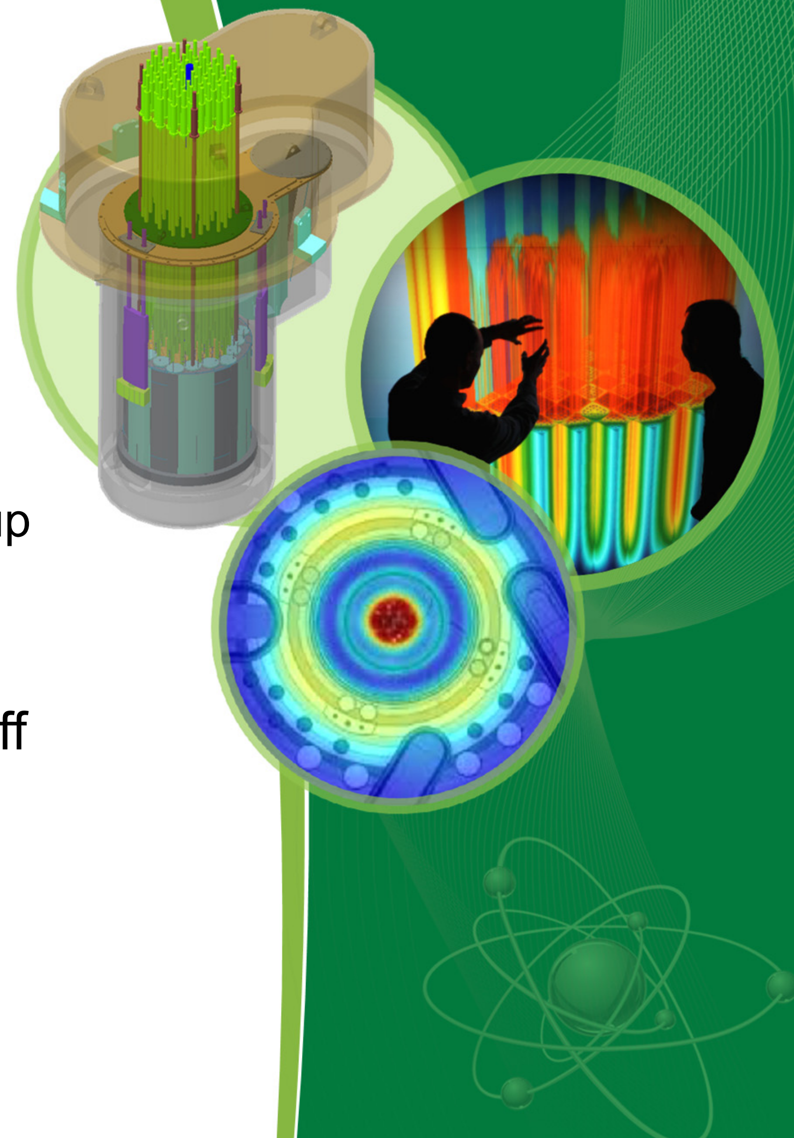
Module 3: Overview of Fuel and Coolant Salt Chemistry and Thermal Hydraulics



Presentation on Molten Salt Reactor Technology by:
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What are "Molten Salts"?

- Salts are ionic compounds formed from a combination of electronegative and electropositive elements
  - At elevated temperatures salts liquefy and are termed "molten salts"
- Halide salts are ionic compounds formed from the combination of a halogen (electronegative) and another electropositive element – commonly, but not exclusively, alkali metals or alkaline earths
  - Examples: LiF, BeF_2, $MgCl_2$, NaCl (aka table salt), ZrF_4, RbF, UF_4, UCl_3

Halogens

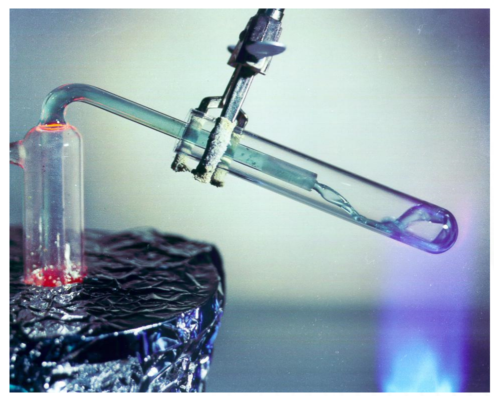
9	F	Fluorine	18.998...
17	Cl	Chlorine	35.45
35	Br	Bromine	79.904
53	I	Iodine	126.90...
85	At	Astatine	(210)
117	Ts	Tennessine	(294)

Alkali Metals

3	Li	Lithium	6.94
11	Na	Sodium	22.989...
19	K	Potassium	39.0983
37	Rb	Rubidium	85.4678
55	Cs	Caesium	132.90...
87	Fr	Francium	(223)

Alkaline Earths

4	Be	Beryllium	9.0121...
12	Mg	Magnesium	24.305
20	Ca	Calcium	40.078
38	Sr	Strontium	87.62
56	Ba	Barium	137.327
88	Ra	Radium	(226)



(left) Solid "Frozen" and (right) Liquid "Molten" $2LiF\text{-}BeF_2$ salt

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Molten Halide Salts Have Attractive Heat Transfer Properties

Coolant (Reactor Concept)	High Working Temperature[a]	High Volumetric Heat Capacity[b]	Low Primary Pressure[c]	Low Reactivity with Air & Water[d]	Coolant & Materials Cost
Water (PWR)	☹	☺	☹	☺	☺
Sodium (SFR)	😐	😐	☺	☹	😐
Helium (GCR)	☺	☹	☹	☺	😐
Salt (FHR/MSR)	☺	☺	☺	☺	☹

[a] High system working temperature desirable for high efficiency power conversion and process heat applications

[b] High coolant volumetric heat capacity enables ~constant temperature heat addition / removal ($\eta_C = 1 - T_C/T_H$ ~ Carnot cycles), compact system architectures, and reduces pumping power requirements

[c] Low primary system pressure reduces cost of primary vessel and piping and reduces energetics of pipe break accidents

[d] Low reactivity with air and water reduces energetics of pipe break accidents

Molten Salts Are Attractive Coolants for Very High Temperatures

Compared to 20°C water

Fluorides:
- ~ 2X density
- ~ 1/2X heat capacity
- ~ 1–5X viscosity
- ~ 2X thermal conductivity
- ~ 1X coefficient of expansion as a liquid
- Very low vapor pressure

Chlorides:
- ~ 1 1/2X density
- ~ 1/4X heat capacity
- ~ 1 1/2X viscosity
- ~ 1X thermal conductivity
- ~ 1 1/2X coefficient of expansion as a liquid
- Very low vapor pressure

Characteristics of *Fuel Salts* and *Coolant Salts* Are Available from Review Articles

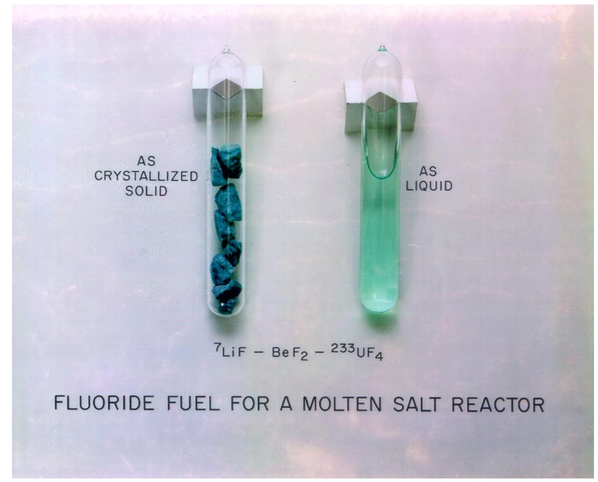
- A fuel salt is a molten salt that contains fissile material
  - C. F. Baes, Jr., “The Chemistry and Thermodynamics of Molten Salt Reactor Fuels,” *Journal of Nuclear Materials*, 51 (1974) 149-162
  - W. R. Grimes, “Molten Salt Reactor Chemistry,” *Nuclear Applications and Technology*, 8(2) (1970) 137–155
  - B. R. Harder, G. Long, and W. P. Stanaway, “Compatibility and Processing Problems in the Use of Molten Uranium-Alkali Chloride Mixtures as Reactor Fuels,” *Nuclear Metallurgy, Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers*, 15 (1969) 405-32
- Coolant salts are molten salts with advantageous heat transfer properties
  - D. F. Williams, *Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop*, ORNL/TM-2006/69

Composition of Fuel Salts Are Tailored to Performance Objectives

- Fuel salts consist of a mixture of
  - Fissile material
  - Fertile material (if used)
  - Solvent (diluent)
    - Lowers melting point
    - Decreases power density
    - Decreases viscosity
  - Fissile oxidation prevention material
    - Preferentially oxidizes to avoid creation of fissile oxide particles due to contamination

$$ZrF_4 + UO_2 \Leftrightarrow ZrO_2 + UF_4$$

  - Fission products (upon use)



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Fuel Salts Must Integrate Reactor Physics, Heat Transfer, and Material Compatibility

- Reactor physics requirements
  - Low neutron absorption
    - Thermal neutron absorption is of lower importance for fast spectrum reactors
  - Radiolytic stability under in-core conditions
  - Dissolve fissile materials
- Both chloride and fluoride salts are industrially used as heat transfer fluids
  - High heat capacity, high boiling point, low thermal conductivity fluids
  - Melting point must be below ~525°C
  - Relatively insensitive to fission products
- Both fluoride and chloride salts, under mildly reducing conditions, are reasonably compatible with high temperature structural alloys and graphite

Elements or Isotopes Which may be Tolerable in High-Temperature Reactor Fuels

Material	Absorption Cross Section (barns at 2200 m/sec)
Nitrogen-15	0.000024
Oxygen	0.0002
Deuterium	0.00057
Carbon	0.0033
Fluorine	0.009
Beryllium	0.010
Bismuth	0.032
Lithium-7	0.033
Boron-11	0.05
Magnesium	0.063
Silicon	0.13
Lead	0.17
Zirconium	0.18
Phosphorus	0.21
Aluminum	0.23
Hydrogen	0.33
Calcium	0.43
Sulfur	0.49
Sodium	0.53
Chlorine-37	0.56
Tin	0.6
Cerium	0.7
Rubidium	0.7

Source: Grimes, “Molten Salt Chemistry,” *Nuclear Applications and Technology* 8(2) (1970) 137-155.

Fuel Salts Have Multiple Subclasses

- Thermal spectrum reprocessing optimized fluoride salts
  - FLiBe (2^7LiF-BeF_2) solvent provides optimal neutronic performance
    - Lithium to beryllium ratio selected to minimize melt temperature with acceptable viscosity
    - High tritium production – need isotopically separated lithium
  - NaF-ZrF_4 solvent does not require isotopic separation
    - Much lower tritium production
    - Higher vapor pressure
  - ~1% fissile loading
  - Fertile loadings vary but are typically much higher (~20%)
- Fast spectrum and thermal spectrum, once-through fuel cycle optimized fluoride salts
  - Much higher fissile loading (actinide-rich eutectics)
  - Adequate fissile material content is a significant design challenge
- Chloride salts
  - Enables harder neutron spectrum and enhanced breeding
  - Isotopically separated chlorine preferable - ^{35}Cl from ^{37}Cl
    - ^{35}Cl has a moderate capture cross-section (n,γ) E < 0.1 MeV < E (n,p)

European Fast Spectrum MSR starting fuel composition LiF-ThF_4-UF_4-$(TRU)F_3$ with 77.7-6.7-12.3-3.3 mol%

Chlorine natural isotopic composition
^{37}Cl = 24.23%
^{35}Cl = 75.77%

Fluoride Fuel Salts Have Substantially More Experimental Data Than Chloride Fuel Salts

- Fluoride salts
  - **Two operating molten salt reactors**
  - Multiple in-pile loops
  - Many capsule tests
  - Fast-spectrum fluoride salts have much less experience
- Chloride salts – laboratory measurements of physical properties
  - No in-core testing of fuel salts
  - Use in pyroprocessing

Thermal Spectrum Fuel Salt Behaves Similarly to Solvent Salt

- MSRE nominal fuel mixture was

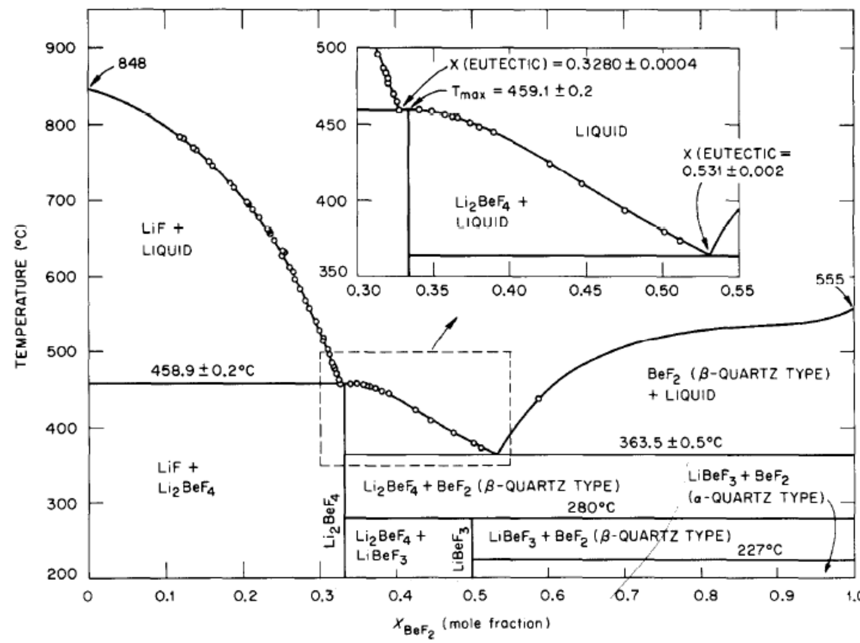
  65 LiF, 29.1 BeF_2, 5 ZrF_4, 0.9 UF_4 (mol %)

- Uranium enriched to 33%
- Uranium trifluoride disproportionates in most molten fluoride solutions

$$4UF_3 \Leftrightarrow 3UF_4 + U^0$$

  – Large UF_4/UF_3 ratio prevents disproportionation

- Isotopically pure ^7Li - nominally 99.993% at MSRE
  – Means to limit tritium production due to large ^6Li cross-section



LiF-BeF_2 Phase Diagram

Source: Benes and Konings, "Thermodynamic properties and phase diagrams of fluoride salts for nuclear applications," *Journal of Fluorine Chemistry*, 130, 2009.

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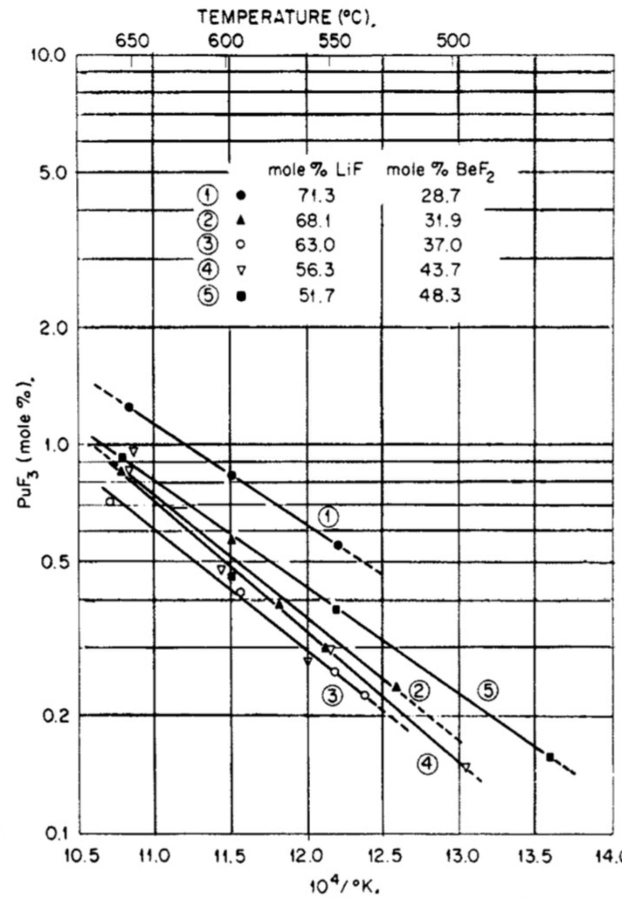
Fluoride Fuel Salts Have Limited Solubility for Actinide Trifluorides

- Fast spectrum systems operate near solubility limits
  - Lanthanide trifluorides compete with actinide trifluorides
    - CeF_3 substantially displaces PuF_3
  - Log of actinide trifluoride solubility is roughly linear versus inverse temperature
- Monovalent solvent fluorides dissolve much higher levels of actinide trifluorides
  - Joint solubility of PuF_3+UF_3 is much less than individual components up to 600°C
  - Solubility has strong temperature dependence
    - Plate out during transients possible
  - Polyvalent fluorides (e.g., ThF_4, UF_4, or BeF_2) substantially reduce solubility



Solubility of PuF_3 in FLiBe

Source: C. J. Barton, "Solubility of Plutonium Trifluoride in Fused-Alkali Fluoride-Beryllium Fluoride Mixtures" *J. Phys. Chem.* , Vol. 64, 1960

Fuel Salt Properties Will Be Impacted by Fission Products

- Fission products may be gaseous, solid, or dissolved
  - Alkaline and alkaline earth fission products (e.g., Cs and Sr) form stable fluorides (or chlorides)
  - Semi-noble fission products plate out on metal surfaces
    - Potential heat load issue following rapid draining
  - Noble fission products form suspended clusters that may plate out
- May elect to actively strip gaseous fission products
  - Lowers the in-core accident source term
  - Requires cooling fission product traps
  - Bubble formation and collapse results in reactivity burps
- Fluoride salts have been extensively examined
  - Reactors, in-pile loops, capsules
  - Some uncertainty remains - especially about impact of long-term build up of fission products
- Chloride fuel salts almost entirely untested in core environments
  - Potential for development of undesirable compounds and phases

"I am pleased, without benefit of rack and thumbscrew, to recant. More realistic calculations based on the single-region 'reference design' MSBR heat exchangers indicate that peak afterheat temperatures, while still uncomfortably high, will be much lower than originally anticipated."

J. R. Tallackson, ORNL-TM-3145

Fission Product Solubility Changes Along Decay Chain

A few elements are very sensitive to redox changes:

Nb behavior changed during MSRE operation after addition of Be°

Transitional (*soluble → gas → soluble*) decay example:

24 sec. half-life		*4-min. half-life*		*6 % cumulative ^{235}U fission yield*
^{137}I	→	^{137}Xe	→	^{137}Cs

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	*Zn*	*Ga*	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	*Cd*	*In*	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	*Hg*	*Tl*	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr															

soluble

insoluble

sometimes soluble

Cover Gas Handling System Is a Key Element of Any MSR

- Distribution of fission products is a central safety issue
  - Reduction of fission products in the core limits potential fuel accident source term
  - Fission products away from core change decay cooling requirements and radionuclide containment requirements
- Cover gas will inevitably contain some fission products
  - Aggressive sparging may result in up to 40% of fission products in cover gas (nearly all of the fission products with gaseous precursors)
  - Results in substantial heat load in short term fission product trap
  - Longer term fission product traps contain much lower levels of activity
- Transition from fission product barrier function to waste handling system along carbon beds is conceptually significant
  - ^{85}Kr emerging from final stage could be vented
- Some fuel salt fissile components have significant vapor pressures
  - UCl_4 boils at 791°C
- Some solvents vaporize incongruently
  - ZrF_4 sublimes resulting in snow-like deposits in exhaust piping

NRG (Petten) Recently Began Irradiation Tests of Fuel Salt Capsules

- SALIENT program is trilateral collaboration between NRG, JRC, and TUD
- Fluoride salts initially
  - Chlorides later stage
- Goals
  - Handling experience
  - Salt–graphite interaction
  - Fission product stability / redistribution
  - Metal particle size distribution
- Longer term
  - Waste route for spent molten salt fuel
  - In-pile molten salt loop for the HFR Petten

Cartoon of potential Petten MSR loop

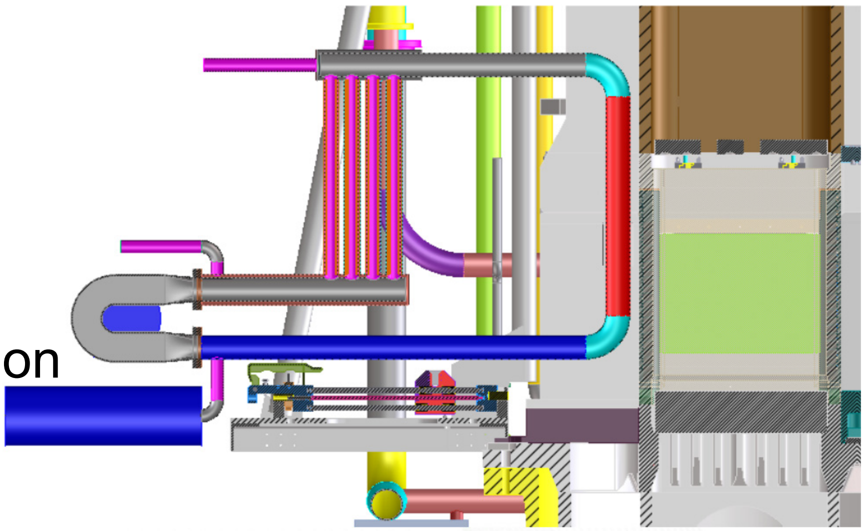


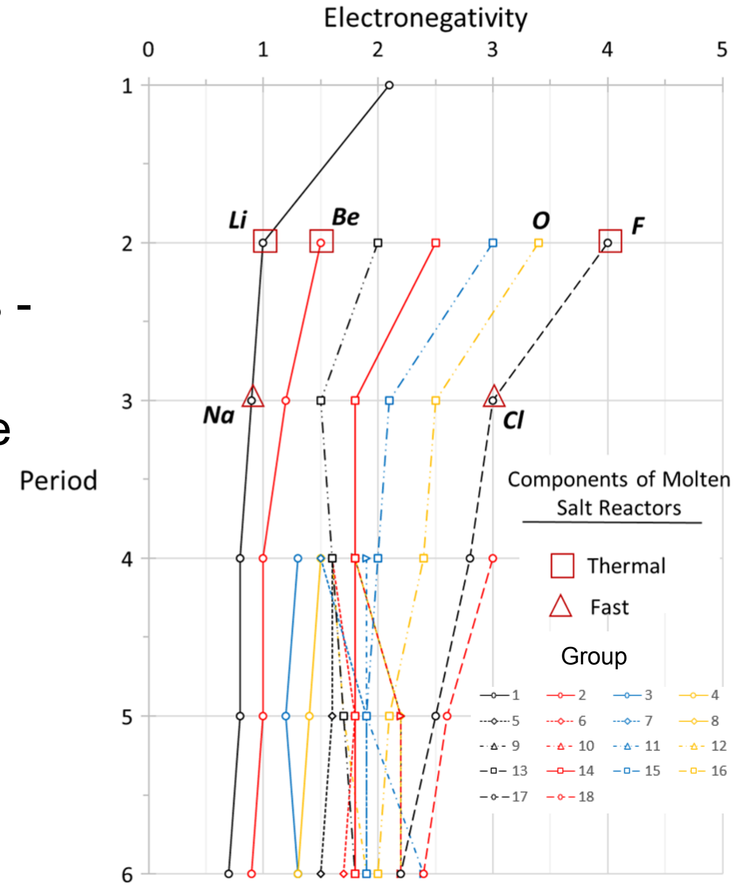
Image provided by NRG; used with permission.

Isotope Separation Is a Significant Issue for Both Fluoride and Chloride MSRs

- Lithium enables optimal reactor physics
  - Lithium-6 is a large cross-section thermal neutron absorber that yields tritium
  - Lithium isotope separation is also necessary for fusion and PWR chemistry control
  - Mercury amalgam-based lithium isotope separation was performed at industrial scale in the 1950s for defense purposes
- Chlorine
  - Absorption reactions in ^{35}Cl both produces ^{36}Cl (long-lived radionuclide) and results in a reactivity penalty
  - Lack of chlorine isotope separation technology was a key element in US decision in 1956 to pursue thermal breeder MSR

Removing Oxygen Is a Key Technology Requirement for Both Fluorides and Chlorides

- Salts containing excess oxygen are much more corrosive
- Hydrofluorination for fluoride salts
  - HF is highly corrosive - performed offline
  - Also removes other electronegative impurities - sulfur and chlorine
  - Ammonium hydrofluoride - NH_4HF_2 alternative
- Carbochlorination for chloride salts – phosgene ($COCl_2$) or carbon tetrachloride used as reactant
  - $MO_2 + CCl_4 \rightarrow MCl_4 + CO_2$
- Oxygen can also be removed from some chloride melts by precipitation as aluminum oxide
  - $AlCl_3 + UO_2 \rightarrow AlO_2 + UCl_3$



Source: Taube EIR-332; p.156

Tritium is Significant Issue For Lithium-Bearing Salts

- Tritium is produced by neutron reactions with lithium, beryllium, and fluorine as well as being a ternary fission product
  - Tritium production levels are similar to HWRs
- Tritium chemical state in salt is determined by redox conditions
  - TF (oxidizing) or T^+ (reducing)
- Above 300°C tritium readily diffuses through structural alloys
  - Heat exchangers represent largest surface area for diffusion
- Escape through power cycle is potential route for radionuclide release into environment

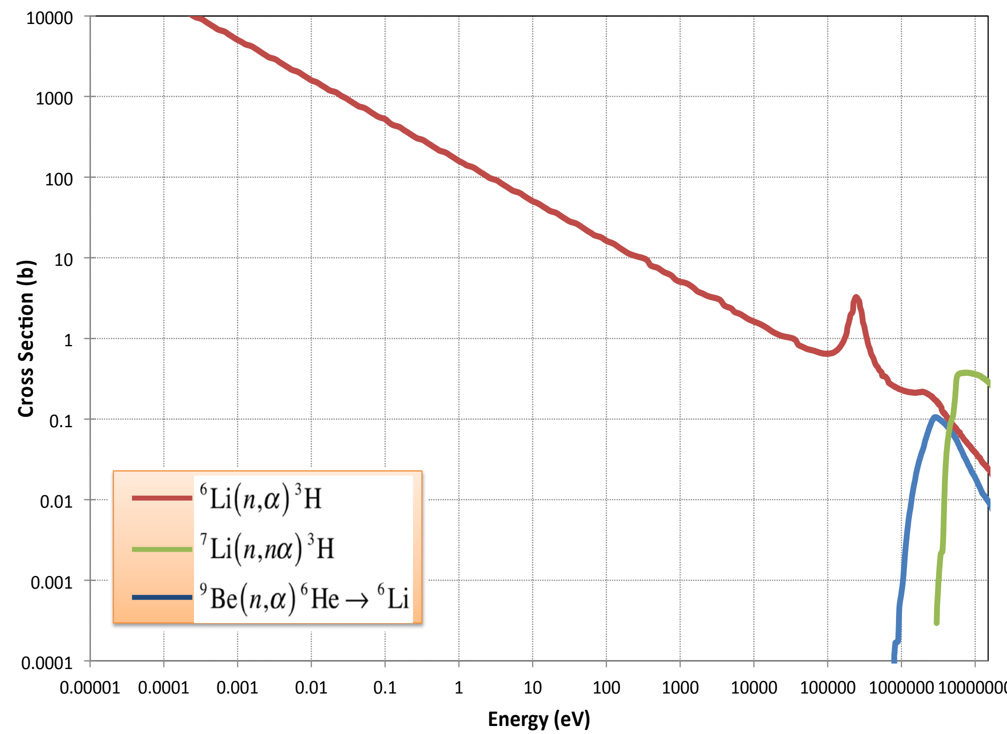


Table 1. Sources and rates of production of tritium in a 1000-MW(e) MSBR[a]

	Production rate (Ci/day)
Ternary fission	31
$^6Li(n,\alpha)^3H$	1210
$^7Li(n,n\alpha)^3H$	1170
$^{19}F(n,^{17}O)^2H$	9
Total	2420

[a]From Ref. 1.

Source: Mays, ORNL/TM-5759

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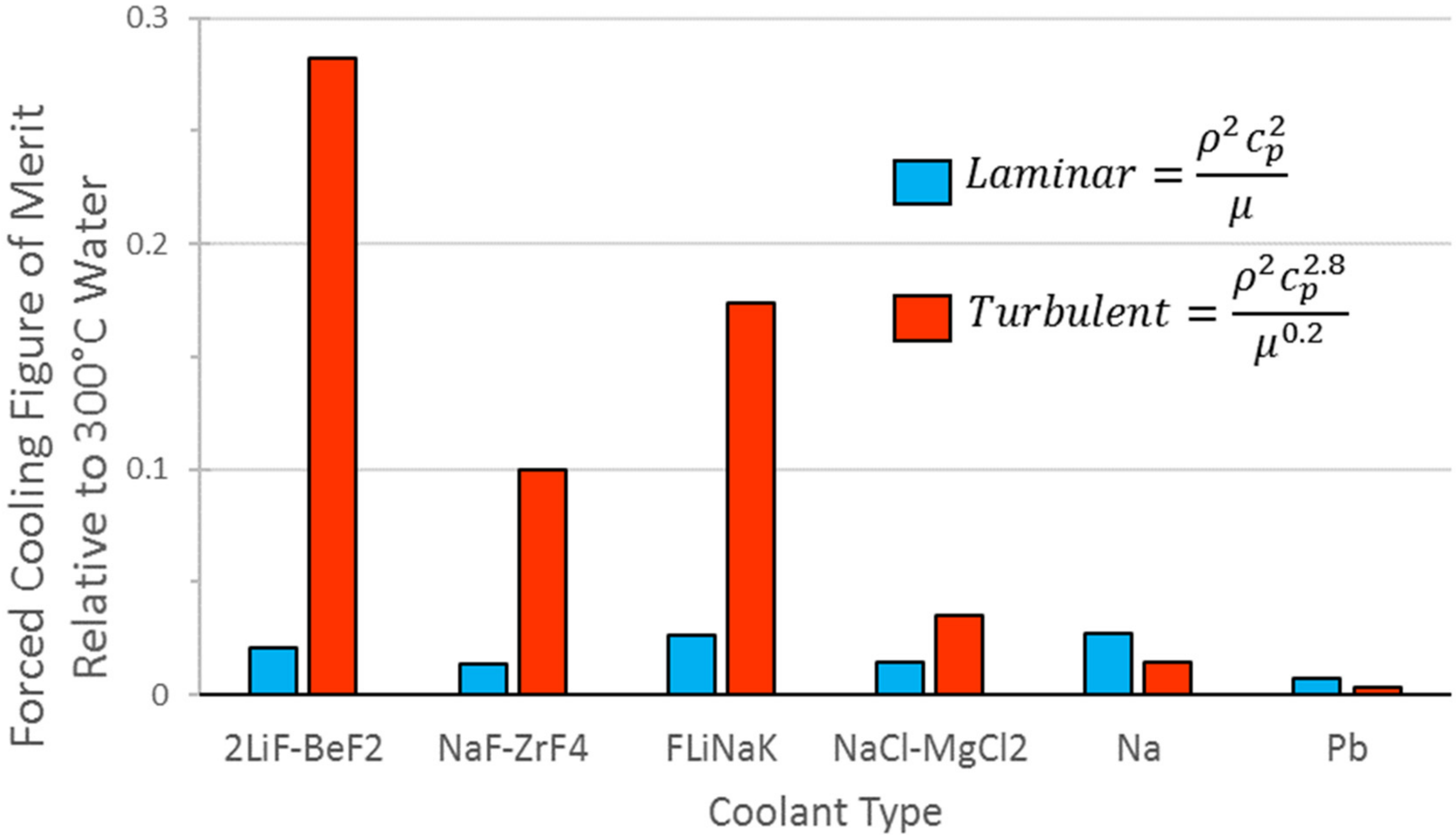
Tritium Mitigation Methods Include Stripping, Blocking, and Trapping

- Largest technical challenge for stripping is the small diffusion of tritium in salt
  - Necessitates intimate mixing of salt and stripping material
    - Gas sparging or spraying in gas space using fine droplets
    - Turbulent flow (to promote mixing) across large surface area window (e.g., double-walled heat exchanger)
    - Flow through packed bed of absorbers
  - Palladium alloys have highest tritium diffusion coefficient
    - Nickel may be acceptable and is much less expensive
  - Carbon traps tritium at operating temperatures - desorbs at high temperatures (peak storage at ~800°C)
    - Nickel coating carbon improves trapping kinetics
    - Irradiation damage significantly increases number of traps
  - Several lanthanides form stable tritides (e.g., Y or Sm)
- Tritium trapping in coolant salt was demonstrated in NaF-$NaBF_4$ (8–92 mol%) at engineering scale for MSBR

Molten Salts Have Attractive Heat Transfer Properties

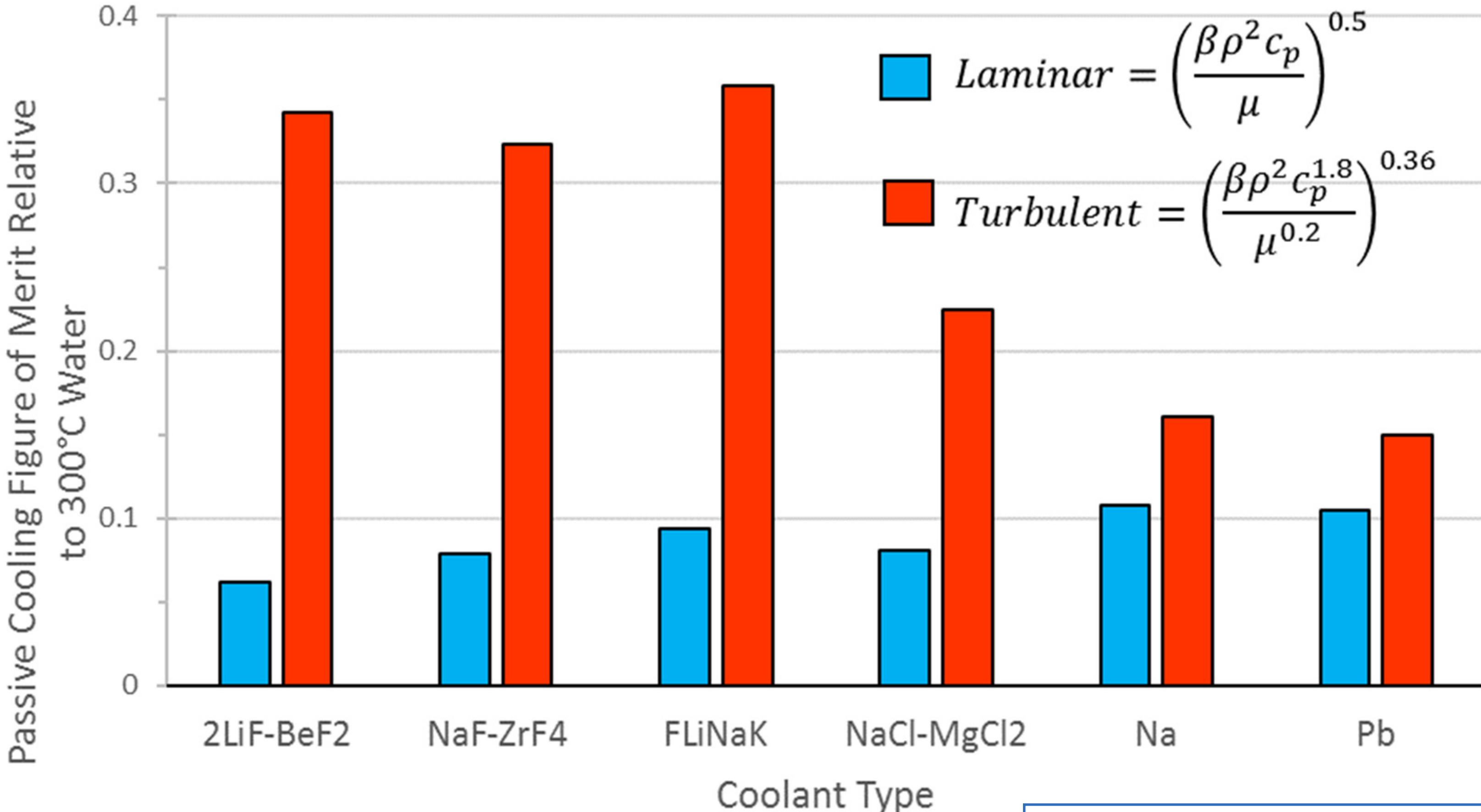


- Large heat capacity and low viscosity are key properties

Source:
Nuclear Engineering Handbook 9-90,
D. F. Williams et al., ORNL/TM-2006/12

ρ = density
c_p= heat capacity
μ = dynamic viscosity
β = volumetric expansion coefficient

Molten Salt Passive Cooling Characteristics are Favorable

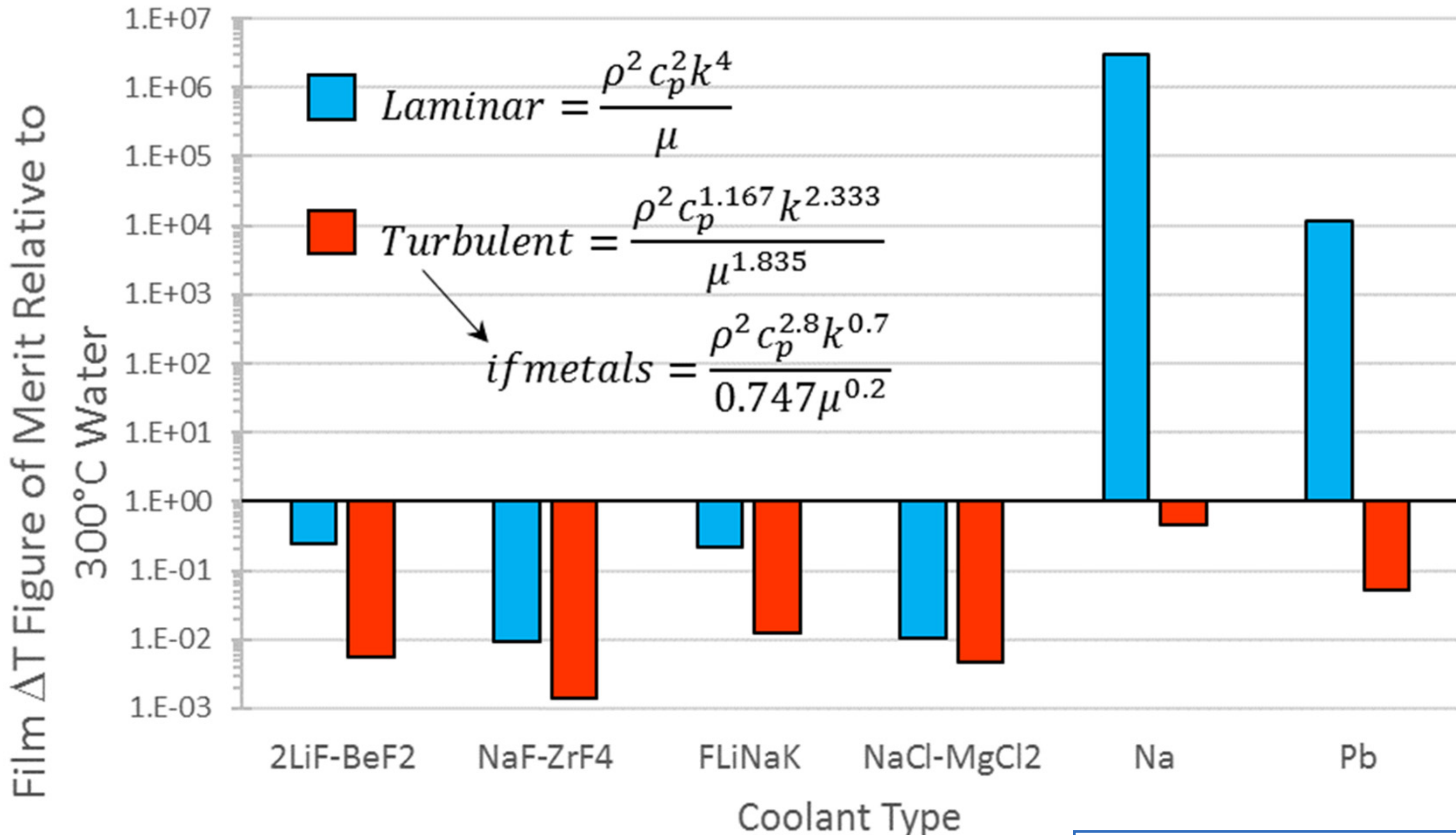


ρ = density
c_p= heat capacity
μ = dynamic viscosity
β = volumetric expansion coefficient

- Volumetric expansion with temperature provides buoyancy driving force

Source:
Nuclear Engineering Handbook 9-90,
D. F. Williams et al., ORNL/TM-2006/12

Salts Have Sharp Boundary Layer (High Prandtl Number)

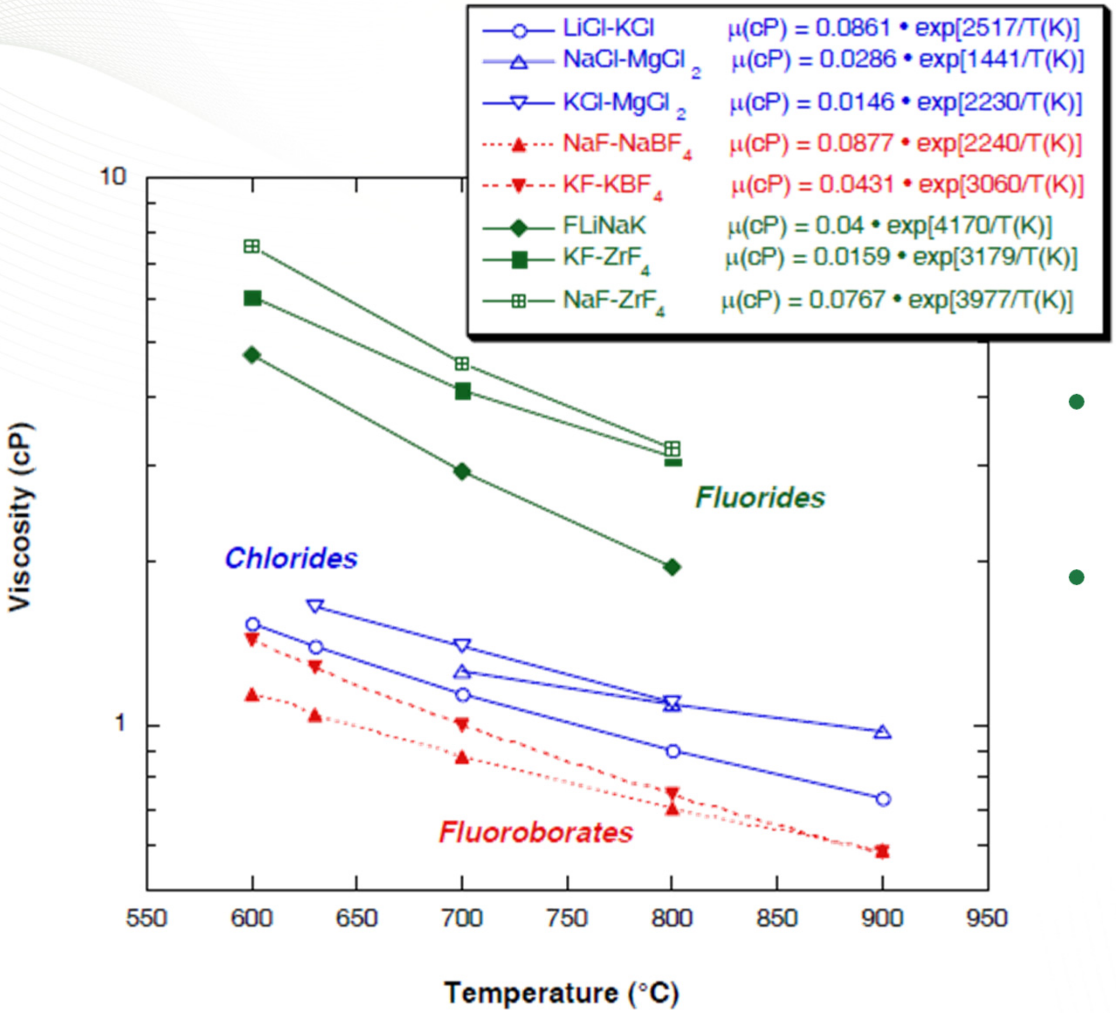


ρ = density
c_p= heat capacity
μ = dynamic viscosity
β = volumetric expansion coefficient

- Turbulence is required for effective heat transfer (or tritium stripping)

Source:
Nuclear Engineering Handbook 9-90,
D. F. Williams et al., ORNL/TM-2006/12

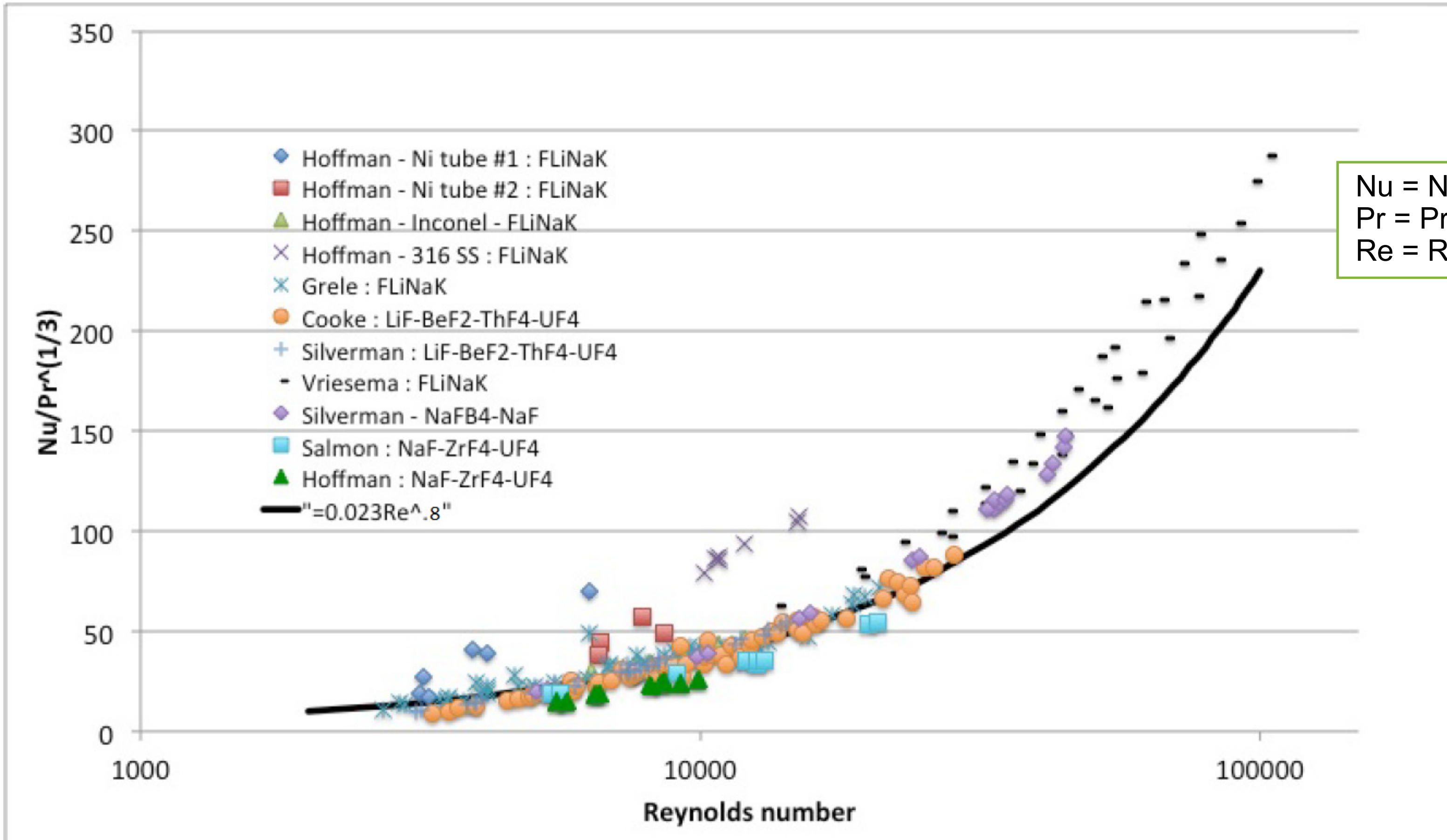
Salt Viscosity Decreases with Temperature



- Flow increases to hotter regions
- Improves temperature uniformity

Source:
D. F. Williams et al., ORNL/TM-2006/12
D. F. Williams, ORNL/TM-2006/69

Significant Uncertainty Remains in Fluoride Salt Turbulent Heat Transfer



Nu = Nusselt number
Pr = Prandtl number
Re = Reynolds number

Source: Yoder, ICAPP 14332, 2014

- Little experimental data with few material combinations and geometries
- Y-axis is a common heat transfer correlation for fully developed turbulent flow in tubes

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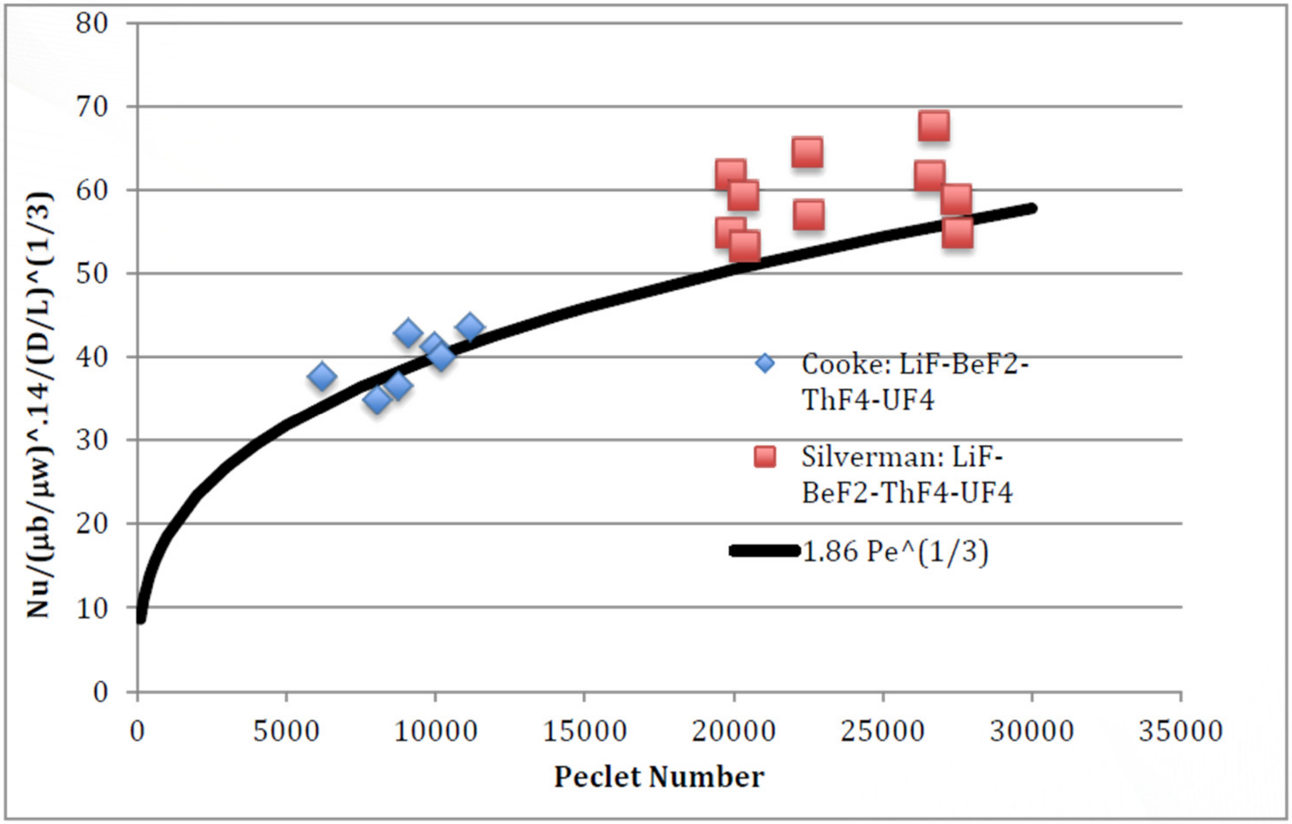
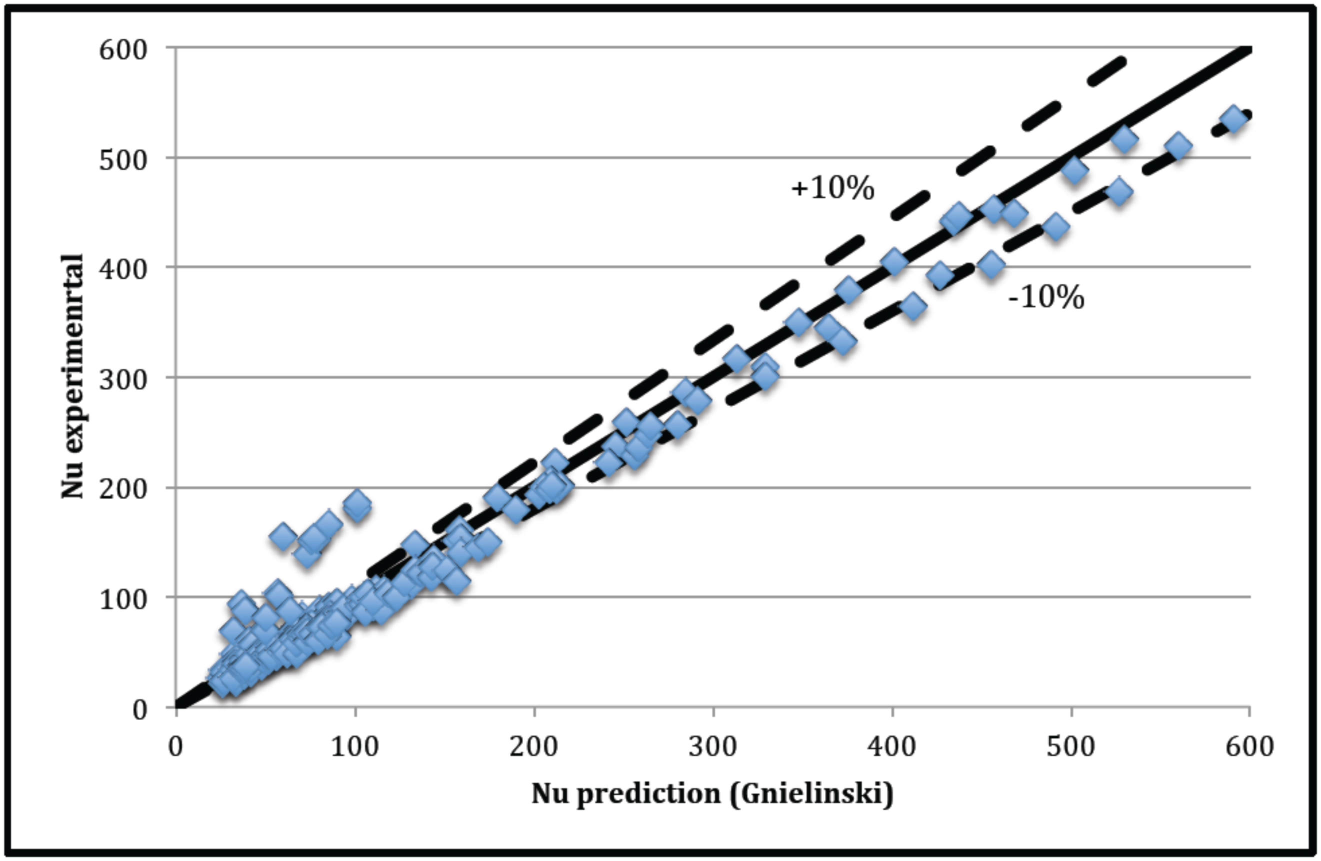
Laminar Flow Heat Transfer Also Has Significant Remaining Uncertainty



Source:
Yoder,
ICAPP 14332, 2014

- Axes selected to enable comparison with prior laminar flow correlations (Seider and Tate)
- Peclet number is a dimensionless ratio of the thermal energy convected to the fluid to the thermal energy conducted within the fluid

Significant Remaining Uncertainty in Prediction of Conductive / Convective Heat Transfer Ratio



Source:
Yoder,
ICAPP 14332, 2014

- Plot compares experimental and predicted conductive/convective heat transfer ratios
  - Prediction based upon reference Gnielinski correlation - commonly used for heat transfer comparisons

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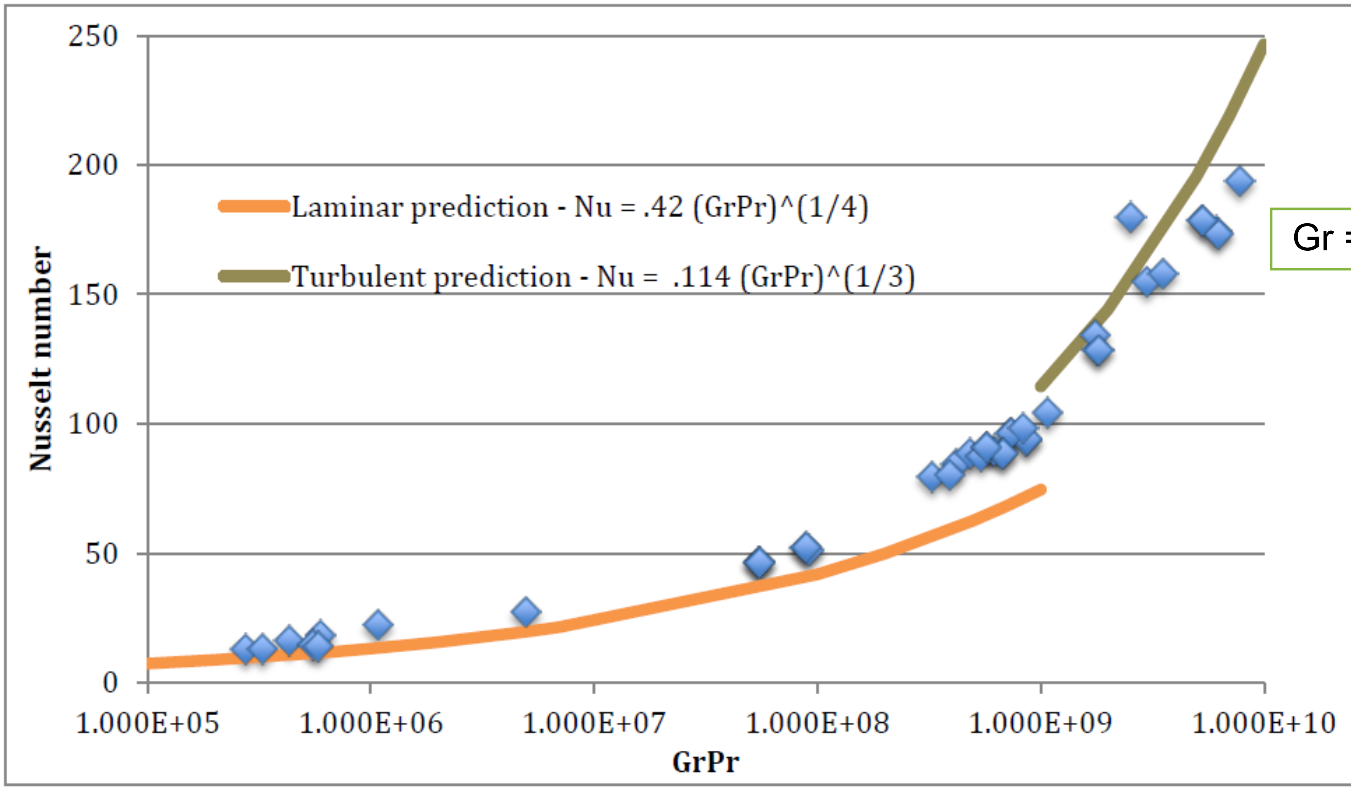
Natural Circulation Heat Transfer Has Significant Remaining Uncertainty



Gr = Grashof number

Source:
Yoder,
ICAPP 14332, 2014

- Product of Grashof and Prandtl number (X-axis) is the Rayleigh number associated with buoyancy-driven flow
  - Above critical Rayleigh number heat transfer is primarily convection below primarily conduction
  - Y-axis is ratio of convective to conductive heat transfer

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Heat Transfer Uncertainties Affect Operating Margin Calculations

- Material combinations and geometries of interest to MSRs have not been thoroughly characterized in past experiments
- Sources of experimental uncertainty include:
  - Salt purity and purification during the experiment
  - Film layers/deposits on heated surfaces
  - Temperature
- More targeted, controlled experimental data is required to improve the confidence in thermophysical property correlations

Molten Fluorides Are Highly Thermodynamically and Radiolytically Stable

- Salts are combinations of strongly electronegative elements with strongly electropositive metals
  - Very high bond energies
  - Negative change in Gibbs free energy ($-\Delta G_f$) > 100 kcal/mol-F
  - Structural metal fluorides have Gibbs free energies at least 20 kcal/mol-F less negative
    - MSRE graphite and Hastelloy N exposed to coolant salt was untouched after ~3 years of operation
  - Salt radiolysis is overwhelmed by recombination at operating temperatures

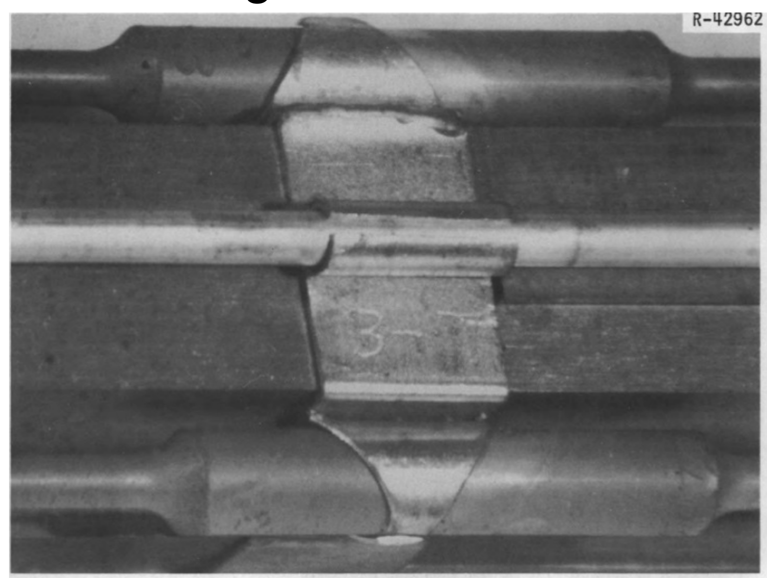


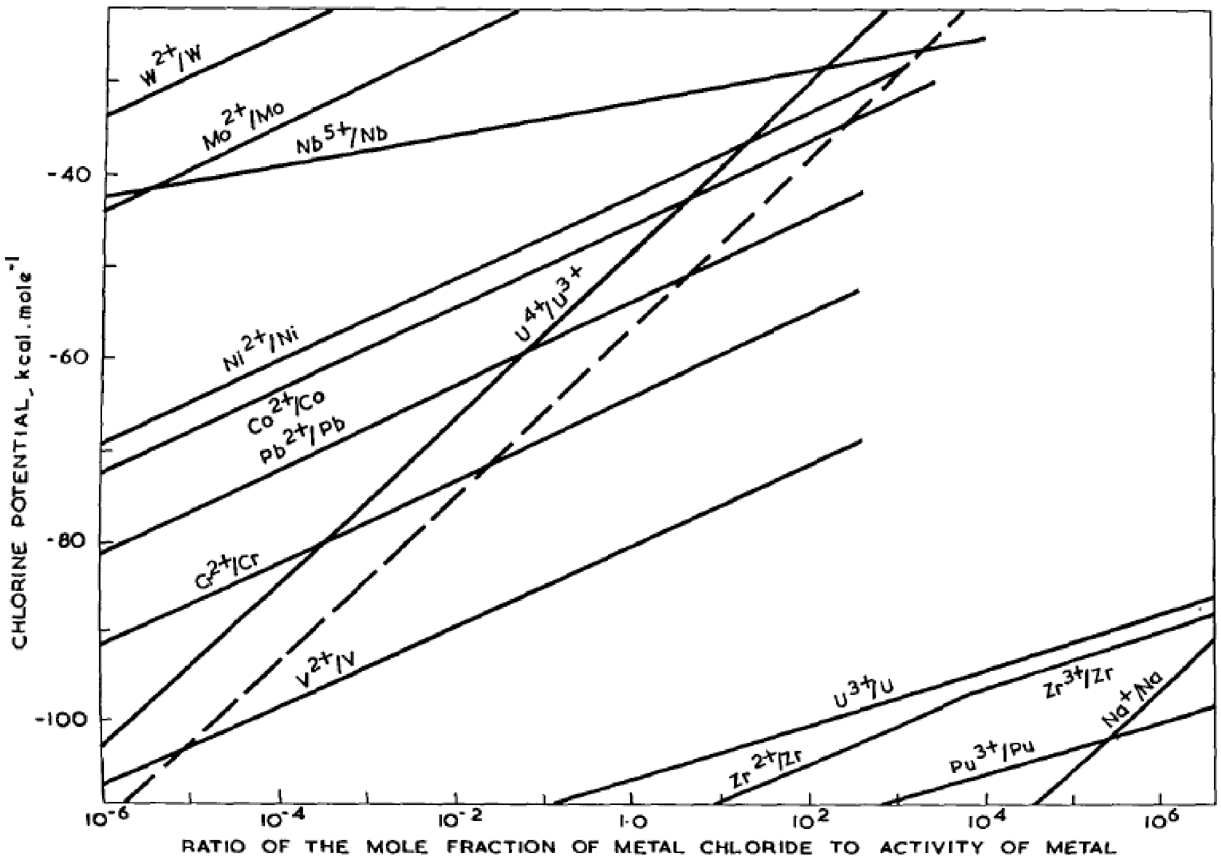
Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

Source: ORNL/TM-4174

Thermochemical Stability Drives Both Corrosion and Fissile Solubility

- Increased free chlorine results in larger amounts of dissolved structural alloy chlorides
- Increasing ratios of UCl_4/UCl_3 restrict acceptable choice of structural alloys
- Use of nickel-based structural alloys restricted to UCl_4/UCl_3 ratios of roughly 0.003 to 5%
  - Smaller amounts of UCl_4 results in disproportionation of UCl_3

    $4UCl_3 \rightleftarrows UCl_4 + U^0$
- Refractory coatings would enable higher UCl_4/UCl_3 ratios



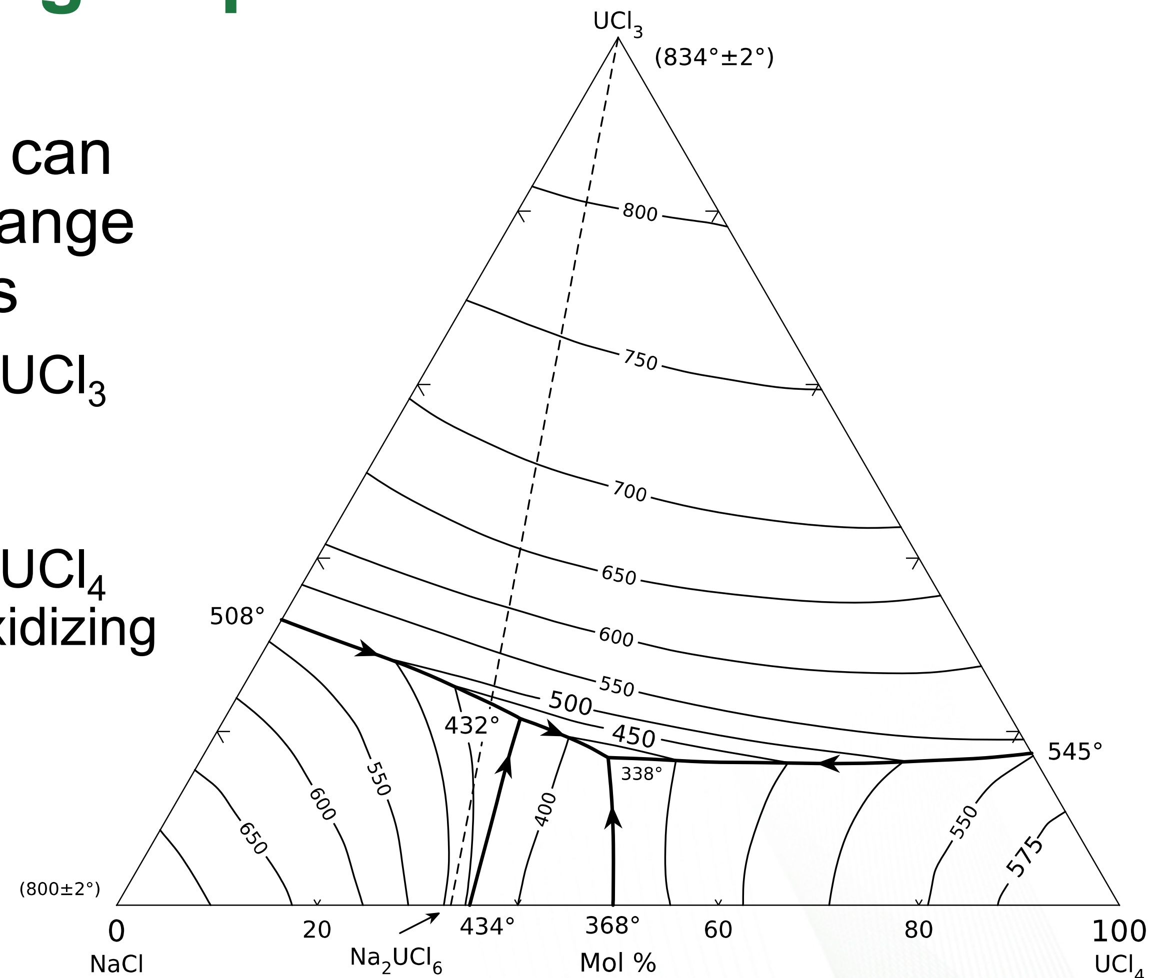
1. Chlorine Potential Diagram at 1000°K.

Source:
Harder, Long, and Stanaway, *Nuclear Metallurgy* 15:405-432, 1969.

- $PuCl_3$ disproportionation is less favorable than that of UCl_3

Phase Diagrams of Chloride Fuel Salts Show Fuel System Design Options

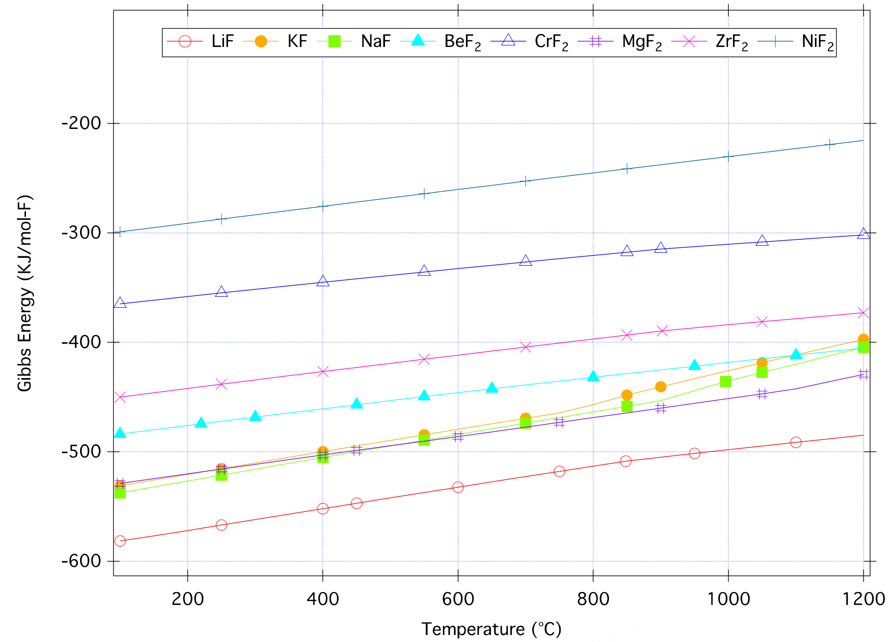
- A ~500°C melt point can be achieved with a range of UCl_3 to UCl_4 ratios
  - Systems with higher UCl_3 fractions have lower uranium loading
  - Systems with higher UCl_4 fractions are more oxidizing (corrosive)



Source: V. N. Desyatnik et al. *At. Energ.*, 31 [6] 631-633 (1971); *Sov. At. Energy* (Engl. Transl.), 31 [6] 1423-1424 (1971). Fig. 05953—System NaCl-UCl4-UCl3

Maintaining Mildly Reducing Redox Conditions Key to Enabling Use of Engineering Alloys

- Use of a circulating redox buffer provides means to maintain redox condition
  - Fission changes oxidation state of salts
- Ratio of U^{4+}/U^{3+} serves as a measure of the redox potential of the salt
  - Applicable to both fluoride and chloride salts
  - Adding beryllium to FLiBe
- Fluoride salts will likely have an ideal ratio of ~10–100



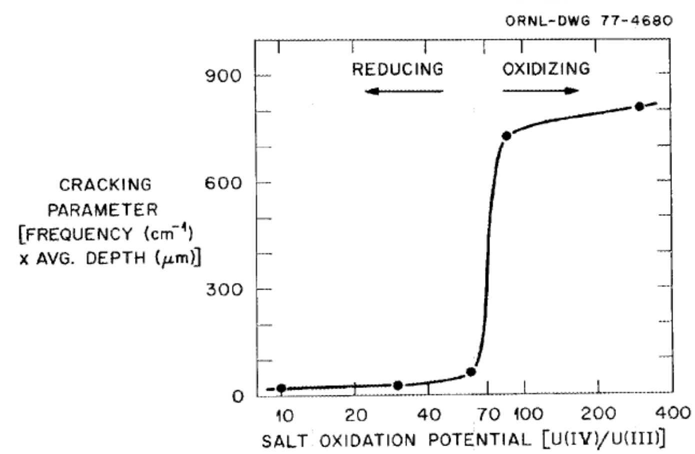


Fig. 12. Cracking Behavior of Hastelloy N Exposed 260 hr at 700°C to MSBR Fuel Salt Containing $CrTe_{1.266}$.

Source:
Baes,
Keiser, ORNL/TM-6002

Fission Process Continuously Alters the Fuel Salt Redox Conditions

- When a U or Pu ion fissions, the available electrons will rearrange on each fission product to satisfy its valence requirements and produce either net oxidizing or reducing conditions in the melt
  - For ^{235}U (as UF_4) four F ions are released. The fission products require less than four and thus there will be an excess of F ions with net oxidizing conditions
  - For ^{239}Pu (as PuF_3) three F ions are released. The fission products require more than three and thus there will be a F ion deficit with net reducing conditions
- MSRE periodically added metallic beryllium (strong reducing agent) to maintain UF_4/UF_3 ratio

Salt Type	Fission Product	Oxidation State (Z)	Yield (Y) [atoms]	Cl atoms reacted (Y*Z)
Chloride Salt (UCl_3)	Kr, Xe	0	25	0
	Rb, Cs	1	19	19
	Sr, Ba	2	10	20
	Rare Earths	3	46	138
	Zr	3	22	66
	Nb, Mo	0	2	0
	Te, I	0	6	0
	Pd, Re, Rh Ag, Cd	0	61	0
	Total Cl atoms reacted out of 300 available			243
Fluoride Salt (UF_4)	Br, I	-1	1.5	-1.5
	Kr, Xe	0	60.6	0
	Rb, Cs	1	0.4	0.4
	Sr, Ba	2	7.2	14.4
	Lanthanides, Y	3	53.8	161.4
	Zr	4	31.8	127.2
	Nb	0	1.4	0
	Mo	0	20.1	0
	Tc	0	5.9	0
	Ru	0	12.6	0
	Total F atoms reacted out of 400 available			301.9

Sources: Baes (fluoride salts), Harder (chloride salts)

Because Chemical Activity in Molten Salts Is Controlled by Melt Composition…

- Monovalent salts are “basic” in that they supply fluoride ions (F^-)
- Polyvalent salts are “acidic” in that they form complexes with F^-
- Lewis acid/base coordination equilibria are established
  - $ZrF_4 + 3F^- \leftrightarrow ZrF_7^{3-}$
  - $BeF_2 + 2F^- \leftrightarrow BeF_4^{2-}$
- The chemical reactivities of these and other metal ions are higher when they are not sufficiently coordinated with fluoride ions
- In the absence of the extra fluoride ions supplied by LiF component, for example, ZrF_4 and BeF_2 would be volatile and distill from the system

Fission Products and Contaminants Would Alter Fuel Salt and Cover Gas Properties

- Oil leak along MSRE pump shaft resulted in foaming in pump bowl
  - Foam overflowed into gaseous waste handling system
- Noble fission products do not dissolve into salt and consequently lack a surface tension inhibition for entering cover gas (i.e., they readily enter the cover gas)
- Contamination particles, solid oxide precipitate, etc., may form a scum layer on the salt surface

Source:
Yoder et al., ORNL/TM-2014/499

Fluoride Salts Are Vulnerable to Radiolytic Decomposition at Low Temperatures

- Intense radiation creates more free fluorine than is recombined below ~200°C
- Experience with chloride salts is almost nonexistent
  – Likely has similar vulnerability as fluoride salts
  – Pyroprocessing salts and conditions are different from fuel salts
- Free fluorine can react with structural materials resulting in dramatically increased corrosion or converting solid UF_4 to gaseous UF_6
  – Origin of the issue with the stored MSRE fuel salt in the 1990s

Source:
Haubenreich, ORNL-TM-3144, 1970

Long Term Waste Forms from MSRs Remain Unproven

- Primary US work remains “Applied Technology”
- Offgas sorbent could serve as ultimate fission gas disposal medium
  - Charcoal beds were employed for MSRE
- May be possible to make fluorides more stable by conversion to a fluorophosphate
- Chlorides are currently converted to a *salt-cake* waste form as part of the ongoing EBR-II processing campaign
- Synthetic rock process developed by ANSTO appears applicable
- Dutch SALIENT project has primary objective to develop final waste form for their test salts

Characteristics of MSRs Derive from the Chemistry and Physics of Halide Salts

- Low pressure, high temperature operation
- Dissolve useful amounts of fissile material
- Chemically compatible with engineering alloys in mildly reducing environments
- Strong passive safety features
  - Negative reactivity feedback
  - Natural circulation-based decay heat removal
  - Reduced potential for radionuclide release
- Fluoride salts have substantially more experimental data than chloride salts for reactor operations
- Tritium production from lithium-bearing salts can be mitigated by stripping, blocking, and trapping