U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Waste Form Performance Model Development

Material Recovery & Waste Form Development

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Conceptual Approach for Waste Form Performance Models

- Objective of waste form performance models is to predict radionuclide release rates from engineered waste forms over the service life of a disposal system to (1) develop durable waste forms and (2) provide mechanistic bases for source term models used in site assessments.

- Demonstrating a mechanistic understanding of the corrosion processes that result in radionuclide release is the single most important factor in justifying the long-term predictions of waste form performance models…

  …but a detailed numerical model that takes all mechanistic processes into account explicitly is not required to make those predictions.

- The actual prediction can be based on the process that significantly impacts radionuclide release consistent with the mechanistic understanding.

Model Development

- **Empirical Observations**
  - Trends measured under various test conditions to determine corrosion behavior to be modeled
- **Mechanistic Models for Individual and Coupled Processes**
  - Identify reactions and processes contributing to observed responses and functional dependencies
- **Conceptual Models**
  - Represent evolving contributions and couplings of processes fo revolving surfaces and solutions
- **Waste Form Degradation Model**
  - Analytical equation to calculate waste form degradation rate with environmental dependencies; consistent with mechanistic understanding of controlling process(es)

- **Radionuclide Source Term Model**
  - Analytical form to calculate radionuclide fractional release rates based on waste form degradation rate, surface area, and inventory; suitable for incorporation in PA

WF deg. rate (g WF/A/y) x WF area (A) x RN inventory (Ci/g WF) = RN release rate (Ci/y)

WF Performance Model Development

Scientific Basis Model

Individual process tests and models

Coupled process tests and models

Simulation tests and models

Mechanistic description and model

Key process →

Source Term Model

Analytical expression consistent with mechanistic models

Lumped parameters

Empirical values

Bounding values

Performance model for GDSA

<u>Key Processes:</u>

UO_2 fuel solution redox establishes surface potential and fuel dissolution rate (UFD)

Glass: secondary phase formation kinetics coupled with glass dissolution kinetics

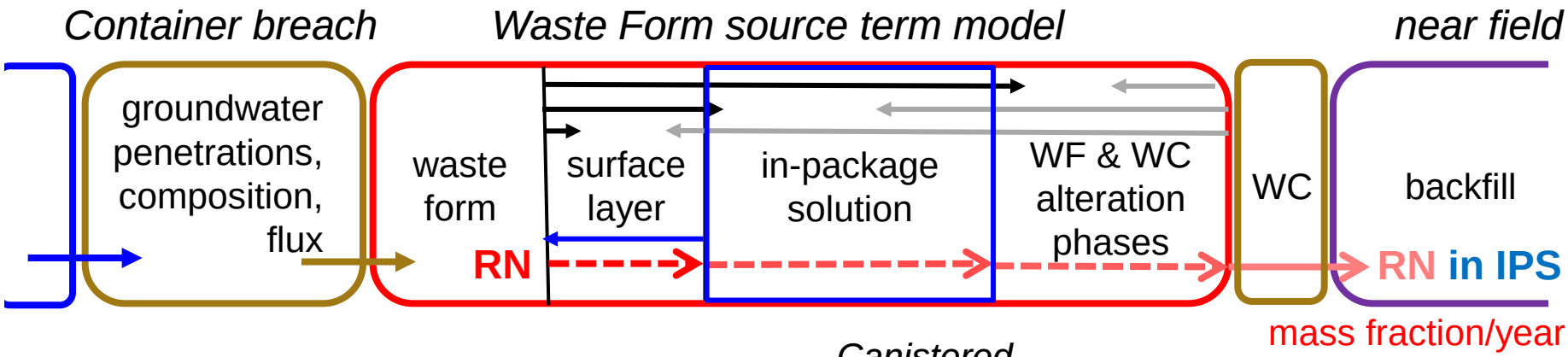
Alloy: active/passive oxidation reactions and oxide dissolution

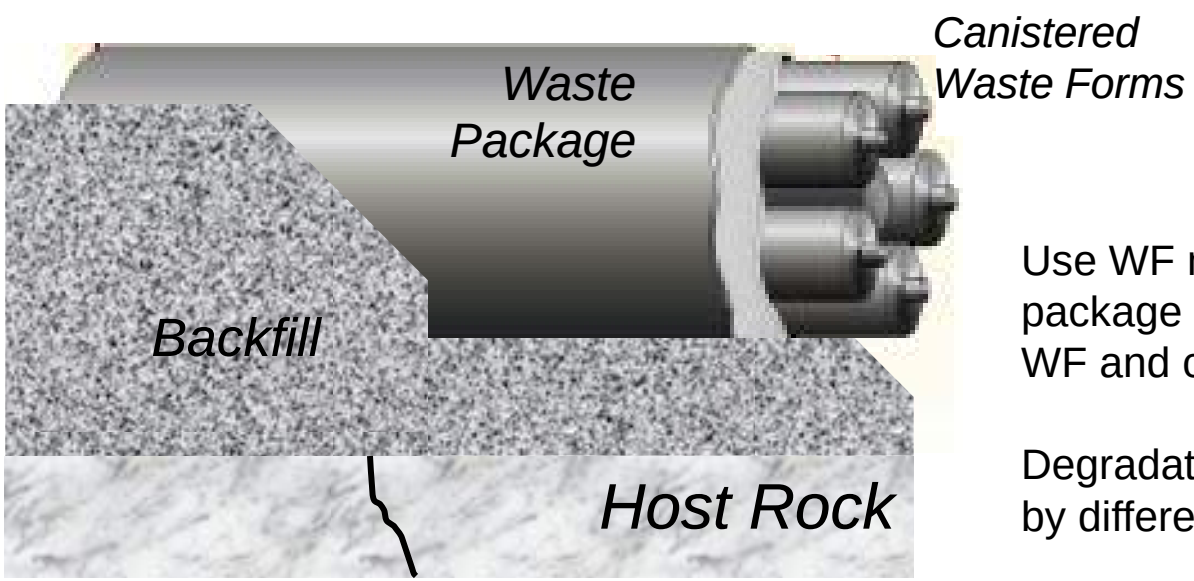
Ceramic: host phase solubility controls waste form degradation by chemical dissolution (TBV)

Glass-ceramic: (TBD)

Role of Waste Form Degradation Models in GDSA

Flexibility in the WF models and interfaces: WF models not constrained by GDSA model.

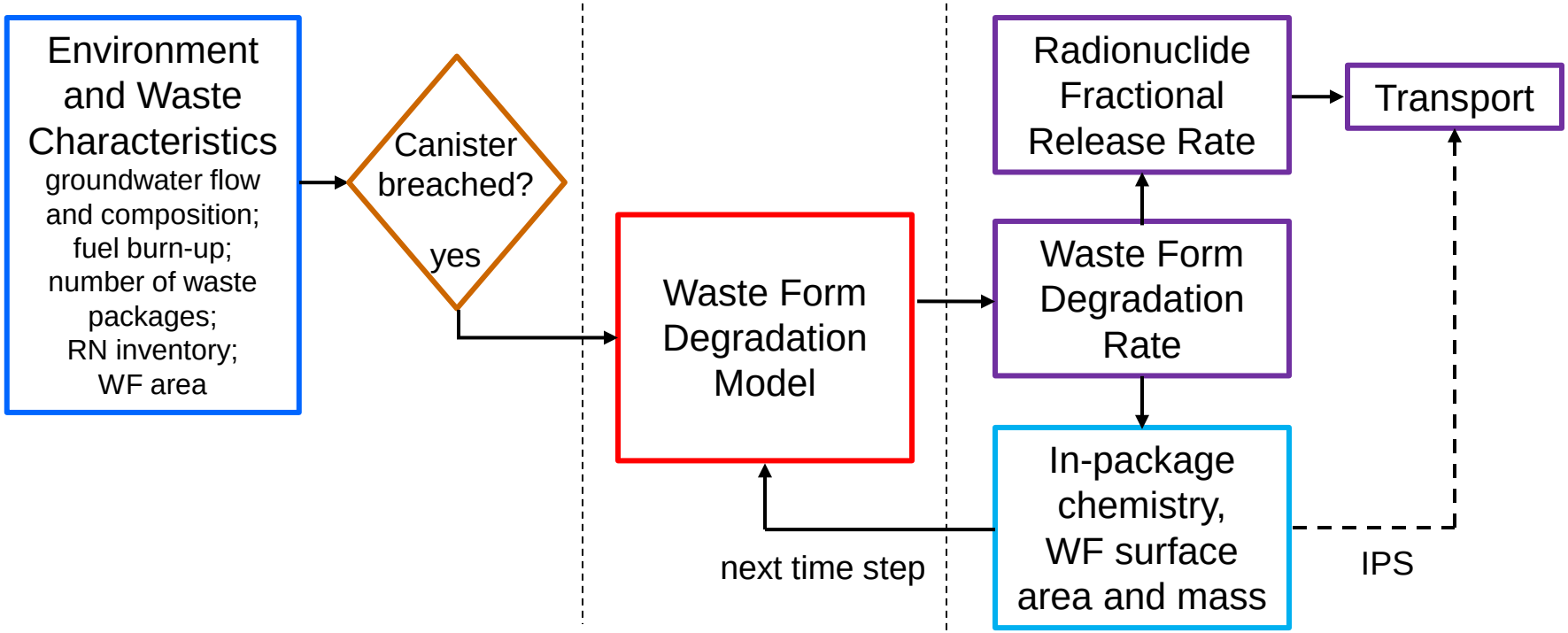




Use WF model to track evolution of in-package solution composition due to WF and canister/container degradation.

Degradation of different WFs affected by different species.

Information Flow Diagram in GDSA



Develop models for engineered waste forms that plug into the same input/output interfaces with the same formats, childish time steps, etc. being developed for used fuel FMDM model.

Updated parameter values stored in PFLOTRAN

UO_2 Fuel Matrix Degradation Model

- **Conceptual model based on experimental observations (mostly from literature)**
  - Concurrent rapid oxidative-dissolution and slow chemical dissolution pathways
  - Threshold potential for oxidative-dissolution to occur
  - Radiolysis and steel corrosion add oxidants and reductants to groundwater
  - Key oxidants are dissolved O_2 and radiolytic H_2O_2 (crystalline and argillite) or $HClO/ClO_3^-$ (salt)
  - Key reductant is H_2 generated during steel corrosion

- **Kinetics of key redox reactions used to calculate surface potential at UO_2 surface with electrochemical mixed potential theory to calculate dissolution rate**
  - Rate calculated as sum of all electrochemical dissolution reactions and chemical dissolution

$$UO_2^{fuel} \rightarrow UO_2^{2+} + 2e^-$$
$$UO_2^{fuel} + 2CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} + 2e^-$$
etc.
$$UO_2^{Fuel} \rightarrow U(OH)_4(aq)$$

- **Effects of radiolysis, homogenous interactions with solution, diffusion, steel corrosion (TBD), and precipitation of U-bearing phases taken into account in FMDM to calculate total dissolved U, effective dissolution rate, change in area and fuel mass, gap/grain boundary (TBD), and RN release rate.**

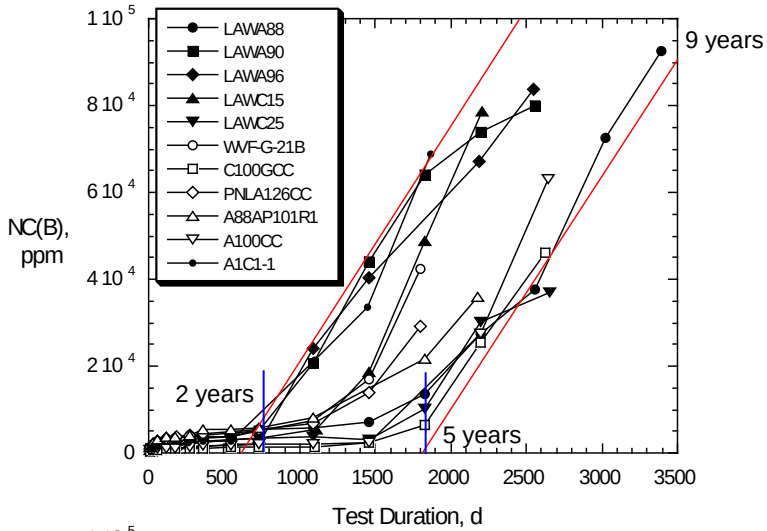
Compared to Previous CSNF Models

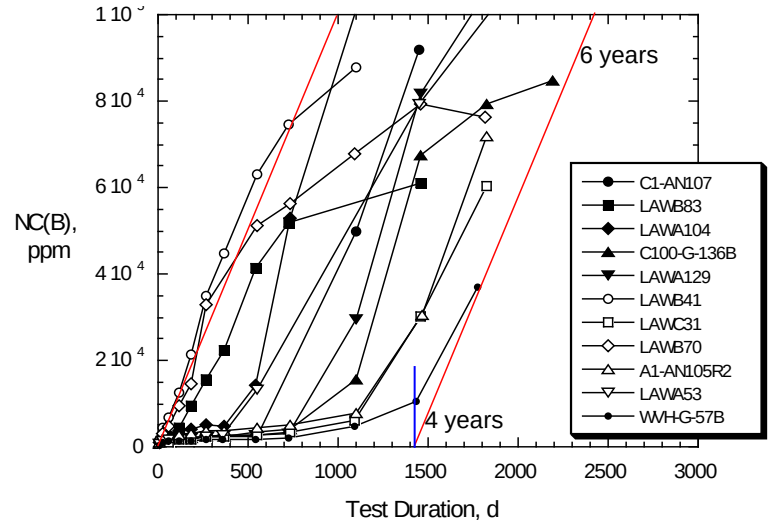
- **Mechanistic basis for model (rather than purely empirical) provides confidence in long-term predictions**
- **Quantifies effect of H_2 mitigating oxidation of U(IV) to U(VI) to decrease fuel dissolution rate**
- **Environmental sensitivities of contributing reaction kinetics taken into account through specific processes, including effects of radiolysis and secondary phase formation.**
- **Track solution composition in GDSA calculations: pH, [H_2], [O_2], [H_2O_2] to calculate surface potential, [CO_3^{2-}], [Fe^{2+}], all U-bearing species (UO_2^{2+}, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, etc.) to calculate fractional release**
- **FMDM is semi-mechanistic model that can be simplified if necessary.**

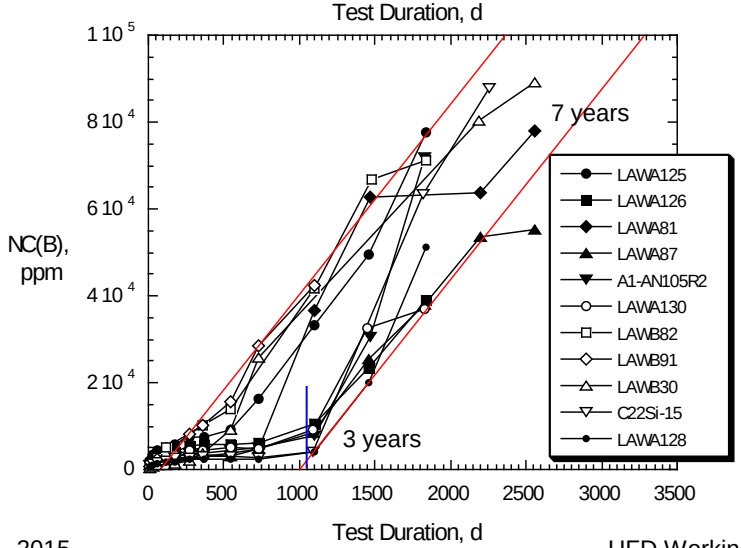
Long-term Tests with Glass at 90 °C

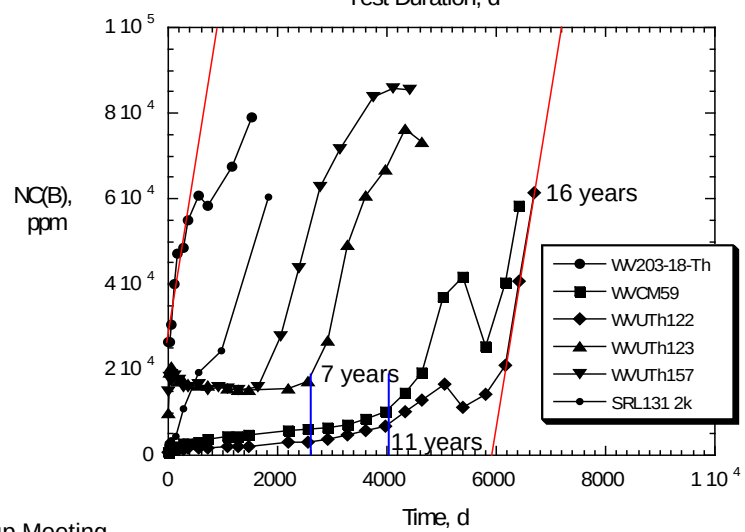
static test with crushed glass at representative S/V

W.L. Ebert (2014). *An Evaluation of the ALTGLASS Database for Insights into Modeling Stage 3 Behavior*, FCRD-SWF-2014-000616.

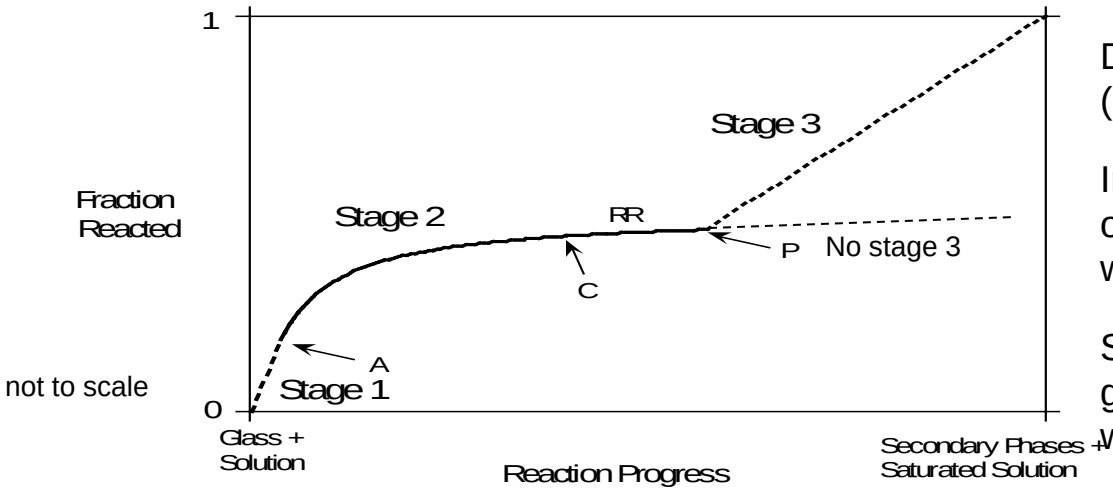


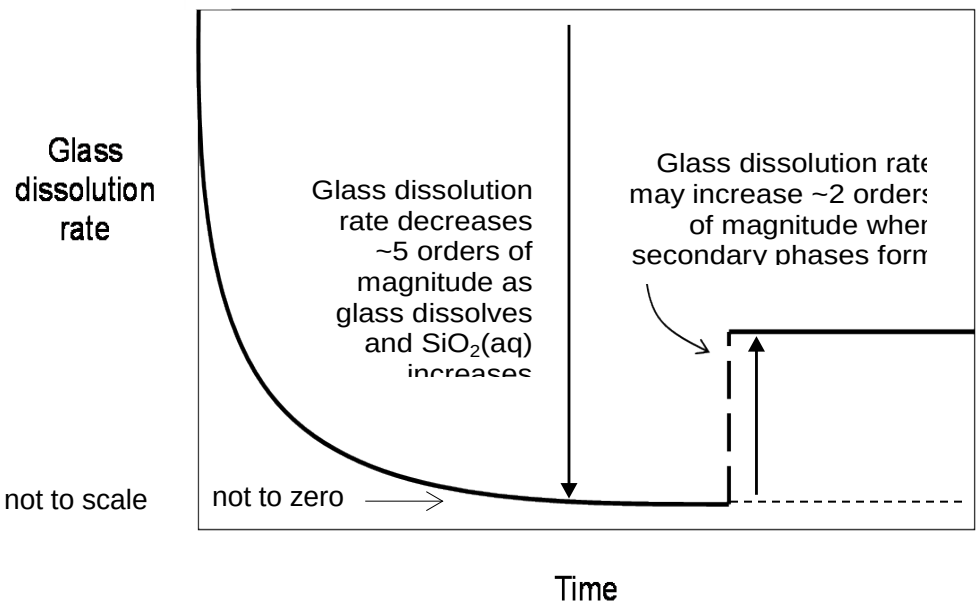






Empirical Observations Model





Dissolution slows to low residual rate (RR) in static solutions (but not zero).

Increased rate (Stage 3) has been observed in laboratory tests with many waste glasses, but not all.

Similar RR and Stage 3 rates for many glasses, but significant variability in when Stage 3 is triggered.

Understanding scientific basis of why Stage 3 rates occurs (or does not) needed to predict long-term behavior.

Conditions necessary to trigger Stage 3 (at Point P) may not be attained during tests or during disposal.

Model developed to predict initial decrease (Stage 2), residual rate (RR), and if/when increase will occur (Stage 3) as glass corrodes.

Glass Waste Form Modeling Approach

- **Conceptual model**
  - Glass degradation controlled by hydrolysis of Si-O bonds
  - Net hydrolysis rate decreases as SiO_2(aq) accumulates in solution due to condensation reactions (Stage 2), which generate surface layer
  - Mass transport through surface layer may limit dissolution rate
  - Glass degradation rate changes when certain secondary phases precipitate (Na-chabazite, analcime, phillipsite, etc.): rate may decrease (RR) or increase significantly (Stage 3) depending on precipitation kinetics
  - Waste glasses thermodynamically driven to transform to assemblage of secondary phases. Glass durability is due to slow glass dissolution kinetics and restricted nucleation kinetics of secondary phases
  - Coupling of glass dissolution and secondary phase precipitation kinetics through material transfer (most importantly Al) results in a constant steady-state rate: either slower residual rate or faster Stage 3 rate

W.L. Ebert (2015). *Stage 3 Model for Coupled Glass Dissolution and Secondary Phase Precipitation Reactions*, FCRD-SWF-2014-000246.

Glass Waste Form Degradation Model

- **Analytical Glass Dissolution Model**

Si-O hydrolysis rate increases with temperature and is catalyzed by H^+ and OH^-,

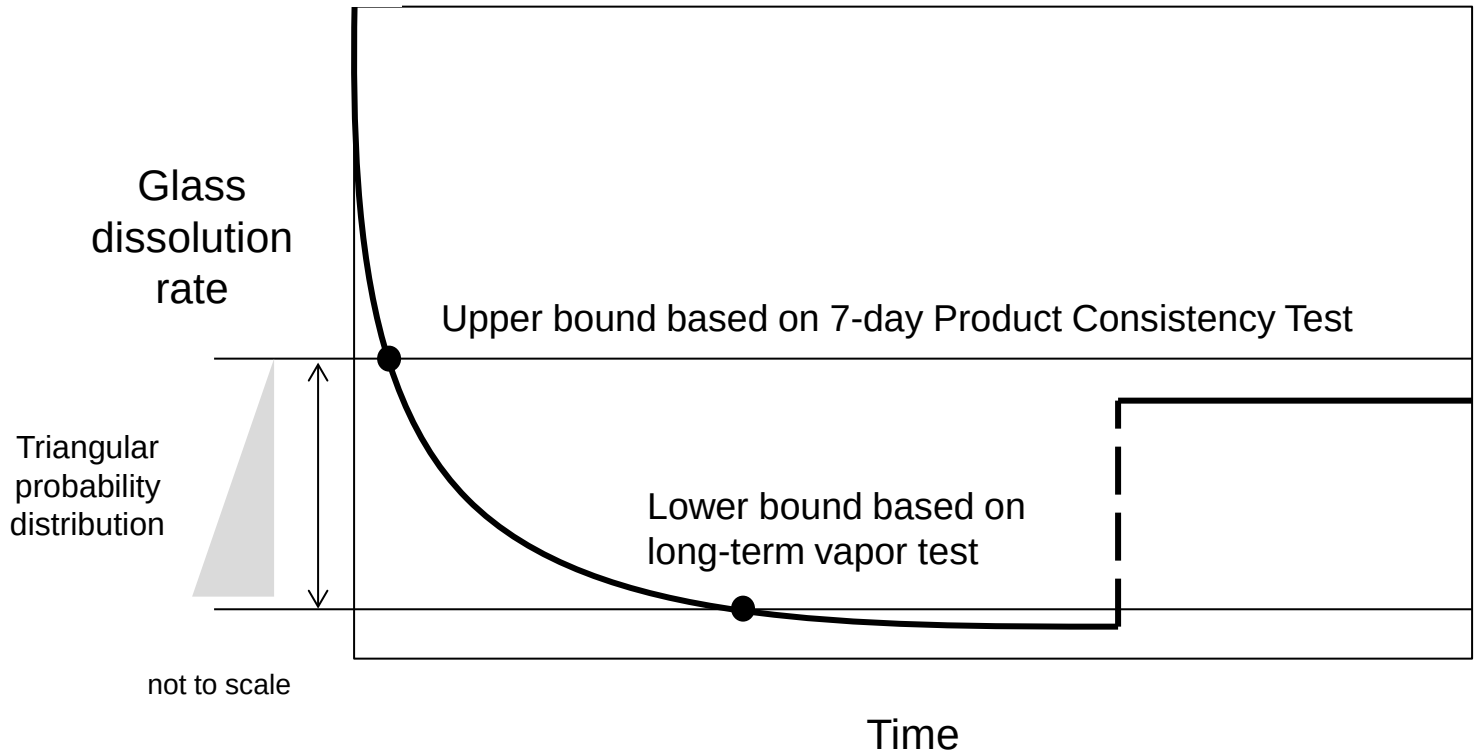
$$\frac{rate}{A} = k_0 \bullet \exp\left(\frac{-E_a}{\mathrm{RT}}\right) \bullet (a_{H^+})^{\eta} \bullet \lambda \bullet fn(\Delta G_r)$$

but net dissolution rate is attenuated by transport and thermodynamic reaction affinity term

- Analytical rate law used since mid 1980's; but understanding of affinity term has evolved
- Analytical form and value of reaction affinity term depends on solution composition and changes when different secondary phases form.
- Different reaction affinity terms $fn(\Delta G_r)$ for different controlling processes
  - Stage 1: no attenuation; glass dissolves at kinetic rate
  - Stage 2: effects of SiO_2(aq) build-up and transport limits; glass dissolves at decreasing rate
  - Residual rate: slow growing secondary phase (e.g., clay); glass dissolves at steady state rate
  - Stage 3: rapid growing secondary phase (e.g., zeolite); glass dissolves at steady state Stage 3 rate

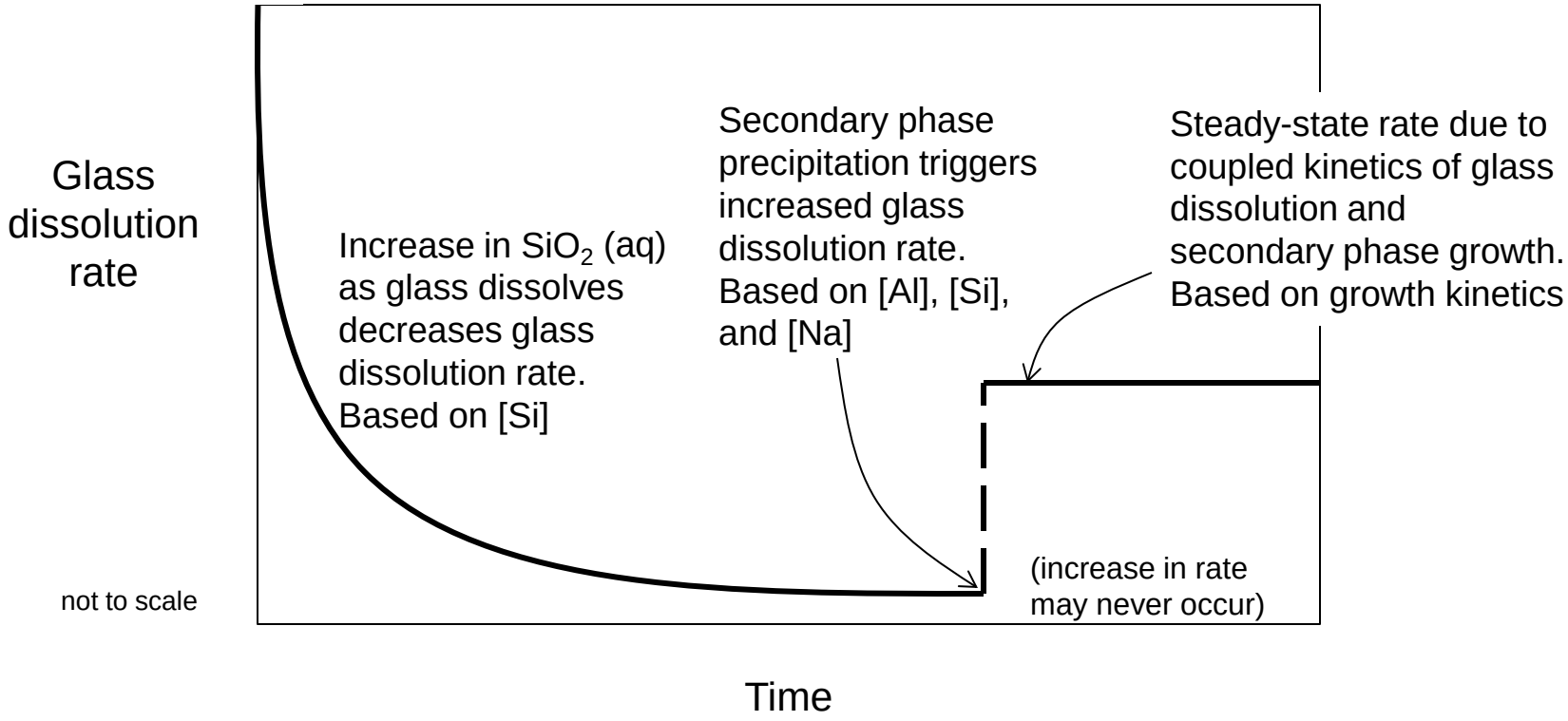
Previous Glass Degradation Model

Didn't know forms of $fn(\Delta G_r)$ to determine trigger points or calculate long-term rates.
Had to use empirical bounding values.
Transport code didn't track dissolved glass constituents.



New Glass Degradation Model

Will be able to determine trigger point and long-term rate using effective $fn(\Delta G_r)$ values based on solution composition.
NEUP looking at Stage 3 triggers and rates for a wide range of glass compositions.



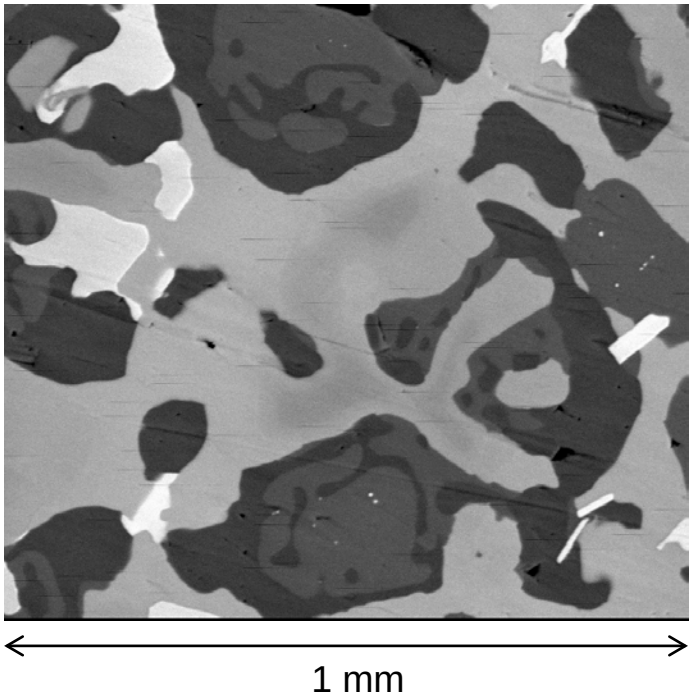
W.L. Ebert (2015). *Stage 3 Model for Coupled Glass Dissolution and Secondary Phase Precipitation Reactions*, FCRD-SWF-2014-000246.

Compared to Previous Glass Models

- **Very similar conceptual model**
- **Mechanistic basis for rate increase (rather than purely empirical bounding maximum and minimum values) provides more realistic rates and confidence in long-term predictions**
- **Environmental sensitivities of contributing reaction kinetics taken into account**
- **Different values of** $fn(\Delta G_r)$ **used to represent glass dissolution before and after secondary phases form based on their precipitation kinetics**
- **Track pH and [Al], [Na], and [Si] in GDSA calculations to trigger changes in rate and calculate long-term rate based on values of** $fn(\Delta G_r)$ **term (TBD)**

Alloy Waste Form

- **Developed for steel cladding hulls and metallic fuel wastes from electrochemical (EChem) treatment**
- **Fuel wastes are primarily Zr, epsilon phases, and residual contamination levels of U/TRU**
- **Multi-phase waste form comprised of several intermetallics and solid solution phases**
- **Radionuclides report to specific phases:**
  - Fe-Ni-Zr-U/TRU
  - Zr-Pd-U/TRU
  - Fe-Cr-Mo-Tc
  - steel-Tc
- **Initial studies on alloy/oxide composites with LN-oxide phases (NEUP)**



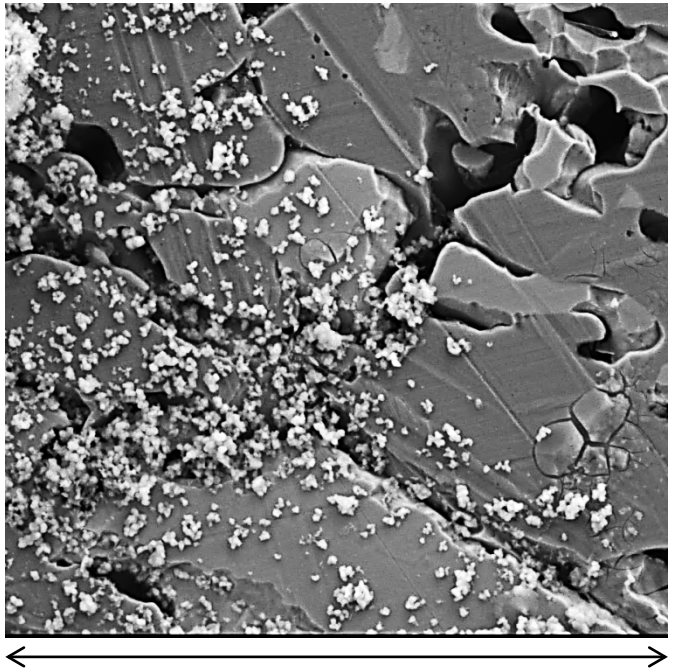
Multi-phase surrogate metallic waste form comprised of Fe-Ni-Zr-U, Zr-Pd-U, Fe-Cr-Mo-Tc intermetallic and steel-Tc solid solution phases.

Alloy Waste Form Modeling Approach

- **Electrochemical tests at various fixed potentials to ID corroding phases, measure corrosion parameters and effects of environmental variables, and measure releases of Tc and U/TRU**
- **Conceptual alloy degradation model**
  - 2-step oxidative-dissolution mechanism
  - active-passive anodic oxidation coupled with affinity-controlled oxide dissolution
- **Developed analytical oxidative-dissolution degradation model based on same electrochemical theory as FMDM, but more empirical due to multiple alloy phases**
- **Currently parameterizing model for specific alloy waste forms**

W.L. Ebert (2013). *Alloy Waste Form Testing Strategy Roadmap*, FCRD-SWF-2013-000226.

Observation:



Multi-phase surrogate metallic waste form reacted in acidic brine showing preferential dissolution of Fe-Ni-Zr-U intermetallic phase and no dissolution of Zr-Pd-U or Fe-Cr-Mo-Tc intermetallics.

Alloy Waste Form Degradation Model

- **Analytical Oxidative-Dissolution Model**
  - Metallic components are oxidized by reaction with ground water
  - Cr-bearing alloys passivate
  - Oxides dissolution limited by their solubilities and form surface layer

Bare surface oxidation rate is moderated by passivation and dissolution affinity

$$FR(RN) = B\left(Eh, pH, T\right) \times P\left(Eh, Cl^{-}\right) \times D\left(T, RN\right)$$

- Different parameter values for different radionuclides (sum for all host phases)
- Track pH, Cl, and dissolved O_2, H_2O_2, and H_2 (to estimate Eh)

W.L. Ebert (2014). *Radionuclide Source Term Model for Metallic Waste Forms*, FCRD-SWF-2014-000244.

Summary and Future Plan

- Approach to develop degradation models for engineered waste forms to integrate into GDSA calculations follows approach used to integrate oxide fuel FMDM model.
- Will use "standardized" input/output architecture for different WF models to facilitate interfaces with GDSA and other sub-models (e.g., canister corrosion).
- The modular approach being taken in GDSA benefits individual waste form models:
  - Can evolve the in-package solution independently to quantify effects on WF dissolution rate
  - Can include waste form and radionuclide interactions with container materials
  - Can represent corrosion behavior with better fidelity to mechanisms than was possible with previous models for more reliable long-term predictions
- On-going work to determine appropriate analytical representations, measure model parameter values, and identify interfaces with sub-models being developed in UFD.
  - Model for glass waste forms fairly mature and ready for integration: known input/output variables and which species to track. Analytical forms of affinity term being finalized
  - Model for alloy waste forms being developed (ready in about 1 year); several aspects similar to FMDM
- Models for advanced ceramic and glass-ceramic waste forms being developed; both expected to be similar to glass model

Acknowledgements

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