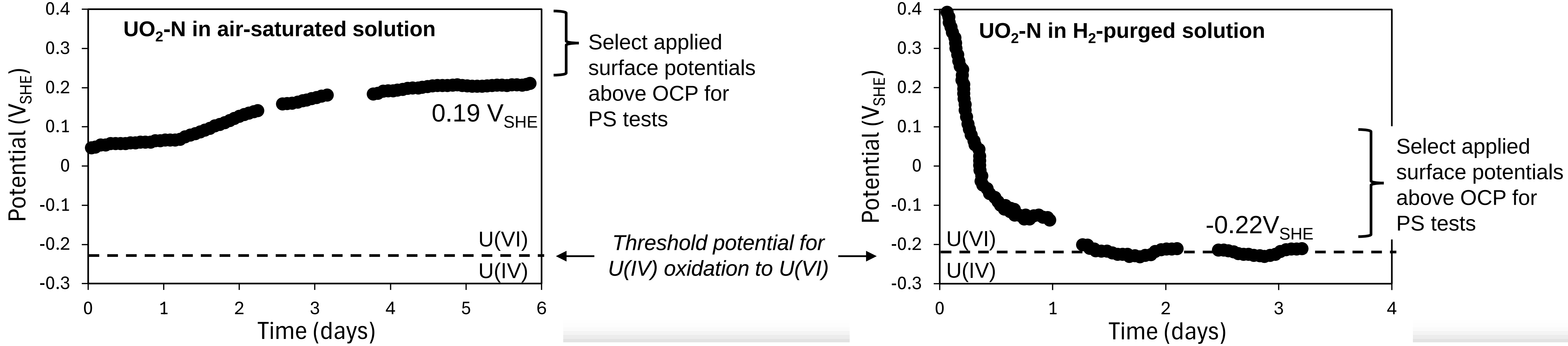
Open circuit potential (OCP) measurements:

- Provide insight into stability of SIMFUEL surface under known exposure conditions
- Are directly compared to FMDM parameter E_{CORR}
- Are used to select fixed surface potentials to apply during potentiostatic (PS) tests that provide insight into surface reaction kinetics

Effect of dissolved H_2 on measured OCP



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Summary

- Electrochemical experiments are designed to quantify the effect of individual variables on surface reaction kinetics by controlling:
  - SIMFUEL composition (e.g., noble metal content)
  - Solution chemistry and temperature
  - SIMFUEL surface potential
- Future electrochemical tests will determine effects of:
  - Concentration and composition of noble metal phases in SIMFUEL
  - Presence of catalytic poisons in solution (e.g., Br^-)
  - Dissolved H_2 concentration in solution
  - Galvanic coupling between cladding, noble metals, and UO_2 matrix
  - System temperature, dissolved carbonate concentration, and pH

Acknowledgements

- **Bert Debusschere, Sandia National Laboratories**
- **Vineeth Gattu, Argonne National Laboratory**

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Questions