Radiolytic Studies of Single-Cycle Extraction Systems

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Single Cycle Processes & Innovative Aqueous Separations Radiation Chemistry

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

Conversion to fuel → Reactor

Plutonium and recovered uranium → Spent fuel → Reprocessing

Waste management and storage

Gaseous Phase
Organic Phase
Aqueous Phase
Precipitation Oxide Layer Structural Materials

Reprocessing radiation chemistry

Water Radiolysis

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

Indirect Radiation Effects

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

Direct Radiation Effects

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

Alkane Radiolysis

\[
\text{R-CH}_3 \rightleftharpoons e^-, \text{RH}^+, \text{RH}^+, \cdot\text{CH}_3, \cdot\text{H}, \text{H}_2
\]

Reprocessing radiation chemistry

Water Radiolysis

$H_2O \rightarrow e_{aq}^-, H^+, \cdot OH$

Direct Radiation Effects

$NO_3^- + NO_3^- \rightarrow NO_3^- + O_2$

Key Transient Species

$e_{aq}^-, H^+, \cdot OH$ from $H_2O$

$\cdot NO_3$ from $HNO_3$

$RH^{\cdot\cdot}$ from $n$-dodecane

$N_2O_4 \rightarrow HNO_2 + HNO_3$

References:
Reprocessing radiation chemistry

Water Radiolysis

\[ \text{H}_2\text{O} \rightarrow e^- + \text{H}^\bullet + \cdot\text{OH}, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_\text{aq}^+ \]

Indirect Radiation Effects

\[ \text{HNO}_3 + \cdot\text{OH} \rightarrow \cdot\text{NO}_3 + \text{H}_2\text{O} \]

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

\[ \cdot\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \cdot\text{NO}_2 + 2\text{OH}^- \]

\[ \cdot\text{NO}_3^- + \text{H}^- \rightarrow \text{HNO}_3^- \rightarrow \cdot\text{NO}_2 + \text{OH}^- \]

\[ \cdot\text{NO}_2 + \cdot\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4 \]

Direct Radiation Effects

\[ \text{NO}_3^- \rightarrow \text{NO}_3^* \rightarrow \text{NO}_2^- + \text{O} \]

\[ \text{HNO}_3 \rightarrow \cdot\text{NO}_3^- \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

Today’s Research Focus

RH\^+ from \textit{n}-dodecane

R - CH\textsubscript{3} \rightarrow e^- , RH^\bullet + , RH^\bullet , \cdot\textsubscript{CH}_3 , H^\bullet , H_2^\bullet

\[ \text{N}_2\text{O}_4 \rightarrow \text{HNO}_2 + \text{HNO}_3 \]

\[ \text{H}_2 \]

\[ \]

References:

Complexation effects

Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å$^3$. (a) [Nd(TEDGA)$_3$]([NO$_3$])$_3$, (b) [Nd(TEDGA)$_3$]Cl$_3$, (c) [Am(TEDGA)$_3$]([NO$_3$])$_3$, and (d) [Am(TEDGA)$_3$]Cl$_3$.

“...in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products.” Kimberlin et al., PCCP, 2022.

- Ilan and Czapski, Biochimica et Biophysica Acta, 1977, 498, 386.
- Kimberlin, Saint-Loius, Guillaumont, Cames, Guilbaid, and Berthon, PCCP, 2022, 24, 9213.
Complexation effects under MRWFD

- Toigawa et al., PCCP, 2021, 23, 1343.
- Celis-Barros et al., PCCP, 2021, 23, 24589.
Transients are detected by optical absorption changes.

Methodology

Psuedo-First-Order Rate Coefficient \( (10^8 \text{ s}^{-1}) \)

\[ \ln(\text{TODGA})^3 (\text{mM}) \]

\[ k(\text{[Yb(TODGA)3] + RH}^+) = (8.58 \pm 1.81) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]

\[ k(\text{[Gd(TODGA)3] + RH}^+) = (2.47 \pm 0.18) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]

\[ A = 7.87 \times 10^9 \text{ s}^{-1} \]

\[ E_a = 0.19 \text{ J mol}^{-1} \]

\[ k(\text{TODGA} + \text{RH}^+) = (9.72 \pm 1.10) \times 10^9 \text{ M}^{-1} \text{s}^{-1} \]

Lanthanide Complexed CMPO Radiolysis

$k([\text{Nd(CMPO)}_n] + \text{RH}^{++}) = (5.13 \pm 0.85) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$

$k([\text{Gd(CMPO)}_n] + \text{RH}^{++}) = (1.09 \pm 0.03) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

$k([\text{Yb(CMPO)}_n] + \text{RH}^{++}) = (1.35 \pm 0.28) \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$

Conclusions

- Complexation has a profound effect on reaction kinetics, from changes in electron distribution to size.
- Understanding the impact of complexation on the radiation-induced degradation mechanisms of reprocessing ligands is essential for accurate estimates of process viability.
- M4 milestone due September 30th, 2022, draft manuscript. On track.

Future Research

- Continued support in evaluating the radiation robustness of next generation ligands.
- Determine the impact of post-VOLOX direct dissolution formulations on metal-loaded ligand radiolysis behavior.

References:
- Horne et al., Does Addition of 1-Octanol as a Phase Modifier Provide Radical Scavenging Radioprotection for N,N,N',N'-tetraoctyldiglycolamide (TODGA)? PCCP, 2020, 22, 24978.
Acknowledgements