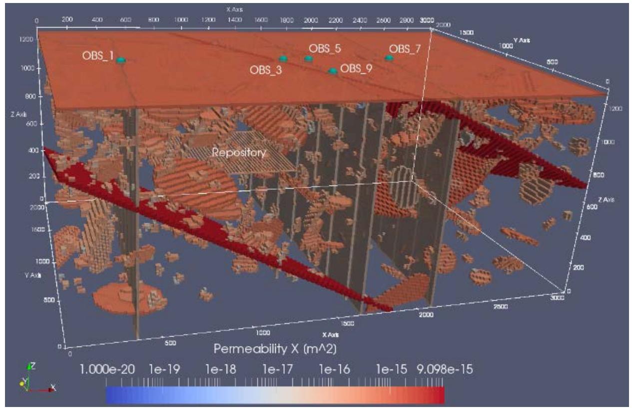

Overview of Commercial SNF Degradation Rate Models

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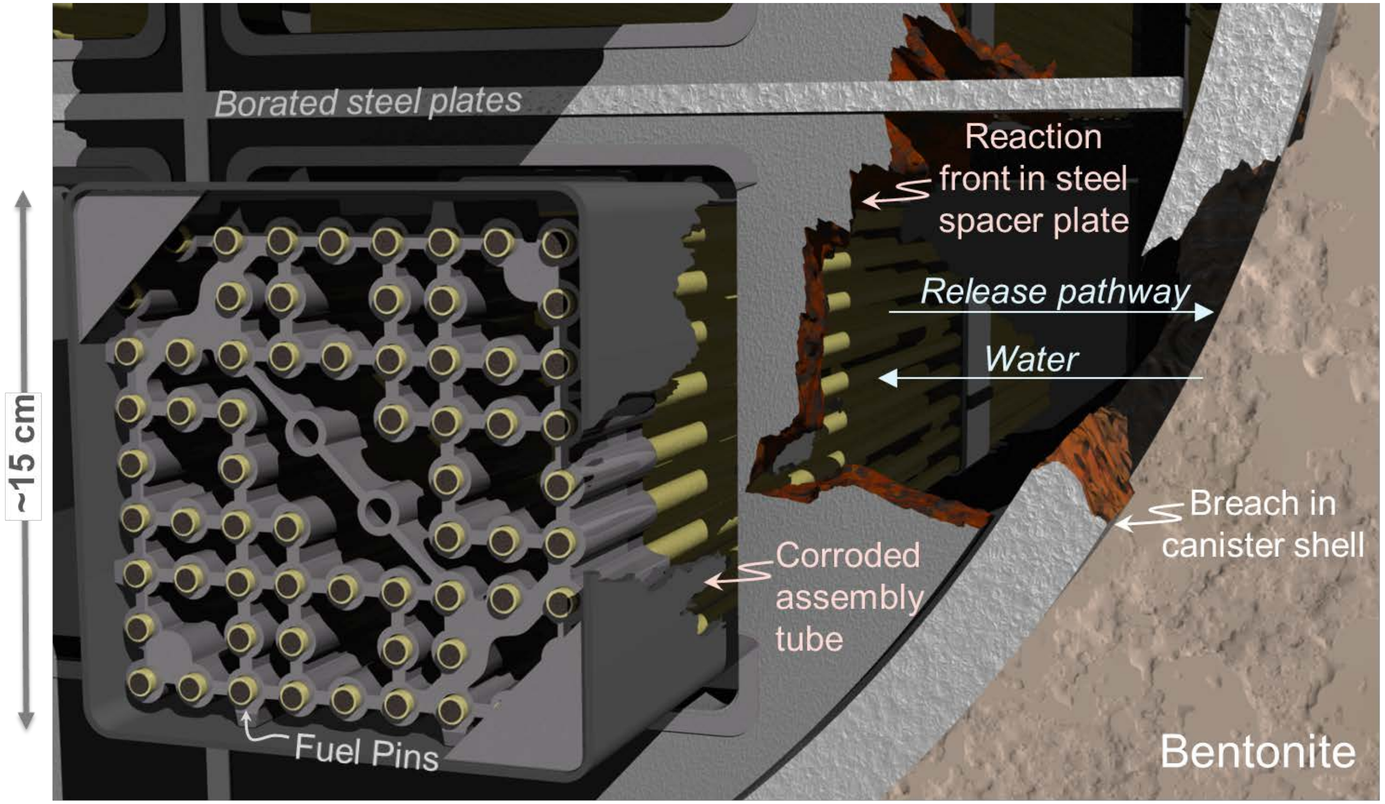
SAND2024-06251PE

Presentation Outline

- Concepts for Degradation Rate of Spent Nuclear Fuel (SNF)
  - Background
    - Concepts for SNF degradation
    - SNF degradation rates for repository system performance assessment (PA)
  - Program models implemented for
    - Process understanding
    - Performance assessment
- The Fuel Matrix Degradation Model
  - Process models – radiolysis model and mixed potential model
  - Primary sensitivities
  - Model couplings and implementation for GDSA
- Strategic Approach for SNF Degradation Testing
  - Methodology for prioritization
  - Activity status/discussion
  - Path forward
- International Collaborations (B. Hanson)

Context: Breached SNF Canister in Repository



Schematic figure of a breached SNF waste canister

Source: Wang et al. (2016)

Waste Package (WP) Breached

- Fluid pathways in/out
- In-package chemistry
  - Incoming water
  - Metal corrosion (WP internals)
  - Spent nuclear fuel (SNF) corrosion drives radionuclides (RN) releases
- Away from the fuel surface RN
  - Interact with corrosion products and bentonite barrier
  - Evaluated for solubility limited concentration

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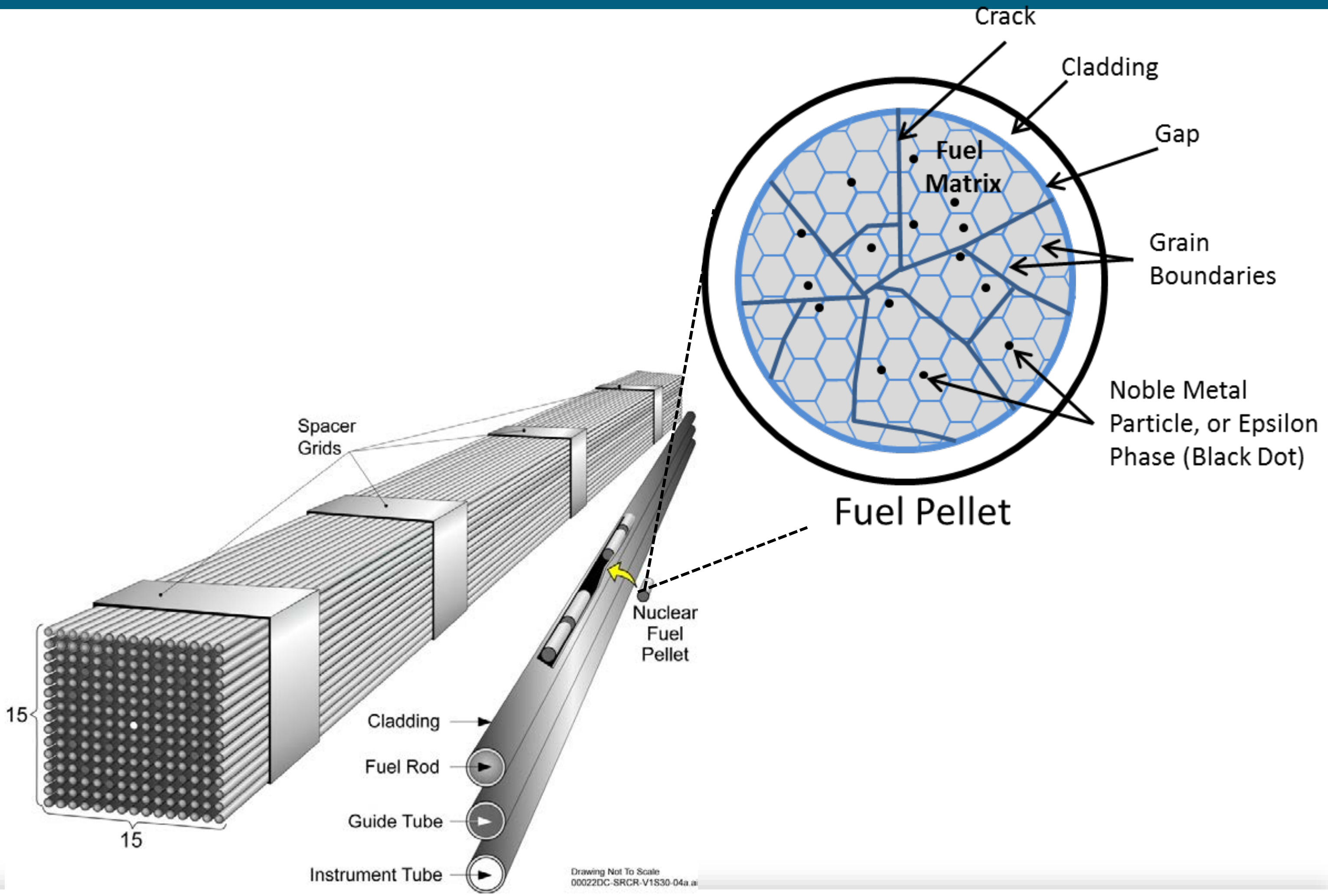
Basic Concepts of SNF Degradation

- First Approximation: SNF as UO_2 – Ore Deposit Analogues
  - Stable for millions/billions of years in saturated/anoxic systems
  - Lower bound on degradation rate from chemical dissolution
    - U (IV) in SNF dissolves to U(IV) species in solution
    - Flux of solvent (or diffusion of dissolved) controls rate to low value
      - This is a reasonable ***MINIMUM*** bound for degradation rate of SNF
- Query: What Else Matters for Reality? (to Increase Rate Above ***MIN***)
  - Oxidation of U(IV) to U(VI) is primary, first-order effect (sources?)
    - Little to none from materials – mainly strongly reducing metals
    - Groundwater influx – possible for future events but not continual/pervasive
    - SNF delta from UO_2 – alpha radiation field – radiolytic generation of oxidants
      - This is the major source of oxidants (e.g., H_2O_2) directly at SNF surface
      - IF the rate of production drives SNF oxidation, this is a reasonable ***MAXIMUM*** bound for degradation rate of SNF
- Query: What Else Matters for Reality? (Potential Sinks for H_2O_2 to Offset ***MAX***)
  - Other reductants
    - Other constituents in SNF (e.g., Am, Pu, etc. – only few percent)
    - Steels are not directly at oxidant source location (mm vs microns, but abundant)
    - Cladding – proximal, but very unreactive at these relevant temperatures
    - Hydrogen (H2) generation – potentially abundant from steel surface corrosion, labile to reach SNF surface, reactive

Conceptual Overview of SNF Degradation Models

- Reducing Disposal Environments
- Two Release Processes Concepts:
  - Instant Release Fraction (IRF)
    - At cladding failure (gap & grain boundaries)
  - Fuel Matrix Degradation (FMD)
    - UO_2 solubility limits (slow)
    - Oxidative Dissolution (faster)
      - Radiolytic oxidants – e.g., H_2O_2
      - Reductants – e.g., H_2
    - Role of Epsilon Phase (Ru, Rh, Pd, Mo, Tc)
      - “Protects” matrix grains from oxidation
      - Cathodic coupling?, catalytic?, both?
    - FMD Model includes all above to assess the SNF matrix degradation rate over time



Spent Fuel Degradation Rates from Other Programs

Table 3-2. UNF dissolution rates relevant to contact with groundwater in crystalline rock under reducing conditions

Source	Rates	Units	Comments
SKB (2006, 3.3.7)	10^{-8} (min) 10^{-7} (mode) 10^{-6} (max)	yr^{-1}	Log-triangular distribution based on Werme et al. (2004)
Pastina and Hellä (2010, 1.4.6)	10^{-7} (reference)	yr^{-1}	Based on model by Werme et al. (2004) and data by King and Shoesmith (2004), Ollila and Oversby (2005), Carbol et al. (2006), and Ollila (2008) that show absence of radiolysis effects in presence of metallic iron (strongly reducing conditions); considered pessimistic (p. 138)
Ollila (2008)	Anoxic: 8.1×10^{-7} (min) 2.2×10^{-6} (max) Reducing: 4.3×10^{-8} (min) 2.2×10^{-7} (max)	yr^{-1}	Static batch dissolution tests, isotope dilution, 0.01 M NaCl; UO_2 doped with 0, 5 and 10% ^{233}U; anoxic conditions from N_2 and 1 ppm S^{-2} (E_h ~ -200 mV); reducing conditions from N_2 and Fe (E_h ~ -400 mV); 2 $cm^2 g^{-1}$ geometric surface area
Röllin et al. (2001)	$6 \times 10^{10} \times U_{max}$	$mg \, m^{-2} d^{-1}$	U_{max} is the aqueous solubility of $UO_{2(c)}$ in $mol \, L^{-1}$; 300 $cm^2 g^{-1}$; reducing conditions (~8×10^{-4} $mol \, L^{-1}$ $H_{2(g)}$); forward reaction rate because measured under flow-through conditions; very low flow rates provided insufficient flux of $H_{2(g)}$ to maintain reducing conditions
Jerden et al. (2015)	FMDM	$mg \, m^{-2} yr^{-1}$	The FMDM code is coupled with PFLOTRAN to calculate the UNF dissolution rate as a function of environmental conditions and surface precipitation (see text); 0.001 $m^2 g^{-1}$ specific surface area recommended (Cachoir and Mennecart 2011; Jerden, J., pers. comm.)

Source: Sassani et al., 2016

Forsmark Site Example

- Fractional dissolution rate range 10^{-6}/yr to 10^{-8}/yr
  - *Corresponding **fuel lifetimes**: ~ 1 Myr to 100 Myr*
- *Dissolution rates for oxidizing conditions (**not anticipated**), up to 10^{-4}/yr*

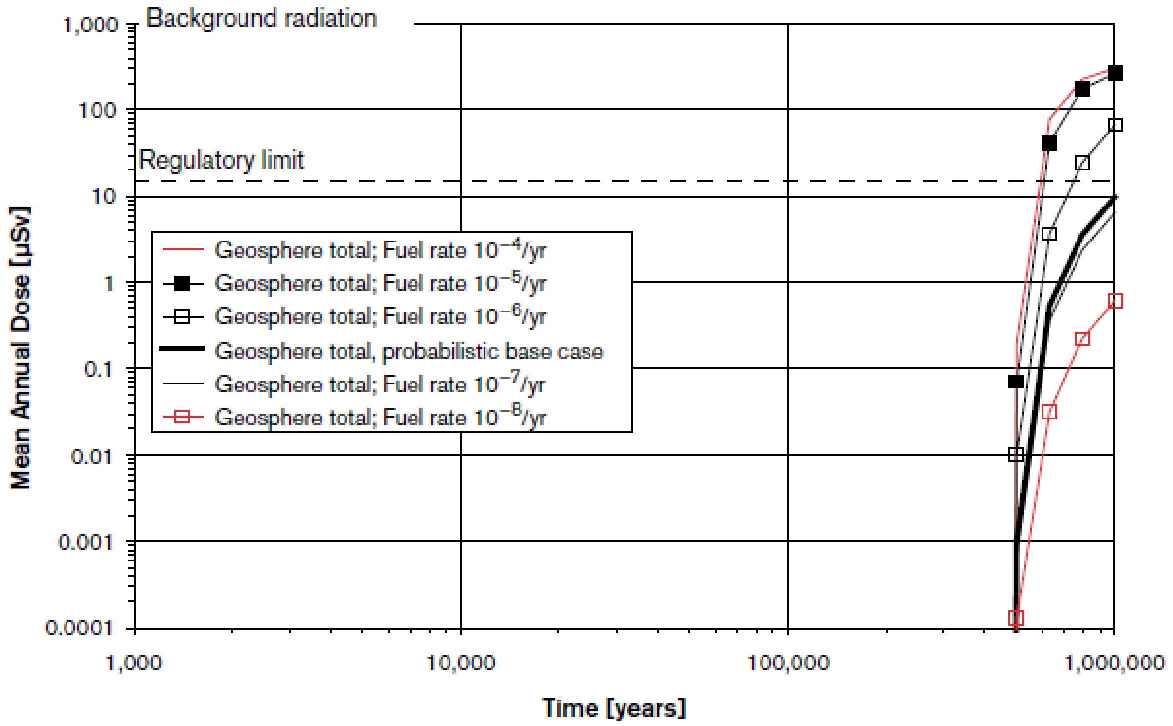
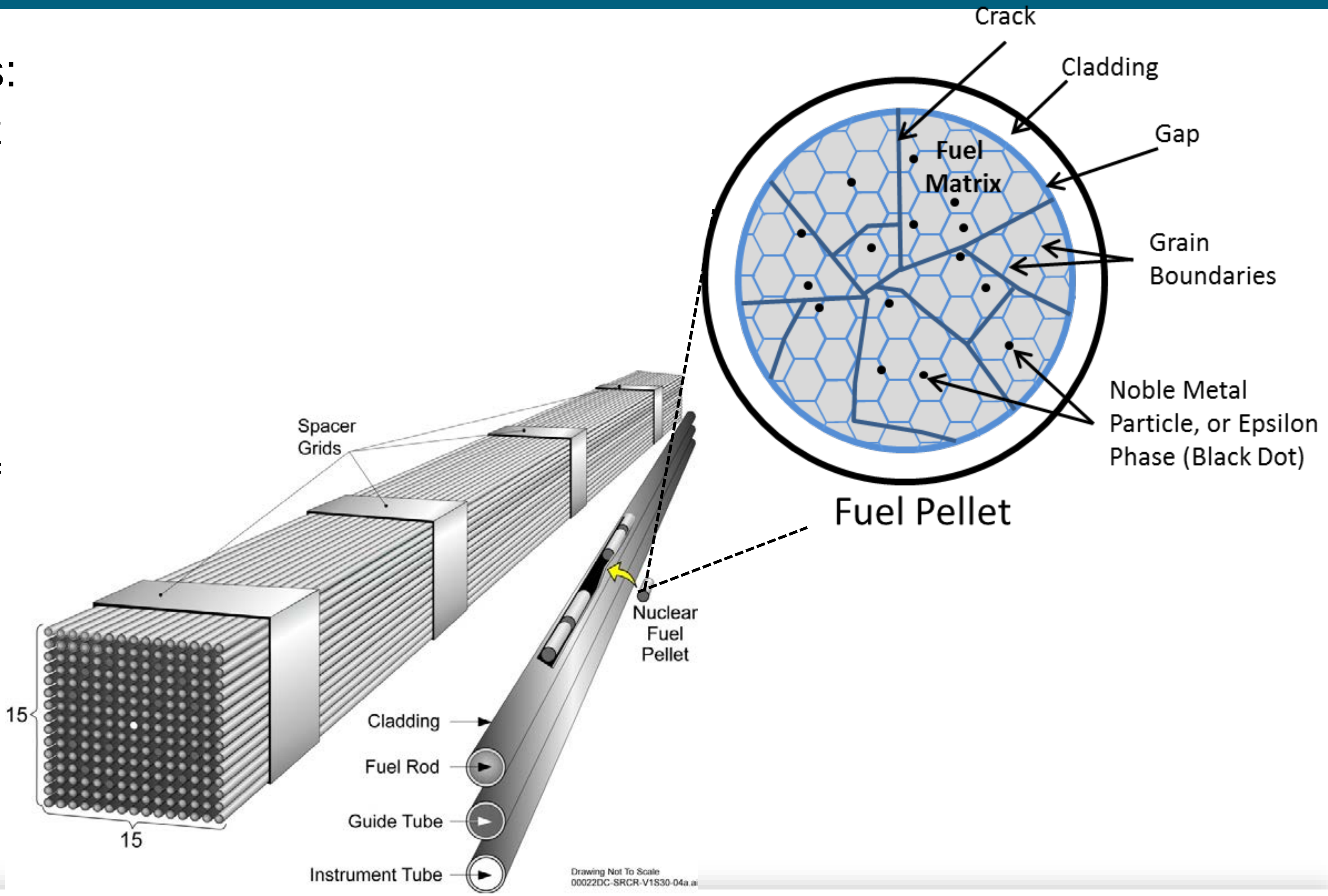


***Figure 10-44.** Sensitivity of the base case result to the fuel dissolution rate. Semi-correlated hydro-geological DFN model for Forsmark. 1,000 realisations of the analytic model for each case.*

Source: SKB 2006, *Long-term Safety for KBS-3 Repositories at Forsmark and Laxemar—a First Evaluation,* TR-06-09, section 10.6.5
Also, SKB 2006, *Fuel and Canister Process Report for the Safety Assessment SR-Can,* TR-06-22, section 2.5.5

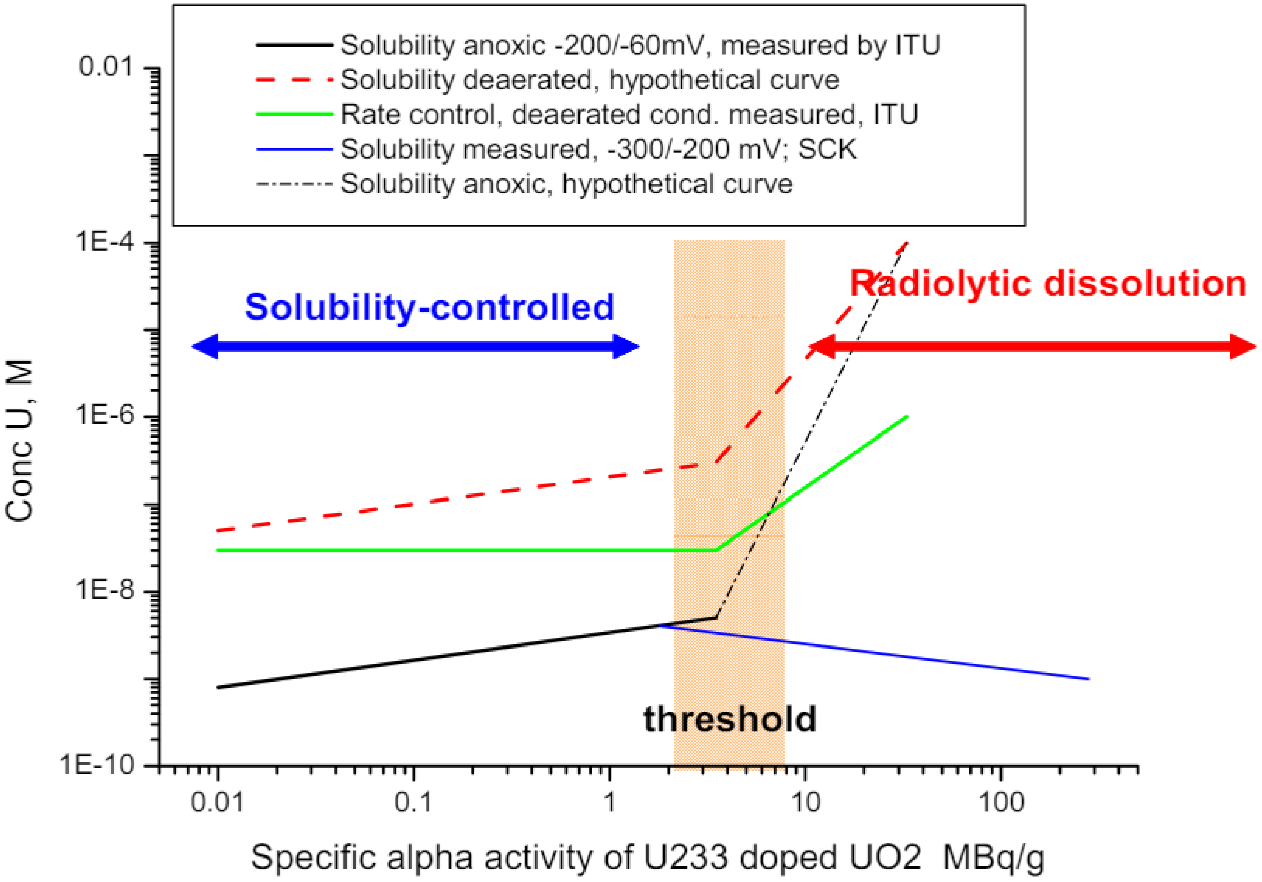
Why Develop a Mechanistic Model?

- Understanding Mechanisms/Processes:
  - Allows consideration of the environment context for the results
  - Provides a basis for interpreting experimentally determined data
  - Permits relating short-term data from experiments to expected long-term system evolution
  - Creates a more transparent construct of application versus random sampling application



UO_2 Dissolution: Mechanistic Representation

- SNF (UO_2) matrix dissolution rate defines release rate of radionuclides (RN) (congruent)
- The FMDM includes:
  - Solubility-limited mechanism during aqueous interactions
  - Effect of dissolved carbonate on UO_2 dissolution rate
  - Effects of radiolysis (α) produced oxidants (H_2O_2)
  - Reaction of H_2 at the fuel surface
  - Electrochemical reactions of oxidant/reductant species via Noble metal particles (NMP)



Effect of alpha (α) activity on solubility and rate controlled release of U from α doped UO_2 (Poinssot et al. 2005; Cachoir et al., 2005)

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FMDM Model Sensitivities

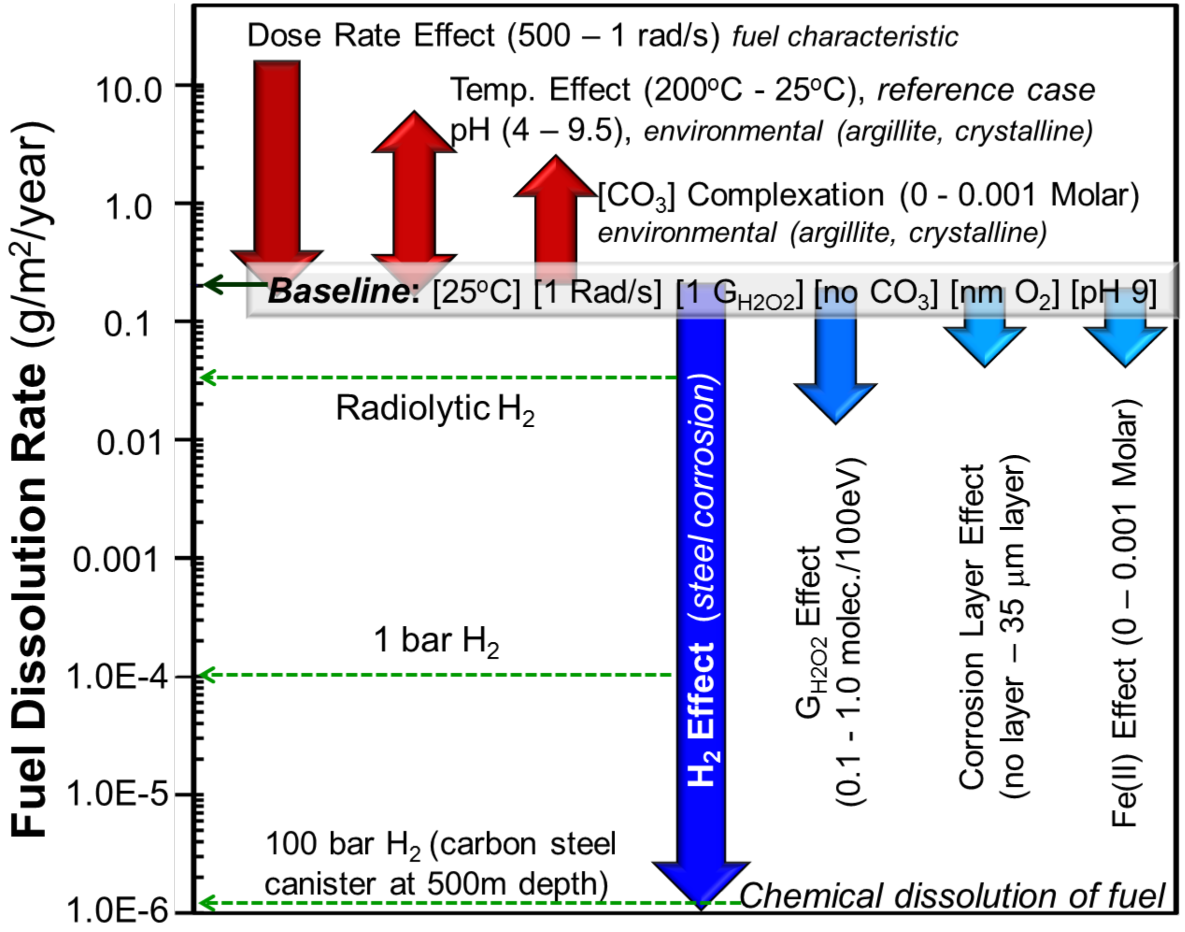
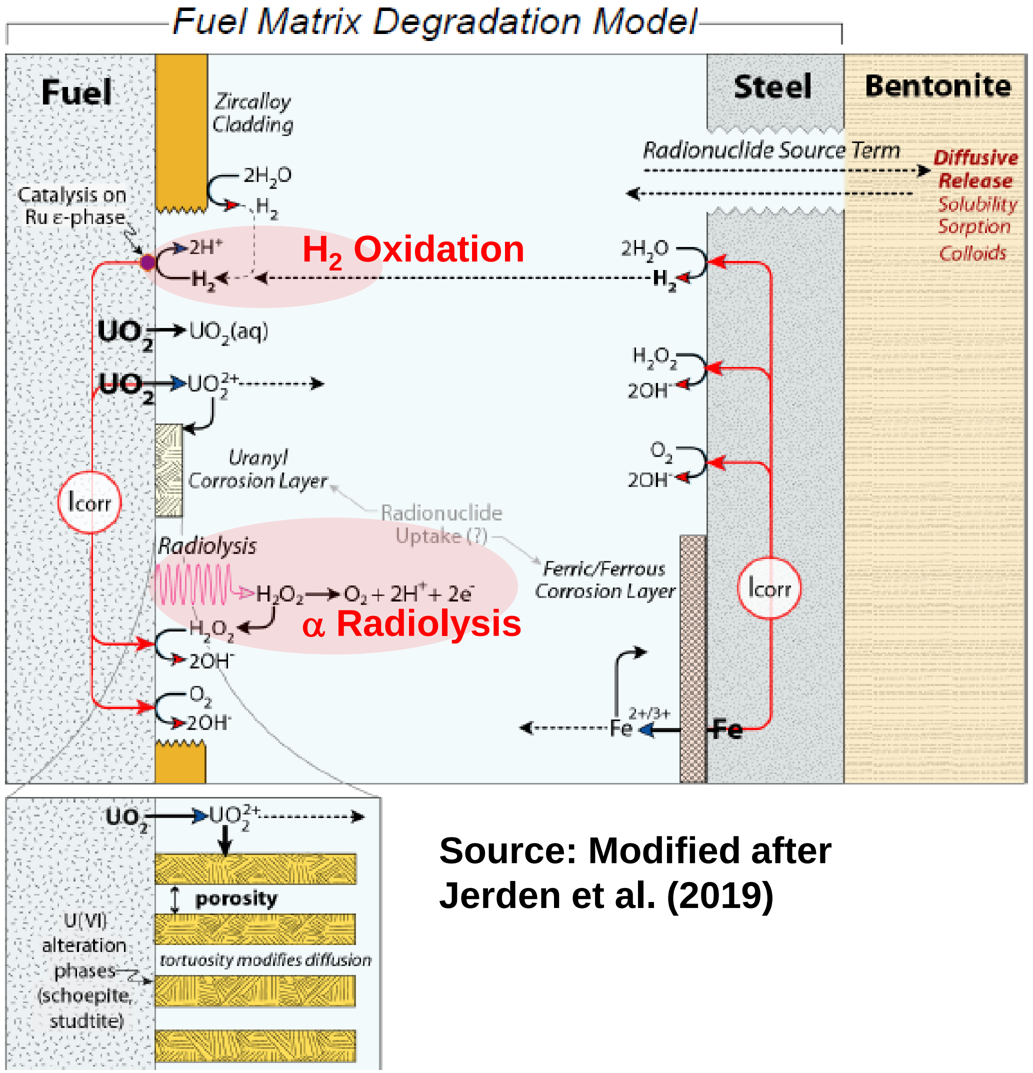


Figure 7. Summary of compiled results from FY2014 MPM V2 sensitivity runs. (from Jove-Colon et al., 2014)

Fuel Matrix Degradation Model (FMDM)



Source: Modified after Jerden et al. (2019)

The Fuel Matrix Degradation Model (FMDM)

- Based on the Canadian Mixed Potential Model (MPM) for UO_2 dissolution (Shoesmith et al., 2003)
- Electrochemical transport model
- Surface potentials based on major interfacial anodic and cathodic reactions
- Reaction rates for the fuel surface reactions used to represent oxidative UO_2 dissolution
- H_2 catalytic oxidation by noble metal particles (NMPs)
- H_2O_2 generated by α irradiation field (extends to ~35 microns from fuel surface)
- 1-D diffusive transport of chemical species
- Surface precipitates (e.g., schoepite/studtite)

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FMDM Electrochemical (E-chem) Reactions at the SNF Surface

SNF Surface Half Reactions

Number	Reaction	Type
1	$UO_2 \rightarrow UO_2^{2+} + 2e^-$	Anodic
2	$UO_2 + 2CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} + 2e^-$	Anodic
3	$UO_2 \rightarrow UO_{2(aq)}$	Chemical
4	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	Anodic
5	$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$	Anodic
6	$H_2O_2 + 2e^- \rightarrow 2OH^-$	Cathodic
7	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Cathodic

NMP Surface Half Reactions

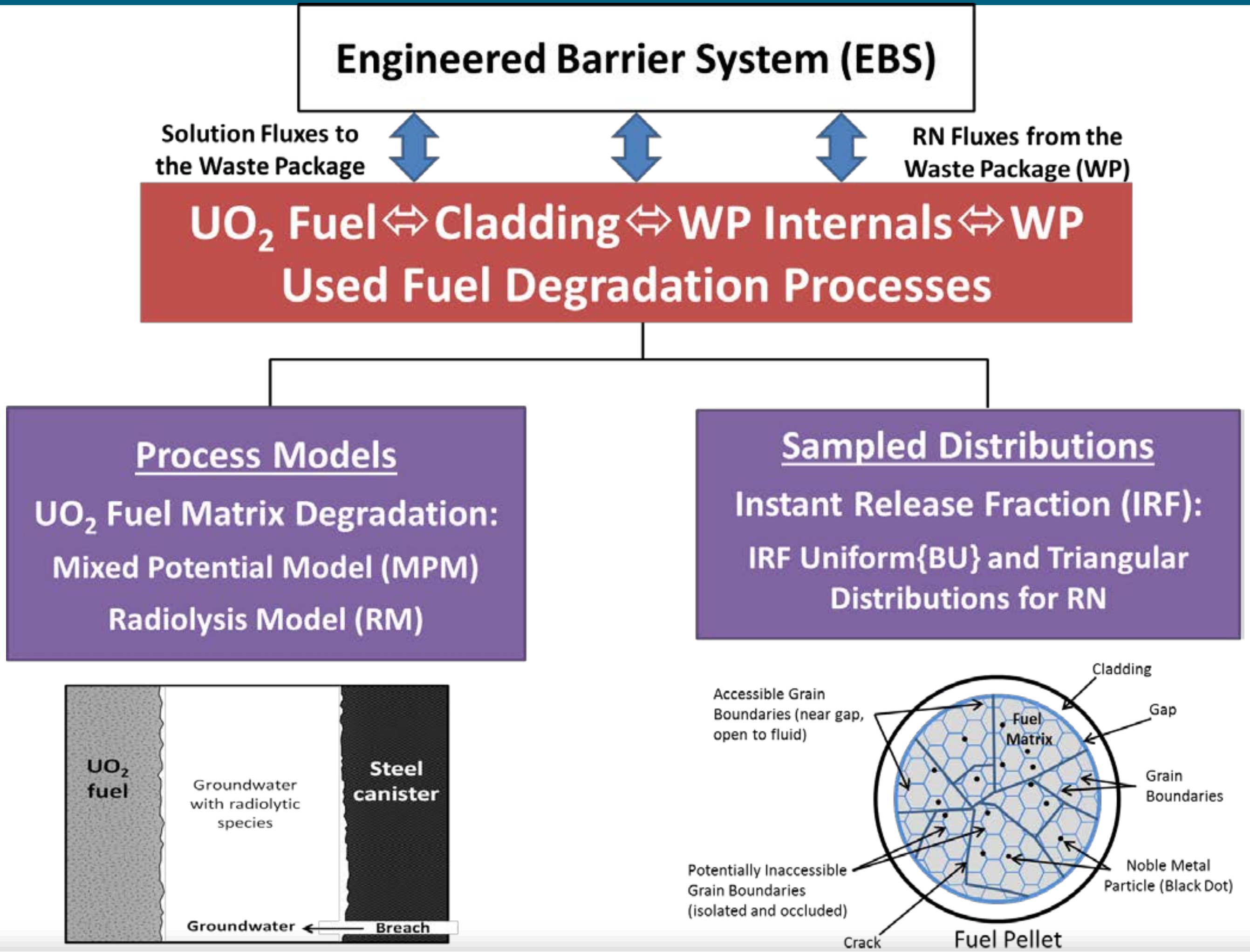
Number	Reaction	Type
8	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	Anodic
9	$H_2O_2 + 2e^- \rightarrow 2OH^-$	Cathodic
10	$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$	Anodic
11	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	Cathodic

The Fuel Matrix Degradation Model (FMDM)

- Anodic/cathodic e-chem reactions applied to UO_2 and NMP surfaces
- UO_2 oxidative dissolution rate is represented by the net current densities of e-chem reactions
- E-chem reaction rates determine the current densities
- SNF degradation rate is calculated from total U flux into solution (translates to a fractional degradation rate)

Source: Thomas (2024), Fuel Matrix Degradation Process Model Documentation, in prep.

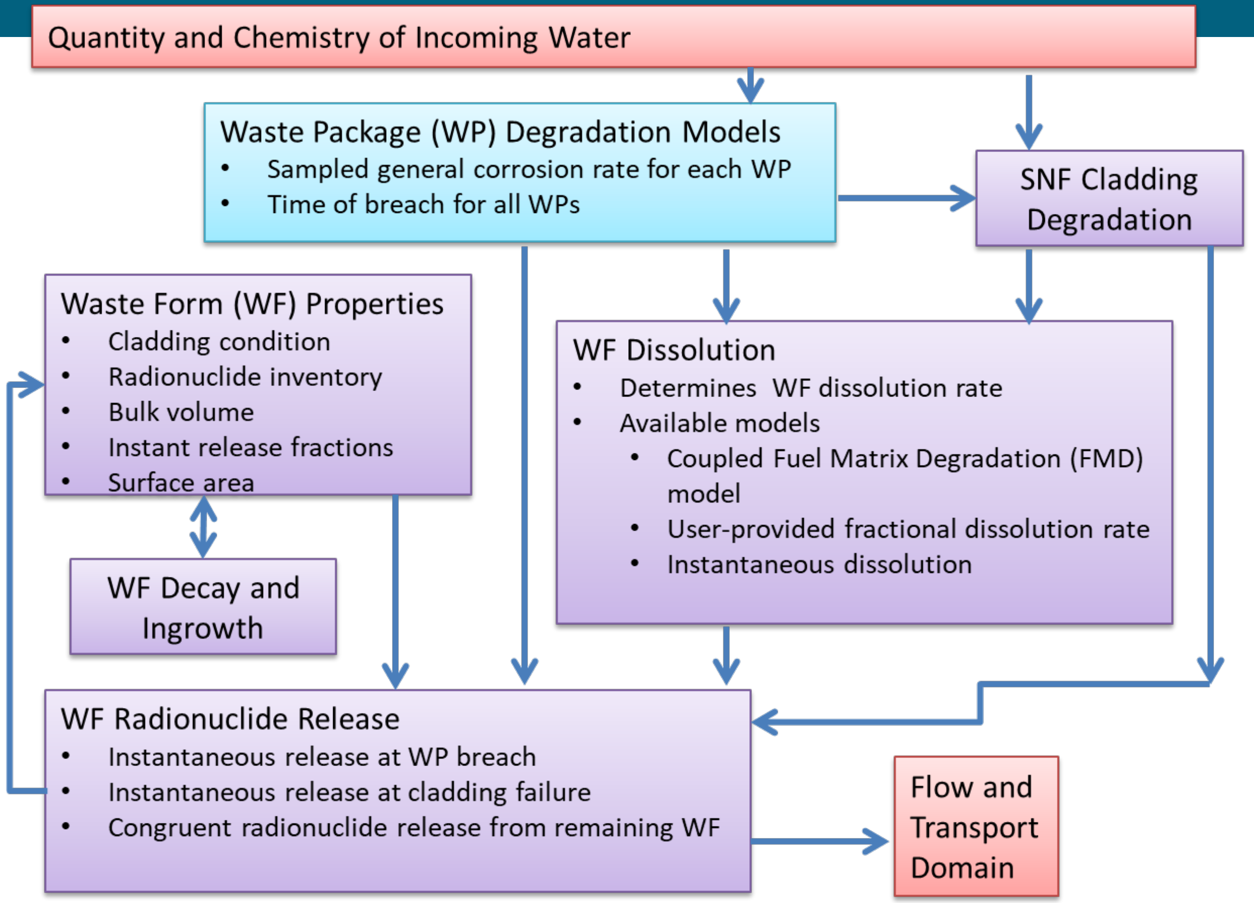
Original Context for the Source Term in System Model



Ongoing and Future FMDM Activities (SNL)

Summary:

- FMDM describes SNF degradation
  - Includes effects of NMP catalysis, radiolytic oxidants, and H_2 from steel corrosion
  - Development considers literature and experimental SNF degradation data
- Enhancements to the Geologic Disposal Safety Assessment (GDSA) Framework
- Strategic testing activities for SNF degradation



Conceptual Framework for Source Term Processes in GDSA (Adapted from Mariner, et al., 2019)

Developing Strategic Testing Plan for SNF Degradation

- Review Conceptual Processes to Identify Gaps
  - Relate to existing models and data
    - Process understanding (technical bases)
  - Integrate within performance assessment approach
    - Features, events, and processes (FEP) screening (include/exclude)
    - Uncertainty treatment
    - Fundamental gap
- Apply Grading Approach to Prioritize Gaps
  - Use current approach for Program Activities (evolving)
  - Risk-informed
- Evaluate Testing Methods to Address Highest Priority Gaps
  - Assess/rank available methodologies to answer open questions
    - Efficacy, duration, resource needs
  - Plan highest priority testing strategy
  - Iterate for next level(s) gaps as appropriate

Prioritization Method – Importance to Safety (Sevougian et al., 2019)

Post-Closure Safety Impact	Post-Closure Safety Description	PCSS Numerical Value
High importance to post-closure safety	Knowledge gained by closing identified gap strongly affects one of the post-closure safety assessment elements.	**5**
Medium importance to post-closure safety	Knowledge gained by closing identified gap moderately or weakly influences one of the post-closure safety assessment elements.	**3**
Low importance to post-closure safety	Knowledge gained by closing identified gap is of a supporting nature and does not strongly affect one of the post-closure safety assessment elements.	**1**

Prioritization Method – State of the Art Level (Sevougian et al., 2019)

SAL Description	SAL Definition	SAL Numerical Value
Fundamental Gaps/Data Needs	The representation of a subject area is under development, and/or the data or parameters in the representation of a subject area are being gathered.	**5**
Improved Representation	Methods and data exist, and the representation may be reasonable but there is not widely agreed upon confidence in the representation.	**4**
Improved Defensibility	Focuses on improving the technical basis and defensibility of how a subject area is represented by data and/or models.	**3**
Improved Confidence	The representation of a subject area is technically defensible, but improved confidence would be beneficial.	**2**
Well Understood	The representation of a subject area is well developed, has a strong technical basis, and is defensible.	**1**

Prioritization Method – Scores Merged (Sevougian et al., 2019)

SAL / PCSS	1	2	3	4	5
High (5)	L	M	M	M-H	H
Medium (3)	L	M	M	M	M
Low (1)	L	L	L	L	L

Status and Path Forward

- Status of Testing Strategy Development
  - Preliminary Gap definitions
  - Preliminary prioritization of Gaps
    - Based on 2019 RoadMap Reevaluation (Sevougian et al., 2019)
- Path Forward
  - Use FEP Tool to map Gaps to FEP (detailed sub-FEP level)
  - Assess Scoring methodology updates (FEP based)
    - Details of risk-informed bases for Post-closure safety score
    - Review FEP context for State-of-the Art Level
  - Revise Prioritization
  - Assess methods available for highest priority FEP Gaps
  - Develop Strategy for further SNF Testing

Recent International Collaborations

- European Joint Programme on Radioactive Waste Management (EURAD)
  - FIRST Nuclides (Fast/Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel) Associated Group 2012-2014
  - DisCo (Modern Spent Fuel Dissolution and Chemistry in Failed Container Conditions) Associated Group 2017-2021
- International-Nuclear Energy Research Initiative (I-NERI)
  - JRC/ITU, BAM, NAGRA (Germany and Switzerland)
  - KAERI (South Korea)
- Studsvik Cladding Integrity Project (SCIP) IV 2019-2024
- International Atomic Energy Agency (IAEA)
  - Spent Fuel Performance Assessment and Research (SPAR) IV 2016-2020

Ongoing and Future International Collaborations

- IAEA
  - Spent Fuel Research and Assessment (SFERA)
  - Challenges, Gaps and Opportunities for Managing Spent Fuel from Small Modular Reactors
- EURAD-2
  - Release of safety relevant radionuclides from spent nuclear fuel under deep disposal conditions (SAREC)
- International Spent Fuel Workshop
  - Spain 2022
  - France 2024

Summary

- The Fuel Matrix Degradation Model
  - Couples process models – radiolysis model and mixed potential model
    - Radiolytic oxidants drive SNF degradation rate
  - Evaluated sensitivities show H_2 pressure primary variable
  - Model implemented in GDSA as alternative to fractional degradation rate sampling
  - GDSA evaluation of surrogate models for faster performance (next presentation)
- Strategic Approach for SNF Degradation Testing
  - Methodology for prioritization is being updated with revised program work
  - Status is “ongoing”
  - Path forward
- International Collaborations
  - Moving forward with EURAD-2 and IAEA integration

Questions?

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