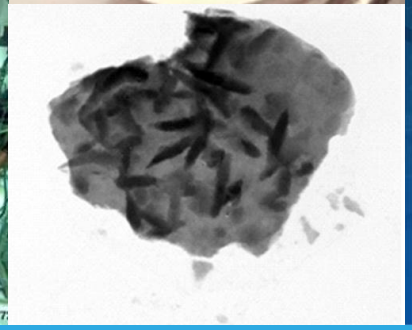

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Steven D. Herrmann

Principal Investigator
Idaho National Laboratory

Parametric Study of Used Nuclear Oxide Fuel Constituent Dissolution in Molten LiCl-KCl-UCl_3

INL/MIS-21-62631

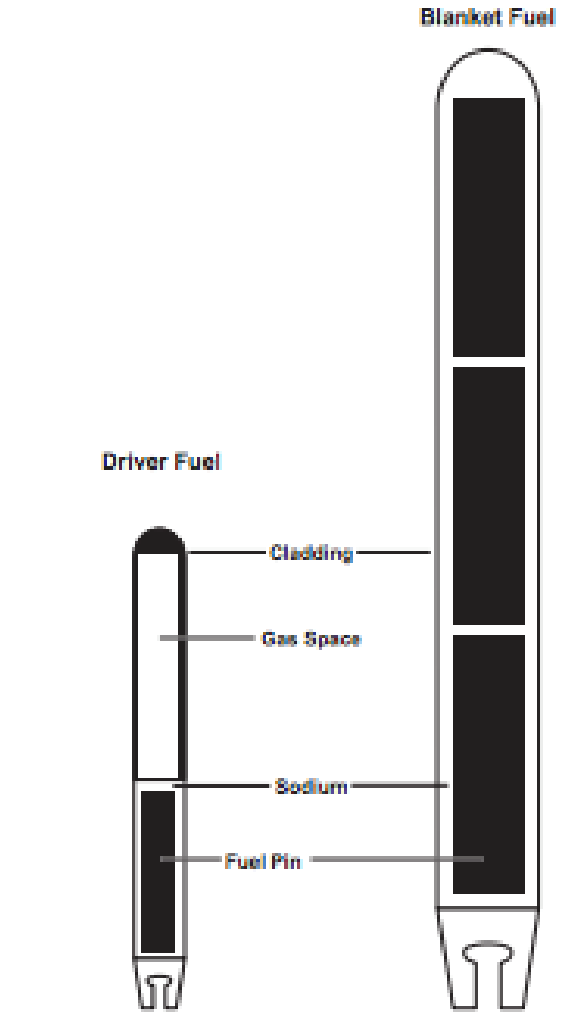
Idaho National Laboratory

Outline

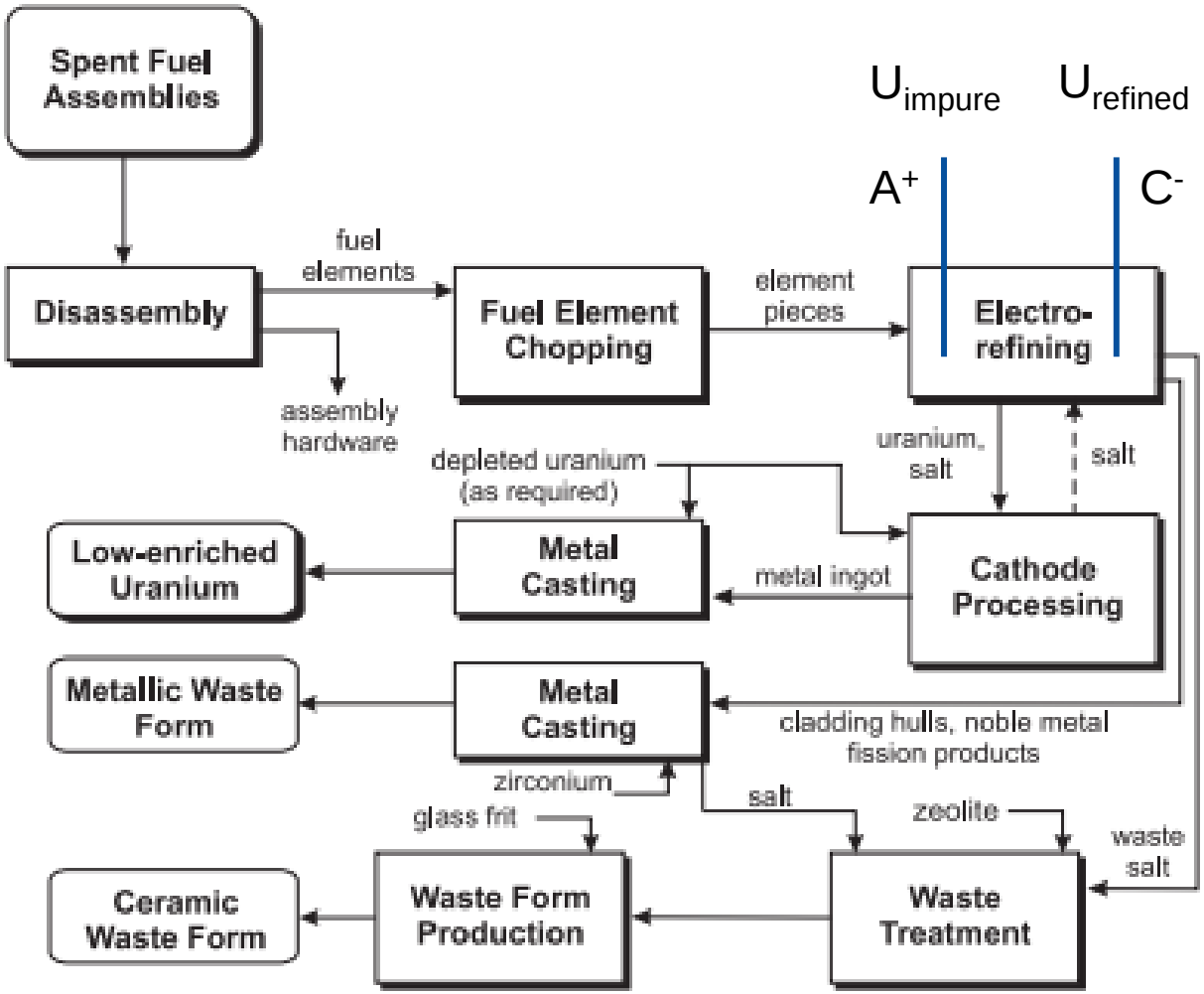
- Purpose – Discuss outcome of experimental study on used nuclear oxide fuel constituent dissolution in LiCl-KCl-UCl_3.
- Background
  - Electrometallurgical Treatment (EMT) process
  - Oxide Reduction
- Objectives and approach of three-part progressive study
  - Scoping study
  - Electrolytic dissolution study
  - Chemical-seeded dissolution study
- Test conditions, equipment, materials, results, observations, discussion, and conclusions of each study.
- Summary
- Future Work

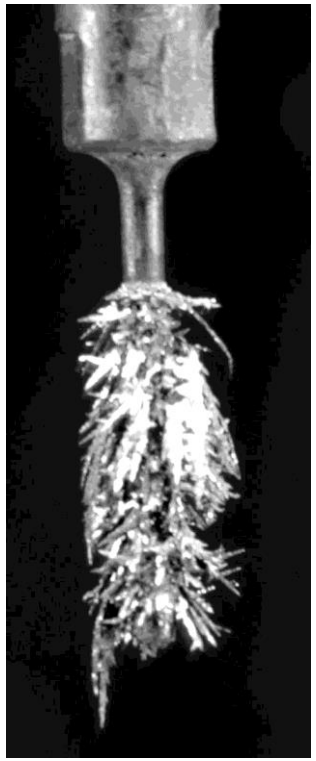
Background – Electrometallurgical Treatment (EMT) Process

- EMT is a proven process and well-suited for treating sodium-bonded used metallic fuels (e.g., EBR-II).
- Demonstrated in 1996-1999
  - Independent review by a National Research Council (NRC)
  - Selected by DOE for treatment of 26 metric ton (MT) of used fuel
- Continues to operate today for treatment of EBR-II driver and blanket fuel
- Uses electrorefining technology with a molten salt electrolyte of LiCl-KCl-UCl_3 at about 500°C



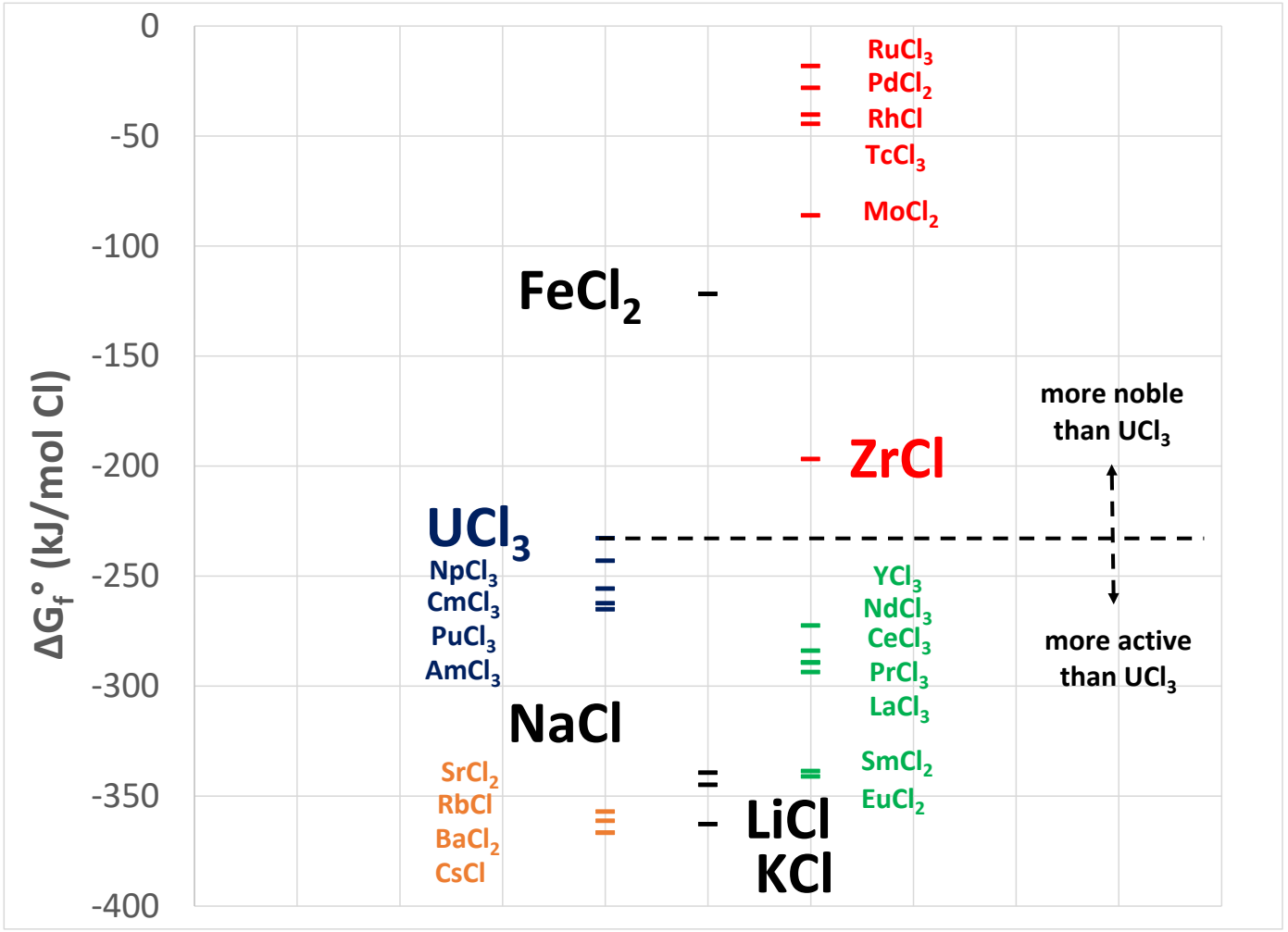
EMT Summary Flow Diagram





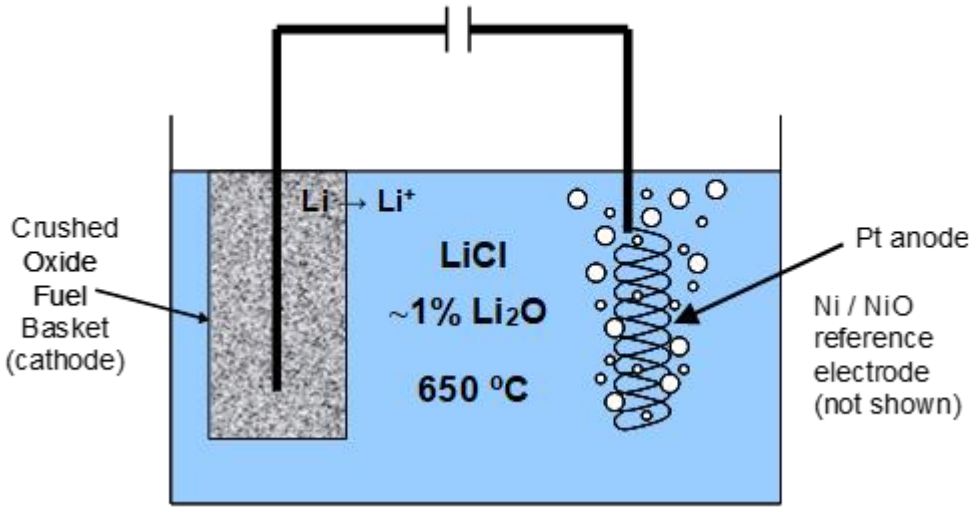
refined U deposits on cathode rod

Distribution of Fuel Constituents in EMT Process – Thermodynamic Basis



Extension of EMT to Used Nuclear Oxide Fuels

- Background of Oxide Reduction processes
  - Lithium-based metallothermic process to reduce uranium oxide to metal as a head-end step to electrorefining
    - $4\ Li + UO_2 \xrightarrow[650C]{LiCl} U + 2\ Li_2O \quad \Delta G_{Rx,650C} = -26\ kJ$
  - Electrolytic reduction process to convert UO_2 to U
    - Cathode: $UO_2 + 4e^- \rightarrow U + 2\ O^{2-}$
    - Anode: $\underline{2\ O^{2-} \rightarrow O_2(g) + 4\ e^-}$
    - Full Cell: $UO_2 \rightarrow U + O_2(g) \qquad E° = 2.40\ V$



Simplified electrochemical cell diagram for electrolytic reduction process

Electrolytic Reduction Process Performance

- Typical reduction performance with used oxide fuels
  - >98% reduction of uranium in PWR fuels
  - >87% uranium, >54% transuranium (TRU) in fast reactor MOX
  - Group 1 (Cs, Rb), group 2 (Ba, Sr), group 16 (Te), and group 17 (Iodine) partition and accumulate in LiCl-Li_2O electrolyte.
- Transfer of reduced fuel to a uranium electrorefiner invariably introduces some oxide species.
- Fate of fission products from reduced fuel in electrorefiner
  - Metals: Anodic dissolution or chemical reaction with UCl_3
    - $3/z\ M + UCl_3 \rightarrow 3/z\ MCl_z + U$; where M = active metal
  - Oxides: $M_xO_y + UCl_3 \rightarrow MCl_z + UO_2$ **(???)**
- Prior work* w/ anodic dissolution of partially reduced MOX fuel (29% U, 16% Pu, 2% lanthanide metals) in LiCl-KCl-UCl_3 at 500°C
  - Nearly all TRU and lanthanides dissolved into molten salt.

* S. D. Herrmann, et al., "Separation and Recovery of Uranium and Group Actinide Products from Irradiated Fast Reactor MOX Fuel vie Electrolytic Reduction and Electrorefining," *Separation Science and Technology*, **47**, 2044 (2012).

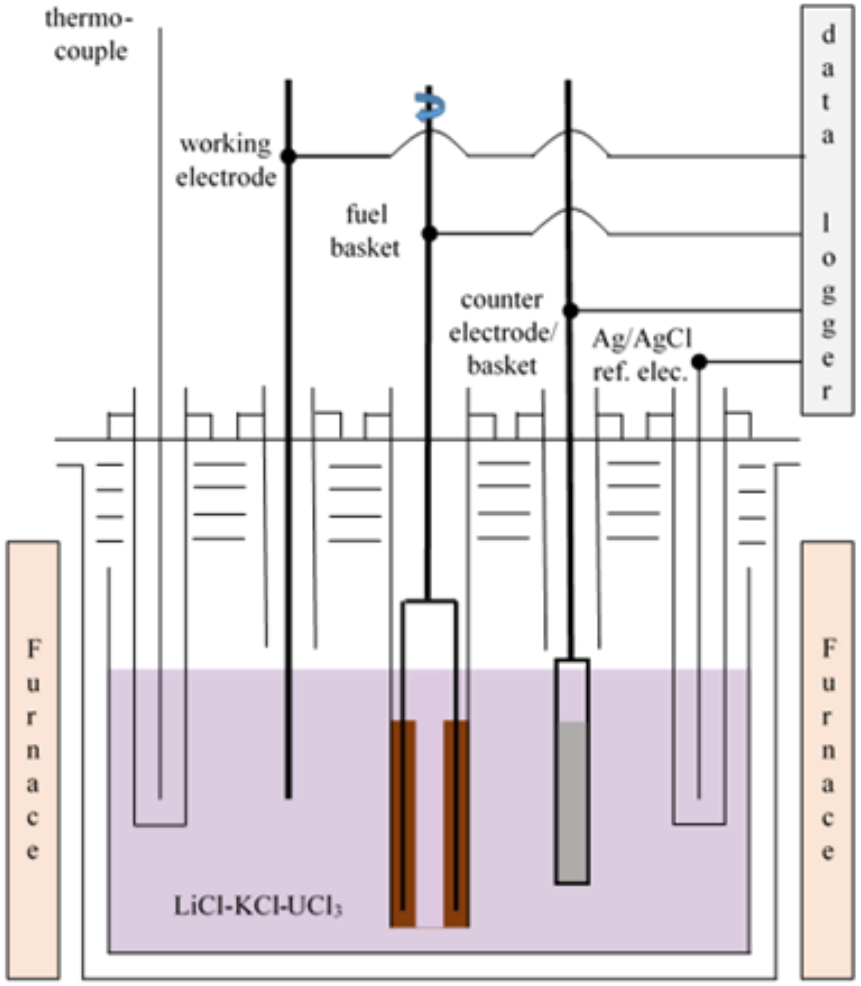
Objective and Approach of this Study

- Objective: Investigate parameters and reaction mechanisms associated with dissolution of used nuclear oxide fuel constituents in LiCl-KCl-UCl_3.
- Approach: Series of 3 progressive studies
  - Scoping study – compare performance with 3 different fuel types
    - Oxidized EBR-II driver fuel
    - Crushed PWR fuel (UO_2) from Belgium Reactor 3 (BR3)
    - Voloxidized fuel from BR3 ($UO_2 \rightarrow U_3O_8$)
  - Electrolytic dissolution study with preconditioned BR3 fuel
    - Create reducing conditions in fuel bed electrolytically
    - Additional effects of temperature and UCl_3 concentration
  - Chemical-seeded dissolution study with preconditioned BR3 fuel
    - Blend fuel with depleted uranium (DU) metal particulate
    - Additional effects of temperature

Summary of Test Conditions

run	[U] as UCl_3 in LiCl-KCl	Fuel Loading		DU metal mass	Temp.
	(wt%)	type	mass (g)	(g)	(°C)
1. Scoping Study					
1.1	9	Oxidized EBR-II fuel	24.7	50	500
1.2		Crushed BR3 fuel	28.3		
1.3		Voloxidized BR3 fuel	28.7		
2. Electrolytic Dissolution Study					
2.1	6, 19	Pre-conditioned BR3 fuel	30.6	59.9	500, 650
3. Chemical-Seeded Dissolution Study					
3.1.	19	Pre-conditioned BR3 fuel + uranium metal particulate	24.4 oxide, 16.5 metal	Seeded in each basket, then deposited on Ta rod	650, 725, 800
3.2			20.2 oxide, 14.3 metal		
3.3			13.1 oxide, +16.5 metal		

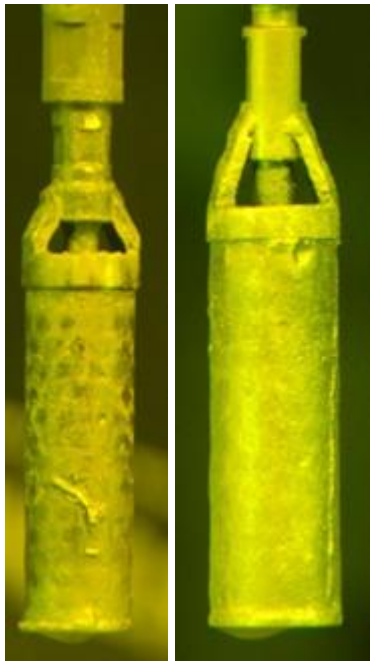
Equipment



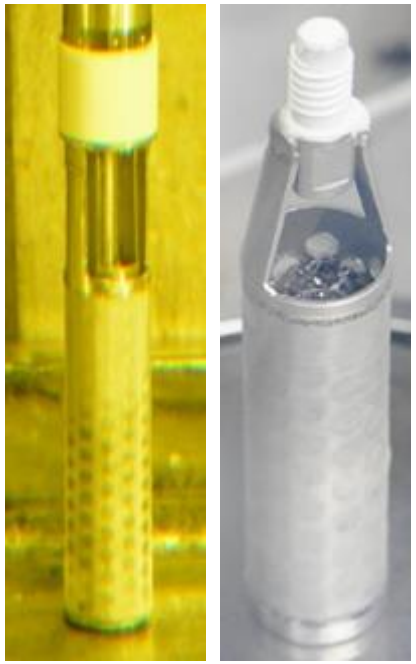
Simplified electrochemical cell configuration for series of dissolution studies

Hot Fuel Dissolution Apparatus (HFDA) in Hot Fuel Examination Facility (HFEF)

Components and Materials



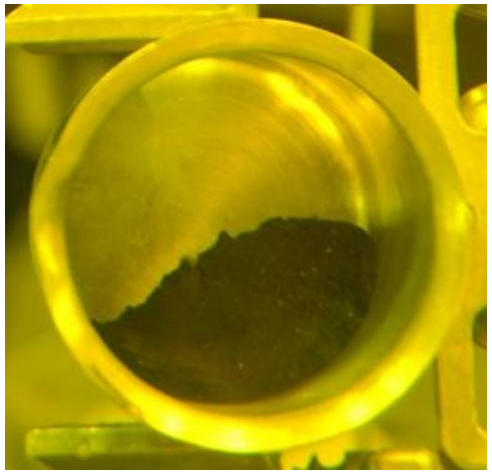
Scoping study baskets – oxide fuel (left), DU metal (right)

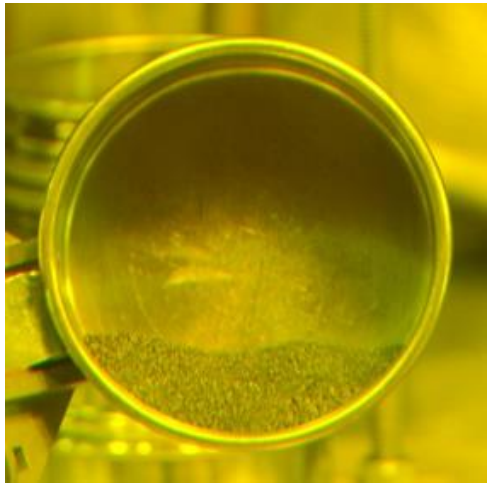


Electrolytic dissolution baskets – oxide fuel (left), DU metal (right)

Chemical-seeded dissolution basket and stirrer (center and right), Ta rod (left)

Oxidized EBR-II fuel (top); crushed BR3 fuel (bottom)



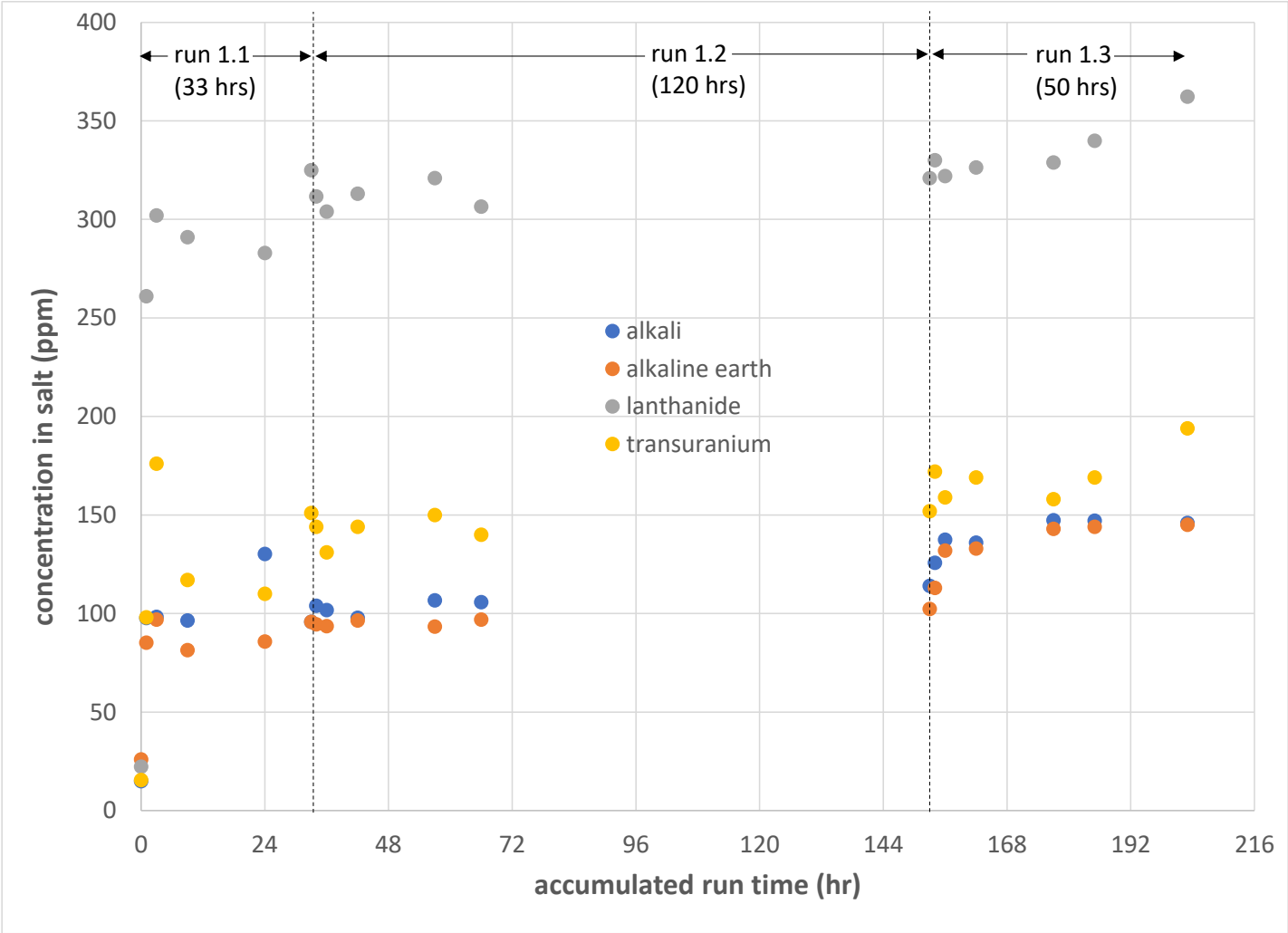


Calculations

- Chemical equilibrium model (HSC, Gibbs energy minimization model) was run to identify reaction mechanisms.
  - Assumptions: Unit activities and ideal mixing; lanthanide and transuranium (TRU) oxides were limited to trivalent form due to reducing conditions in salt system, i.e., no tetravalent forms.

Eq.	Reaction Mechanism	ΔG_{Rx} (kJ)			
		500C	650C	725C	800C
1	$Cs_2O + UCl_3 \rightarrow UOCl + 2\ CsCl$	-504	-501	-503	-505
2	$BaO + UCl_3 \rightarrow UOCl + BaCl_2$	-266	-265	-264	-264
3	$Nd_2O_3 + 3\ UCl_3 \rightarrow 3\ UOCl + 2\ NdCl_3$	-159	-156	-154	-157
4	$Pu_2O_3 + 3\ UCl_3 \rightarrow 3\ UOCl + 2\ PuCl_3$	-142	-139	-138	-141

Consolidated Results of Salt Sample Analyses (Gamma Spectroscopy, ICP-OES, and ICP-MS)



Sample Analysis Results (cont.)

- Extent of fuel constituent dissolution in LiCl-KCl-UCl_3 at 500°C

Constituent	Run 1.1	Run 1.2	Run 1.3
Alkali	99.5%	21.6%	93.7%
Alkaline earth	93.5%	24.0%	59.3%
Lanthanide	93.9%	14.0%	13.9%
Transuranium	91.5%	19.4%	12.4%

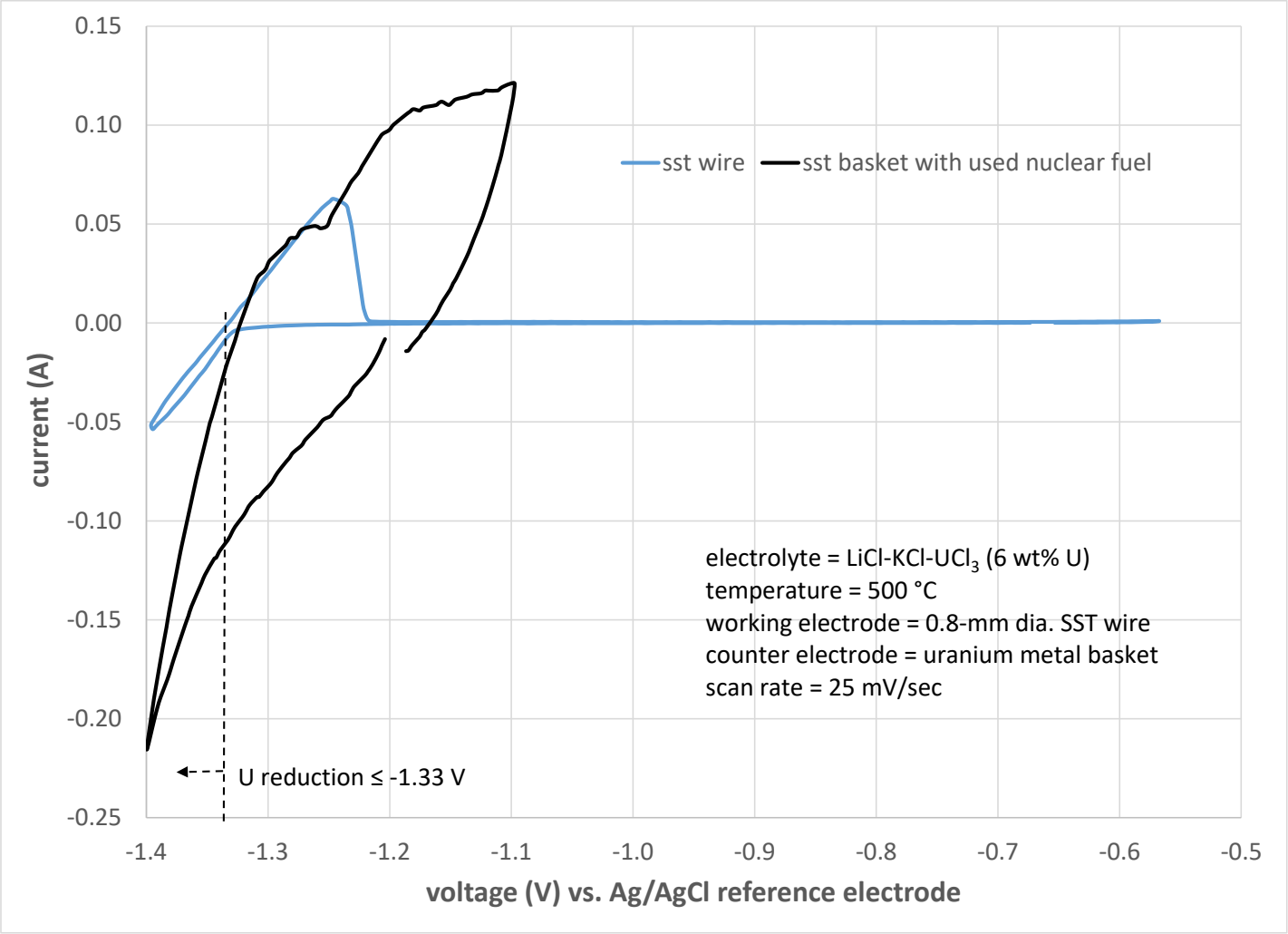
- Uranium-235 concentrations in salt and fuel phases

iso%	Run 1.1		Run 1.2		Run 1.3	
	pre-test	post-test	pre-test	post-test	pre-test	post-test
Fuel	57.4	30.2	3.39	4.42	4.93	5.50
Salt	0.356	7.42	--	7.06	--	9.45

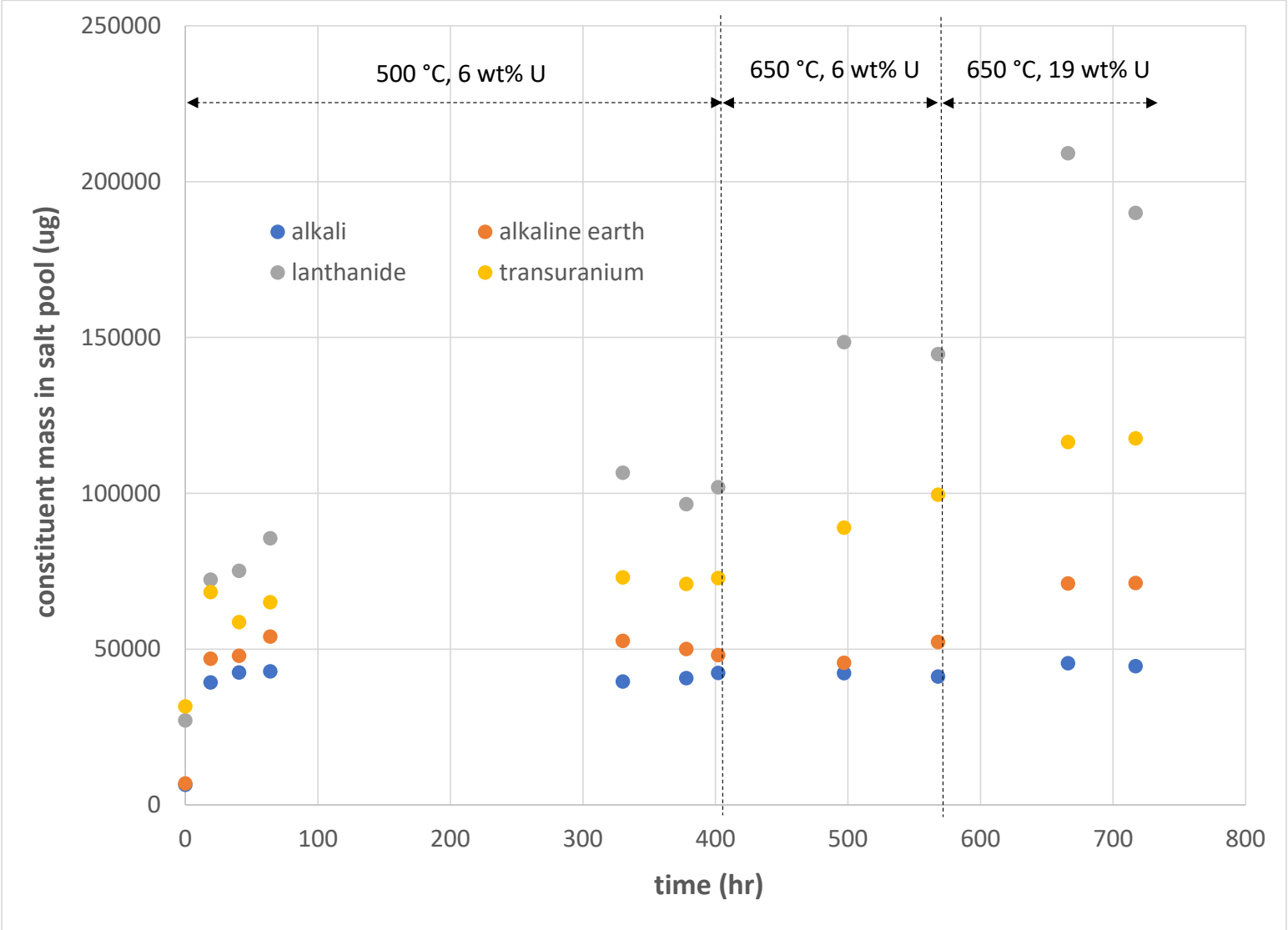
Scoping Study – Discussion

- Observed stark contrast in extent of fuel constituent dissolution between oxidized EBR-II fuel and BR3 fuels
- Observed appreciable difference between BR3 fuel forms
- Observations prompted subsequent metals analysis of EBR-II fuel, revealing a 30.2% uranium metal fraction – similar to prior work with MOX fuel dissolution (at 29% uranium metal fraction).
- Chemical equilibrium modeling for possible reaction mechanisms
  - $UO_2 + UCl_3 \rightarrow UOCl + UOCl_2$ $\quad \Delta G_{Rx,500C} = +45.1$ kJ
  - $3\ UO_2 + 2\ UCl_3 + U \rightarrow 6\ UOCl$ $\quad \Delta G_{Rx,500C} = -26.2$ kJ
  - Former is not thermodynamically spontaneous.
  - Latter is thermodynamically favored, creating a system in which U in the salt phase (UCl_3) has the same valency as U in a solid oxychloride phase (UOCl).
  - UOCl stability questionable; reaction reverses >1190°C.
- Conclusions: Reduced U in fuel matrix and preconditioned BR3 fuel promote fuel constituent dissolution.

Electrolytic Dissolution Study – Cyclic Voltammetry



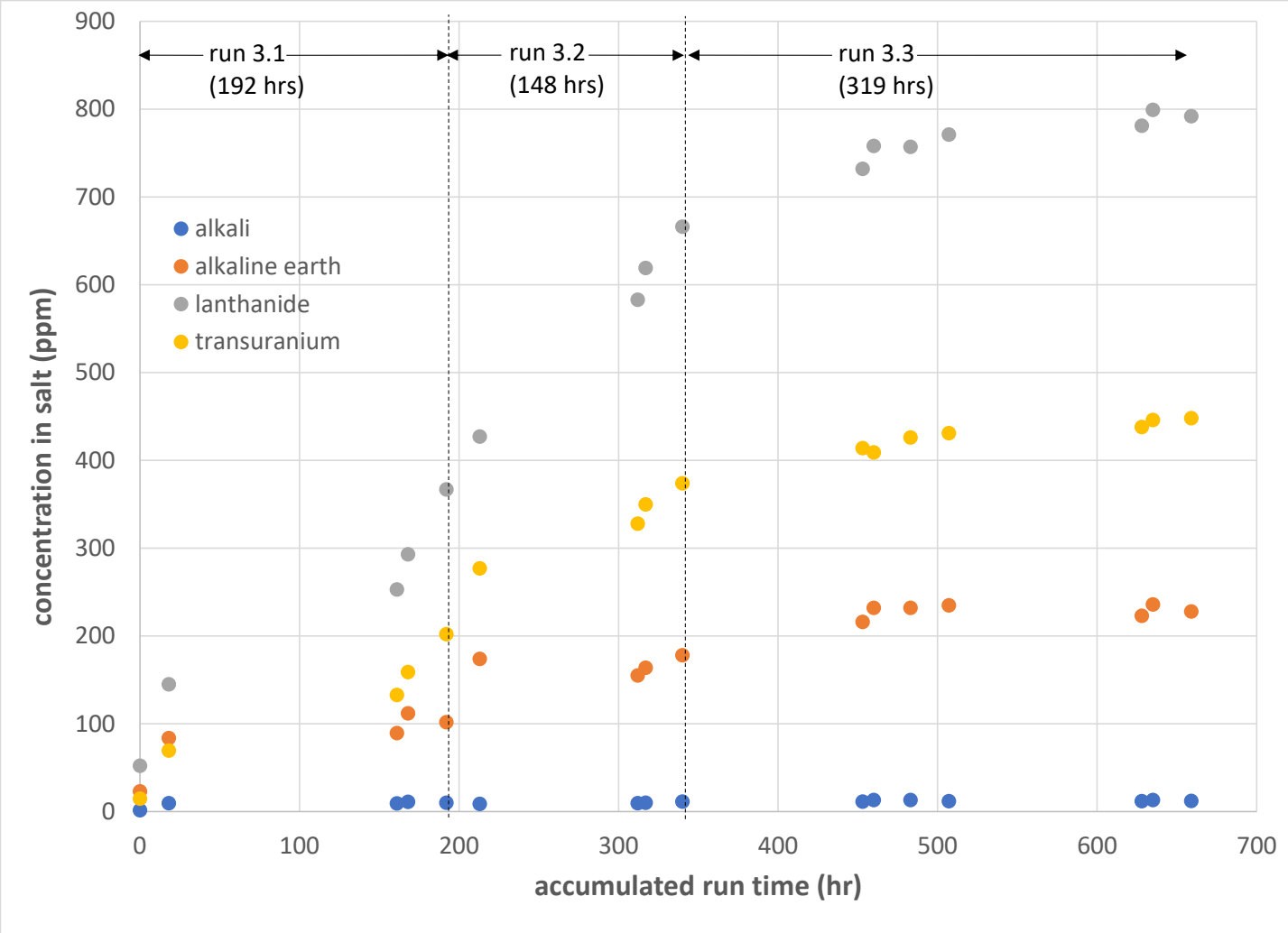
Consolidated Salt Sample Analysis Results



Fuel Sample Analysis Results and Discussion

- Extent of fuel constituent dissolution in molten salt
  - Alkali = 99.6%
  - Alkaline earth = 82.6%
  - Lanthanide = 66.2%
  - Transuranium = 62.6%
- Discussion and conclusions
  - Extents of dissolution trended with thermodynamic spontaneity.
  - Higher system temperature and uranium fraction in salt phase promoted alkaline earth, lanthanide, and transuranium constituent dissolution.
  - Run time was substantially longer than in the scoping study, due to operational limitations and low imposed currents.

Chemical-Seeded Dissolution Study – Consolidated Salt Sample Analysis Results



Chemical-Seeded Dissolution Study – Discussion

- Extent of fuel constituent dissolution in LiCl-KCl-UCl_3

	Run 3.1	Run 3.2	Run 3.3
Alkali	99+%	99+%	>92%
Alkaline earth	97.7%	97.6%	97.7%
Lanthanide	89.8%	92.9%	93.0%
Transuranium	86.2%	90.4%	90.4%

- Uranium-235 concentrations in salt and fuel phases

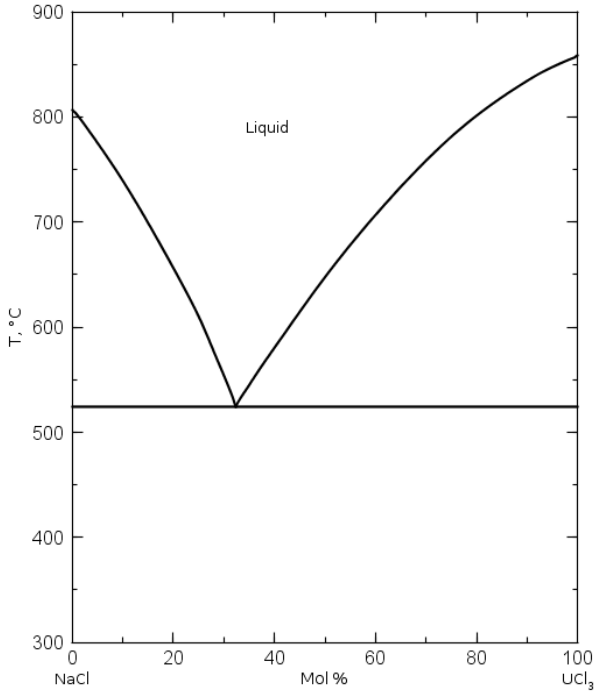
iso%	Run 3.1		Run 3.2		Run 3.3	
	pre-test	post-test	pre-test	post-test	pre-test	post-test
Fuel	3.55	1.11	3.55	1.09	3.55	1.26
Salt	0.336	0.543	--	0.723	--	0.760

Conclusions

- Collectively, the series of progressive studies identified increased rates and extents of used oxide fuel constituent dissolution in LiCl-KCl-UCl_3 by:
  - Imposing a uranium metal fraction of at least 25% in an oxide fuel matrix ($3\ UO_2 + 2\ UCl_3 + U \rightarrow 6\ UOCl$);
  - Preconditioning an oxide fuel via voloxidation and pre-heating to 1200°C;
  - Increasing system temperature from 500 to 800°C; and
  - Increasing the uranium fraction in the salt phase from 6 to 19 wt%.
- Application of the above preferred parameters yielded extents of alkali, alkaline earth, lanthanide, and transuranium constituent dissolution above 90%.
- Patent was issued for this dissolution technique.
  - US 8,734,738 B1

Future Work

- Repeat dissolution experiments in FY21 with three successive runs.
  - NaCl-UCl_3 (19 wt% U) electrolyte
  - 800°C
  - Run 1 – Preconditioned BR3 fuel + sodium metal (chemical-seeded dissolution)
  - Run 2 – Preconditioned BR3 fuel + DU metal particulate (chemical-seeded dissolution)
  - Run 3 – Preconditioned BR3 fuel (electrolytic dissolution)
- Fuel and salt sample analysis results by Oct. 2021



NaCl-UCl_3 phase diagram (above); chemical-seeded basket/stirrer and Ta cathode rod (right)

Thank you for your attention!