A Simplified and More Environmentally Benign Spent Nuclear Fuel Dissolution Process

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Standard reprocessing regimes use some version of the PUREX process:

- Hot nitric acid (8 to 12 M) oxidizes UO$_2$ to UO$_2^{2+}$
- Dissolves everything except noble metal phase
- NO$_x$ and fission gases released
- Large volume of gases goes up exhaust stack
- Iodine is volatile from hot nitric acid. Must be scrubbed from stack gases.

Leaves waste products:
- Neutralized aqueous radioactive waste
- Radioactive and organic mixed waste
Carbonate Dissolution of UO\textsubscript{2}

- Uranium oxides dissolve in carbonate solutions under oxidizing conditions.
- UO\textsubscript{2}\textsuperscript{2+} forms a series of stable, soluble anionic carbonate complexes.
- Carbonate solutions have been used to leach uranium ores since the 1950s.
- Carbonate leaching is well known mechanism for transport of radionuclides at fuel repository.
- A few groups have investigated dissolution of simulated (unirradiated) spent nuclear fuel with carbonate solutions.
Carbonate Dissolution of Fuel

- Uranium is known to dissolve. Well established chemistry.
- Most fission products are known to be insoluble in carbonate solution.
- pH of carbonate solution is about 10 (depending on the cation). Halogens are not volatile. Ru is not volatile.
- No nitric acid necessary. No NO\(_x\).
- Room temperature chemistry.
- Much smaller volume of stack gases. Easier control of stack emissions.
We chose (NH₄)₂CO₃ for the carbonate solution and H₂O₂ as the oxidizing agent:

- (NH₄)₂CO₃ is volatile and does not add mass to the spent fuel solution
- (NH₄)₂CO₃ can be recovered and recycled in a processing system
- H₂O₂ decomposes to H₂O and O₂(g), adding no mass and leaving benign decomposition products
Carbonate Dissolution of UO$_2$

- Dissolution stoichiometry for UO$_2$:

\[
UO_2 + H_2O_2 + 3(NH_4)_2CO_3 \Rightarrow (NH_4)_4UO_2(CO_3)_3 + 2NH_4OH
\]

- Uranium carbonate complexes go on to form temporary peroxide complexes:

\[
UO_2(CO_3)_3^{4-} + H_2O_2 \Leftrightarrow UO_2(CO_3)_2O_2^{4-} + 2H^+ + CO_3^{2-}
\]

- Decomposition of O$_2^{2-}$ consumes H$^+$:

\[
2O_2^{2-} + 4H^+ \Leftrightarrow 2H_2O_2 \Rightarrow 2H_2O + O_2(g)
\]

- pH should not change materially because solution is buffered by ammonium and carbonate ions.
Three spent fuel segments from commercial reactors:

- **ATM-105**
  - 30 GWd/MTU
  - 27 years out of reactor

- **ATM-106**
  - 45 GWd/MTU
  - 28 years out of reactor

- **ATM-109**
  - 60 GWd/MTU
  - 16 years out of reactor

Spent fuel in cladding. Photo taken through leaded hot cell glass.
During dissolution, each piece of fuel was expected to form a rind of undissolved or reprecipitated fission products and transuranics.

Rind could be knocked off using milling balls and tumbling equipment, except we have:
- Highly radioactive slurry
- Gas pressure due to decomposition of H₂O₂

Crushing the fuel was an expedient way to expose as much surface area as possible to aqueous solvents:
- Crushed with commercial (piston-in-cylinder) crusher
- Passed through 212-μm soil sieve
Experimental: Dissolution

- ~13 g of each spent fuel was placed in a 500 mL Tantalum crucible
- Reagents added:
  - 150 mL saturated \((\text{NH}_4)_2\text{CO}_3\)
  - 30 mL 30% \(\text{H}_2\text{O}_2\)
- Orbital shaker and alumina milling balls:
  - Agitate slurry to keep solids from settling and becoming unavailable for dissolution
- Solids allowed to settle overnight
  - Solution removed
  - Fresh \((\text{NH}_4)_2\text{CO}_3\) and \(\text{H}_2\text{O}_2\) added
  - \(\text{H}_2\text{O}_2\) added every few hours
- Repeated for several days. Dissolution considered complete when removed solution no longer yellow
Experimental: Dissolution

- Dissolution didn’t need as much time as we gave it.
- U forms highly soluble mixed carbonate-peroxide complexes, which decompose within hours.

\[
\text{UO}_2 \rightarrow \text{UO}_2(\text{CO}_3)_2(\text{O}_2)^{4-} \rightarrow \text{UO}_2(\text{CO}_3)_3^{4-}
\]

fuel → soluble species → less soluble species

- Dissolution proceeded fast enough to cause re-precipitation of \((\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3\) after peroxide complexes decomposed.

Solution must be frequently removed and replaced with fresh carbonate-peroxide to avoid re-precipitation of uranium.
Post-Dissolution Processing

Irradiated UO₂ fuel

Solution:
- \( \text{UO}_2(\text{CO}_3)_3^{4-} \)
- An, Ln carbonates
- Cs⁺, I⁻, Br⁻
- Fission Products
- ~0.6M (NH₄)₂CO₃

Heat to 80-90°C to Evaporate (NH₄)₂CO₃

Breakdown of Np, Pu, Am, Cm carbonate complexes → precipitation

Solids:
- An, Ln, Sr carbonates
- An, Ln hydroxides
- Fission products
- Noble metal phase

Filtration

Solids:

Solution:

Filtration
Post-Dissolution Processing

Solids → 0.5 M HNO₃ → Solids → 0.5 M HNO₃ → FP Fraction

Solids → 0.5 M HNO₃ → Sat. NH₄OH → Sr Fraction

Solution → Ion Exchange Column → Cs Fraction

Solution → Ion Exchange Column → U Fraction
Dissolution Results

Noble metal phase:
- Insoluble black residue left after all post-dissolution chemistry
  - Pure noble metal phase contains Mo, Tc, Ru, Rh, and Pd
  - Our insoluble residue also has FP and high alpha activity
- Had a tiny fraction of the gamma activity of the starting fuel
  - $^{125}\text{Sb}$, $^{137}\text{Cs}$, $^{154}\text{Eu}$, and $^{155}\text{Eu}$ most prominent
- Mass of noble metal phase is $< 2\%$ of the starting fuel mass and varies with burnup:

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Starting mass (g)</th>
<th>Ending mass (g)</th>
<th>Fraction Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATM-105</td>
<td>13.087</td>
<td>0.0266</td>
<td>0.998</td>
</tr>
<tr>
<td>ATM-106</td>
<td>13.167</td>
<td>0.1214</td>
<td>0.991</td>
</tr>
<tr>
<td>ATM-109</td>
<td>12.054</td>
<td>0.2320</td>
<td>0.981</td>
</tr>
</tbody>
</table>
Distribution of Major Fission Products in Various Process Fractions

The bar chart shows the distribution of major fission products in various process fractions. The chart includes the following nuclides:
- Sr-90
- Sb-125
- Cs-137
- Eu-154
- Eu-155

The chart is color-coded as follows:
- Noble Metal Phase
- F.P. Fraction
- Sr Fraction
- Cs Fraction
- U Fraction

Each nuclide is represented by a bar, and the height of the bar indicates the fraction of the total inventory for that nuclide in each process fraction.
Distribution of Actinides in Various Process Fractions

The chart illustrates the distribution of various actinide nuclides across different process fractions. The y-axis represents the fraction of total inventory, while the x-axis lists different nuclides, including Total U, Np-237, Pu-238, Pu(239+240), Am-241, Cm-242, and Cm(243+244). Each nuclide is color-coded to show its distribution across different fractions:

- Noble Metal Phase
- F.P. Fraction
- Sr Fraction
- Cs Fraction
- U Fraction

The chart provides a visual representation of how each nuclide is distributed among these fractions, allowing for a clearer understanding of their relative abundance in each process.
The uranium fractions removed from the hot cell still contained significant amounts of dissolved Np, Pu, Am, and Cm.

Solutions were heated in a fume hood to expel most of the \((\text{NH}_4)_2\text{CO}_3\)

- Loss of carbonate causes actinide carbonate complexes to fall apart
- Precipitation of actinides

Solution filtered with 0.45mm filter

- Solids labeled **Second Precipitate**
- Solution labeled **Final Solution**
Distribution of Major Fission Products in Various Process Fractions, 2nd Precipitation

![Graph showing the distribution of major fission products in various process fractions.](image)

Legend:
- Noble Metal Phase
- F.P. Fraction
- Sr Fraction
- Cs Fraction
- U Fraction

Axes:
- Y-axis: Fraction of Total Inventory: ATM-10€
- X-axis: Sb-125, Eu-154, Eu-155
Distribution of Major Fission Products in Various Process Fractions, 2\textsuperscript{nd} Precipitation
Distribution of Actinides in Various Process Fractions, 2nd Precipitation

The diagram illustrates the distribution of various actinides in different process fractions. The y-axis represents the fraction of total inventory in ATM-10e units, ranging from 0 to 1.0. The x-axis lists the isotopes and fractions: Pu (239+240), Am-241, Cm-242, and Cm (243+244). The chart includes a legend indicating different phases: Noble Metal Phase, F.P. Fraction, Sr Fraction, Cs Fraction, and U Fraction.
Distribution of Actinides in Various Process Fractions, 2nd Precipitation

- Noble Metal Phase
- F.P. Fraction
- Sr Fraction
- Cs Fraction
- U Fraction

Pu (239+240) data is shown in the graphs.
**Distribution of Actinides in Various Process Fractions, 2nd Precipitation**

<table>
<thead>
<tr>
<th></th>
<th>Sr-90</th>
<th>Sb-125</th>
<th>Cs-137</th>
<th>Eu-154</th>
<th>+240</th>
<th>Am-241</th>
<th>+244</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Final solution</strong></td>
<td>0.003</td>
<td><strong>0.441</strong></td>
<td>0.013</td>
<td>0.053</td>
<td>0.055</td>
<td>0.011</td>
<td>0.011</td>
</tr>
<tr>
<td><strong>Both precips</strong></td>
<td>0.013</td>
<td>0.169</td>
<td>0.0003</td>
<td><strong>0.933</strong></td>
<td><strong>0.937</strong></td>
<td><strong>0.962</strong></td>
<td><strong>0.974</strong></td>
</tr>
<tr>
<td><strong>Cs frac</strong></td>
<td><strong>0.598</strong></td>
<td>0.109</td>
<td><strong>0.983</strong></td>
<td>0.0001</td>
<td>0.008</td>
<td>0.019</td>
<td>0.014</td>
</tr>
<tr>
<td><strong>Sr frac</strong></td>
<td><strong>0.385</strong></td>
<td>0.051</td>
<td>0.003</td>
<td>0.0001</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.001</td>
</tr>
<tr>
<td><strong>noble metals</strong></td>
<td><strong>0.230</strong></td>
<td>0.0001</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

We have developed a promising alternative spent nuclear fuel reprocessing scheme using $(NH_4)_2CO_3$ and $H_2O_2$:

- > 98% dissolution of solid spent fuel
- Simple heating and precipitation provide ~95% separation of Pu, Am, Cm, and Eu
- All reagents are volatile
  - Volume of products can be made quite small
  - Some reagents can be recycled
- Uses more benign materials than traditional reprocessing schemes.
- Leaves $UO_2^{2+}$ in the well characterized carbonate form
Conclusions

From this process, it is possible to simplify spent fuel disposal.

- Current plans call for disposing of all spent fuel constituents together, requiring all components to be treated the same as the most hazardous ones.
- With additional development, our process could be used to produce more manageable waste components:
  - Sr + Cs → short term storage (~300 years)
  - Transuranics → Light water reactor, fast reactor, repository
  - Other Fission Products → low dose, small volume, safe chemical form of our choosing
Acknowledgements

The authors would like to acknowledge the Advanced Fuel Cycle Initiative Separations Campaign for financially supporting this work.

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy (DOE) by Battelle under Contract DE-AC05-76RL1830.