Multiscale Evaluation of Acetohydroxamic Acid (AHA) Radiolysis Under Used Nuclear Fuel Reprocessing Solvent System Conditions

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Radiation Chemistry and Used Nuclear Fuel Reprocessing

Solvent Extraction Reprocessing
Ligands/organic diluent: $\text{HNO}_3/\text{H}_2\text{O}$
($\pm$ additives)

- Gaseous Phase
- Organic Phase
- Aqueous Phase
- Oxide Layer
- Structural Materials

- Uranium mine
- Conversion to fuel
- Reactor
- Spent fuel
- Plutonium and recovered uranium
- Reprocessing
- Waste management and storage
**Advanced Used Nuclear Fuel Reprocessing**

Solvent Extraction Reprocessing
Ligands/organic diluent: HNO₃/H₂O
(± additives)

- **Gaseous Phase**
- **Organic Phase**
- **Aqueous Phase**
- **Precipitation**
- **Oxide Layer**
- **Structural Materials**

**Figure 1.** Concentration of NpO₂⁺ (■) and NpO₂²⁺ (●) ions as a function of absorbed gamma dose for formally 2 mM NpO₂²⁺ in 0.5 M HNO₃.

\[ \text{Np}^{4+}/\text{NpO}_2^{2+} \rightarrow \text{Extractable} \]

\[ \text{NpO}_2^{2+} \rightarrow \text{Inextractable} \]
Radiation Chemistry in Nitrate and Nitric Acid Solutions

Water Radiolysis

\[ \text{H}_2\text{O} \leftrightarrow e_\text{aq}^-, \text{H}^+, \cdot\text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_\text{aq}^+ \]

Indirect Radiation Effects

\[ \text{HNO}_3 + \cdot\text{OH} \rightarrow \cdot\text{NO}_3 + \text{H}_2\text{O} \]
\[ \text{NO}_3^- + e_\text{aq}^- \rightarrow \text{NO}_3^{2-} \]
\[ \text{NO}_3^{2-} + \text{H}_2\text{O} \rightarrow \cdot\text{NO}_2 + 2\text{OH}^- \]
\[ \text{NO}_3^- + \text{H}^+ \rightarrow \text{HNO}_3^- \rightarrow \cdot\text{NO}_2 + \text{OH}^- \]
\[ \cdot\text{NO}_2 + \cdot\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \]
\[ \text{N}_2\text{O}_4 \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

Direct Radiation Effects

\[ \text{NO}_3^- \leftrightarrow \text{NO}_3^-* \rightarrow \text{NO}_2^- + \text{O} \]
\[ \text{HNO}_3 \leftrightarrow \text{HNO}_3^* \rightarrow \text{HNO}_2 + \text{O} \]
\[ \text{NO}_3^- \leftrightarrow \cdot\text{NO}_3 + e^- \]
\[ \text{HNO}_3 \leftrightarrow \cdot\text{NO}_3 + \text{H}^- \]

The Role of AHA and its Radiolytic Behavior

Concentration of AHA, BTPS, and H$_{aq}^+$ vs. gamma dose for 2 h of AHA hydrolysis.

“...concentrations for both molecules (AHA and SO$_3$-Ph-BTP) are practically invariable with dose...”

“...the separation factor between Eu and Am to remain essentially unchanged.”

“...to scale up these kind of processes an in-depth knowledge of their resistance and long-term behavior is still required...”

“...it is essential to design reliable simulating strategies to predict the long-term performance of extraction systems...”

Experimental Methodology

**Steady-State Gamma Radiolysis**

**Time-Resolved Pulsed Electron Radiolysis**

Multiscale Modeling Irradiated Solutions

- 100 ps

- 50
- 100
- 150
0
50
100
150

-100
0
50
100
150

1. Track Structure Simulation
2. Physicochemical Processes
3. Nonhomogeneous Diffusion-Reaction Kinetics
4. Homogeneous Bulk Chemistry

Energy Transfer and Track Structure
Ultra-fast Chemistry
Intra-track Chemistry
Reaction of Long-lived Radiolysis Species

<1 femtosecond
<1 picosecond
<1 microsecond
>1 microsecond

Acetohydroxamic Acid (AHA) Radiolysis

- Loss of AHA by radiolysis and hydrolysis processes from the irradiation of 0.5 M AHA in 0.2 M NaNO₃ (▼) and HNO₃ (▲): (A) 51 Gy min⁻¹ at 36 °C; (B) 150 Gy min⁻¹ at 40 °C; and (C) 250 Gy min⁻¹ at 42 °C.
Dissolved Degradation Product Formation

Yields of **Acetic Acid** and **HA** from the irradiation of 0.5 M AHA in 0.2 M NaNO$_3$ (▼) and HNO$_3$ (▲): (A) 51 Gy min$^{-1}$ at 36 °C; (B) 150 Gy min$^{-1}$ at 40 °C; and (C) 250 Gy min$^{-1}$ at 42 °C.
Gaseous Degradation Product Formation

- Yields of $\text{N}_2\text{O}$ and $\text{H}_2$ from the irradiation of 0.5 M AHA in 0.2 M NaNO$_3$ (▼) and HNO$_3$ (▲): (A) 51 Gy min$^{-1}$ at 36 °C; (B) 150 Gy min$^{-1}$ at 40 °C; and (C) 250 Gy min$^{-1}$ at 42 °C.

Dominant Reaction Mechanisms

\[
\begin{align*}
\text{H}_\text{aq}^+ \text{, H}_2\text{O} & \quad + \quad \text{HNO}_2 \\
\text{N}_2\text{O} & \quad + \quad \text{H}_2\text{C}_2\text{O}_4
\end{align*}
\]
Conclusions and Future Research

• Loss of AHA by hydrolysis > radiolysis.

• Radiolysis of AHA predominantly by oxidizing radicals (\(\cdot\text{OH}, \text{NO}_3\cdot\), and AHA\(\cdot\)).

• Multiscale model accurately predict loss of AHA in representative single cycle aqueous phase conditions.

• Biphasic conditions promote negligible changes in AHA and ligand (TBP, DEHBA, and DEHiBA) radiation chemistry.

• What is the impact of metal ions?
Impact of Metal Ions

\[ (\text{HEH}\{\text{EHP}\}/\text{DD}) = 4.75 \times 10^{-4} \text{ kGy}^{-1} \]

\[ (\text{HEH}\{\text{EHP}\}/\text{DD} + \text{La}^{3+}) = 6.55 \times 10^{-4} \text{ kGy}^{-1} \]

**Table 1. Summary of second-order \( \text{RH}^{\cdot+} \) rate coefficients measured or revised by this work for TBP, DEHBA, and DEHBA in 0.5 M DCM/n-dodecane solutions with and without \( \text{UO}_2^{2+} \) present.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{RH}^{\cdot+} ) Rate Coefficient ((10^{10} \text{ M}^{-1} \text{ s}^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>TBP</td>
<td>1.36 ± 0.07</td>
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<tr>
<td>([\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2])</td>
<td></td>
</tr>
<tr>
<td>DEHBA</td>
<td>0.93 ± 0.02</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{NO}_3)_2(\text{DEHBA})_2])</td>
<td>2.49 ± 0.06</td>
</tr>
<tr>
<td>DEHBA</td>
<td>1.14 ± 0.04</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{NO}_3)_2(\text{DEHBA})_2])</td>
<td>1.59 ± 0.08</td>
</tr>
</tbody>
</table>

Acknowledgements