

Insights into the Coordination, Aggregation, and Transport of Trivalent Metals in the LiCl-KCl Eutectic

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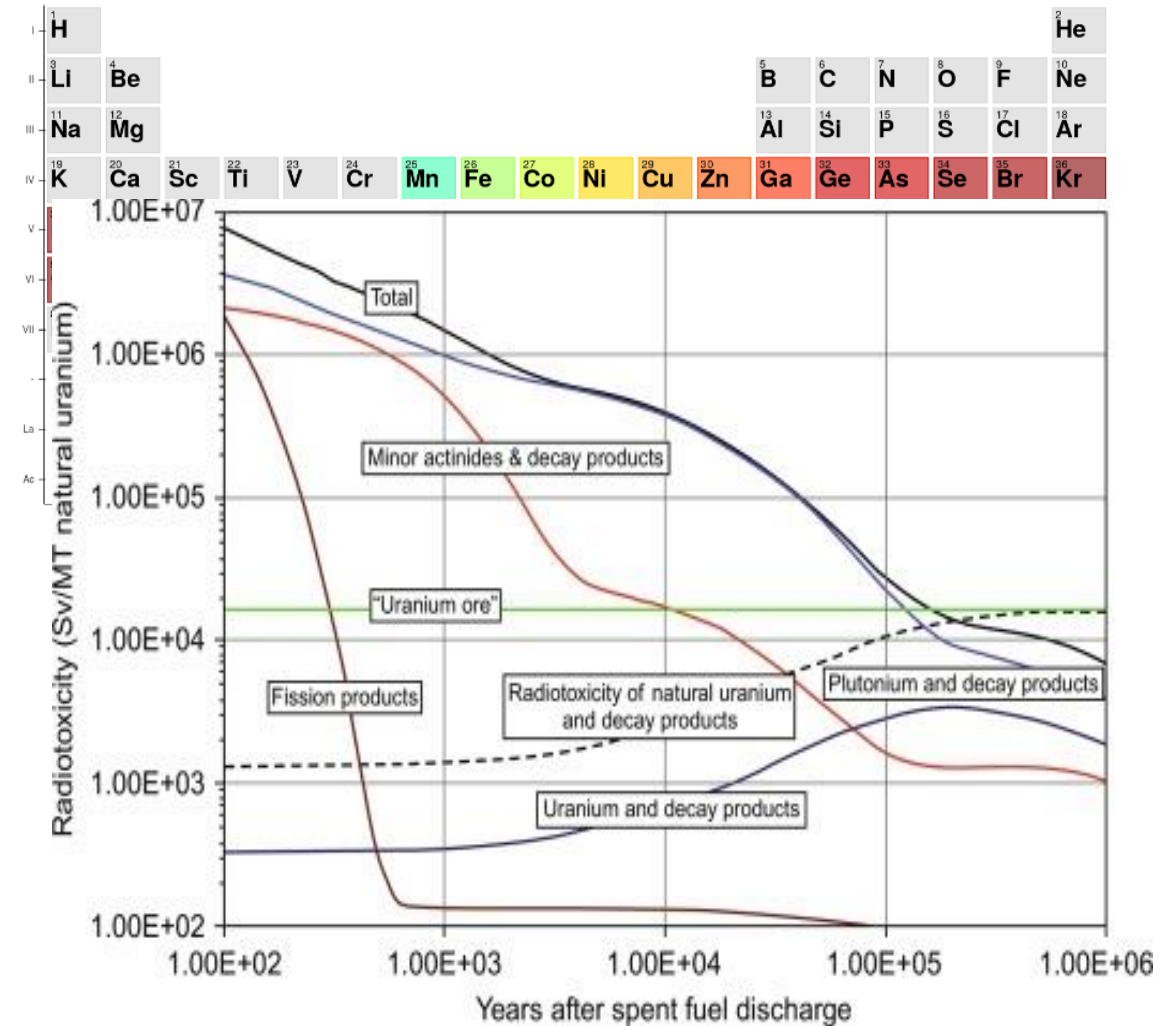
ETI Annual Workshop

February 20 – 21, 2024, Golden, CO



Motivation – The Potential of UNF

- Used nuclear fuel (UNF) contains useful elements
 - Fuel isotopes (U/Pu)
 - Rare earth elements (REEs)
 - Neutron absorbing fission products
 - High radiotoxicity isotopes
- Isolation of these species improves the fuel cycle
 - Improved utilization of fuel isotopes
 - Collection of REEs
 - Reduced radiotoxicity timeline for fuel wastes

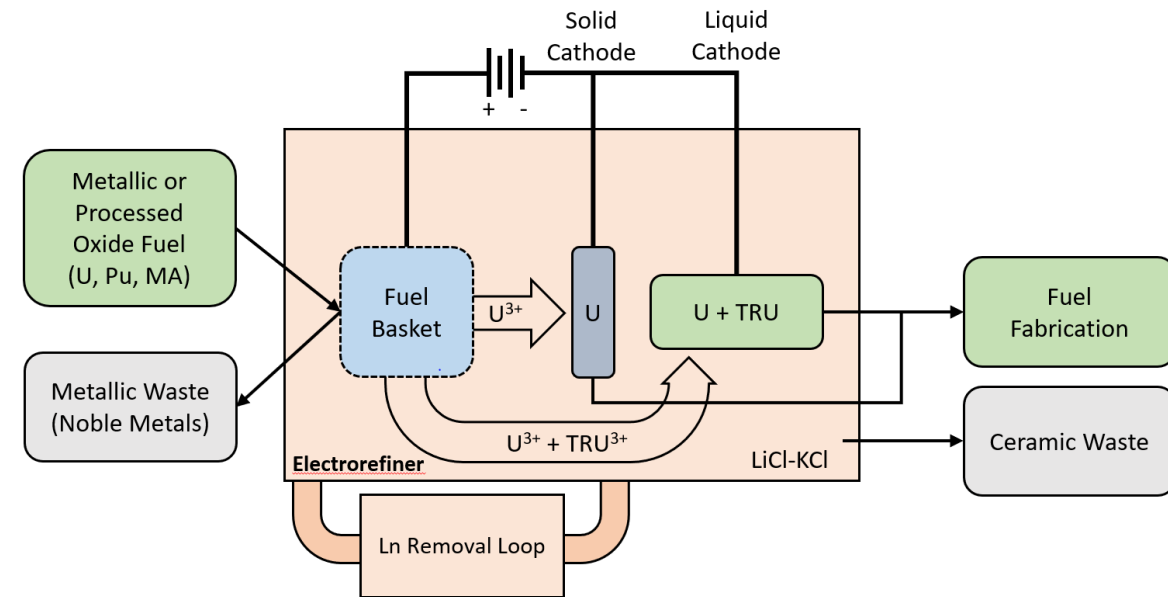


1. Touran, N. What about the waste? Data Source - ENDF/VII.1

2. Joyce, M. Chapter 15 In *Nuclear Engineering*, 357–78. Butterworth-Heinemann, (2018). doi:10.1016/B978-0-08-100962-8.00015-9.

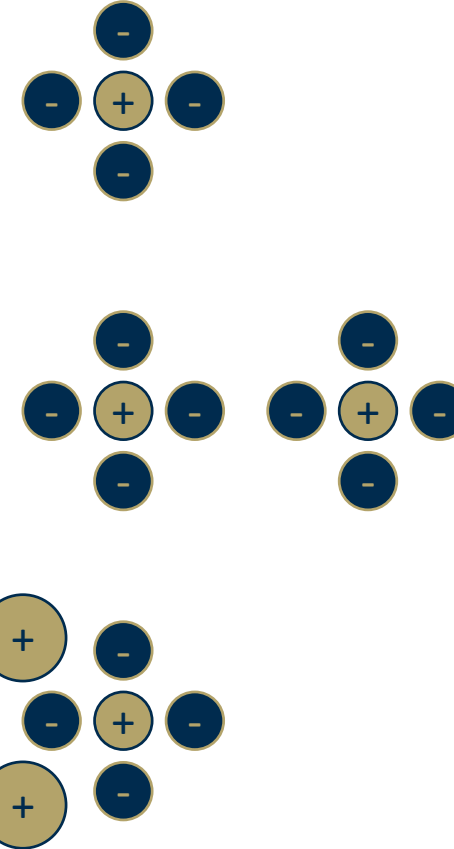
Pyroprocessing – An Overview

- Processing method that could allow for online reprocessing in certain reactors
 - Chloride salts are the most prominent design
 - Monitoring is critical for process security
 - Salts are atypical compared with aqueous systems
- Promising method for handling UNF, but requires knowledge of salt properties
 - Thermophysical and transport properties
 - Liquid structures – networks involving uranium
- Primary components of the electroplating process are:
 - Diffusion of ion species
 - Electron transfer efficiency at the electrode



The Critical Role of Coordination

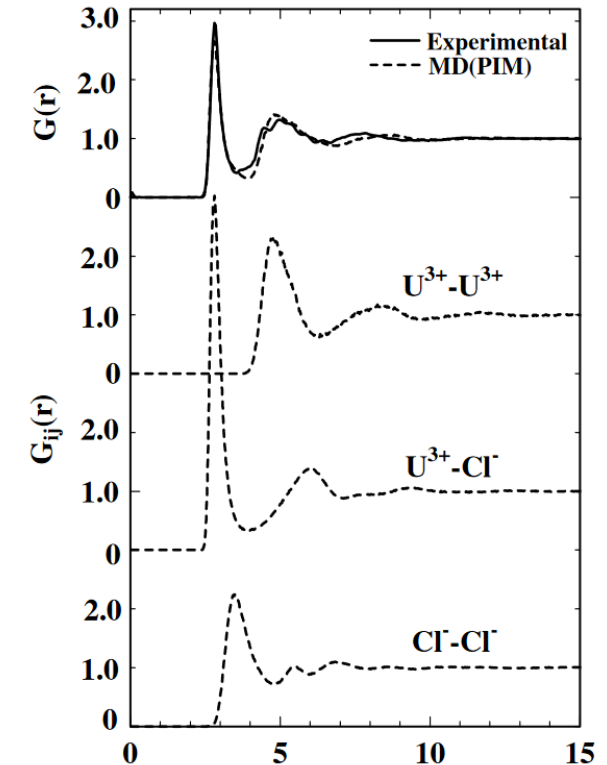
- Both the diffusion regime and electron transfer of ions rely heavily on the coordination environment
 - Diffusion can be impacted by complexing anions or by extended network interactions
 - Electron transfer is influenced by the strength of coordination to other ions
- Experiments probing coordination can be challenging to conduct
 - Corrosive salts
 - High temperatures (500 – 700 C)
 - Radioactive species
- Molecular dynamics (MD) can help predict salt properties and nano-scale behaviors of systems that have not been experimentally tested.



1. Hege, N., et al. Journal of The Electrochemical Society, 170, 1, (2023), p. 016503. doi:10.1149/1945-7111/acafa9.

Prior Efforts in Chloride Salt Coordination Chemistry

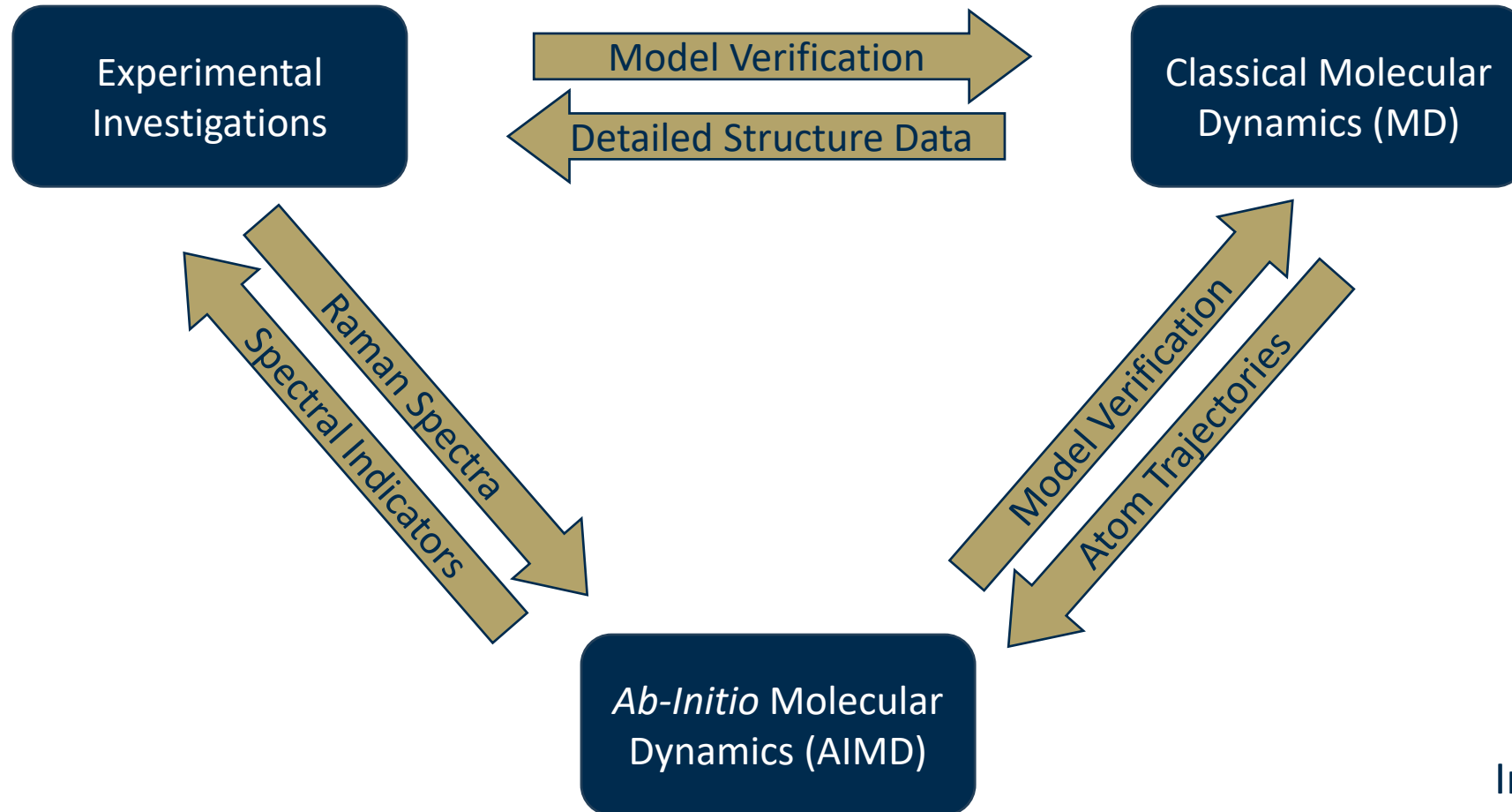
- Experimental Investigations of MCl_x -LiCl-KCl salts
 - Electrochemical properties (Redox potentials and diffusion coefficients)
 - Thermodynamic properties
 - Limited - Coordination by spectral techniques (Raman, UV-Vis, EXAFS)
- Computational Investigations by Molecular Dynamics
 - Basics of coordination in ternary salts
 - Basics of transport and thermodynamic properties in ternary salts
 - Effects of temperature and MCl_3 concentration on transport properties and polymer sizes
 - Limited calculations of Raman spectra
- Knowledge Gaps
 - Detailed analysis of M^{3+} coordination environment in LiCl-KCl
 - Impacts of fission products on U^{3+} coordination environment in quaternary systems



Project Outline

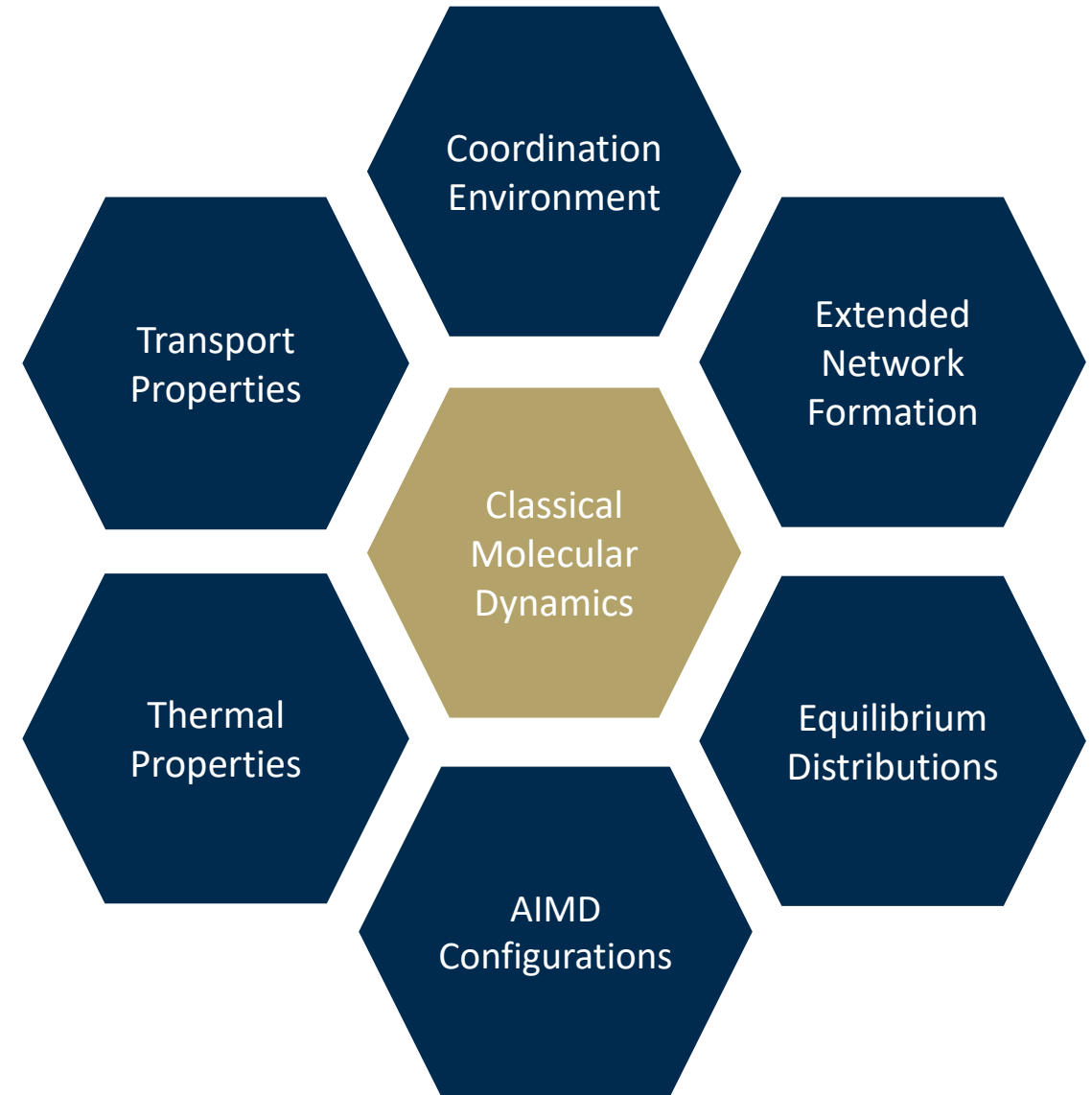
Objective

Develop online monitoring capabilities for pyroprocessing of used nuclear fuel (UNF) by association of optical indicators (Raman/UV-Vis) to nanoscale behavior of the molten salts



Analysis with Classical Molecular Dynamics

- Investigating the systems in ways that can and cannot be probed experimentally
 - Transport properties
 - Thermodynamic properties
 - Basic coordination environment
- Dynamics of coordination
 - Ion coordination times
 - Partitioned contributions to diffusion
 - Inter/intra species aggregation
 - Aggregate size distributions



Highlighting the Role of Many-Body Effects

- U^{3+} diffuses faster than Sc^{3+} in 5 mol% MCl_3 systems

System	M^{3+} Self-Diffusion Coefficient [10^{-5} cm ² /s]	Viscosity [mPa-s]	CN_{M-Cl} [-]
5 mol% UCl_3	0.91	2.46	6.4
5 mol% $ScCl_3$	0.73	2.15	5.6

- Prior work suggests prevalent monomer species in both systems
 - Some dimer species in UCl_3 systems
 - Aggregates may have weak influence over diffusion at this concentration
 - U^{3+} aggregates more readily as MCl_3 concentration increases
- Number of coordinating Cl^- is higher for U^{3+} than Sc^{3+}
 - Suggests that diffusion is influenced by inner and outer sphere effects

1. Wang, S., et al. *Electrochimica Acta*, 306, (2019), pp. 366–76. doi:10.1016/j.electacta.2019.03.123.

Principles of Coordination in 5 mol% MCl_3

- Ions exhibit varied coordination spheres
 - U^{3+} maintains a broad set of coordination numbers ($CN_{M-Cl} = 6, 7, \text{ and } 8$)
 - Sc^{3+} remains octahedral

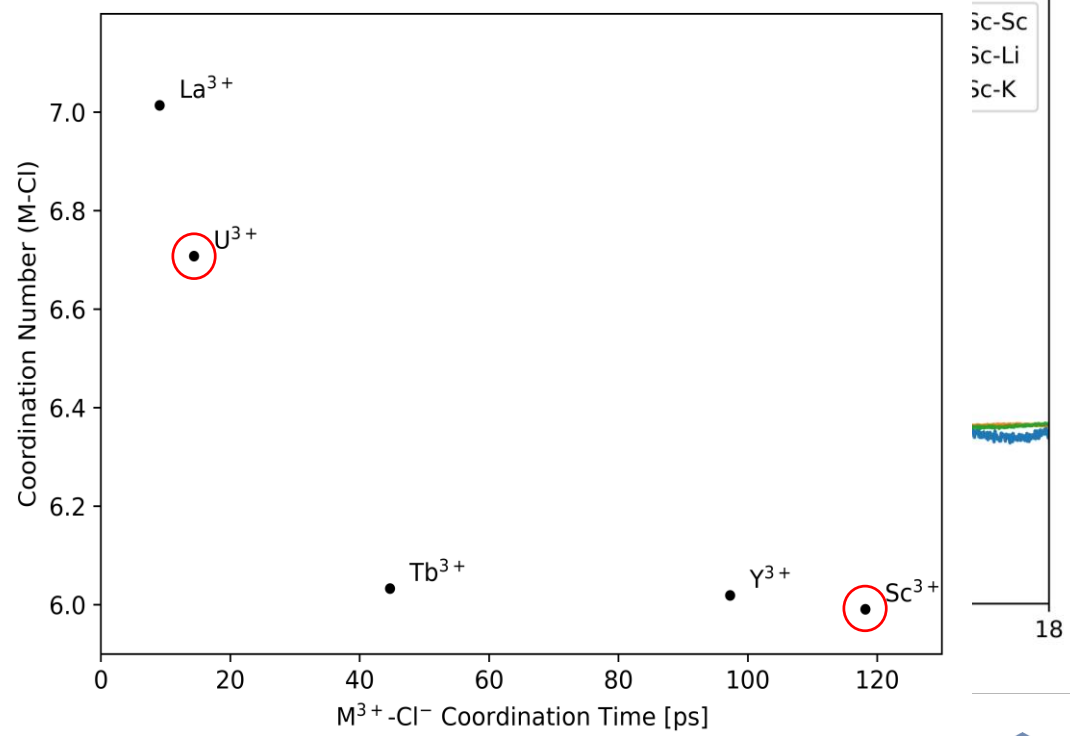
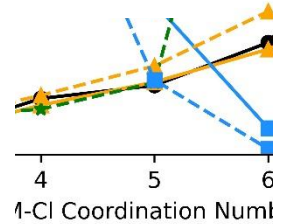
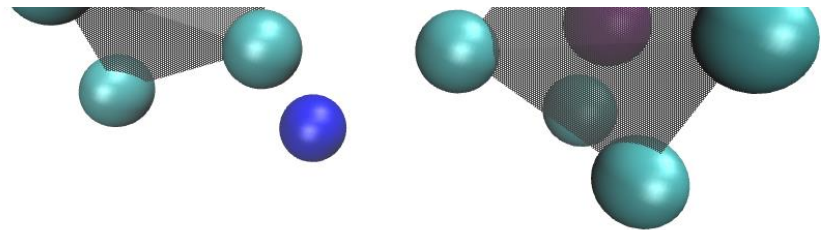
- $M^{3+}-Cl^-$ coordination times vary with cation radius

- Cations can coordinate via
 - Direct Cl^- sharing
 - Solvent cation sharing of co



Reduced $M^{3+}-Cl^- - M^{3+}$ interactions for favored $M^{3+}-Cl^- - K^+$ coordination

Parameter		5 mol% UCl_3	5 mol% $ScCl_3$
M-Cl Coordination Length	[Å]	2.79	2.49
M-Cl Coordination Time	[ps]	14	118
Induced Cl- Dipole	[D]	0.52	0.68
Activation Energy ($E_a - M^{3+}-Cl^-$) @ 773 K	[KT]	4.32	7.34



Cation Aggregation in 5 mol% MCl_3

- Systems remain monomeric by anion sharing
- Considering solvent cation coordination generates system-sized aggregates
- N-mers formed by complex anions remain short-lived

Parameter		5 mol% UCl_3	5 mol% $ScCl_3$
Average CN_{M-Cl}	[-]	6.4	5.6
Aggregate Size [Cl ⁻ Sharing]	[-]	1.2	1.0
Aggregate Size [Solvent Sharing]	[-]	57.0	36.7
Activation Energy ($E_a - M^{3+}-Cl^-$)	[KT]	4.32	7.34
Activation Energy ($E_a - M^{3+}-M^{3+}$)	[KT]	1.48	1.47
Activation Energy ($E_a - M^{3+}-K^+$)	[KT]	1.28	1.48
Activation Energy ($E_a - M^{3+}-Li^+$)	[KT]	1.15	1.06

Consequences of the M^{3+} Coordination Environment

- Lifetime of the complex anion controls diffusion more than the weak aggregation at 5 mol% MCl_3
 - Diffusion coefficients of long-lived species are suppressed
 - System viscosities exhibit minor reduction with smaller aggregates

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Concluding Remarks

- Both U^{3+} and Sc^{3+} preferentially coordinate with K^+ by Cl^- sharing
 - Cl^- sharing interactions between Sc^{3+} - Sc^{3+} are particularly rare
 - Preferential K^+ coordination driven by poor ability of K^+ to polarize Cl^-
- Weaker polarization ability of U^{3+} leads to short-lived complex anions, allowing U^{3+} to diffuse independently of Cl^- , compared with long-lived Sc^{3+} species
 - U^{3+} diffuses faster than Sc^{3+}
- Weakly interacting network has little impact on transport properties at this concentration

Future Work

- Seeking to complete work with other fission product cations
- Extending analysis capabilities
- Integrating experimental data sets into validation of calculations

ETI Impact

National Laboratory Collaboration

- Pacific Northwest National Laboratory



Internships

- Nicole Hege – PNNL
- Jacob Tellez – PNNL



ACKNOWLEDGEMENTS

This material is based upon work supported by the Department of Energy / National Nuclear Security Administration under Award Number(s) DE-NA0003921.

Advisors

Dr. Jen Shafer, Dr. David Wu

Dr. Michael Servis

Collaborators

CSM – Nicole Hege

WSU – Dr. Will Smith, Dr. Aurora Clark

PNNL – Dr. Neil Henson

