INL/CON-24-76838-Revision-0

Electrorefiner Speciation and Phase Model for Prediction of Operation Lifetime

March 2024

Changing the World's Energy Future

Jacob Allen Yingling, Guy L Fredrickson, Tae-Sic Yoo, Toni Y Karlsson

Idaho National Laboratory

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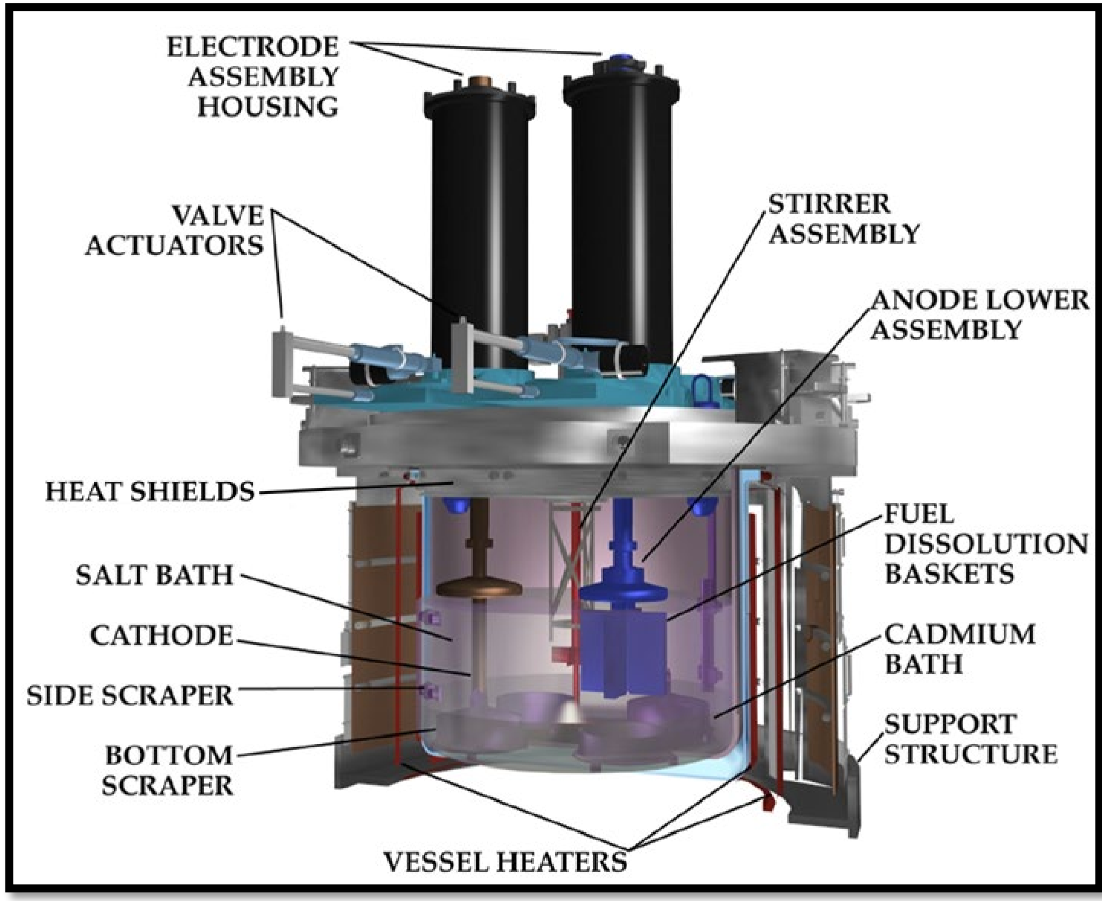
About the Presenter

- Jacob A. Yingling, Postdoctoral research associate, Ph.D
- Thermodynamics via computation of phase diagrams (CALPHAD)
- Veteran Naval Officer (Nuclear Power Training)
- Fuel salt synthesis for the Molten Chloride Reactor Experiment
- Thermodynamics in support of pyrochemical processing of used nuclear fuels
- Collaborators
  - Idaho National Laboratory: Toni Karlsson, Tae-Sic Yoo, Guy Fredrickson,
  - University of South Carolina: Juliano Schorne-Pinto, Jorge Palma, Clara Dixon
- Jacob.Yingling@inl.gov

Historical context: EBR-II

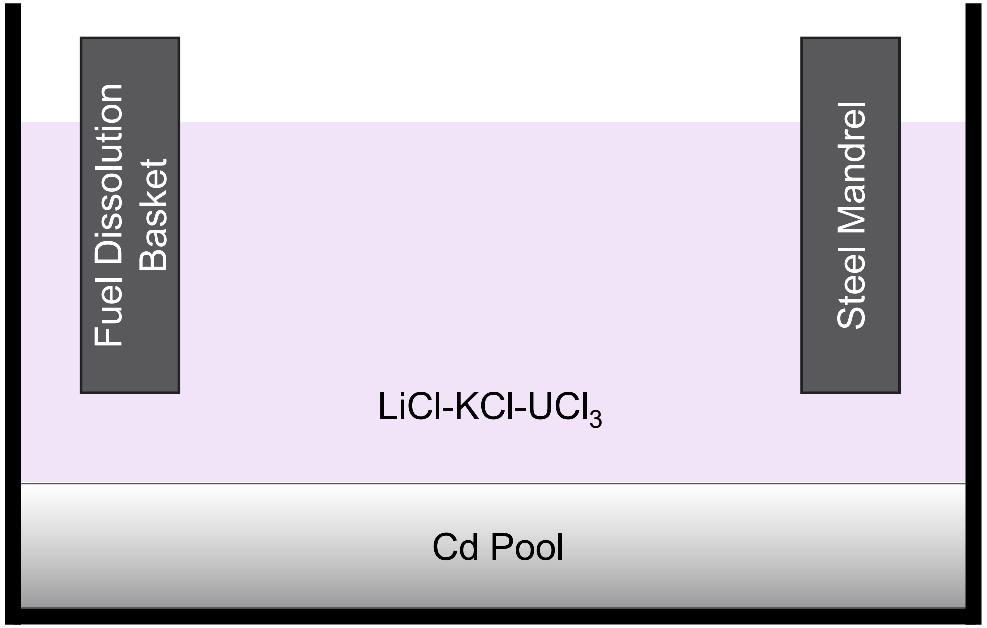
- Na cooled fast breeder (1964-1994)
  - Stainless steel clad, Na bonded metallic fuel
  - Facility power and testing of fast reactor fuels
- Integral Fast Reactor prototype intended to demonstrate reprocessing
  - Changed to a Pu disposition strategy with recovery of U
  - Challenging since fission yield produces a wide distribution of elements
- IFR reprocessing equipment repurposed to processing of EBR-II driver fuel

Mk-IV Electrorefiner



G. L. Fredrickson *et al.*, "History and status of spent fuel treatment at the INL Fuel Conditioning Facility," *Progress in Nuclear Energy*, vol. 143, p. 104037, Jan. 2022, doi: 10.1016/j.pnucene.2021.104037.

Mark IV Electrorefiner



Modes of Operation

Cell Configurations	Anode	
	FDBs	Cadmium Pool
Cathode		
Steel mandrel	Direct transport	Deposition
Cadmium pool	Anodic dissolution	Trivial

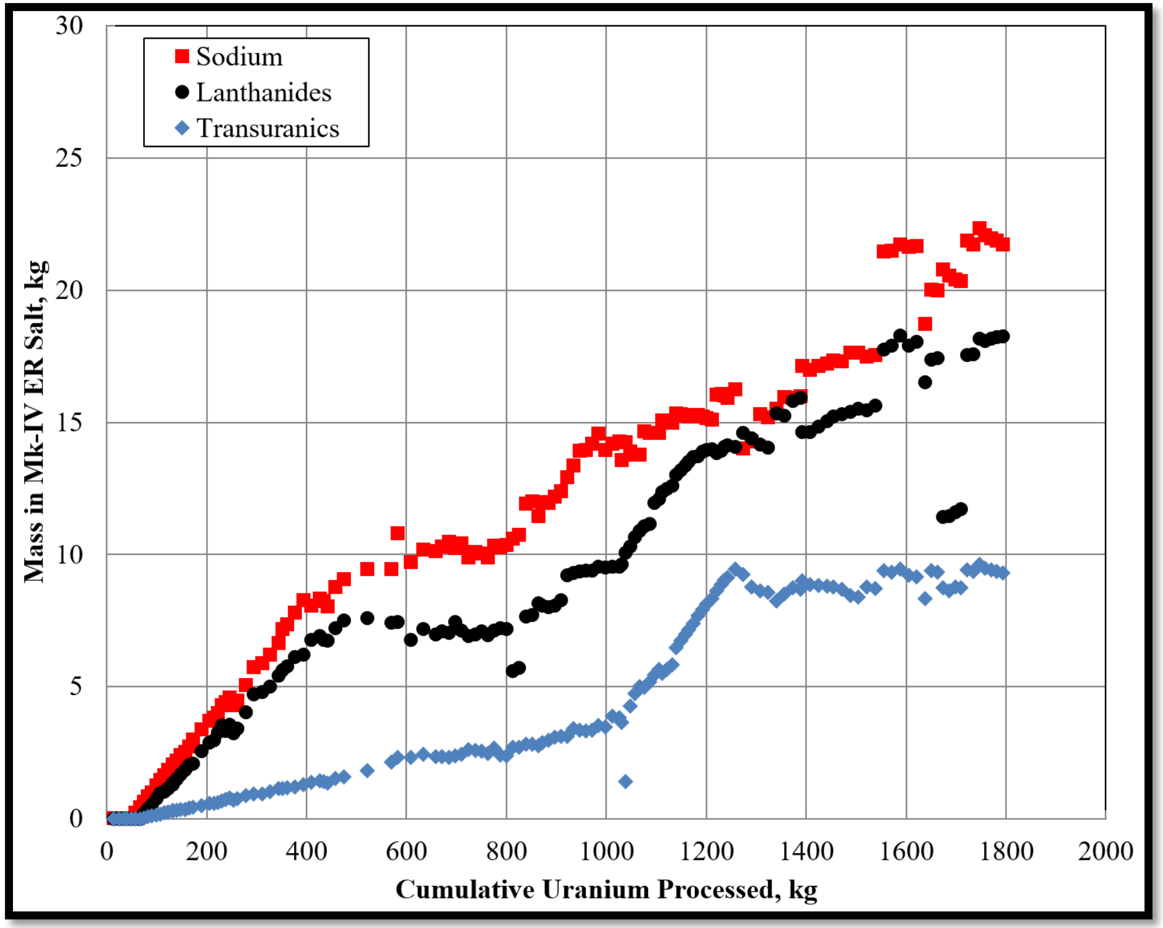
- Used fuel can be transported to the steel mandrel directly or indirectly
  - Cd as secondary electrode
  - Cd as intermediate electrode
- Complex distribution of species present within electrolyte and Cd pool
  - Significant material balance challenge

S. X. Li, "Experimental Observations on the Roles of the Cadmium Pool in the Mark-IV Electrorefiner," *Nuclear Technology*, vol. 162, no. 2, pp. 144–152, May 2008, doi: 10.13182/NT08-A3941.

Progressive accumulation of chlorides

- LiCl-KCl-UCl_3 electrolyte
- Oxidation of impure uranium and elements more electropositive
- Reduction of highly pure uranium
- Other elements remain in electrolyte
- 500°C max operating temperature
- Accumulation of NaCl steadily increases the melting point (801°C)

Species Accumulation in Electrolyte



Which Species Matter?

Compound	NaCl	UCl3	LiCl	NdCl3	PuCl3	CsCl	CeCl3	BaCl2	LaCl3	PrCl3	SmCl3	SrCl2	YCl3	RbCl	NpCl3	EuCl3	GdCl3
KCl	0.109	0.078	0.220	0.038	0.020	0.004	0.017	0.005	0.005	0.005	0.004	0.001	0.001	0.000	0.000	0.000	0.000
NaCl	0.000	0.040	0.083	0.023	0.014	0.004	0.012	0.004	0.004	0.004	0.003	0.001	0.001	0.000	0.000	0.000	0.000
UCl3	0.000	0.000	0.061	0.022	0.013	0.003	0.012	0.004	0.004	0.004	0.003	0.001	0.001	0.000	0.000	0.000	0.000
LiCl	0.000	0.000	0.000	0.032	0.017	0.004	0.015	0.004	0.005	0.004	0.003	0.001	0.001	0.000	0.000	0.000	0.000
NdCl3	0.000	0.000	0.000	0.000	0.009	0.003	0.009	0.003	0.003	0.003	0.003	0.001	0.001	0.000	0.000	0.000	0.000
PuCl3	0.000	0.000	0.000	0.000	0.000	0.002	0.006	0.003	0.003	0.003	0.002	0.001	0.001	0.000	0.000	0.000	0.000
CsCl	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.000
CeCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.003	0.002	0.002	0.001	0.001	0.000	0.000	0.000	0.000
BaCl2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.000
LaCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.000	0.001	0.000	0.000	0.000	0.000
PrCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.000
SmCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000
SrCl2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000									0.000
YCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000									0.000
RbCl	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000									0.000
NpCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000									0.000
EuCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000									0.000
GdCl3	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Negligible

Duplicates

$$ACl - BCl_a$$

$$F_{contrib} = x'(1 - x')[(1 - x') + ax'][x_A x_B]$$

$$x' = \frac{ax_B}{ax_B + x_A}$$

Contribution parameter calculated as the weighted average of binary Førland fractions → weighted asymmetric contributions

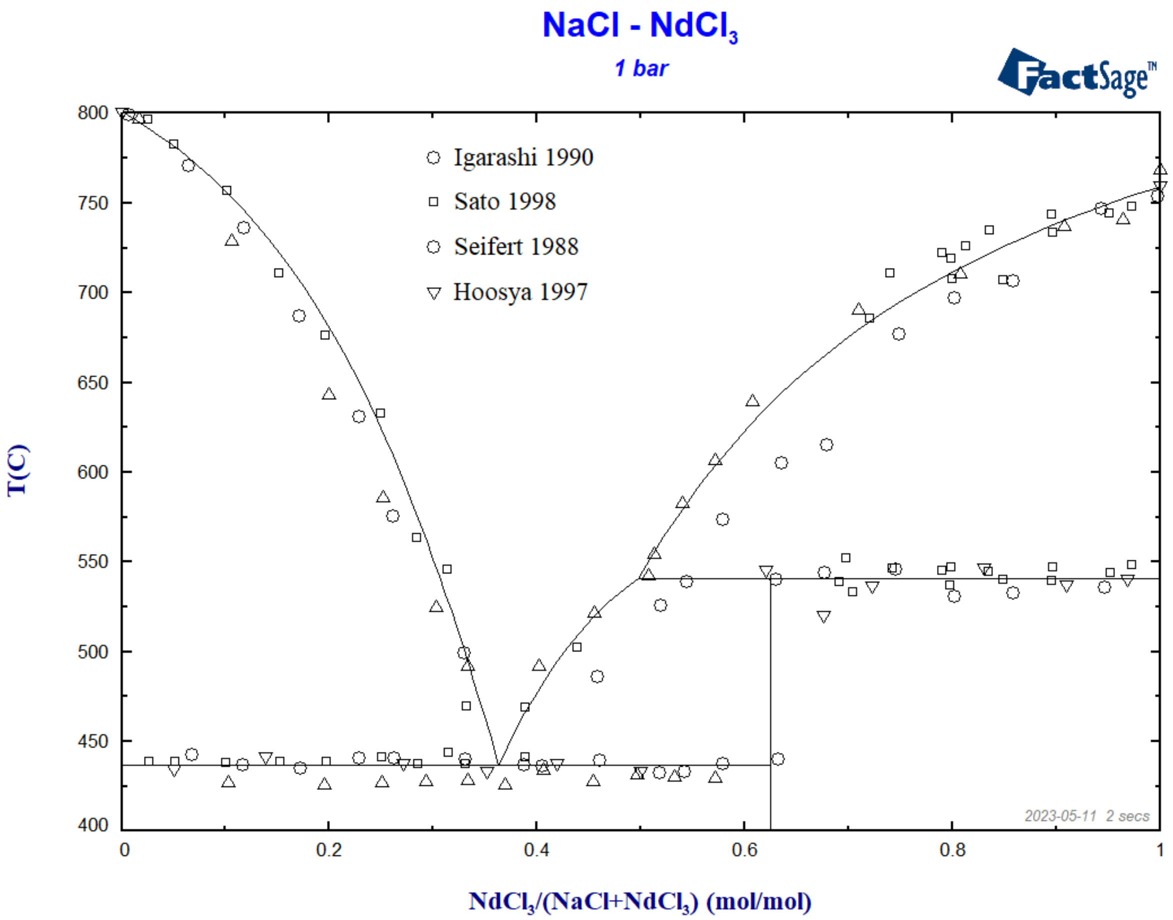
Thermochemical Modeling

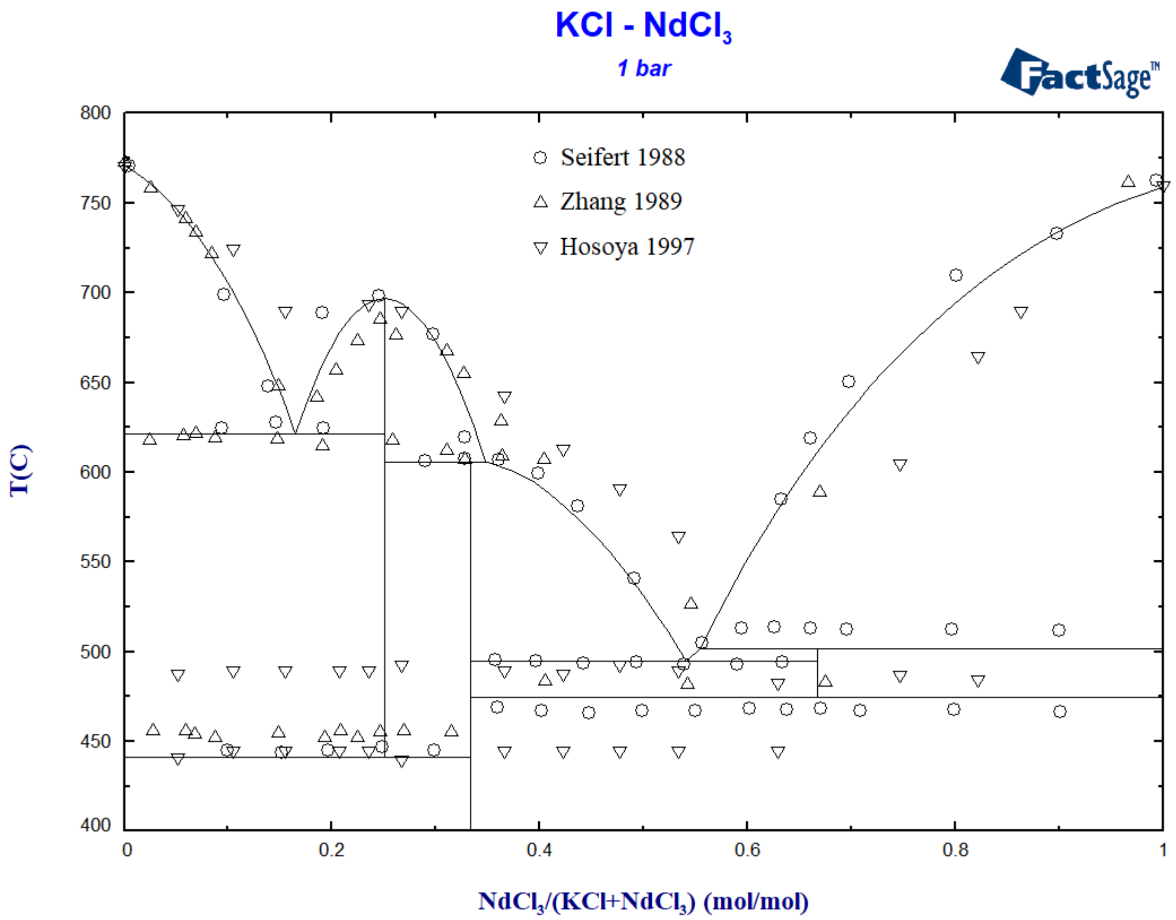
- Models based on Molten Salt Thermal Properties Database – Thermochemical (MSTDB-TC)
  - Modified quasi-chemical model in quadruplet approximation

$$(\boldsymbol{A} - \boldsymbol{X} - \boldsymbol{A}) + (\boldsymbol{B} - \boldsymbol{X} - \boldsymbol{B}) = \mathbf{2}(\boldsymbol{A} - \boldsymbol{X} - \boldsymbol{B}) \rightarrow \boldsymbol{\Delta}\mathbf{G}_{\mathbf{AB/X}}$$

- Model developer chooses parameterization of $\boldsymbol{\Delta}\mathbf{G}_{\mathbf{AB/X}}$=A+BT+CTlnT+D/T+…+
- Accounts for short-range ordering of non-ideal Gibbs energy contributions
- Order of importance: KCl, LiCl, NaCl, UCl_3, $NdCl_3$, $PuCl_3$ …
  - $NdCl_3$ systems not included in MSTDB-TC v2.0 and earlier
- Assessed systems: ACl-$NdCl_3$ (A=Li,Na,K,Cs)
  - Model parameterization constrained based on available experimental data
  - Optimized using experimental weights for phase equilibria, and enthalpy of mixing

Selected calculated phase diagrams



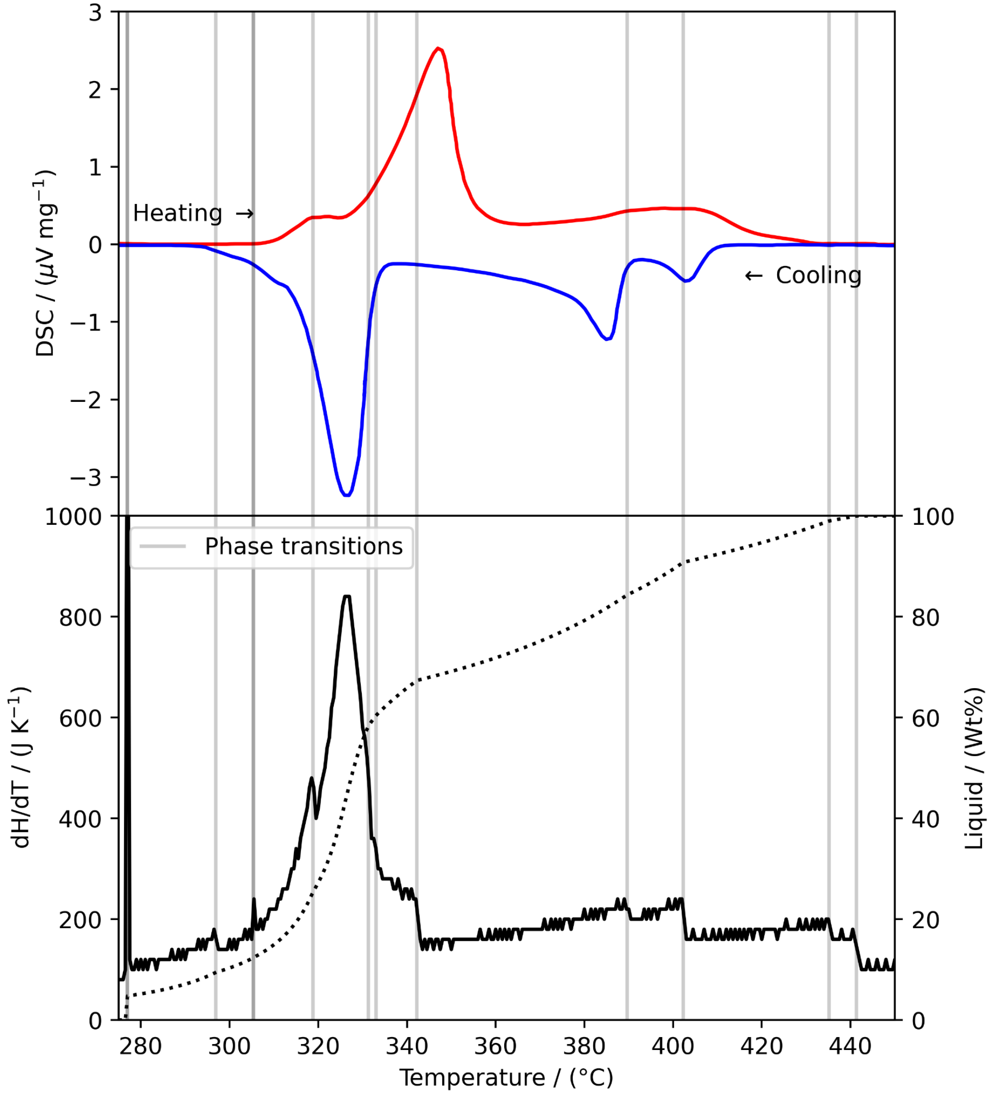


Fitting data includes phase equilibria, $\Delta_{mix}H$, and ΔH^{o}_{298}

$\Delta \mathrm{G}_{\mathrm{AB/X}}$=A+BT+CTlnT+D/T+…+ reduced to A+BT or less for each eutectic

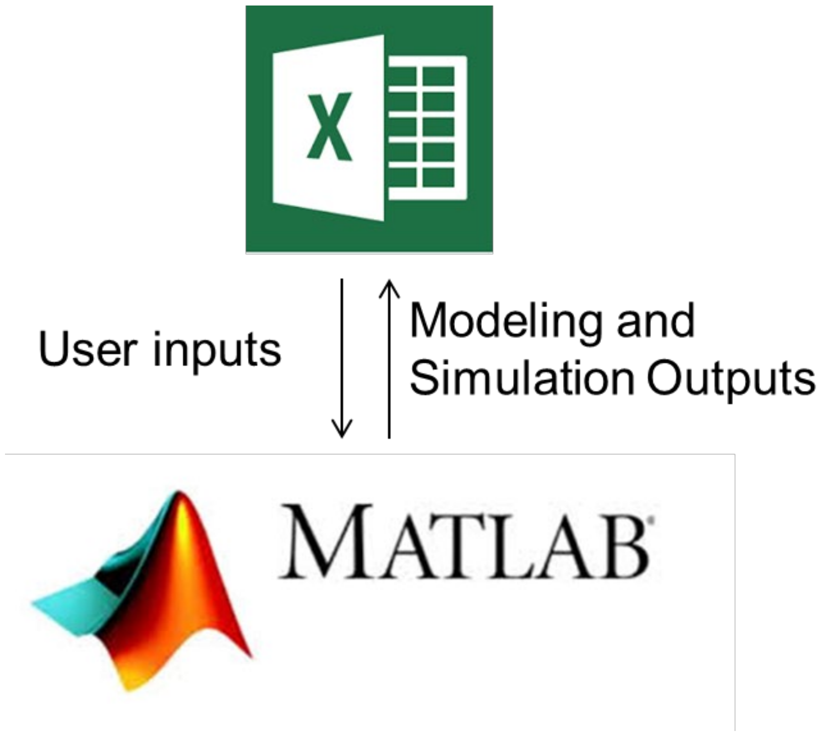
Thermal measurements of Mk-IV salt

- Differential Scanning Calorimetry heating and cooling at 5C/min
- MSTDB-TC v3.1 (pre-release)
  - Includes ACl-$NdCl_3$ models developed in this work
- Calculated equilibrium transitions and solution enthalpy
- DSC minus background compares well to calculated dH/dT
- Calculated transition temperatures appear to agree very well with thermal measurements.



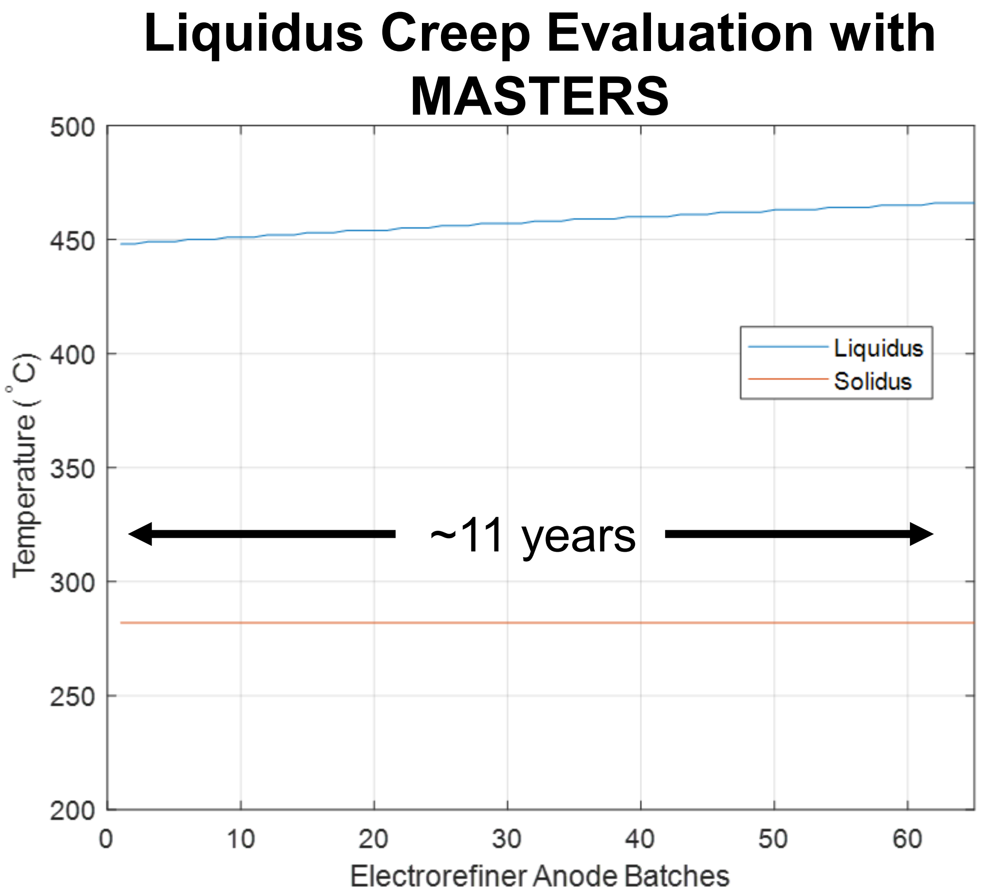
MASTERS (Modeling And Simulation Tool for Electrochemical Recycling Systems)

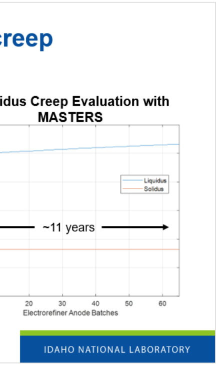
- MASTERS based on MatLab and Microsoft Excel
- Recent Python interface addition for Factsage/Chemapp
- Tracks over over 1000 isotopes
- Flexible code system to simulate various fuel processing scenarios



Strategies to minimize liquidus creep

- Dilute with LiCl-KCl
- Extract NaCl
- Extract TRU
- Extract Lanthanides
- ER operation in 2-phase region
- All options can be studied with MASTERS. A draft documenting selected strategy evaluation with MASTERS is underway





Conclusions

- MQMQA is a highly effective tool for evaluating many component salts
- Pseudo-binary models developed for the LiCl-$NdCl_3$, NaCl-$NdCl_3$, KCl-$NdCl_3$, CsCl-$NdCl_3$ salts
- Models contributed to MSTDB-TC
- Mk-IV ER operation may continue for several years without salt processing
- Missions beyond EBR-II driver fuel processing will require strategies for mitigating liquidus increase

Questions?

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