U.S. DEPARTMENT OF ENERGY

NTRD Nuclear Technology Research & Development

Future Research Directions
DOE-NE Molten Salt Chemistry Workshop
April 10-12, 2017

2017 ORNL Molten Salt Reactor Workshop
Oak Ridge National Laboratory Conference Center, Oak Ridge, TN
October 3-4, 2017

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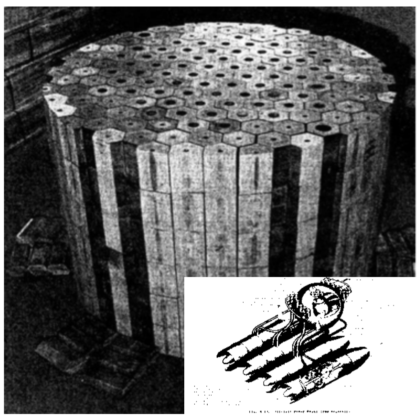
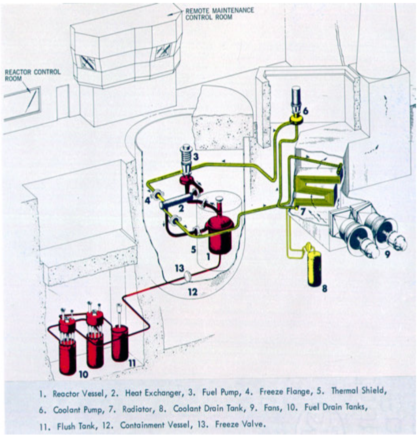
Background

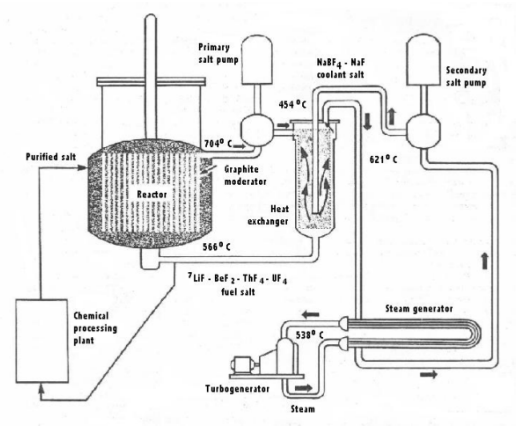
- Much of our current knowledge on molten salt reactors is based on research from ORNL (1950-1970's)
  - Aircraft Reactor Experiment (NaF-ZrF_4-UF_4)
  - Molten Salt Reactor Experiment (^7LiF-BeF_2-ZrF_4-UF_4)



(a) High-temperature thermal propulsion short duration engine (Aircraft Reactor Experiment)



(b) Extended multi-functional test reactor (Molten Salt Reactor Experiment)



(c) Thermal breeder reactor design (Molten Salt Breeder Reactor)

- New concepts from an industry-led MSR Technology Working Group (TWG) requires additional knowledge to support development

Molten Salt Reactor TWG →

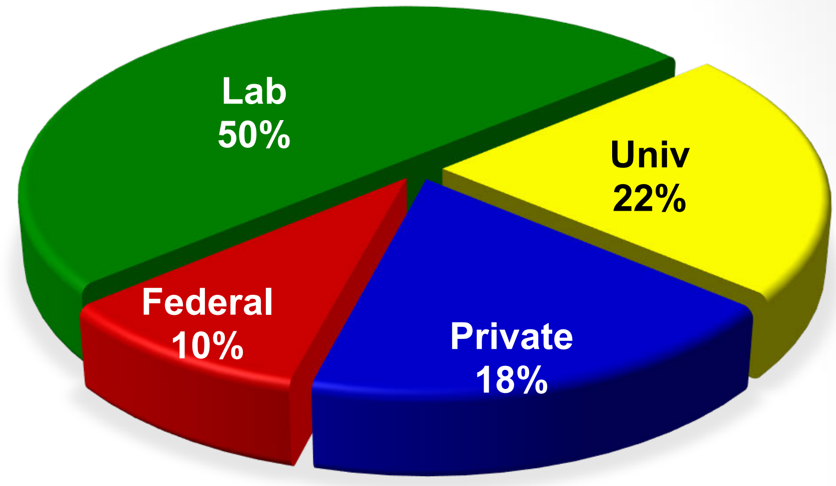
ONE	TWO	THREE	FOUR	FIVE	SIX
TerraPower	**Thorcon**	**Terrestrial Energy**	**Flibe Energy**	**Transatomic Power**	**Elysium Industries**
Fast Breeder Liquid Fuel Salt Cooled Uranium (Could use Th)	Thermal Burner Liquid Fuel Salt Cooled Thorium	Thermal Burner Liquid Fuel Salt Cooled Uranium (Could use Th)	Thermal Breeder Liquid Fuel Salt Cooled Thorium	Hybrid Burner Liquid Fuel Salt Cooled Uranium	Fast Breeder Liquid Fuel Salt Cooled Uranium

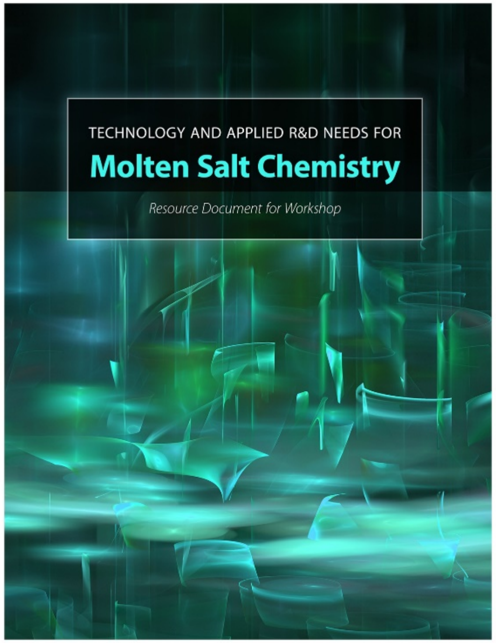
R+D

From Nick V. Smith, MSR TWG Perspective,
DOE-NE Molten Salt Chemistry Workshop, Oak Ridge, April 10-12, 2017

Workshop Attendance

- Workshop goal was to engage broad scientific communities to advance the knowledge and technology base of molten salt chemistry
- Invited attendees: 72
  - National Labs: 7
  - Universities: 13
  - Private: 11
- Factual documents prepared before the workshop which defined where we are and where we need to be





Workshop Attendees

Workshop Goal

- To identify science-based, technology-driven, innovative research opportunities to transform the performance, efficiency, and economic competitiveness of molten salt reactors while reducing technical risk
- Breakout Panels
  - Physical Chemistry and Salt Properties
  - Analytical Chemistry
  - Molten Salt Fission Product Chemistry and Radiolysis
  - Material Compatibility
  - Computational Chemistry and Materials Sciences

Workshop Guidelines

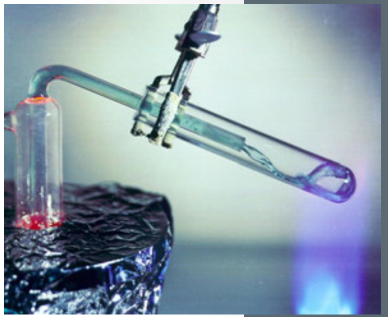
- Panel discussion focused on:
  - Defining R&D critical to breaking through today's technology bottlenecks and make a transformational technological advance in the field
  - Focus on use-inspired basic and applied research to make revolutionary breakthroughs in 5-10+ years
  - Providing inspiration and vision to the research community to address the challenges in molten salt chemistry
- Panel output identified
  - Future Research Directions that might accelerate MSR technology development and deployment
  - Opportunities to use recent advances in characterization tools (e.g. x-ray and neutron scattering) and computational modeling to advance technology development

Workshop Output: Future Research Directions

- Panels identified *fourteen* research directions that were combined to formulate six Future Research Directions*
  1. Understanding, Predicting and Optimizing the Physical Properties of Molten Salts
  2. Understanding the Structure, Dynamics, and Chemical Properties of Molten Salts
  3. Understanding Fission and Activation Product Chemistry and Radiation Chemistry
  4. Understanding Materials Compatibility and Interfacial Phenomena
  5. Guiding Next Generation Materials for Molten Salt Reactors
  6. Creating a Virtual Reactor Simulation

*Disclaimer – these are science based, technology driven research needs which may or may not be a priority of the sponsor

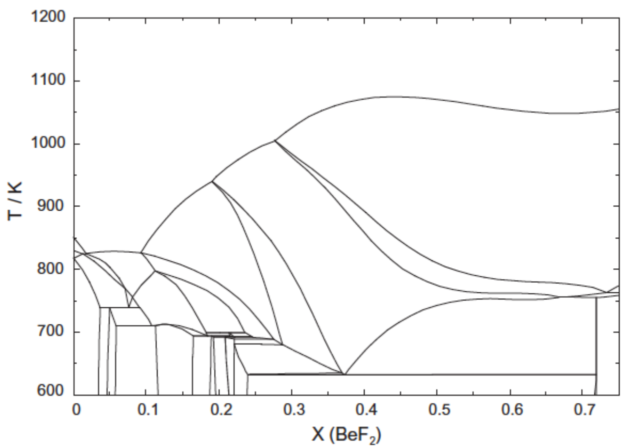
1. Understanding, Predicting and Optimizing the Physical Properties of Molten Salts



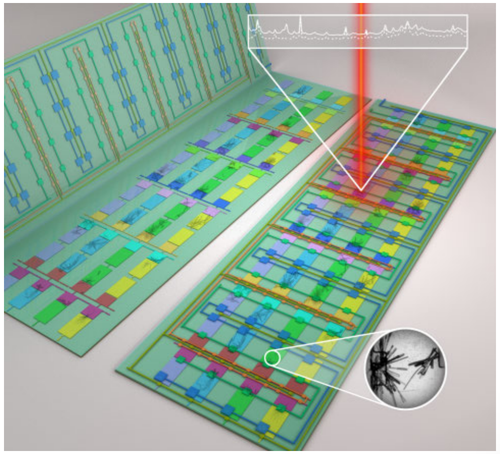
- Preparation of high purity salt
  - Develop validated purification procedures for removal of oxides, sulfides, metals and water and publish results in open literature
  - Establish quality assurance hierarchy for molten salt preparation and characterization
  - Develop a single source of pedigree salt as an analytical standard for the community
  - Develop a series of best practices for the community for handling and characterization of molten salts
- Define phase diagrams
  - Assess prior studies and identify missing data, compositions, and gaps in thermodynamic data (and accuracy) and generate databases

1. Understanding, Predicting and Optimizing the Physical Properties of Molten Salts

- Measure physical properties of individual salts and mixtures including melting point, density, viscosity, heat capacity, thermal conductivity, vapor pressure, fission product and gas solubility, etc.
- High throughput methods are needed that can be miniaturized and are able to operate in an glovebox could greatly accelerate property measurement



(a) Calculated LiF-BeF_2 pseudo-binary phase diagram with fixed concentration of UF_4 (2.55 mol%) and ThF_4 (19.95 mol%).



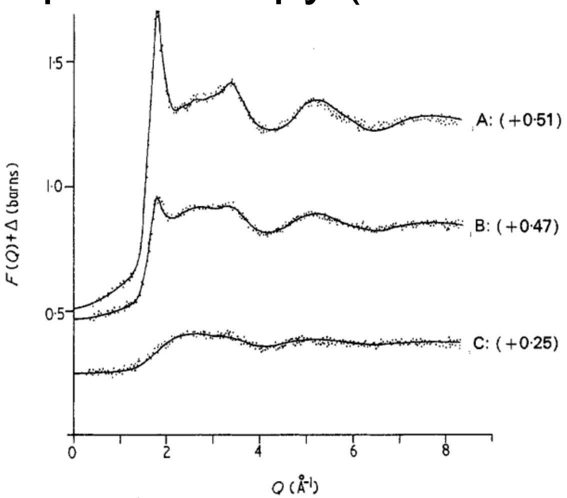
(b) Solid form screening of candidate pharmaceuticals. http://www.scs.illinois.edu/kenis/research.html

1. Understanding, Predicting and Optimizing the Physical Properties of Molten Salts

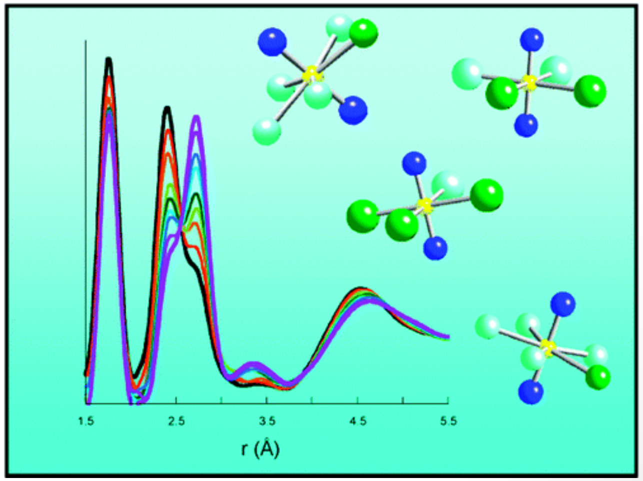
- Use databases and computational methods to accelerate analysis of thermodynamic data and phase diagrams and extrapolate to more complex and difficult to measure systems
  - Validate computational calculations (density functional theory and ab inito molecular dynamics) with experimental data
  - Develop thermodynamics models for predictive insights beyond conditions that can be measured experimentally
  - Develop tools to query databases and visualize information
- Goal is to design molten salts from a combination of simulations and experimental results with appropriate chemical and physical properties that will provide optimal operations of a MSR

2. Understanding the Structure, Dynamics, and Chemical Properties of Molten Salts

- Need to understand how the atomic scale structure and dynamics impact macroscale chemical and physical properties
  - Provide foundational input for computational modeling
    - What is the atomic-scale structure of the molten salt?
    - How are ions (U^{3+}, Th^{4+}, fission products) solvated in molten salts?
  - Take advantage of the advances in x-ray and neutron scattering (x-ray adsorption spectroscopy, pair distribution function) and other spectroscopy (Raman and solid-state NMR)



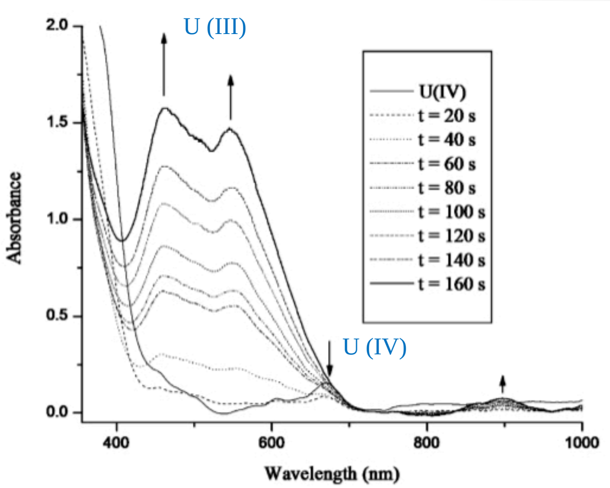
Total structure factor, F(Q), data for liquid $Na^{35}Cl$ (curve A), NaCl (Curve B), and $Na^{37}Cl$ (Curve C) at 875 °C. *J. Phys. C: Solid State Phys.* **1975,** *8(21),* 3483



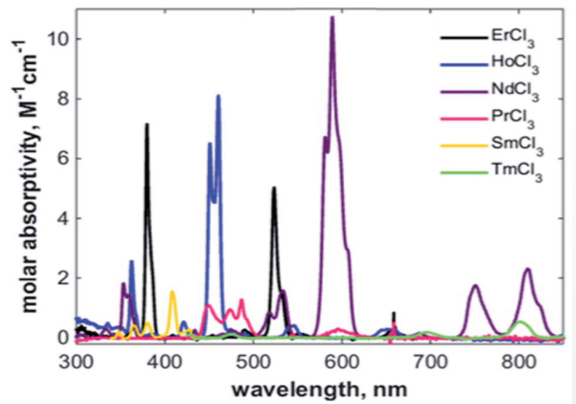
Pair distribution function from x-ray scattering on a series of UO_2^{2+} solution as a function of Cl^- concentration reveal Cl replaces inner-sphere water. *J. Phys. Chem. A* **2011**, *115*, 4959

2. Understanding the Structure, Dynamics, and Chemical Properties of Molten Salts

- Real-time spectroscopic and electrochemical methods are needed for monitoring key chemical species in solution allowing for optimization of reactor performance and lifetime
  - Need to maintain a reducing environment in the reactor to minimize corrosion
  - Optical basicity scale is needed for molten salts (to determine corrosivity and solubility of actinides)



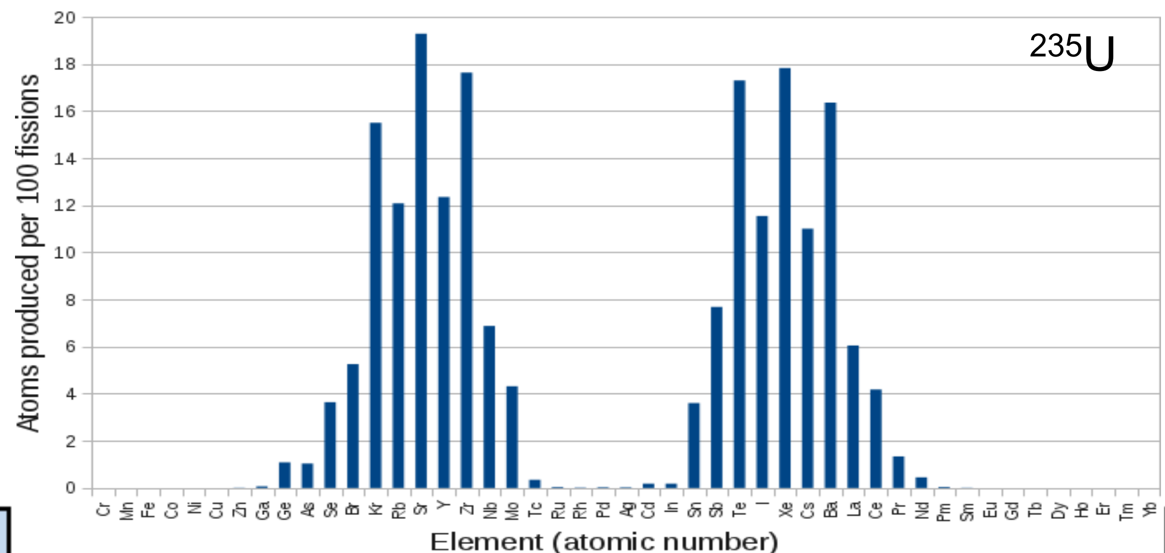
UV-vis absorption spectra following the reduction of U(IV) to U(III) within an alkali chloride molten salt. *Inorg. Chem.* **2008**, *47*, 7474

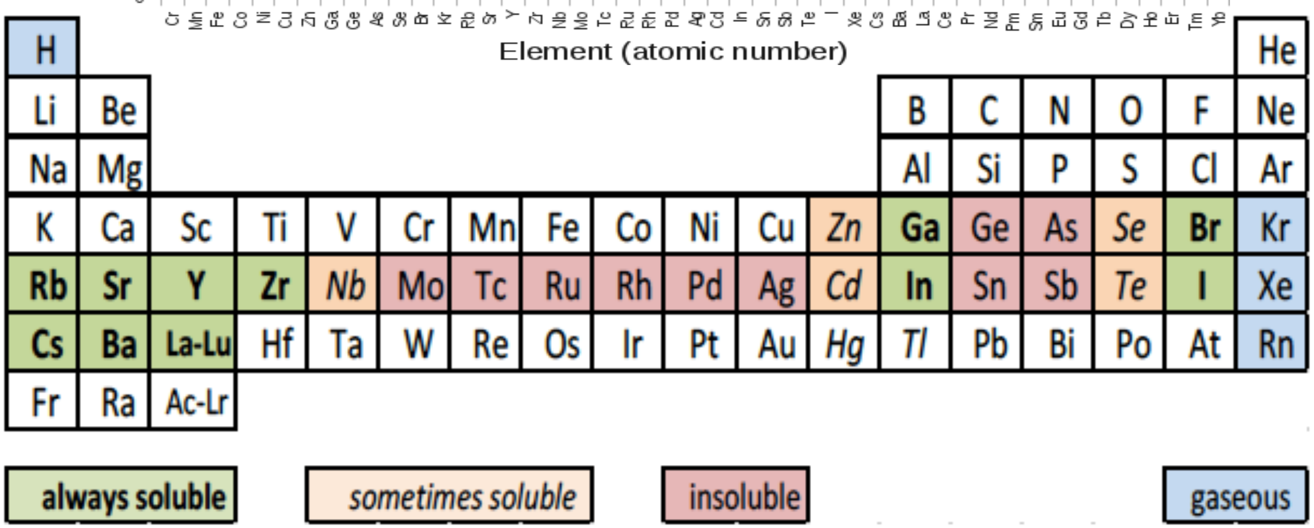


UV-vis absorbance spectra of lanthanides within alkali chloride molten salt. *Anal. Methods–UK* **2016**, *8*, 7731.

3. Understanding Fission and Activation Product Chemistry and Radiation Chemistry

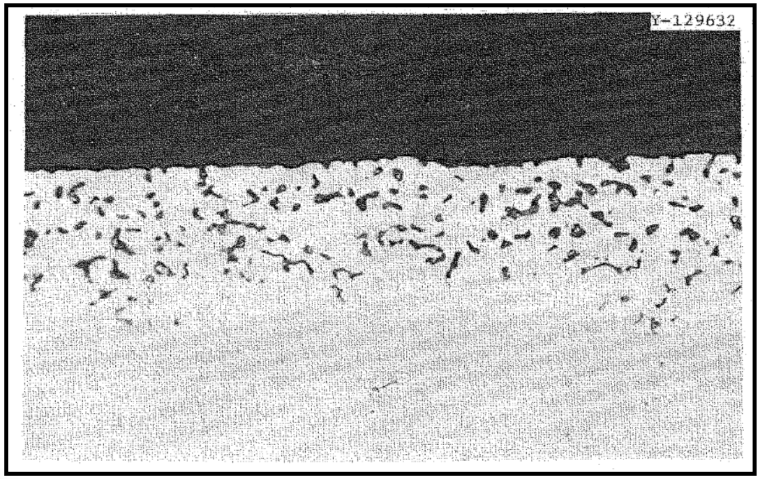
- Understand the fate of fission products (soluble, insoluble, sometimes soluble or gas) and impact on bulk properties



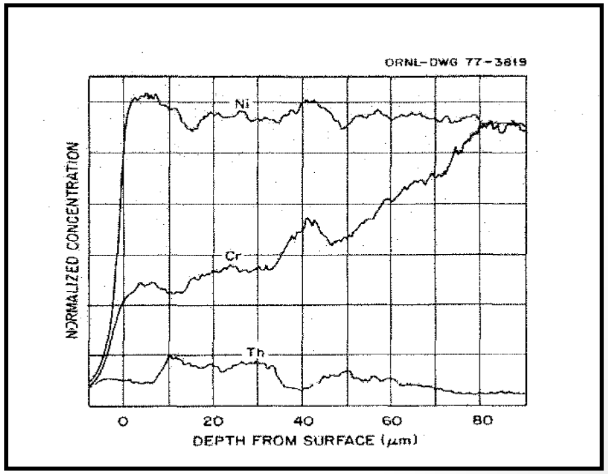


3. Understanding Fission and Activation Product Chemistry and Radiation Chemistry

- Couple experimental data and computational model to gain a predictive insight into impact of fission products on chemical and physical properties
- Need to understand the impact of fission and activation products on corrosion
  - Tellurium, a fission product, contributed to surface cracking in Hastelloy N in the molten salt reactor experiment by leaching Cr



Inconel 601 (Ni-22.5Cr-14Fe) exposed 721 h at 704° C in MSBR fuel salt. ORNL/TM-5783, May, 1977



Microprobe generated line profiles across corroded area of Inconel 601 sample

3. Understanding Fission and Activation Product Chemistry and Radiation Chemistry

- Correlate fission and activation product behavior with surrogates (but be sure surrogates possess representative chemical and physical properties)
- Understand physical and chemical impact of short lived isotopes

soluble → *gaseous* → *soluble*

^{137}I → ^{137}Xe → ^{137}Cs

25 sec. | 4-min.

soluble → *sometimes soluble* → *insoluble*

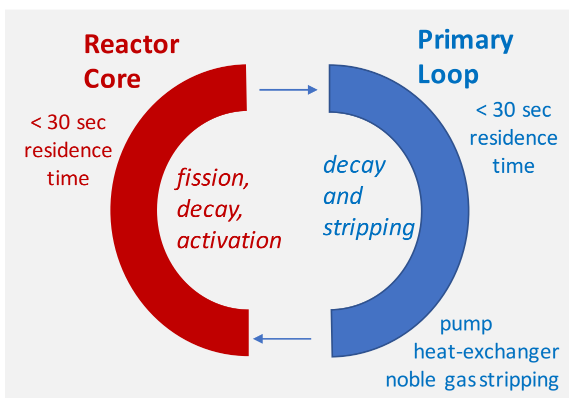
^{99}Zr → ^{99}Nb → ^{99}Mo → ^{99}Tc

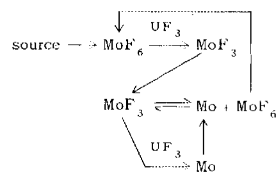
2.1 sec. | 15-sec. | 2.75-day

New capabilities in

- radiation imaging
- multiphysics modeling

could be coordinated with need for neutronics analysis.





~1970 out-of-pile chemistry

soluble → *insoluble* → *sometimes soluble* → *soluble* → *gaseous*

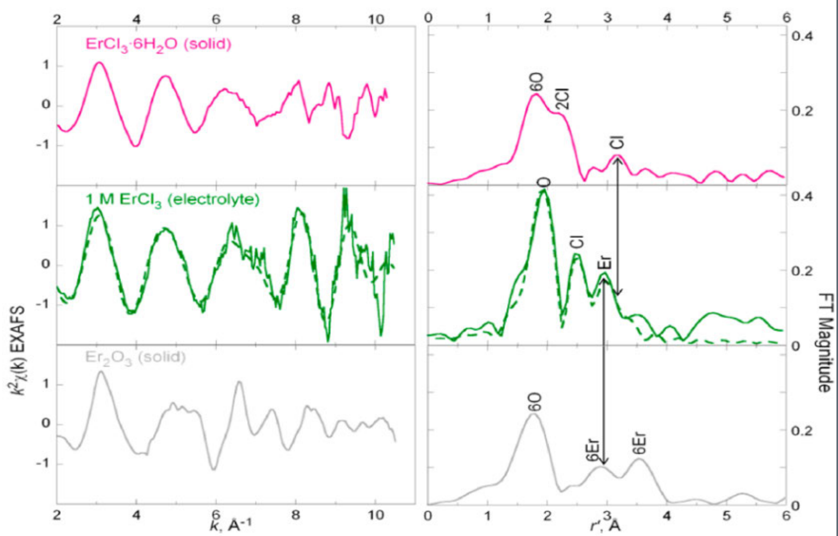
elemental volatility

$^{131,132}Cd$ → ^{131}In → ^{131}Sn → ^{131}Sb → ^{131}Te → ^{131}I → ^{131}Xe

< 1 sec. | < 1 sec. | 1 min. | 23-min. | 25-min. | 8-days

4. Understanding Materials Compatibility and Interfacial Phenomena

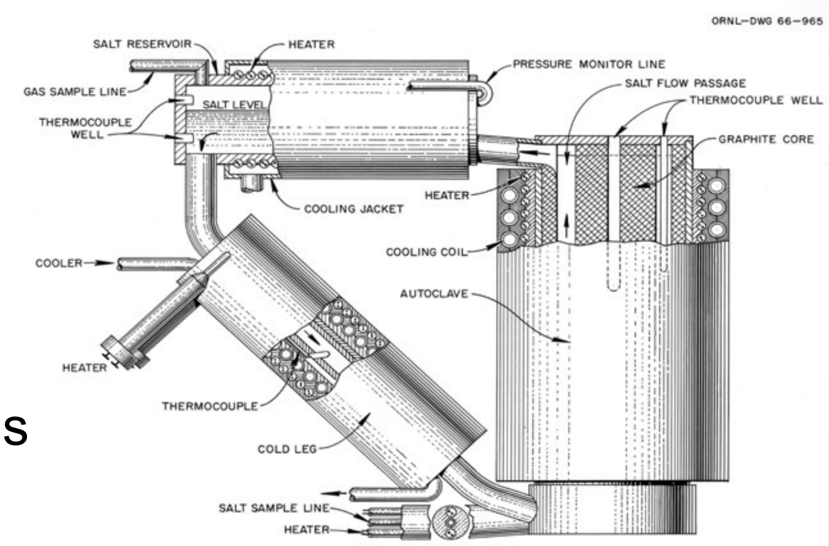
- Characterize the molecular level structure and chemical reactivity of the molten salt/solid interface is needed (to mitigate corrosion, materials precipitation, etc.)
  - Utilize in situ and operando surface sensitive spectroscopy including ATR, diffuse and specular reflectance, RAIR, surface enhanced Raman, sum frequency generation, and x-ray and neutron based techniques (reflectometry and grazing incidence XAFS)



GI-XAFS results reveal unanticipated molecular complex formation at the water/gas interface (Change from $Er(OH_2)_8^{3+}$ in bulk to neutral $ErCl_3(H_2O)_{6-7}$) at interface. *J. Phys. Chem. B* **2015**,*119,* 8734.

4. Understanding Materials Compatibility and Interfacial Phenomena

- Understand degradation mechanisms in MSR environment, especially the synergy between chemical, irradiation, and mechanical effects
  - Corrosion controlled by thermodynamic stability of the bare alloy surface in the salt environment
  - Impurities (HF, HCl, and H_2O) can have major effects
    - Corrosion rates on unpurified salts (167 mm/year) were four orders on magnitude larger than that for pure salts (0.013-0.044 mm/year)
  - Use a flow loop to test materials and analytical method
  - Irradiation of salts and materials in a reactor



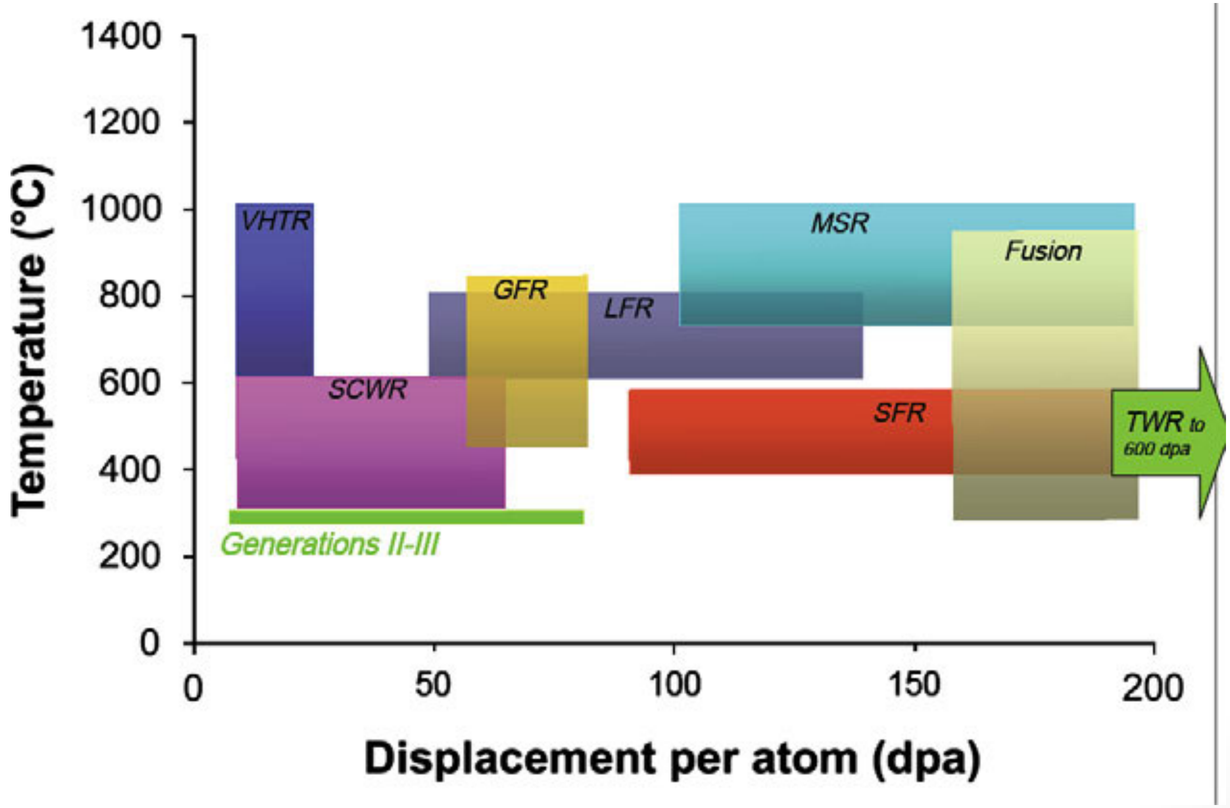
Natural circulation loop used in the Oak Ridge Research Reactor.

4. Understanding Materials Compatibility and Interfacial Phenomena

- Computational prediction of interfacial processes over a wide variety of time scales (ns-year)
  - Predict long time scale processes by scaling up insights from molecular interaction (quantum mechanical molecular dynamics (QM/MD))
    - Predict surface layer formation (metal plating) leading to degradation of reactor and heat exchangers performance
    - Understand gas entrainment and degassing
  - Develop approaches to couple chemical and physical phenomena with microstructure and composition
  - Experimentally validate computational predictions

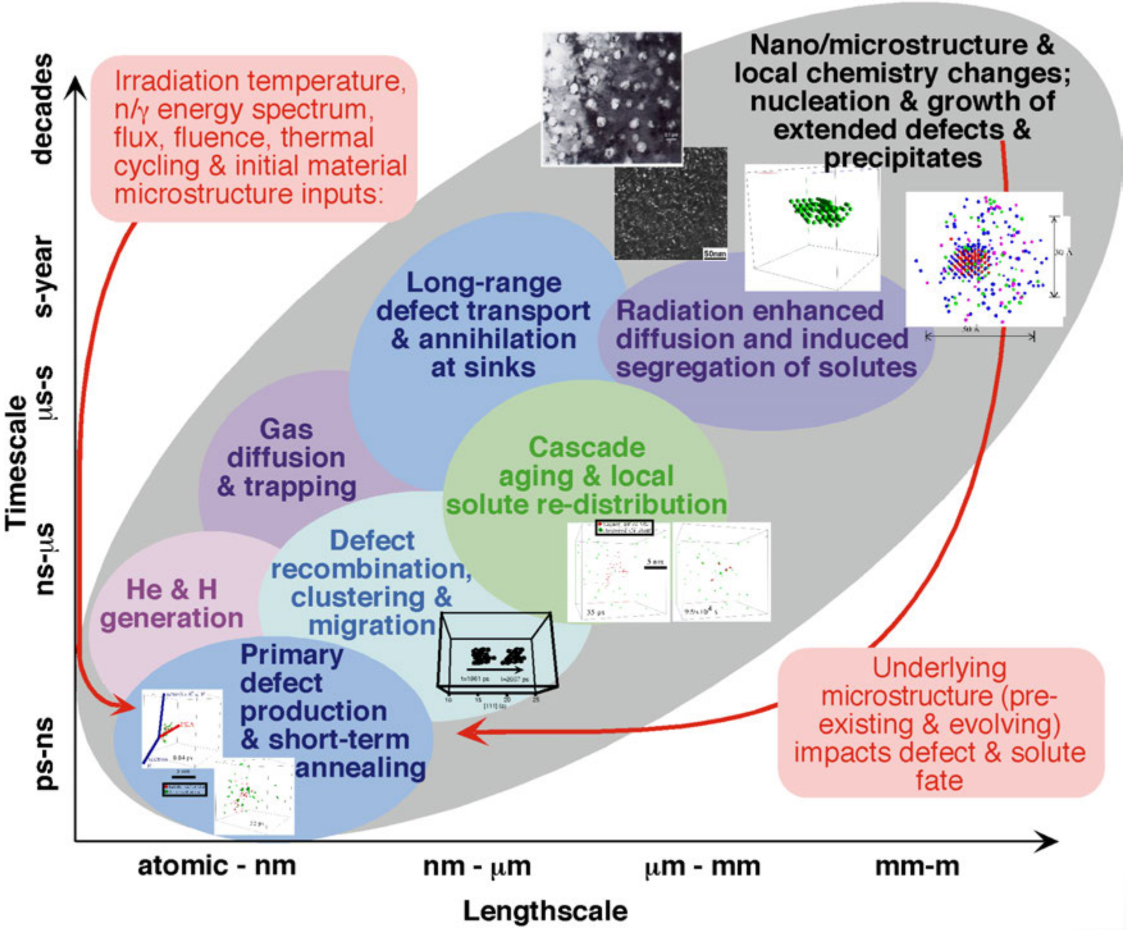
5. Guiding Next Generation Materials for Molten Salt Reactors

- Limited compatible materials - questions on lifetime and durability
  - Develop new methods which combine experimental characterization data with predictive modeling to enable the rapid design of new MSR materials, including superalloys and composites, for extreme environments



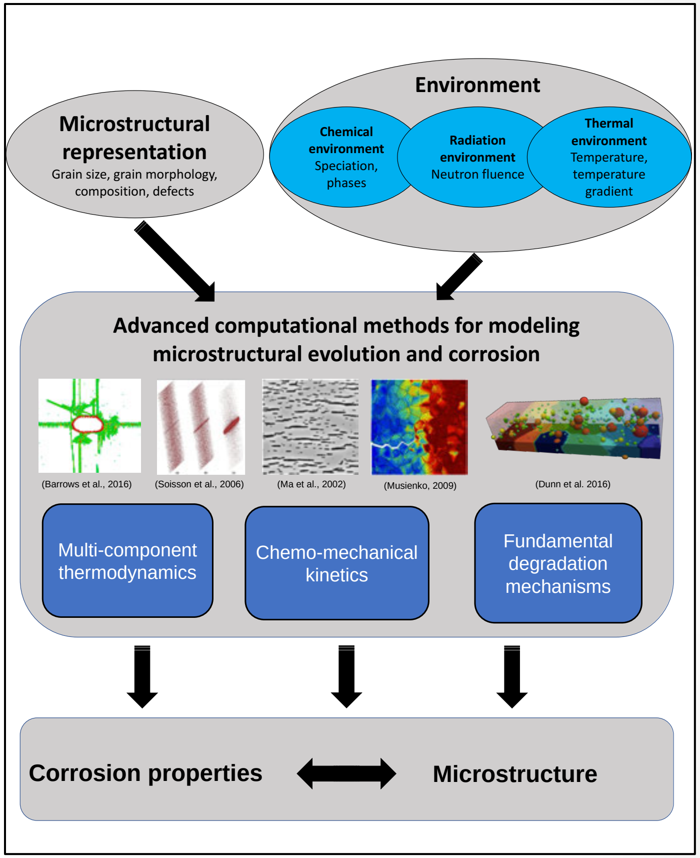
5. Guiding Next Generation Materials for Molten Salt Reactors

- Understand microstructural changes in irradiated materials over a wide range of length and time scales by coupling experimental data with computational methods



5. Guiding Next Generation Materials for Molten Salt Reactors

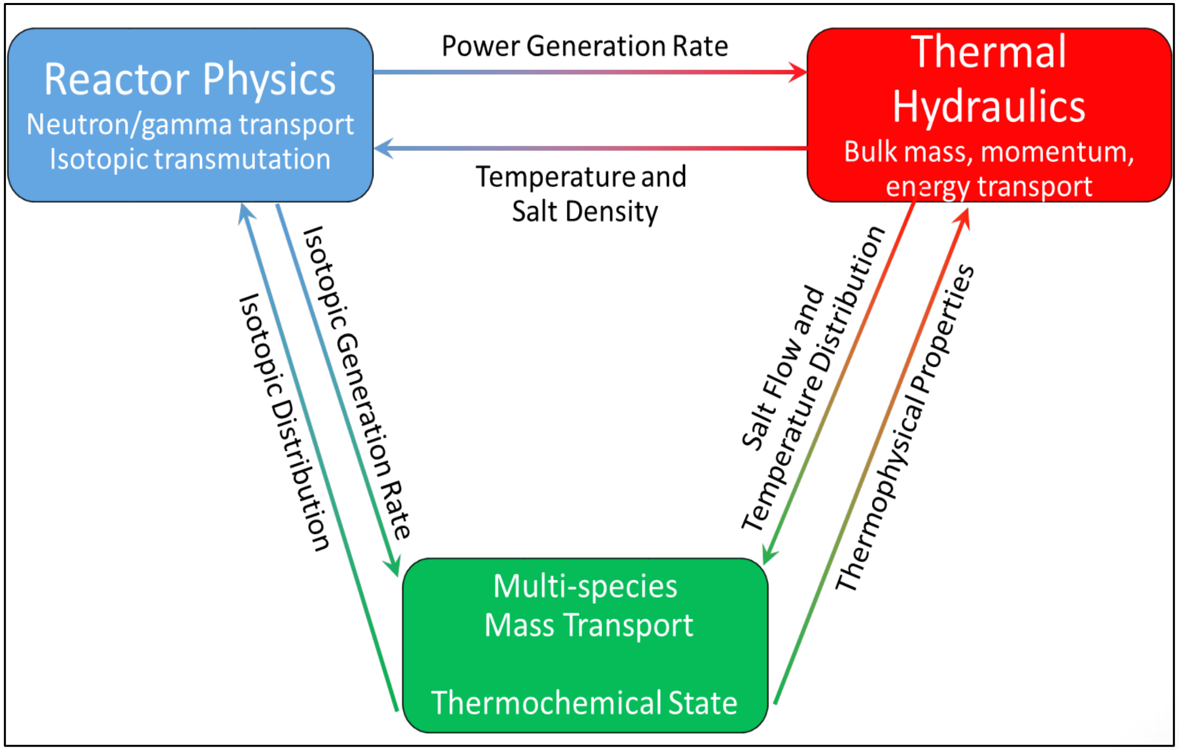
- Methods are needed to predict:
  - Materials behavior in complex molten salt environment
  - Microstructural evolution of materials in dynamic radiation and chemical environment
  - Mechanical degradation processes under MSR conditions
- Accelerate code qualification of new materials



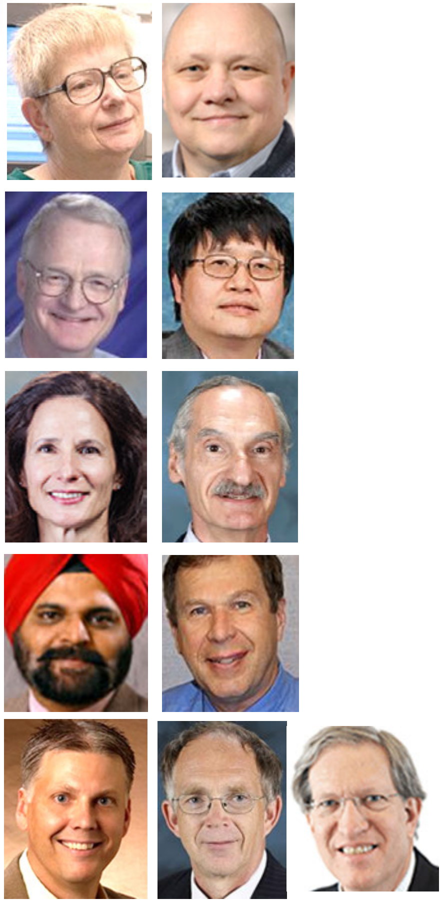
Example of multi-resolution modeling capabilities for microstructure evolution and corrosion. See Molten Salt Chemistry Workshop Report.

6. Create a Virtual Reactor Simulator

- Develop an accurate simulation of a MSR, including reactor core and primary heat exchanger, which describes source term, neutronics, transport, thermal hydraulics, isotope transmutation, thermochemical properties of the fuel, corrosion, refueling, etc.
- The major components of a virtual reactor simulation and the data needed between the various components is shown below.



Molten Salt Chemistry Workshop Panel Leads —
Panel discussions during the workshop provided the foundation of Panel Reports and Future Research Directions



Panel 1: Physical Chemistry and Salt Properties
- **Alexandra Navrotsky** (UC-Davis)
- **Mark Williamson** (ANL)

Panel 2: Analytical Chemistry
- **Sam Bryan** (PNNL)
- **Sheng Dai** (ORNL)

Panel 3: Fission Product Chemistry and Radiolysis
- **Tina Nenoff** (SNL)
- **Bill DelCul** (ORNL)

Panel 4: Materials Compatibility
- **Preet Singh** (Georgia Tech)
- **Jim Keiser** (ORNL)

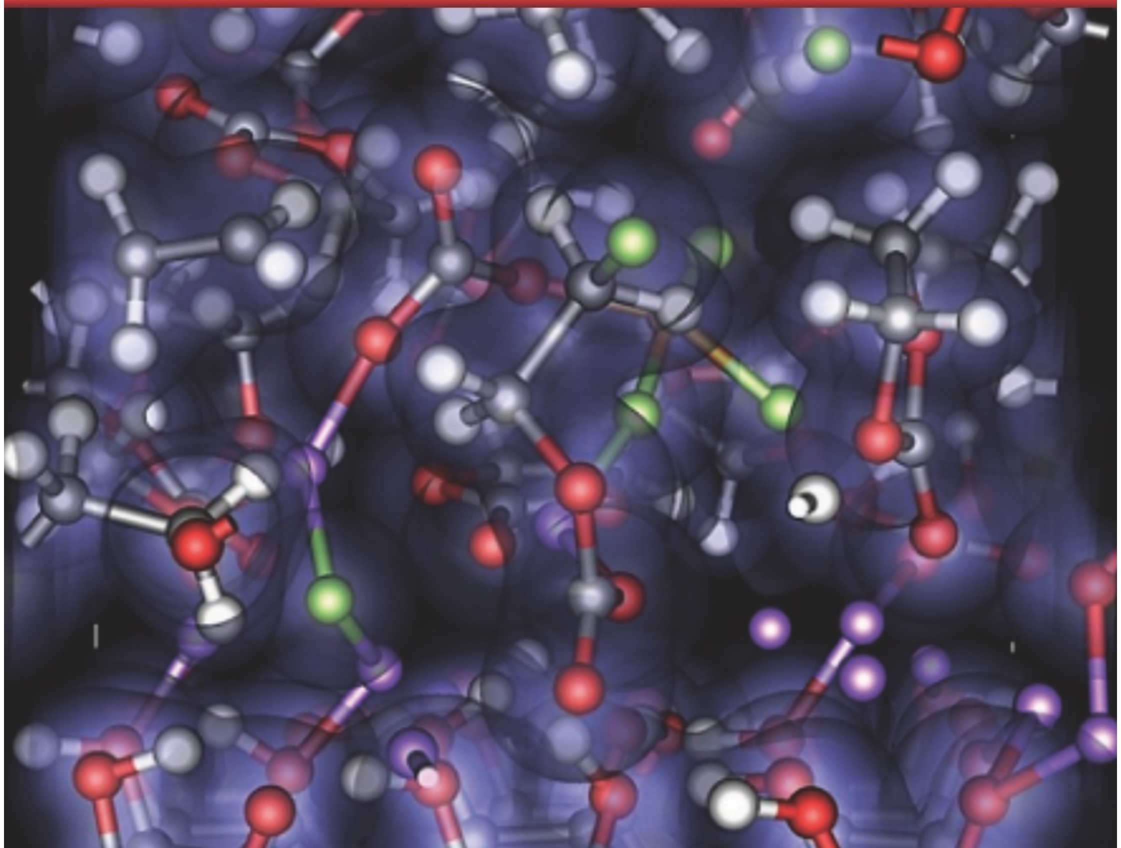
Panel 5: Computational Chemistry and Materials Sciences
- **Brian Wirth** (UTK)
- **Bobby Sumpter** (ORNL)
- **Charles Henager** (PNNL)

Workshop Plenary Speakers:
Alan Icenhour (ORNL); **John Herczeg** (DOE-NE); **Nick Smith** (Southern Company, MSR WG Chair); **Vic Maroni** (ANL); **Steve Zinkle** (Univ Tennessee); **Jim Keiser** (ORNL)

TECHNOLOGY AND APPLIED R&D NEEDS FOR

Molten Salt Chemistry

Innovative Approaches to Accelerate
Molten Salt Reactor Development and Deployment



https://www.ornl.gov/content/molten-salt-chemistry-workshop