Mixed Potential Model for Used Fuel Degradation

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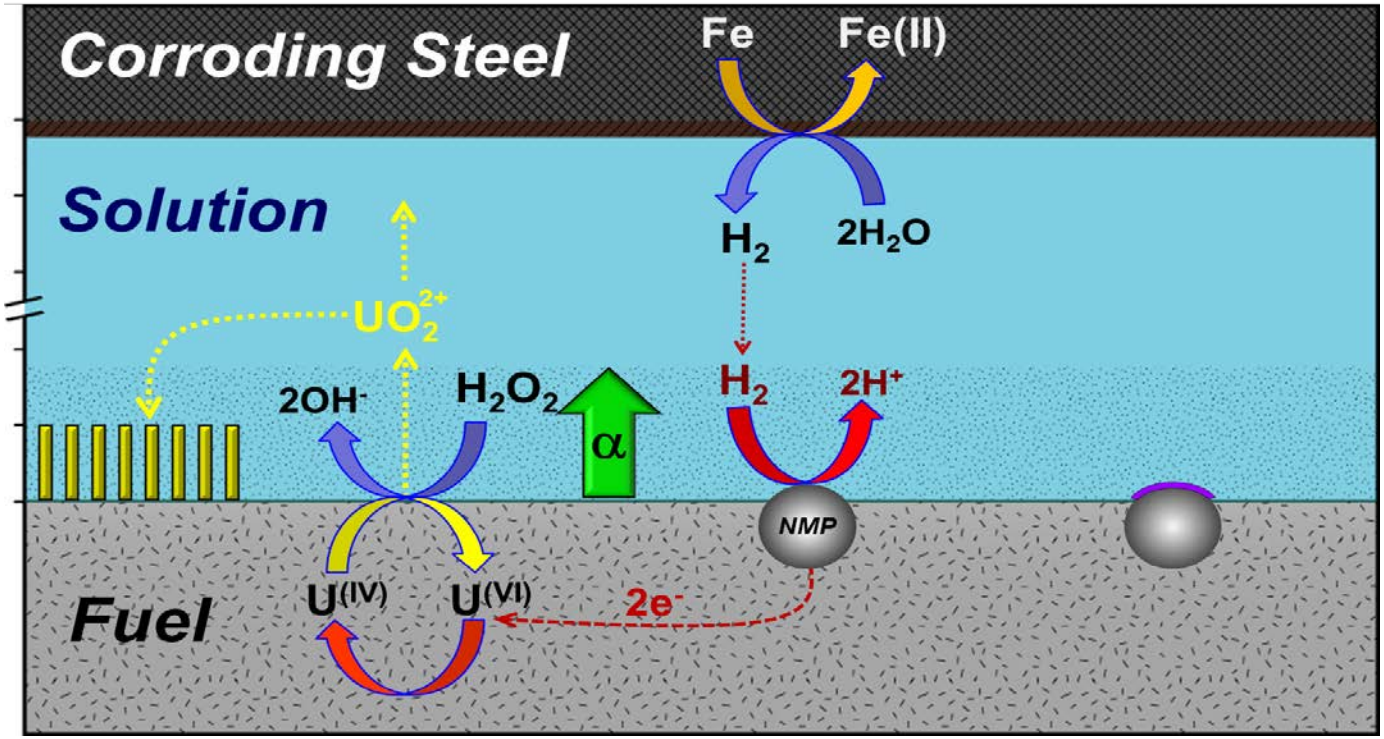
Objective: Mixed Potential Model (MPM)

- Develop model to calculate the dissolution rate of used fuel (g/m^2/years) based on the corrosion potential established at the fuel/solution interface
  - Accounts for interfacial redox reaction kinetics, radiolytic oxidants (H_2O_2), catalysis on noble metal particles (NMP), key solution reactions, and diffusion
  - Accounts for burnup, evolution of waste package T, in-package chemistry
  - Defines fractional fuel degradation rate for PA Source Term

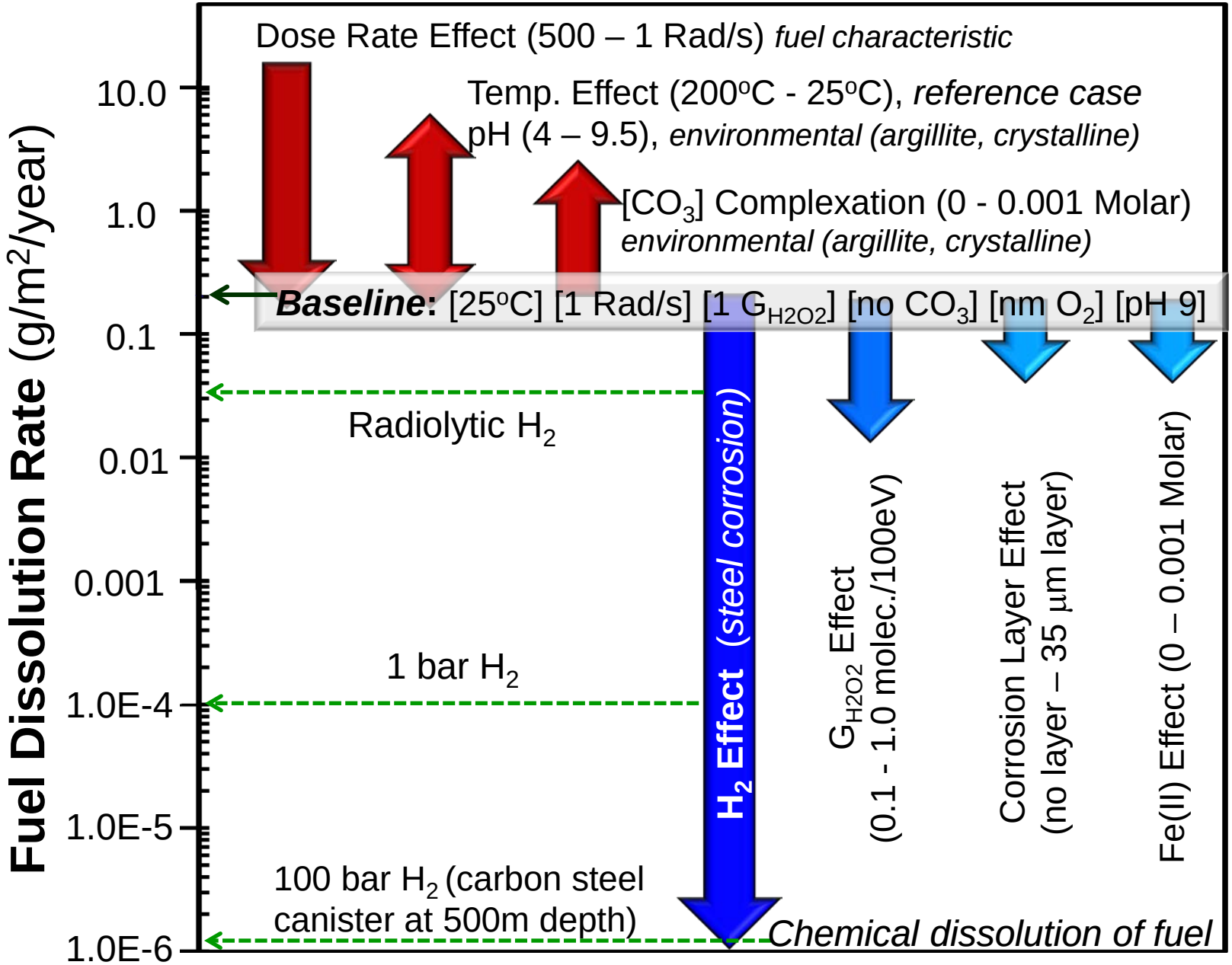


Status and Future Work

- **MPM V.2** *(FY14)*:
  - Added [H_2] Effect - catalysis of redox reactions on noble metal particles (NMP)
  - Added analytical description of Radiolysis Model: conditional G_{H2O2}, [H_2], [O_2]
  - Translated MPM to Fortran 2003 (ongoing)
  - Completed a series of sensitivity runs to determine relative impact of effects
  - Started a literature review for argillite, crystalline environment parameters
  - Milestones: M4 Argillite *(July 14),* M4 Crystalline *(August 15)*

- **MPM V.3** *(FY15)*:
  - Issue Fortran 2003 version of MPM to link with PA
  - Add [H_2] source kinetics: corrosion of steel canister shell and internal structure in collaboration with canister corrosion work package
  - Measure and model processes that counter [H_2] effect: poisoning NMP, effects of halides, SO_4^{2-} *(Requires experimental data)*
  - Replace estimated parameter values with experimentally determined values (H_2 effect, T dependence) – quantify uncertainties*(Requires experimental data)*

Summary of FY2014 MPM V.2 Sensitivity Runs



FY-2015 Priorities

- Link MPM with PA
  - Argillite and crystalline specific parameters: pH, complexation (carbonate, sulfate, halides)
- Couple MPM with H_2 source kinetics: corrosion of waste package steel shell and internal structures
- Measure and model processes that counter H_2 effect on fuel dissolution (poisoning of surfaces, NMP alteration)
- Replace parameter placeholders with experimentally determined values (H_2 effect, T dependence) – *Quantify uncertainties*

Fuel Degradation Model Interfaces with PA

Performance Assessment:
Argillite & Crystalline

Solution Chemistry:
pH $[H_2]$ $[O_2]$ $[CO_3^{2-}]$ $[SO_4^{2-}]$…
Fuel inventory and dose rate
Temperature

Radionuclide release rates
(yr^{-1})

Parameter values database

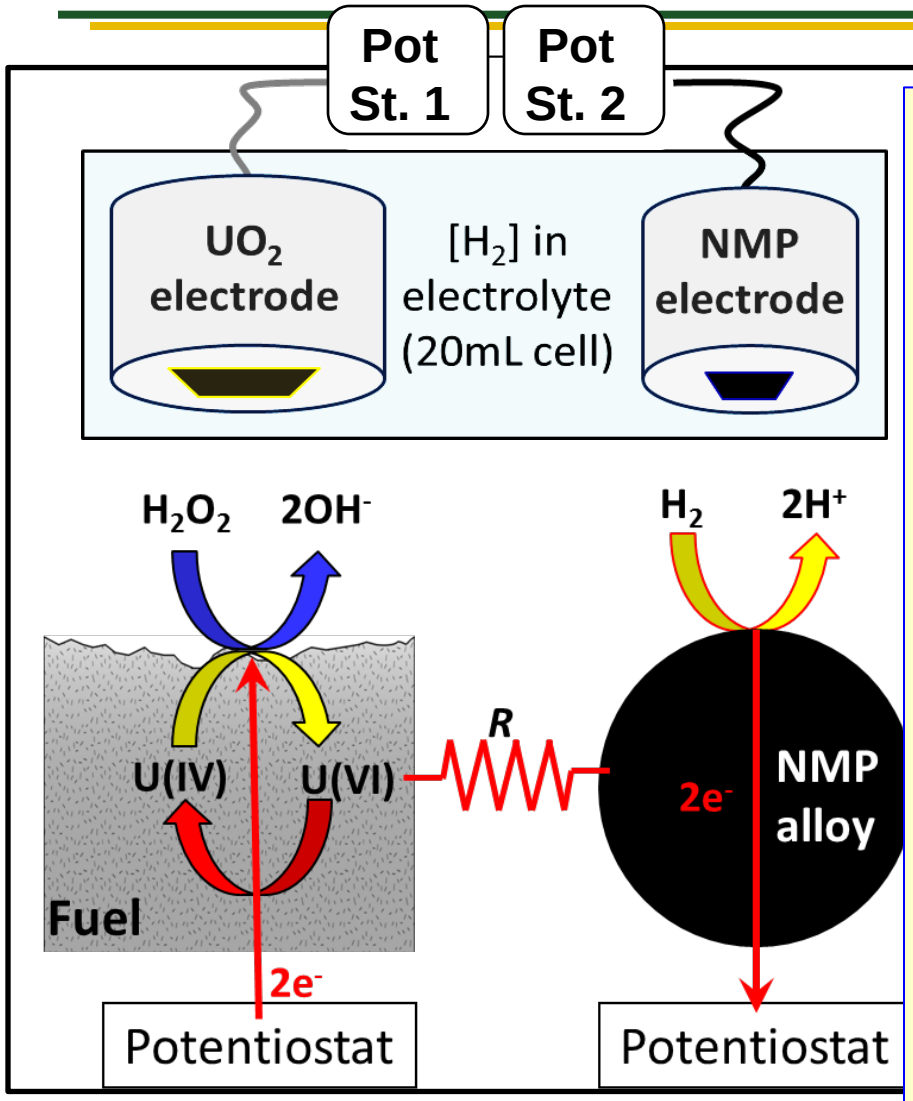
- Steel corrosion kinetics (new in FY 2015)
- Fuel corrosion kinetics
- Interfacial redox chemistry at fuel surface
- Heterogeneous catalysis on NMP including poisoning of catalyst
- Complexation effects
- Temperature dependences
- Appropriate corrosion product phases (saturation)
- Radiolytic effects
- Solution diffusion coefficients

Mixed Potential Model
for matrix degradation
(with radiolysis, catalysis, and container corrosion modules)
+ Instant Release Fraction Model

Discussion Slides

Used Fuel Disposition

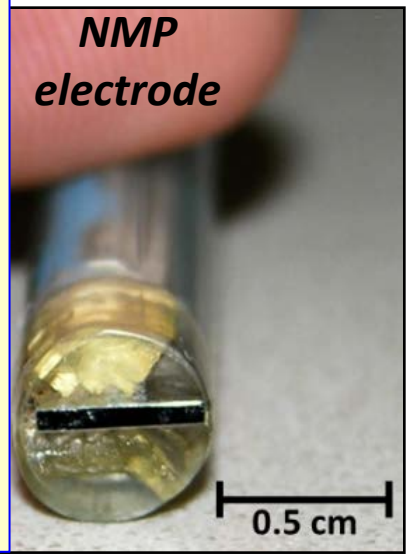
Electrochemical Experiments: argillite and crystalline solutions



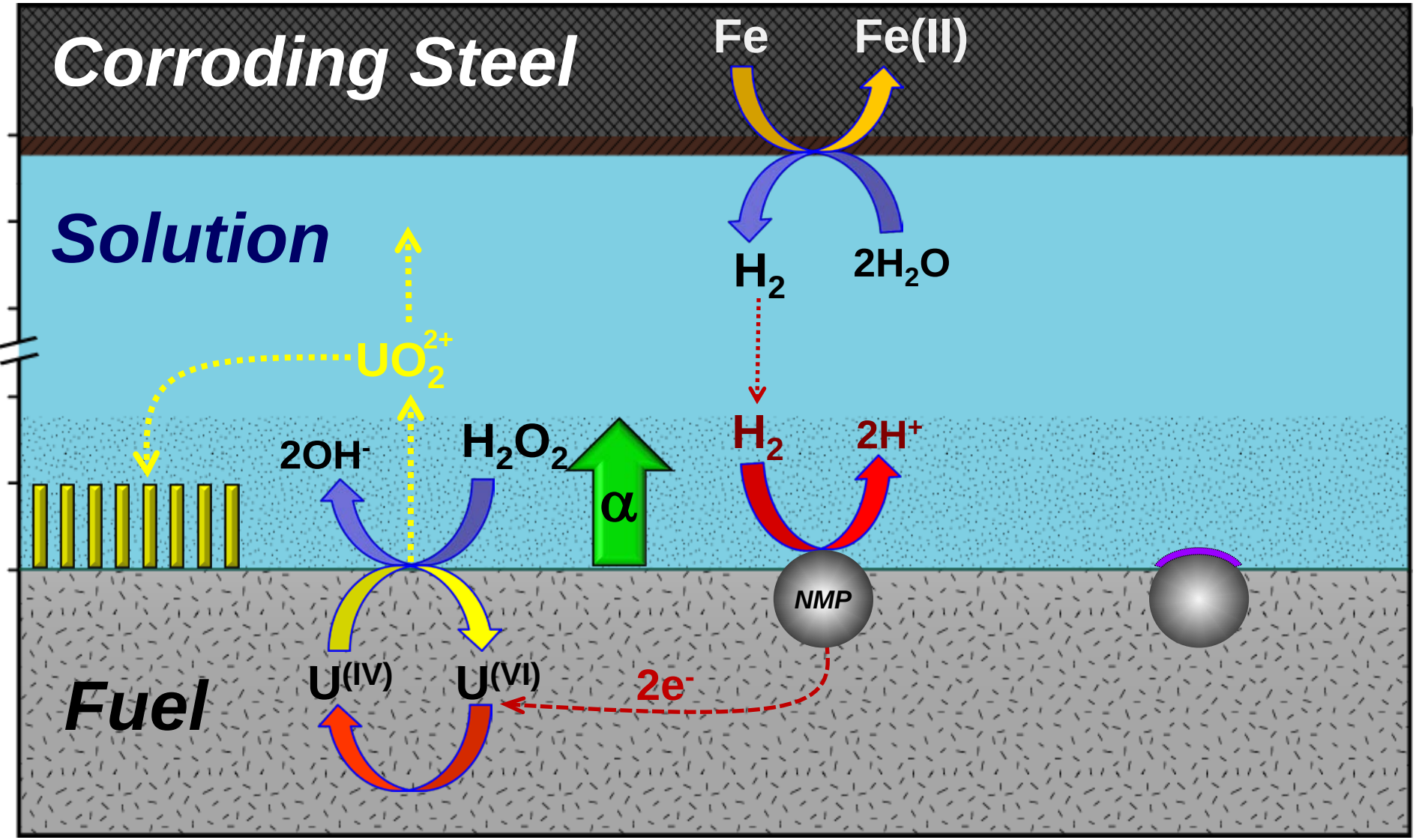
Experimental set-up

Measure:
- Uranium in solution (***dissolution rate***)
- Corrosion potentials
- Corrosion currents
- Characterization of surface alteration (UO_2 and NMP) for relevant solutions
- Poisoning of NMP surface (change in electrochemical properties in the presence of halides, etc.)

Model:
- ***Fuel dissolution rate***
- Corrosion Potential
- Corrosion currents
- Corrosion layer thickness
- Diffusive transport of key species near interface

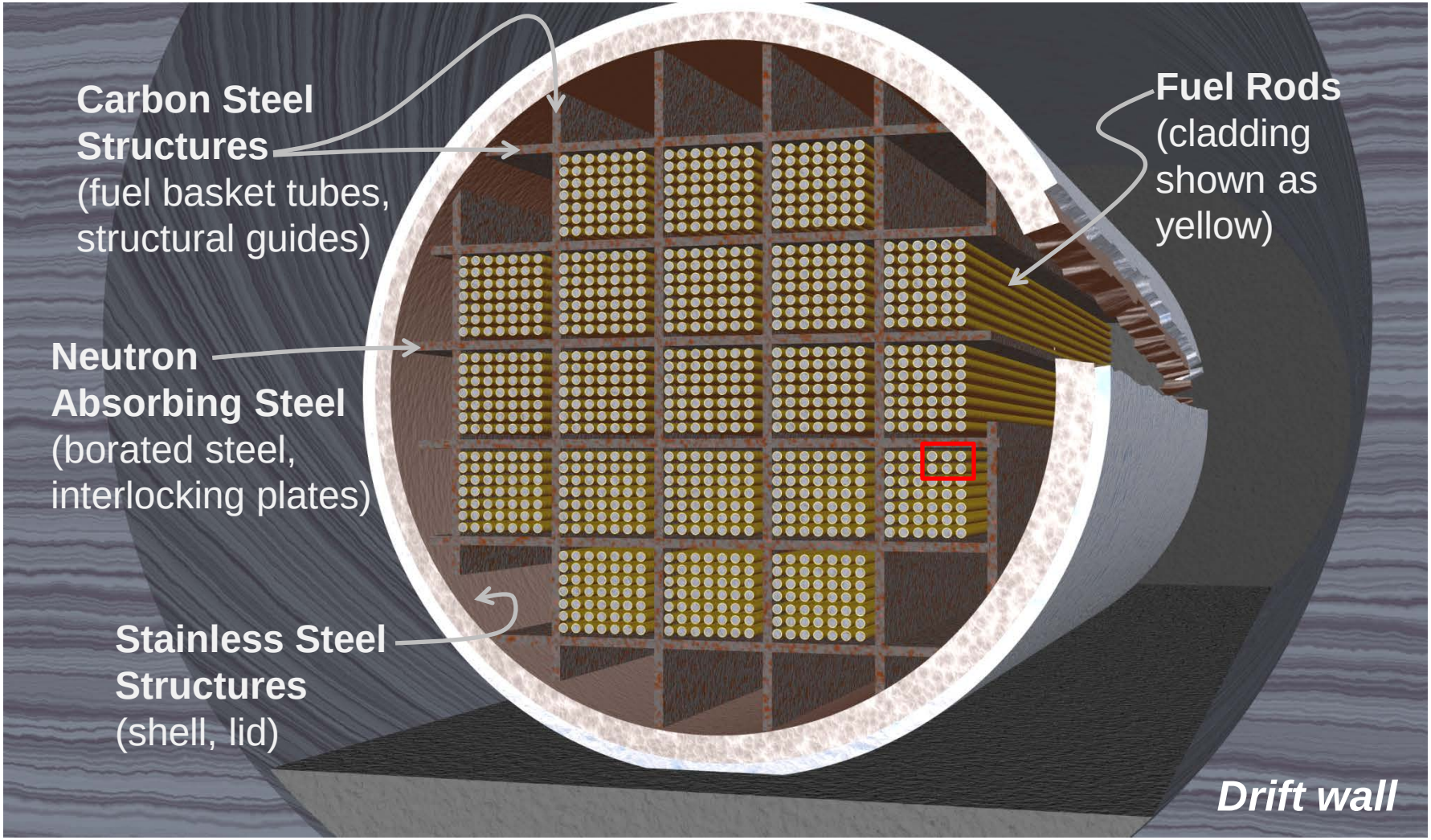


Key Processes Quantified in MPM



Mixed Potential Model Context:

Simplified Cross Section Through Generic Canister



Mixed Potential Module:
Initial settings

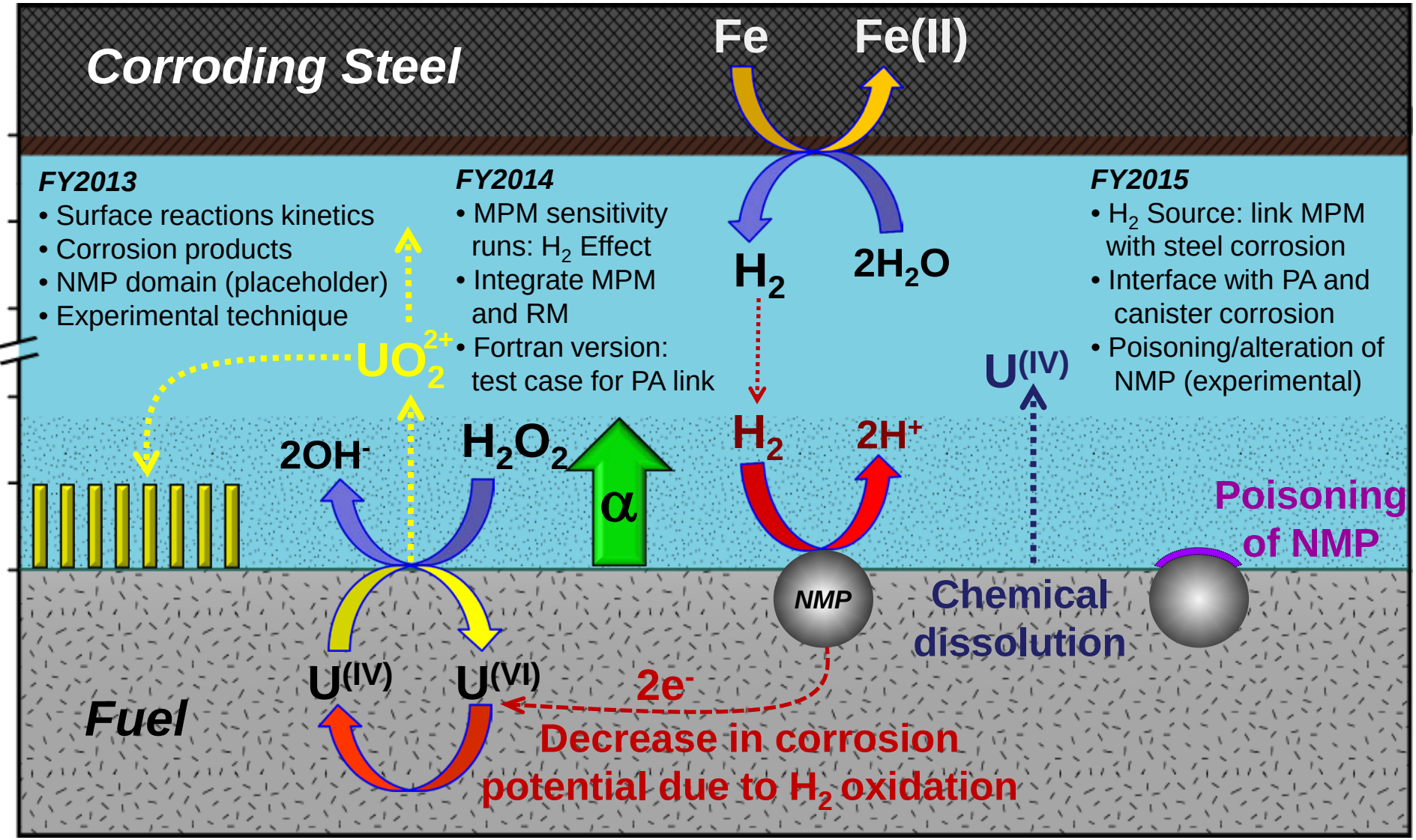
- **Parameters**
  - Alpha-particle penetration depth
  - G_{H2O2} (moles/J)
  - Rate constants *(fT)*
  - Charge transfer coefficients
  - Standard potentials *(fT)*
  - Diffusion coefficients *(fT)*
  - Saturation concentrations U(VI) *(fT)*
  - Activation energies for T dep.
  - Porosity of U(VI) layer
  - Tortuosity of U(VI) layer
  - Resistance between NMP - UO_2
- **Constant (not explicit in model)**
  - pH
  - Pressure
- **Variables**
  - Dose rate
  - Temperature
  - $[O_2]$, $[CO_3^{2-}]$, $[H_2]$, $[Fe^{2+}]$
- **User determined inputs**
  - Length of diffusion cell
  - Number of calc. points in cell
  - Duration of simulation
  - Surface coverage of NMP
- **Calculated by model (output)**
  - Corrosion potential
  - Surf. reaction current densities
  - Surface fluxes
  - Con. all species at each calc. point
  - Corrosion layer thickness

MPM Parameter Database

Mass-Balance Species	Con: C_i (mol/cm^3)	Saturated con: C^{sat}_i (mol/cm^3)	T dependence of C^{sat}_i: ΔH^{sat}_i (J/mol)	Diffusion coeff: D_i (cm^2/s)	Activation energy for D_i: ΔHD_i (J/mol)
UO_2^{2+}	MPM Output	3.20E-08	6.E+04	5.00E-06	15000
$UO_2(CO_3)_2^{2-}$	MPM Output	$5.12[CO_3]^{1.34}$	6.E+04	5.00E-06	15000
U(IV)	MPM Output	----	----	----	----
CO_3^{2-}	Environmental Input *(link to IPC)*	----	----	1.70E-05	15000
O_2	Environmental Input *(link to IPC)*	----	----	1.70E-05	15000
H_2O_2	Radiolysis Model *(PNNL)*	----	----	1.70E-05	15000
Fe^{2+}	Environmental Input *(link to IPC)*	1.00E-08	6.E+04	5.00E-06	15000
H_2	Environmental Input *(link to IPC)*	----	----	Literature	Literature
$UO_3 \cdot 2H_2O$	MPM Output	See Sat. Con.	----	----	----

Used Fuel Disposition

MPM Parameter Database:
Argillite and Crystalline Environments

Anodic reactions on fuel surface	Rate Constant at 25°C	Activation energy (J/mol)	Charge Transfer Coefficient	Standard Potential
$UO_2 \rightarrow UO_2^{2+} + 2e^-$	***pH dependence [Power law exponent]***	6.0E+04 *(estimate)*	0.96	0.169
$UO_2 + 2CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} + 2e^-$	***Concentration and pH dependence***	6.0E+04 *(estimate)*	0.82	-0.173
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	7.40E-06 (literature)	6.0E+04 *(estimate)*	0.41	-0.121
$H_2 \rightarrow 2H^+ + 2e^-$	**Estimate**	Estimate	Estimate	Literature
Cathodic reactions on fuel surface				
$H_2O_2 + 2e^- \rightarrow 2OH^-$	1.20E-10	6.0E+04 *(estimate)*	0.41	-0.973
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	1.40E-10	6.0E+04 *(estimate)*	0.5	-0.426
Precipitation of corrosion product				
$UO_2^{2+} + 2H_2O \rightarrow UO_3{:}2H_2O + 2H^+$	1.0E-3 *(estimate)*	6.0E+04 *(estimate)*	----	----
$UO_2(CO_3)_2^{2-} + 2H_2O \rightarrow UO_3{:}H_2O + 2CO_3^{2-} + 2H^+$		6.0E+04 *(estimate)*	----	----

Key Processes Quantified in MPM