Model Abstraction of Waste Form Degradation in Alternative Disposal Site

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Disclaimer

• This is a joint US NRC staff and CNWRA paper, and views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of any licensing action that may be under consideration at the US NRC.
Introduction

• A variety of potential geological disposal concepts are currently considered for **high-level waste (HLW) and spent nuclear fuel (SNF)** in many countries.

• The degradation of various waste forms of HLW and SNF is important to assess the radionuclide release in the geological disposal system.

• U.S. NRC and CNWRA jointly developed a generic performance assessment model, preliminary *beta-Scoping of Options and Analyzing Risk, β-SOAR*, to provide preliminary insights for a variety of potential HLW and SNF disposal options.

• The five key model components are: Waste Form, Waste Package, Near Field, Far Field, and Biosphere. The **Waste Form Component (WFC)** accounts for the type of waste form, important radionuclides, initial radionuclide inventory, and degradation rate of various waste forms.
Model Implementation

- Two distinct waste forms: SNF and HLW glass associated with reprocessing the SNF. The SNF has two types of commercial SNF and spent mixed-oxide fuel (sMOX).

- Initial inventory of 15 radionuclides: Pu-238, 239, 240, 242, U-232, 233, 234, 235, 236, 238, Np-237, C-14, Cs-135, I-129, and Tc-99, bound on the SNF (or glass) matrix. The selection is based on the performance assessment results of various waste forms in both oxidizing and reducing environments from the literature.

- There is an initial inventory of segregated, unbound radionuclides: C-14, Cs-135, I-129, and Tc-99.

- Each waste package contains a mixed (blended) waste form where the user may specify the ratio of commercial SNF, HLW glass and sMOX.
Model Implementation (continued)

• For the bound radionuclide inventories, the total amount of mobilized radionuclides (M) from waste form dissolution is represented by:

\[ M \, [g] = m \, [\text{fraction year}^{-1}] \times I \, [g] \times t \, [\text{year}] \]

- \( m \): fractional mobilization rate
- \( I \): total inventory of radionuclide
- \( t \): time of waste form contacting aqueous environment

\[ m \, [\text{fraction year}^{-1}] = R \, [g \, \text{cm}^{-2} \, \text{year}^{-1}] \times A \, [\text{cm}^2 \, \text{g}^{-1}] \]

- \( R \): dissolution rate
- \( A \): specific surface area
Key Model Assumptions

• **Radionuclide release:**
  - fission and activation product release: at the fractional mobilization rate
  - actinide release: at constant concentration at or below solubility limit
  - segregated and unbound radionuclides: instantaneous release

• **Dissolution rates of sMOX:** represented by commercial SNF with separate radionuclide inventory of sMOX

• **Dissolution process:** redox-sensitive for commercial SNF and sMOX, not redox-sensitive for HLW glass (pH sensitive)

• For waste form dissolution in a reducing environment, it is assumed that an initial, disturbed oxidizing condition would be replaced by a reducing environment, with residual radiolysis products after a long containment period.
Default Parameters

- Initial radionuclide Inventories assume that waste emplacement by geologic disposal occurs 50 – 100 years before disposal site closure.

- In an oxidizing environment, the contribution to dose from actinides is expected to be significant because of high solubility limits; contribution to the dose from the unbound fission products is also expected to be significant.

- In a reducing environment, fission and activation products will likely be more mobile because of the low solubility limits of actinides.

- The default number of waste packages is 10,000 based on waste loading of current commercial SNF or HLW glass.
The WFC model uses a mixed (blended) waste form inventory which is determined by combining proportions of the commercial SNF, sMOX, and HLW glass radionuclide inventories.

The instant release fractions of commercial SNF and sMOX considers high burnup (>45 GWd/MTU) commercial SNF that may have larger instant release fractions than the lower burnup commercial SNF.

In an oxidizing environment, UO$_2$ matrix will dissolve electrochemically into soluble species with an aid of oxidants such as dissolved oxygen and hydrogen peroxide.

In a reducing environment, UO$_2$ matrix will dissolve chemically into soluble species.
Default Parameters (continued)

• The dissolution of sMOX is assumed to be identical to commercial SNF due to limited data and potential similar UO$_2$ matrix.

• In the HLW glass, radionuclides are assumed to dissolve at the dissolution rate of HLW glass matrix.

• The HLW glass matrix will dissolve chemically with the process controlled by the concentrations of dissolved silica compounds in both oxidizing and reducing environments.
Default Parameters (continued)

• The fractional mobilization rates are assumed to be constant within uncertainty ranges at a given temperature.

• The environmental conditions considered in the dissolution process include a constant range of near field water chemistry, temperature or redox conditions (i.e., reducing, oxidizing or mixed conditions).

• Other environmental effects (e.g., groundwater chemistry or pH) are accounted for by using a broad range of dissolution rates.

• In connecting the dissolution rate to the fractional mobilization rate, the specific surface area is determined by the average fragment size and density of waste form. Other factors such as surface roughness were considered in the calculation of the fractional mobilization rate.
Model Flexibility

- A user defined waste form is available and can be modified by defining specific radionuclide inventories and fractional mobilization rates.

- The user may modify the fractional rate of waste form mobilization by means of a multiplier (by offline calculations): inhibiting effects (e.g., protection by partially failed cladding, redox variation or radionuclide sorption on iron oxides); a fraction of radionuclides unavailable (e.g., intact cladding)

- The effects of temperature on the fractional mobilization rate can also be modeled using an Arrhenius relation for commercial SNF and HLW glass. The temperature corrections using the activation energies are made in the abstraction of dissolution rates.
Reduction of Uncertainties

- Additional data and models for ceramic waste forms, metallic waste forms, sMOX, and higher-loading of HLW glass, with optimization of heat loading

- Expand types of radionuclides, Se-79, Cl-36, Zr-93, Pd-107, Sn-126, Ra-226, Ac-227, Pa-231, and Th-(229, 230)

- Formulate the properties of waste form (e.g., the size of fragments)

- Evaluate temperature and redox relationship as a function of time

- Define the definition of the disposal environment (e.g., redox, temperature, and groundwater chemistry)

- Account for the partial protection by internal waste package structure (e.g., cladding protection or activation product release)
Preliminary $\beta$-SOAR
Input Parameters

- Initial radionuclide inventory of commercial SNF, HLW glass, and sMOX
- Fractional mobilization rate of commercial SNF and sMOX under oxidizing and reducing conditions
- Fractional mobilization rate of HLW glass
- Unbound radionuclide fraction in commercial SNF and sMOX
- Activation energy of commercial SNF, sMOX and HLW glass

[details in backup slides]
The doses shown in the figures also incorporated radionuclide containment and retardation in radionuclide transportation from Waste Package, Near Field, Far Field and Biosphere. The results represented typical example cases for various radionuclide mobilization from the waste form dissolution under reducing conditions.
Conclusions

- The preliminary $\beta$-SOAR considers commercial SNF, sMOX, and HLW glass, with an initial inventory of 15 bound radionuclides, and each radionuclide inventory has its own dissolution rate under reducing, oxidizing or mixed conditions.

- The preliminary $\beta$-SOAR also considers inventories for 5 unbound radionuclides which are rapidly released upon contact with water.

- Each waste package contains a mixed (blended) waste form.

- The preliminary $\beta$-SOAR has flexibility to be run primarily for different types of waste form, different types of environments including redox conditions, various waste loading, various initial mobile radionuclide inventories, multiplier for varying fractional mobilization rates, and more radionuclide types.

- The temperature effects on the fractional mobilization rate can be modeled by an Arrhenius relation.
### Backup Slide – Input Parameters

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Description and Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Inventory of Commercial SNF</strong>&lt;br&gt;(gram per waste package, 1 g = 0.035 oz)</td>
<td>C14, 1.35E+00&lt;br&gt;Cs135, 4.36E+03&lt;br&gt;I129, 1.73E+03&lt;br&gt;Np237, 1.54E+04&lt;br&gt;Pu238, 1.52E+03&lt;br&gt;Pu239, 4.32E+04&lt;br&gt;Pu240, 2.05E+04&lt;br&gt;Pu242, 5.28E+03&lt;br&gt;Tc99, 7.55E+03&lt;br&gt;U232, 1.02E-02&lt;br&gt;U233, 5.76E-02&lt;br&gt;U234, 1.75E+03&lt;br&gt;U235, 6.26E+04&lt;br&gt;U236, 3.84E+04&lt;br&gt;U238, 7.82E+06</td>
<td>The initial radionuclide inventory for Commercial SNF was based on the inventory in DOE (2008) Table 2.3.7-3 as an example case. The inventory was modified to account for the eventual decay of Pu-241 and Am-241 (not tracked in the β-SOAR) into Np-237, by adding the initial values for Pu-241 and Am-241 to the initial value for Np-237 this adjustment prevents the effect of Np-237 from being underestimated.</td>
</tr>
</tbody>
</table>

| **Initial Inventory of HLW Glass**<br>(gram per canister, 1 g = 0.035 oz) | C14, 2.91E-01<br>Cs135, 9.47E+02<br>I129, 9.36E+01<br>Np237, 5.06E+02<br>Pu238, 5.31E+01<br>Pu239, 3.43E+02<br>Pu240, 3.86E+01<br>Pu242, 5.44E+00<br>Tc99, 1.36E+0<br>U232, 1.47E-03<br>U233, 9.39E+00<br>U234, 1.79E+01<br>U235, 3.07E+02<br>U236, 5.96E+01<br>U238, 1.41E+05 | The representative HLW glass radionuclide inventory was based on the radionuclide inventory in DOE (2008) Table 1.5.1-21 as an example case. The radionuclide inventory was derived by selecting the highest value for each radionuclide out of the four glass waste forms (Hanford, SRS, West Valley, and Idaho) presented in the table. Additionally, the initial inventory of Pu-241 and Am-241 are added to the initial inventory of Np-237 to account for in-growth. |
### Initial Inventory of sMOX (gram per waste package, 1 g = 0.035 oz)

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Initial Inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14</td>
<td>2.58E+00</td>
</tr>
<tr>
<td>Cs135</td>
<td>7.17E+03</td>
</tr>
<tr>
<td>I129</td>
<td>3.09E+03</td>
</tr>
<tr>
<td>Np237</td>
<td>4.64E+04</td>
</tr>
<tr>
<td>Pu238</td>
<td>1.50E+03</td>
</tr>
<tr>
<td>Pu239</td>
<td>1.03E+05</td>
</tr>
<tr>
<td>Pu240</td>
<td>7.26E+04</td>
</tr>
<tr>
<td>Pu242</td>
<td>1.84E+04</td>
</tr>
<tr>
<td>Tc99</td>
<td>9.98E+03</td>
</tr>
<tr>
<td>U232</td>
<td>1.01E-03</td>
</tr>
<tr>
<td>U233</td>
<td>2.33E-03</td>
</tr>
<tr>
<td>U234</td>
<td>9.13E+01</td>
</tr>
<tr>
<td>U235</td>
<td>5.62E+03</td>
</tr>
<tr>
<td>U236</td>
<td>2.23E+03</td>
</tr>
<tr>
<td>U238</td>
<td>8.19E+06</td>
</tr>
</tbody>
</table>

The initial radionuclide inventory for sMOX was based on the inventory in the reference [11] (Table 6-2) as an example case. The inventory was modified to account for the eventual decay of Pu-241 and Am-241 (not tracked in the β-SOAR) into Np-237, by adding the initial values for Pu-241 and Am-241 to the initial value for Np-237.

### Mobilization (Degradation) of Commercial SNF and sMOX under the Oxidizing Condition (fraction per year; minimum and maximum)

<table>
<thead>
<tr>
<th></th>
<th>Mobilization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.00E-05, 6.00E-04 (log-uniform)</td>
</tr>
</tbody>
</table>

The oxidizing environment is considered because of the potential alpha radiolysis in the reducing environment and the early waste package failure. The assessment is more based on immersion conditions that are considered in the alternative disposal sites in the future. The dissolution rate of Commercial SNF is assumed to bound that of sMOX under immersion conditions. Both of commercial SNF and sMOX have the particle size of ~ 1 mm after reactor irradiation. Other references include the references of [3] and [7].

### Mobilization (Degradation) of Commercial SNF and sMOX under the Reducing Condition (fraction per year; minimum and maximum)

<table>
<thead>
<tr>
<th></th>
<th>Mobilization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9.00E-07, 2.00E-05 (log-uniform)</td>
</tr>
</tbody>
</table>

An average factor of 0.03 (from 0.01 – 0.1) was factored in the oxidizing case. In the French and Belgian repositories, an average 2 x 10\(^{-6}\)/year was used, similar to the current estimate. To be consistent, the dissolution rate of sMOX was assumed to be same as the rate of commercial SNF.
### Mobilization (Degradation) of Commercial SNF and sMOX under the Combined Condition (fraction per year; minimum and maximum)

| Mobilization (Degradation) of Commercial SNF and sMOX under the Combined Condition (fraction per year; minimum and maximum) | 9.00E-07, 6.00E-04 (log-uniform) | Because the alpha radiolysis may have limited effects on the dissolution rate of commercial SNF and sMOX, the combined case is separated to represent some effects of alpha radiolysis. If we consider the hydrogen effects to be produced by the container corrosion, this combined rate could be conservative. The hydrogen could inhibit the SNF dissolution rate. To be consistent, the dissolution rate of sMOX was assumed to be same as the rate of commercial SNF.

### Mobilization (Degradation) Rate of HLW Glass (fraction per year; minimum and maximum)

| Mobilization (Degradation) Rate of HLW Glass (fraction per year; minimum and maximum) | 1.50E-06, 2.00E-04 (log-uniform) | French and Belgian HLW glass determined the fractional mobilization rate, $1.4 \times 10^{-5}$ per year. Other appropriate data include fractional mobilization rate, $1.4 \times 10^{-5}$ per year at pH $= 7.5$ in the reference [16]. Appropriate pH ranges are: longer-term pH $\sim (8.0 \sim 8.5)$ in the reference [17]; and immersion pH $\sim 8.0$ in the reference [18] as L/year increases. HLW glass has higher dissolution rates per unit area compared with SNF [(in equations (1) and (2)]. However, in the actual calculation of fractional mobilization per year, a bigger chunk of ~10 cm was used compared with ~1 mm of commercial SNF or MOX SNF. This decreases the fractional release rate by a factor of ~100.

### Unbound Radionuclide Fraction in Commercial SNF and sMOX

| Unbound Radionuclide Fraction in Commercial SNF and sMOX | Cs-135, 0.0088 (lower), 0.025 (apex), 0.058 (upper) I-129, 0.0054, 0.11, 0.32 Tc-99, 0.0005, 0.0013, 0.0028 C-14, 0.1 (constant value) | All are measured values from the references [3, 6]. The values used for the radionuclide unbound fractions for commercial SNF were also used for sMOX due to limited data available on sMOX radionuclide release fractions and because of the conservatism in the ranges of values selected. Note the value used for the C-14 unbound fraction is assumed a constant value.

### Activation Energy of Commercial SNF and sMOX

| Activation Energy of Commercial SNF and sMOX | 34,300 | Because the dissolution rate of commercial SNF is assumed to bound that of sMOX, the activation energy of sMOX was also assumed to have a same value to be consistent with the activation energy of commercial SNF. |
Backup Slide – Preliminary β SOAR
Main Dashboard
Backup Slide – Preliminary β SOAR
Source Term Settings Dashboard

Source Term

Waste Form

Waste form proportions tracked in the system:

- Fraction of Waste Inventory that is Spent Nuclear Fuel and Spent Mixed-Oxide Fuel (the remaining fraction is assumed to be High Level Waste): 0.95
- Fraction of the Spent Nuclear Fuel that is commercial SNF (the remaining fraction is assumed to be sMOX): 0.5263

Waste Package

- Waste package material: Stainless Steel, Titanium
- Breach area computation method: Weighted Average
- Check to define waste package thickness (default values used if unchecked)
  - Waste package thickness (cm): 1
  - Number of waste packages: 10000
- Distribution of general corrosion rates: Uniform
- Scale of distribution of general corrosion rates: Linear

Initial Radionuclide Mass in Disposal System

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Mass (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-14</td>
<td>18.5 kg</td>
</tr>
<tr>
<td>Cs-135</td>
<td>5.45 kg</td>
</tr>
<tr>
<td>I-129</td>
<td>2.35 kg</td>
</tr>
<tr>
<td>Pu-238</td>
<td>1.44 kg</td>
</tr>
<tr>
<td>Pu-239</td>
<td>6.85 kg</td>
</tr>
<tr>
<td>Pu-240</td>
<td>4.28 kg</td>
</tr>
<tr>
<td>Pu-242</td>
<td>1.89 kg</td>
</tr>
<tr>
<td>Pu-233</td>
<td>4.36 kg</td>
</tr>
<tr>
<td>Pu-234</td>
<td>8.17 kg</td>
</tr>
<tr>
<td>Pu-235</td>
<td>7.56 kg</td>
</tr>
<tr>
<td>All Radionuclides</td>
<td>7.83e7 kg</td>
</tr>
</tbody>
</table>
Backup Slide – Preliminary β SOAR
Example Model Elements Commercial
SNF Waste Form

Waste Form Initial Inventory (per waste package)
- Initial_Inventory_CSNF
- CSNF_Inventory_Factor_Dashed
- Modified_CSNF_Inventory
- UnboundFractions_CSNF
- CSNF_Unbound_Inventory
- CSNF_Bound_Inventory
- Switch_Releasable_CSNF_Source
- Releasable_CSNF_Distribution
- 3.14 16
- Releasable_CSNF_Used

Waste Form Degradation Rates
- CSNF_DegRates
- DegRate_CSNF_SW
- Switch_EnableCombinedSFDegRate
- WF_DegradationRate_CSNF
- Eq_3F
- WF_TemperatureEnhancementFactor_SF
- ModDegRate_CSNF_Distribution
- ModDegRate_CSNF_Dashboard