Module 4: Salt Heat Transfer and Processing

David E. Holcomb, Ph.D.

Nuclear Energy and Fuel Cycles Division

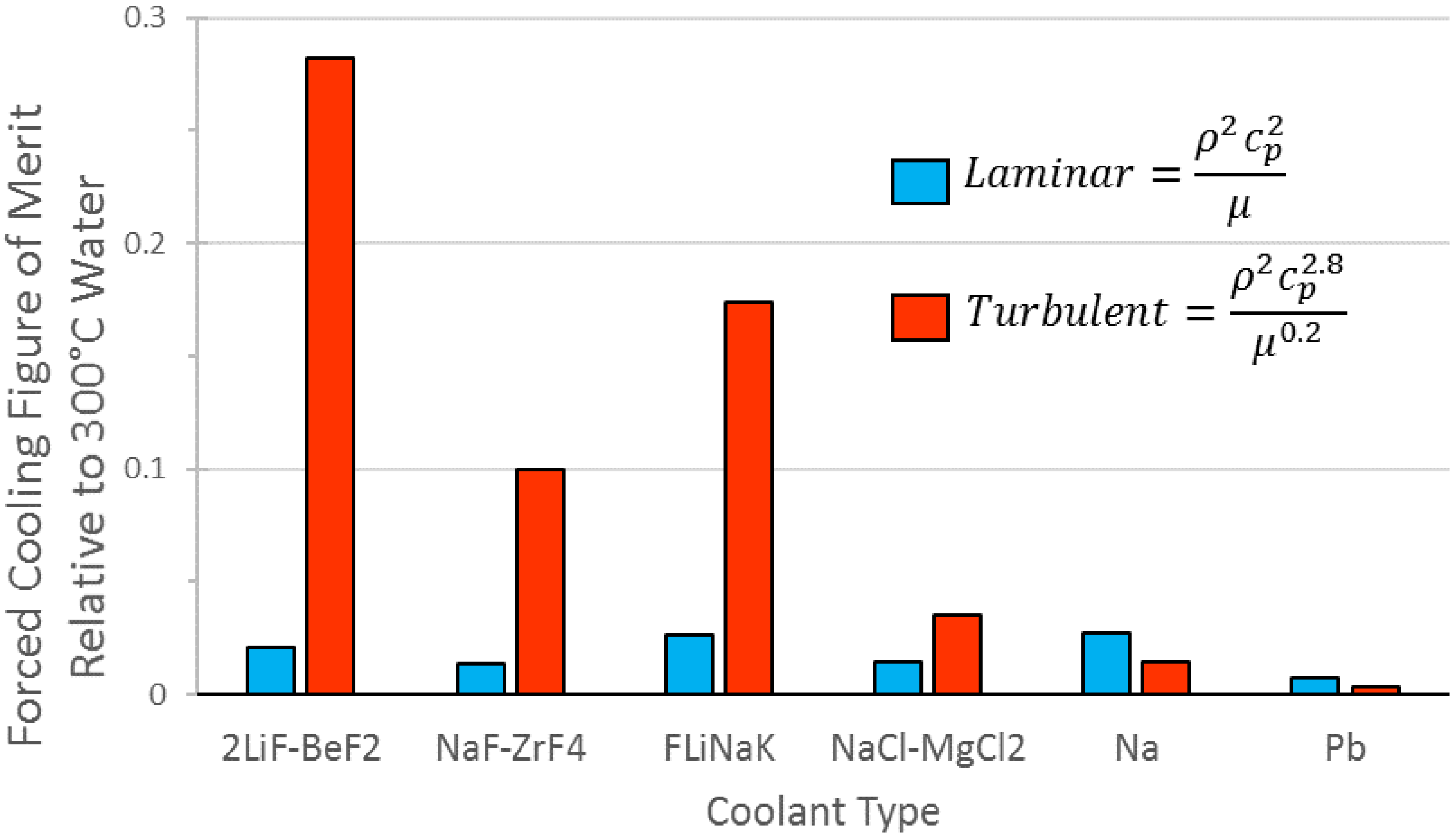
November, 2022

Molten Salts are Both the Nuclear Fuel and Primary Heat Transfer Medium in Liquid-Fuel MSRs

- Module includes
  1. Overview of the heat transfer and fluid flow aspects of molten salts
  2. Current technology status of fuel salt chemical and physical processing
     - Broadly addresses operational and fuel cycle aspects of processing throughout the plant lifecycle
     - Waste stabilization addressed in later waste module

- Some fuel salt processing technology elements have been rapidly advancing
  – Low technology readiness levels (TRLs) necessitate higher degree of speculation

Molten Salts Have Attractive Forced Convection Heat Transfer Properties

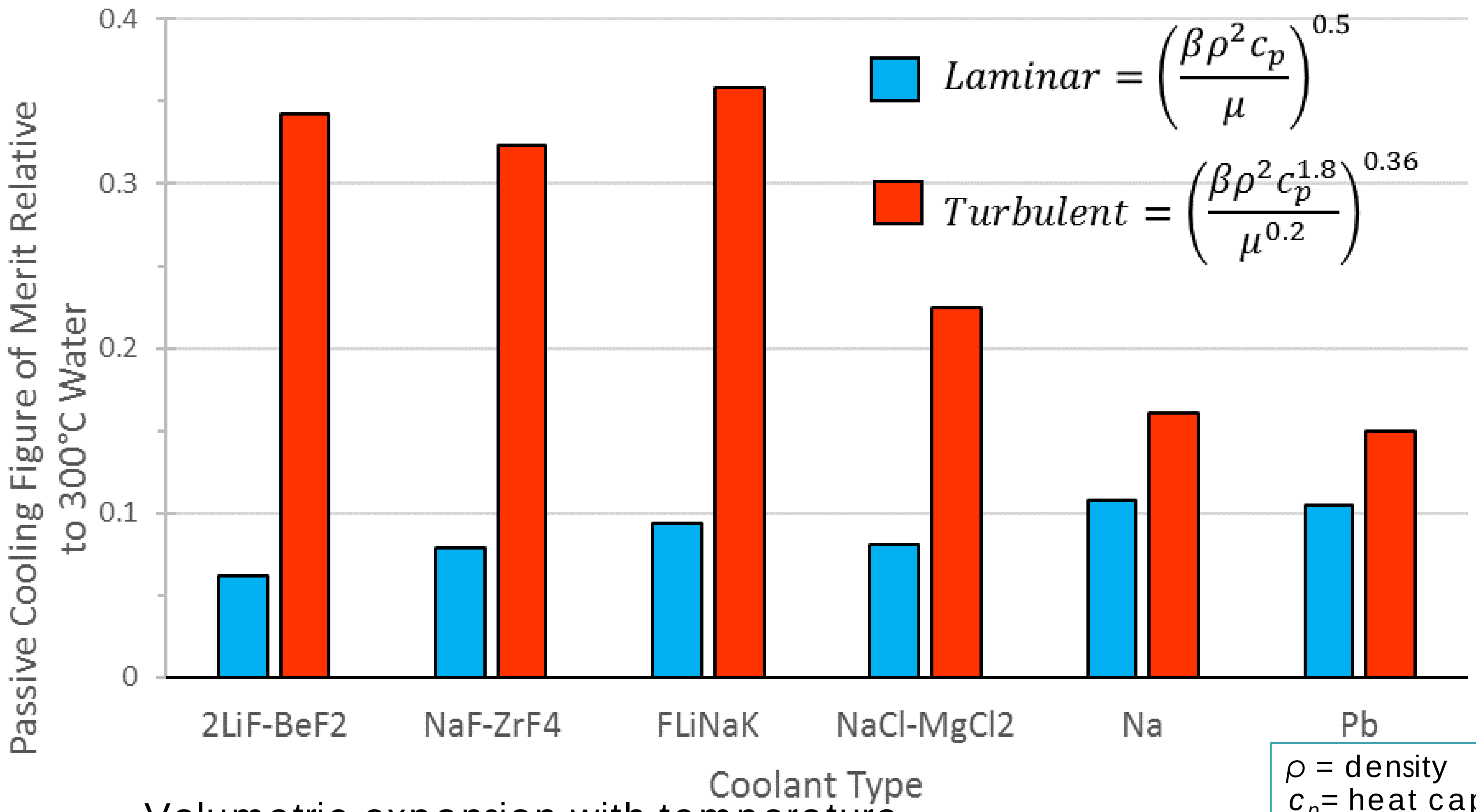


- Large heat capacity and low viscosity are key properties

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

Source:
Nuclear Engineering Handbook – Etherington 1958; 9-90,
D. F. Williams et al., ORNL/TM-2006/12

Molten Salt Passive Cooling Characteristics are Favorable

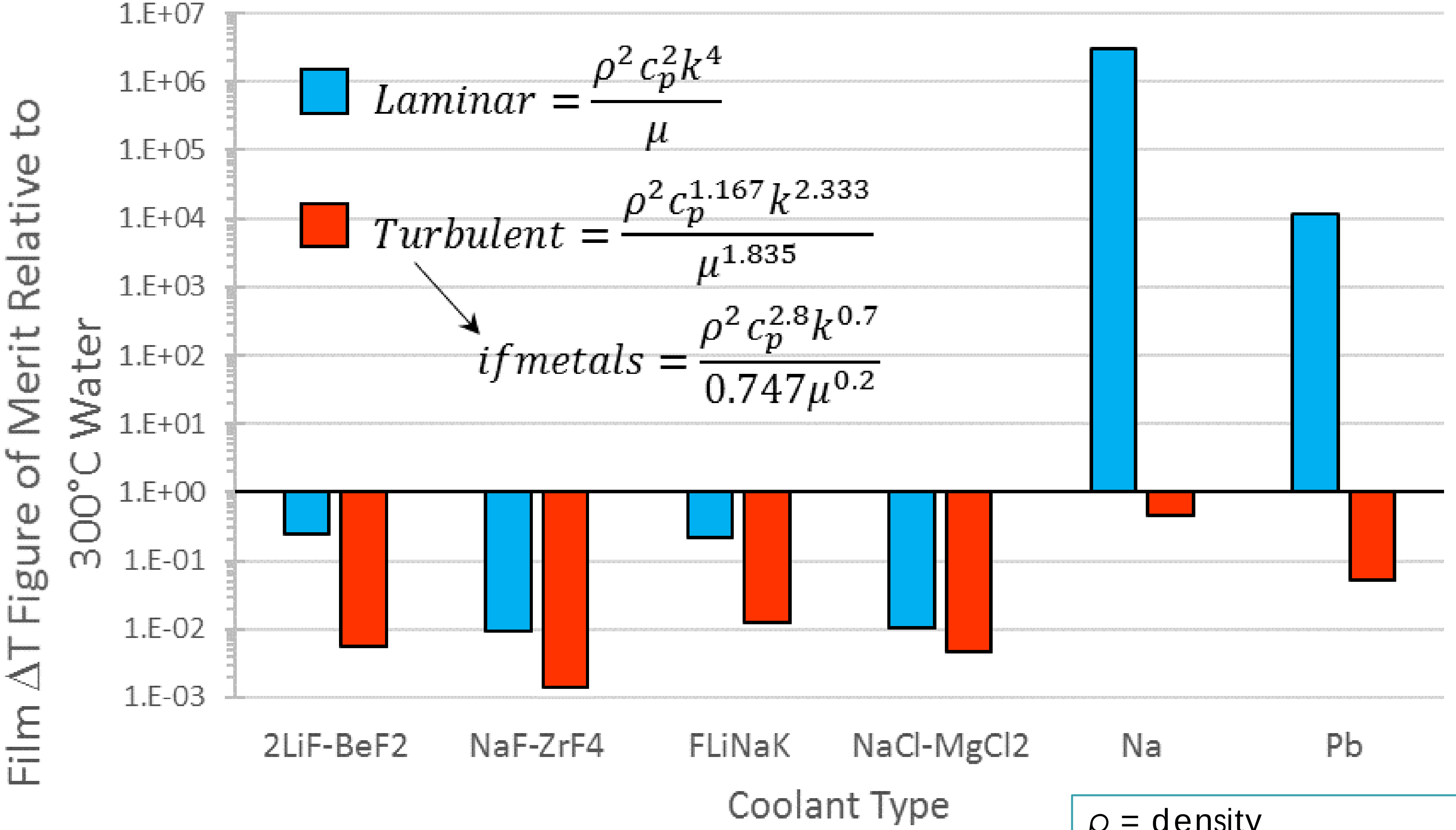


ρ = density
c_p= heat capacity
μ = dynamic viscosity
β = volumetric expansion coefficient

- 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)

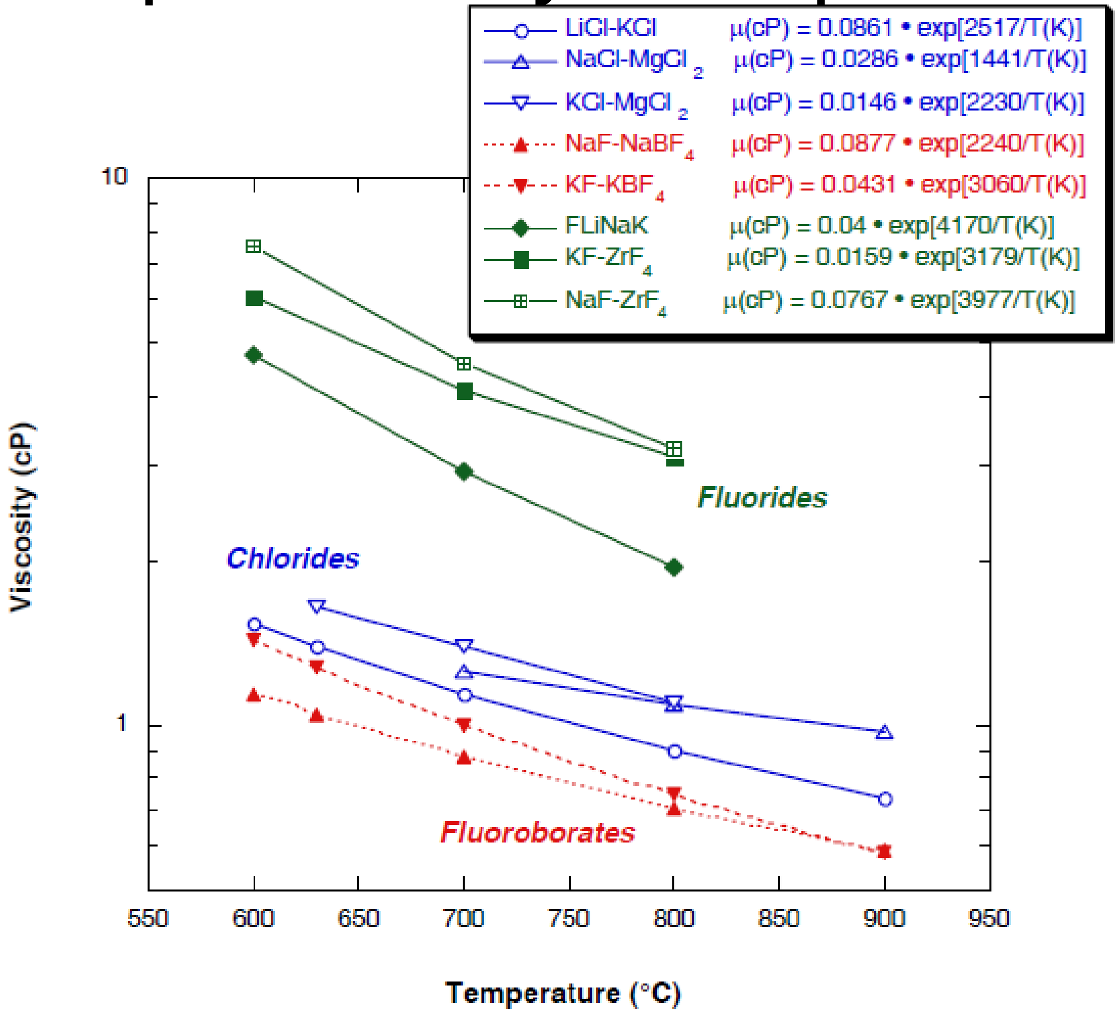


- Turbulence is required for effective heat transfer (or tritium stripping)

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

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

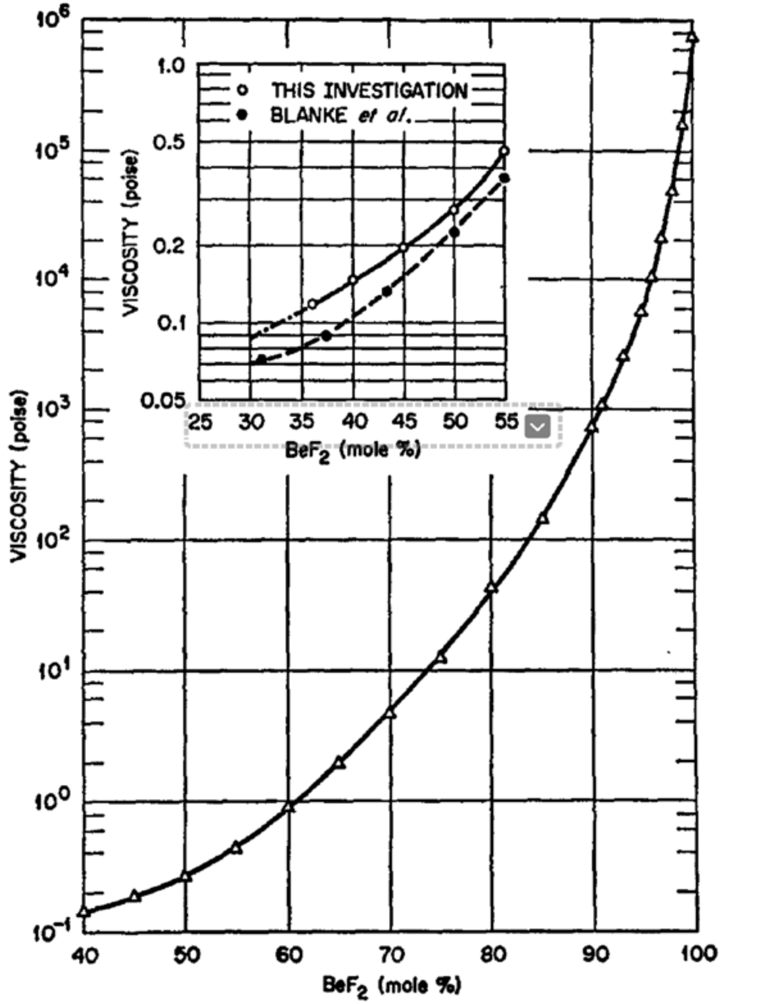
Salt Viscosity Decreases with Temperature and is Strongly Impacted by Composition



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

- Flow increases to hotter regions
- Improves temperature uniformity
- Increasing BeF_2 content
  - Lowers melt point
  - Substantially increases viscosity

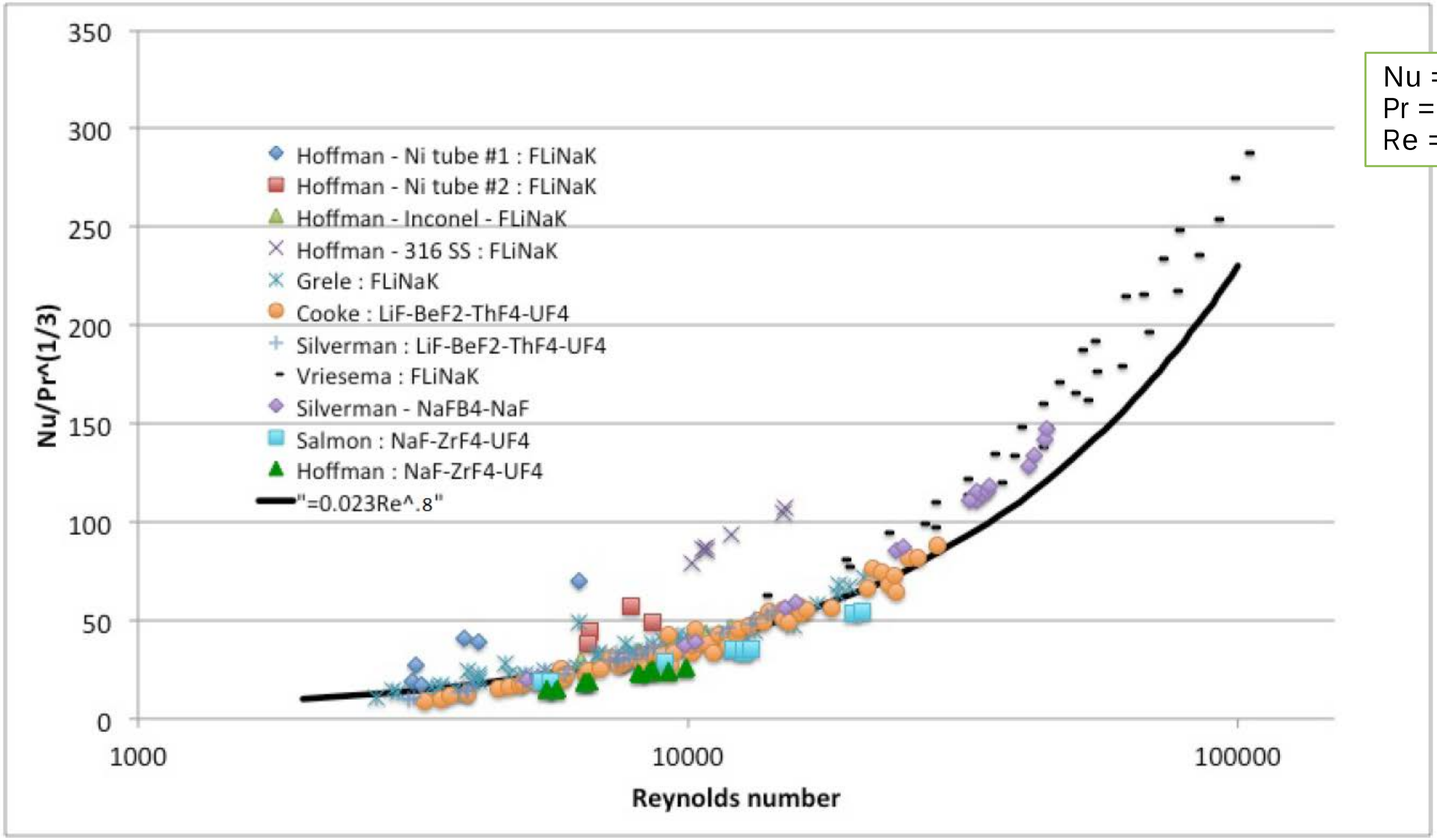
Variance in Viscosity of $LiF\text{-}BeF_2$ at 600 °C with Composition



S. Cantor et al, DOI: 10.1063/1.1671478

OAK RIDGE National Laboratory

Significant Uncertainty Remains in Fluoride Salt Turbulent Heat Transfer

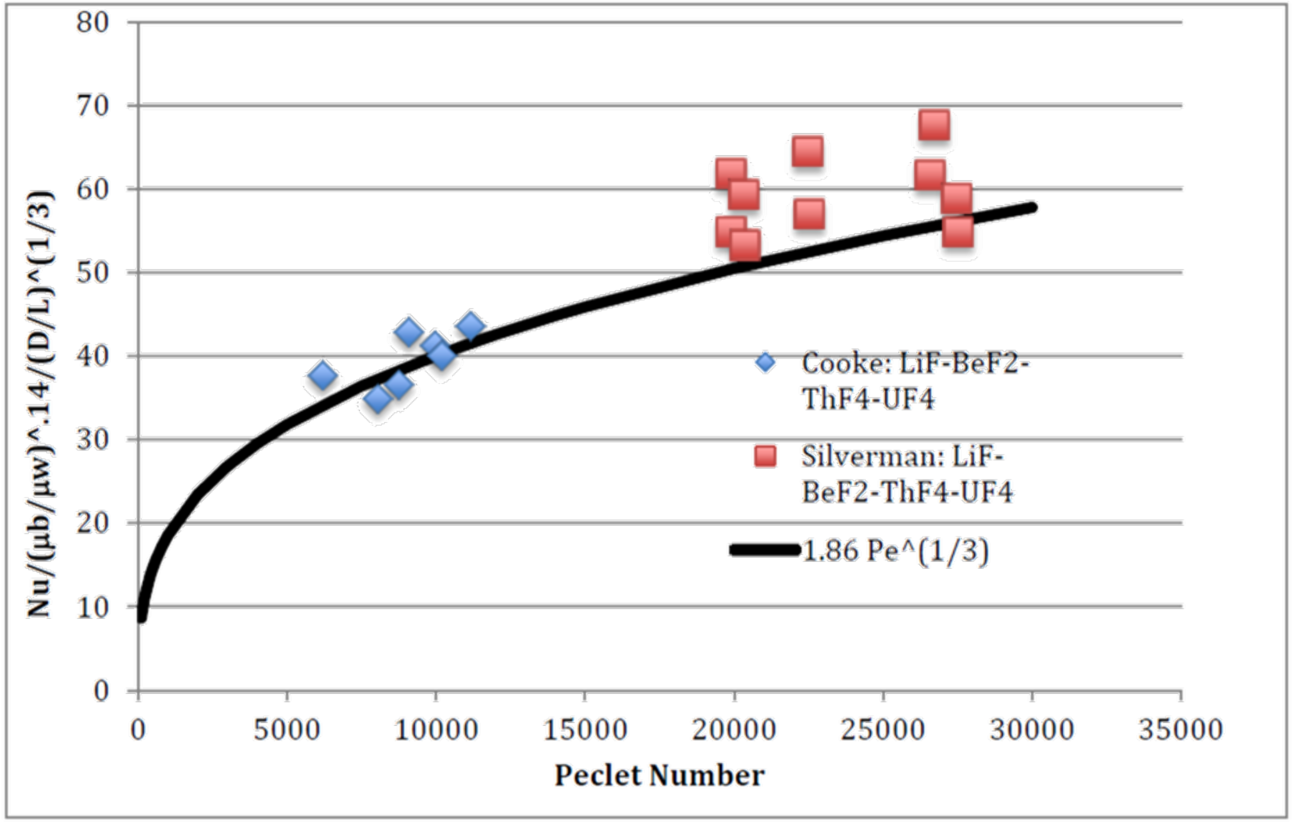


Nu = Nusselt number
Pr = Prandtl number
Re = Reynolds number

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

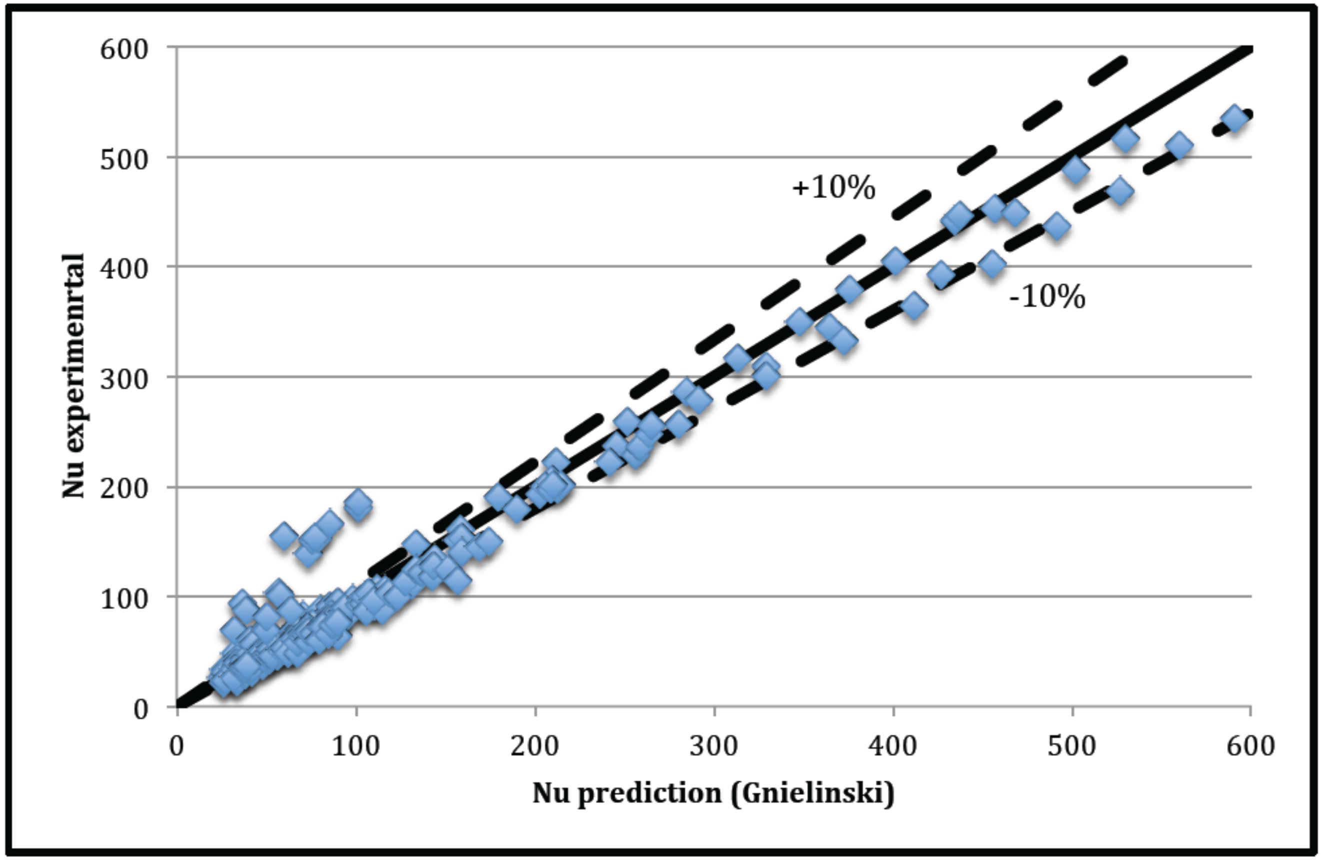
Laminar Flow Heat Transfer Also Has Significant Remaining Uncertainty



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

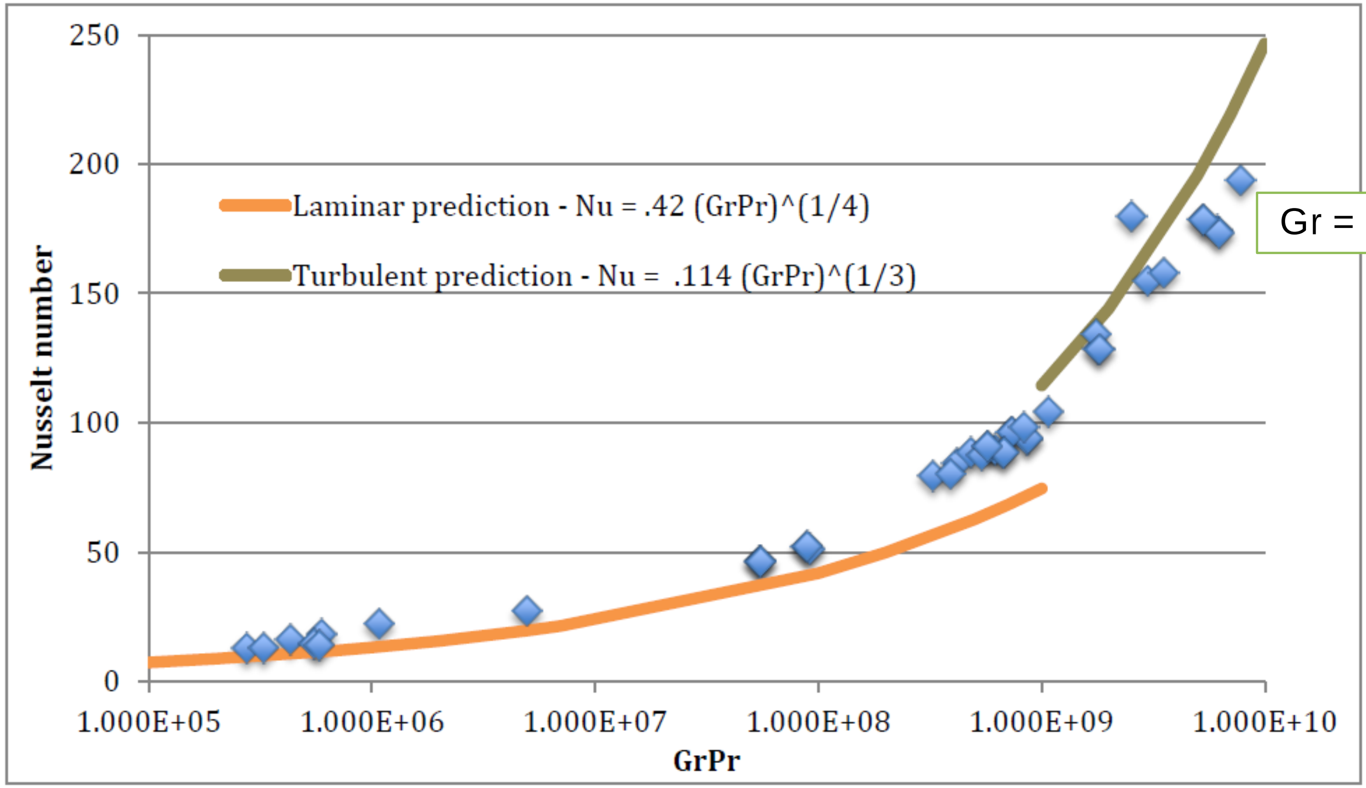
Significant Remaining Uncertainty in Prediction of Conductive / Convective Heat Transfer Ratio



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

Natural Circulation Heat Transfer Has Significant Remaining Uncertainty



Gr = Grashof number

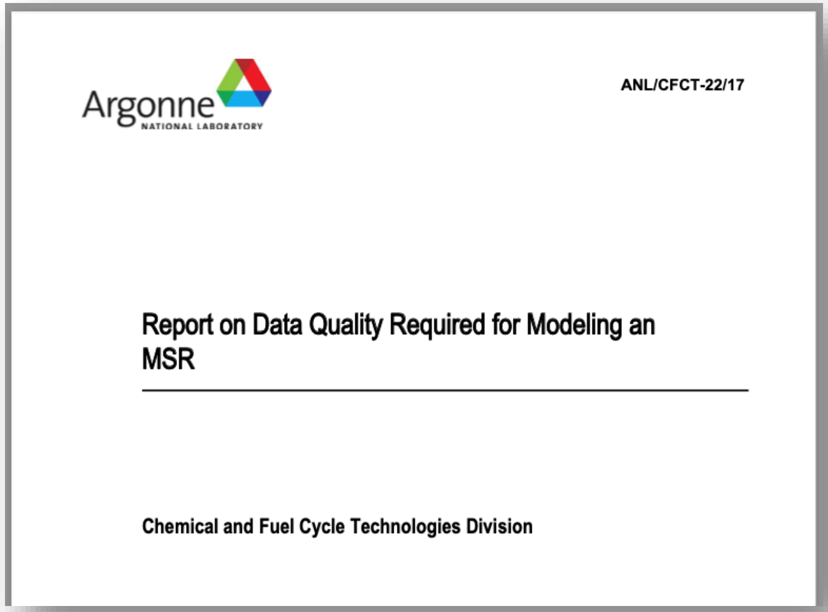
Source:
Yoder,
ICAPP 14332, 2014

- 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

OAK RIDGE
National Laboratory

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


Argonne NATIONAL LABORATORY

ANL/CFCT-22/17

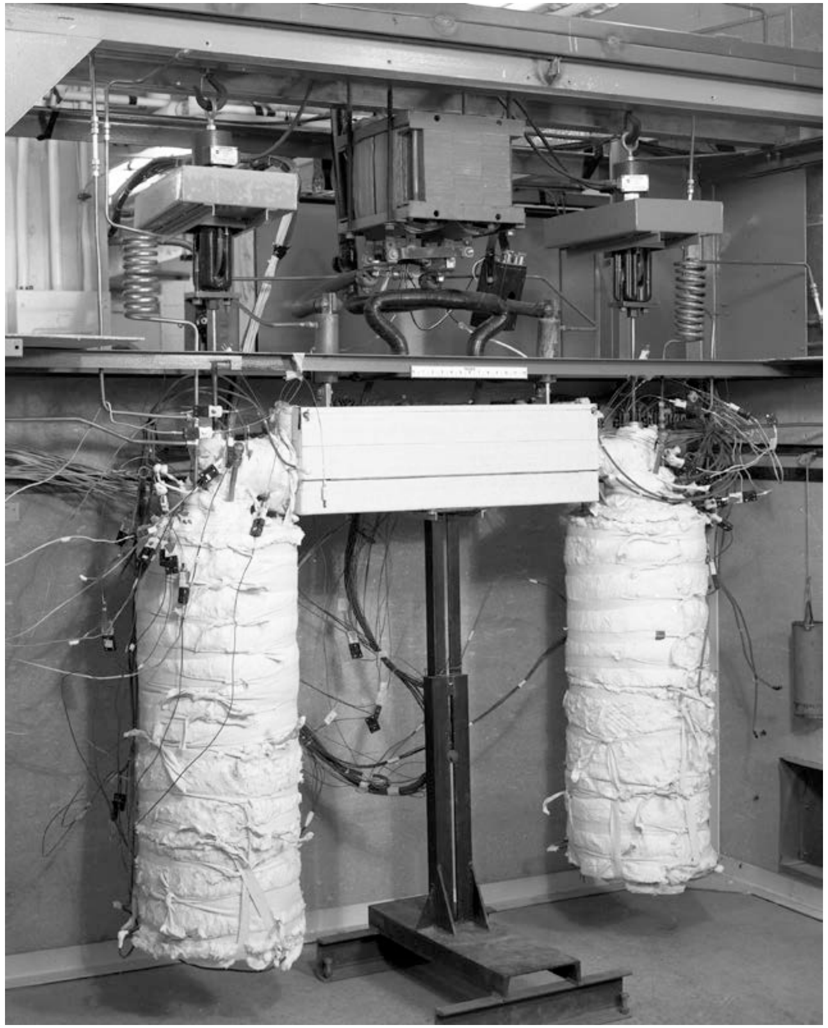
Report on Data Quality Required for Modeling an MSR

Chemical and Fuel Cycle Technologies Division

MSR campaign activities include evaluating impact of fuel salt property data uncertainties

Heat Transfer Characteristics for Fuel Salt Have Been Experimentally Determined

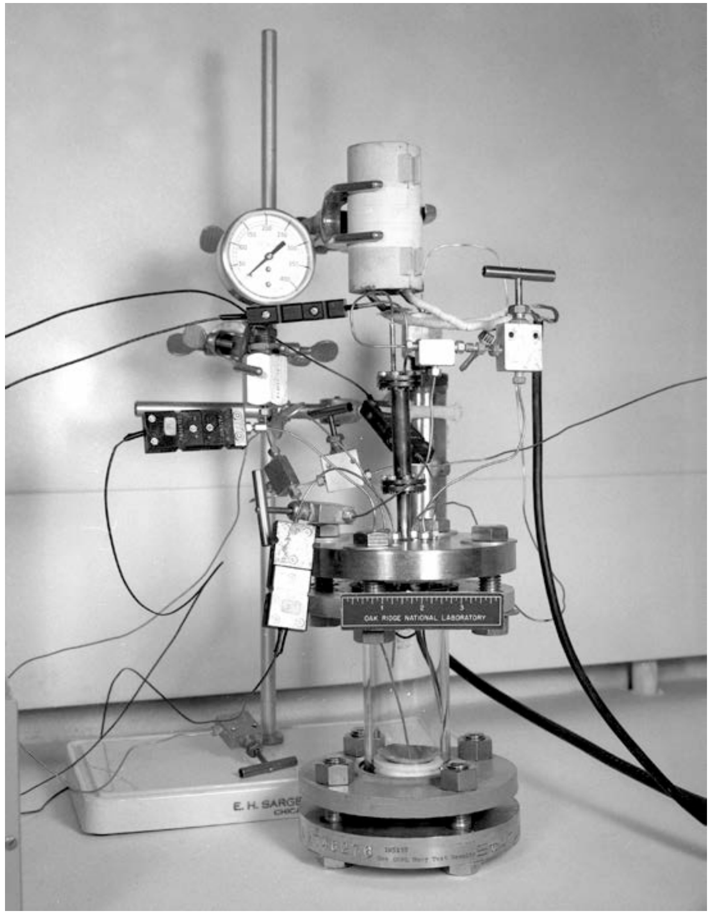
- Two-tank forced flow system
- Measured weight and temperature change under different temperature and flow regimes
- Developed heat transfer correlations
- Demonstrated well behaved heat transfer properties
  - No formation of low-conductance surface films
  - Salt adequately wetted metal surfaces
- Similar apparatus previously employed for sodium hydroxide, nitrate salts, and non-fuel fluoride salt



ORNL Photo 76387
ORNL-TM-4079 – Figure 2

Interaction of Hot Fuel Salt With Water Was Experimentally Verified

- Few grams of fuel salt – LiF-BeF_2-ZrF_4-ThF_4-UF_4; 70-23-5-1-1 mole %) heated and injected into water
- Resolidified salt had an ”exploded popcorn” appearance
- Finely divided droplets of salt found sprayed on the chamber walls and top
- No marked pressure increases
- Only small quantities of oxides or HF detected



Salt Jet Apparatus
ORNL Photo 56520

Fuel Salt Processing Has Multiple Purposes Throughout an MSR's Lifecycle

- Fuel salt synthesis
  - Recover actinides from used LWR fuel
- Minimize corrosion and erosion
  - Filtering suspended solids, remove oxygen, redox control
- Recover medical isotopes
- Parasitic neutron absorber removal
  - ^{135}Xe
- Maintain adequate fissile solubility and minimize neutron poison content
  - Remove lanthanides
- Facilitating breeding especially in Th/U fuel cycle
  - Enabling ^{233}Pa to decay in low-flux environment
- Stabilize wastes

Actinide Oxides from Used Water Reactor Fuel Can Be Converted to Chloride or Fluoride Forms

- Multiple prospective MSR vendors have proposed obtaining their fissile material from used water reactor fuel
- Synthesis is likely to be performed near the used water reactor fuel storage to minimize transportation challenges
  - MSR may be located nearby
- Halide salt chemistry knowledge has markedly increased over the past few decades
  - Likely processes unknown in the first MSR era
- Processing is less likely for the existing US fleet due to the historic US government responsibility to dispose of used LWR fuel
  - Nuclear Waste Policy Act of 1982 establishes the generator's responsibility to bear the costs for permanent disposal – subsequent reactors more likely to recycle

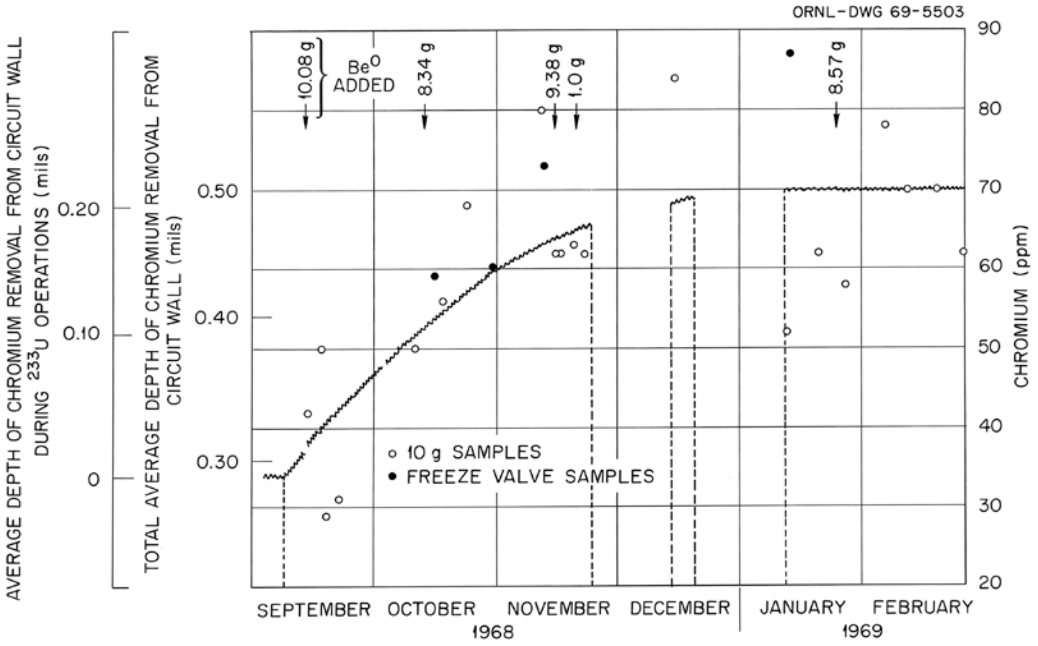
Illustrative Examples - Conversion of Actinide Oxides to Chlorides or Fluorides

- Actinide and rare earth oxides can be converted to chlorides using $ZrCl_4$ in a chloride salt bath (Sakamura et al, 2005)
- Actinide chlorides can then be separated from rare earth chlorides via constant current electrorefining onto a solid aluminum cathode (Conocar, et al, 2005)
- Actinide metals could then be dissolved into barren fuel salt along with chlorinating or fluorinating agent (e.g., ammonium bifluoride or ammonium chloride)
  – LANL developed organo-metallic processes also possible for synthesizing UCl_3 from uranium metal (Monreal, et al, 2011) – licensed for commercial fuel salt production
- Non-aqueous organic routes for direct conversion of UO_2 to UF_4 have recently been demonstrated (Joly et al, 2020)

Fuel Salt Polishing Decreases Corrosivity and Erosivity of Fuel Salt

- Fuel salt polishing indicates conditioning processes likely to be performed on-line
- Common impurities that negatively affect structural materials are oxides, hydroxides, moisture, and sulfur
- Adjusting fuel salt redox via contacting with active metal and/or via applied voltage (cathodic protection)
- Oxygen removal – likely on a side stream (e.g., via carbochlorination)
- Mechanical filtering – suspended particles (e.g., ZrO_2)
  - Floatation – attachment of particles to gas bubbles
- Tritium removal – (e.g., via contacting fuel salt with a compatible physical or chemical trap)

Impact of beryllium additions on chromium content of MSRE fuel salt

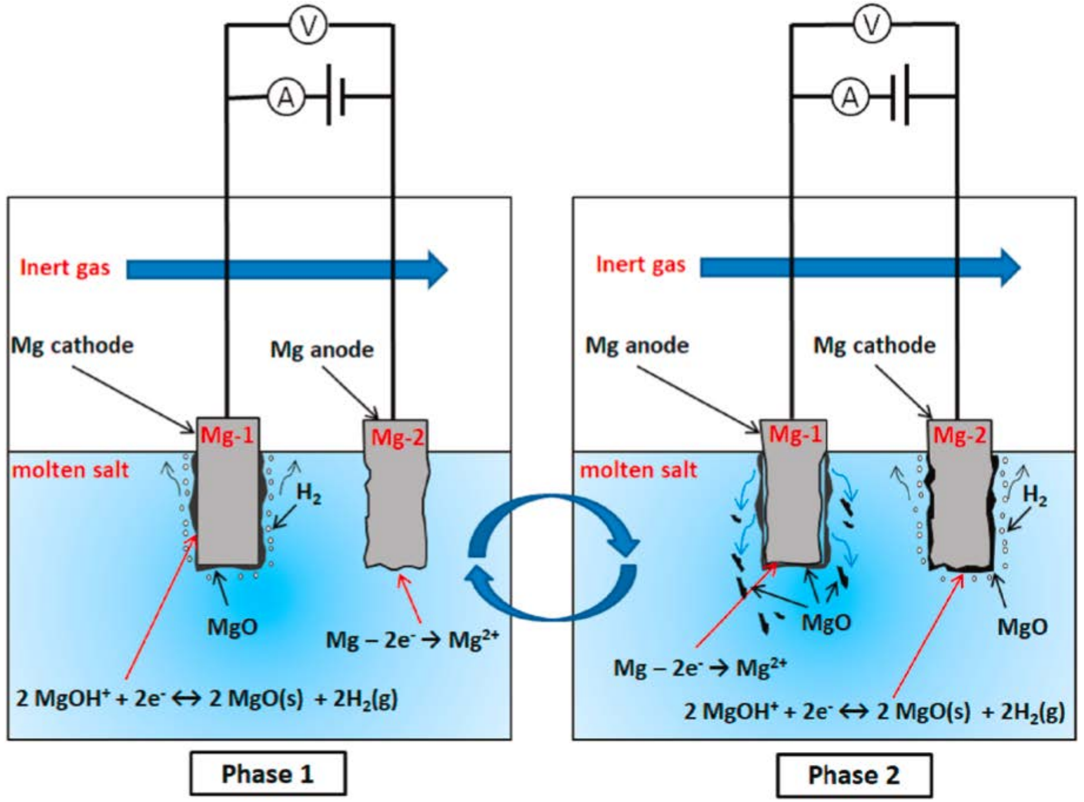


ORNL-4658

OAK RIDGE National Laboratory

Cathodic Protection and Active Metal Contacting Have Recently Been Combined to Minimize Corrosion

- Cathodic protection employs electrical bias to inhibit corrosion reactions
  - Demonstrated at low maturity for both fluoride and chloride salts
  - Widely used in some industries
- Solar thermal storage researchers (Ding, et. al. - 2021) have recently combined cathodic protection with active metal contacting for chloride salts
  - Oxygen precipitated out as MgO
  - Hydrogen released to cover gas



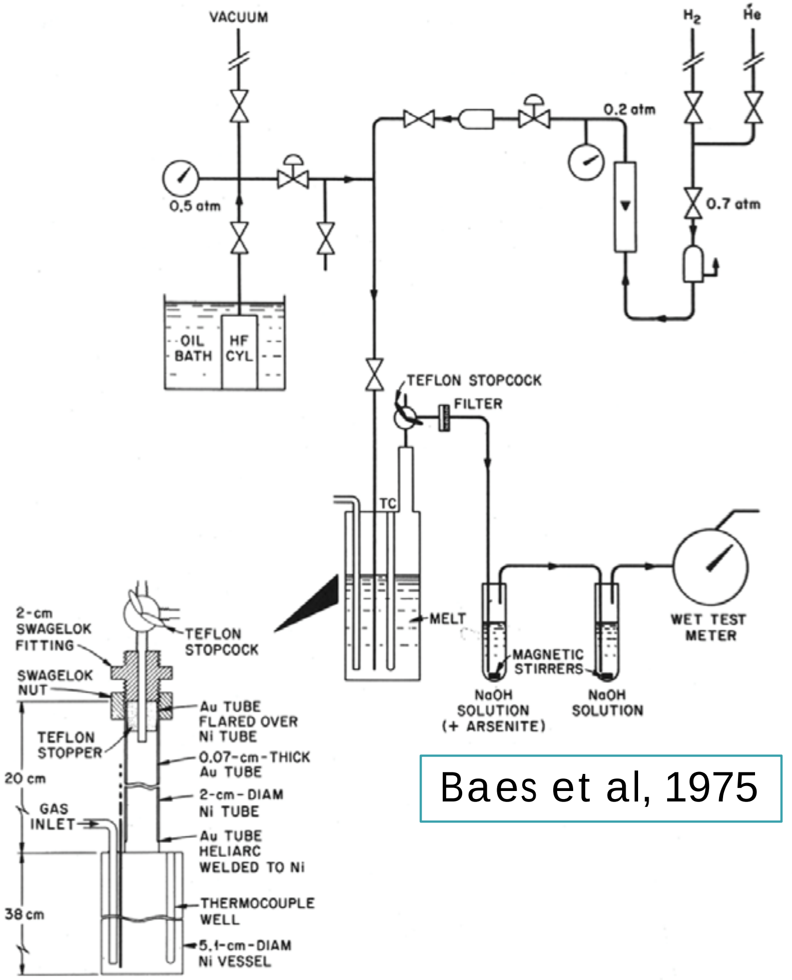
Ding, et. al. - DOI: 10.1016/j.solmat.2021.110979

Fuel Salt May Be Processed to Recover Short-Lived Radioisotopes

- Molybdenum-99 has a large fission yield ~6.1%
  - MoF_6 boiling point – 34 °C
  - $t_{1/2} \approx 66$ h
  - Separated via fluorination
  - Salt re-oxidized
- Xenon -133
  - Separated from fission gas stream
  - $t_{1/2} \approx 5.25$ d
  - Cryogenic distillation or metal-organic frameworks for separation

Xenon-135 and Parent Isotope Removal Would Improve Thermal Spectrum MSR Neutron Efficiency

- Xenon-135 ($t_{½}$ ≈ 9.1 h)
  - Small direct fission yield
  - ~95% from decay of parent isotopes
- ^{135}Te ($t_{½}$ ≈ 19 s) -> ^{135}I ($t_{½}$ ≈ 6.57 h) -> ^{135}Xe
- Stripping method proposed by historic MSR program shifts the redox of a side stream to form volatile HI
  - HF-H_2 sparge
- Also strips ^{129}I ($t_{½}$ ≈ 1.57×10^{7} y) and ^{131}I ($t_{½}$ ≈ 8 day)



Baes et al, 1975

Schematic for stripping iodine from fuel salt

Accumulation of Soluble Fission Products Will Eventually Degrade Fuel Salt Characteristics

- No technology is currently available for selectively removing fission product halides from fuel salt
  - Likely to strip actinides first and then remove fission products
- Particular fuel salt parameter that would first degrade sufficiently to violate technical specifications depends on the reactor
  - Actinide solubility may be limiting characteristic for fast spectrum systems
  - Heat transfer characteristic (e.g., heat capacity or density) may be limiting for thermal spectrum systems
- Multiple different methods are possible for stripping fission products from actinide free halide salts
  - None are at a level to technical maturity suitable for immediate use under reactor conditions
  - DOE MSR campaign provided a technical overview of the technologies in 2018 (PNNL-27723)
  - Zone refining (melt crystallization), oxidative precipitation, vacuum distillation, reactive distillation, and reductive extraction have all been proposed and demonstrated at varying maturity levels

Actinides Can Be Separated From Used Fuel Salt

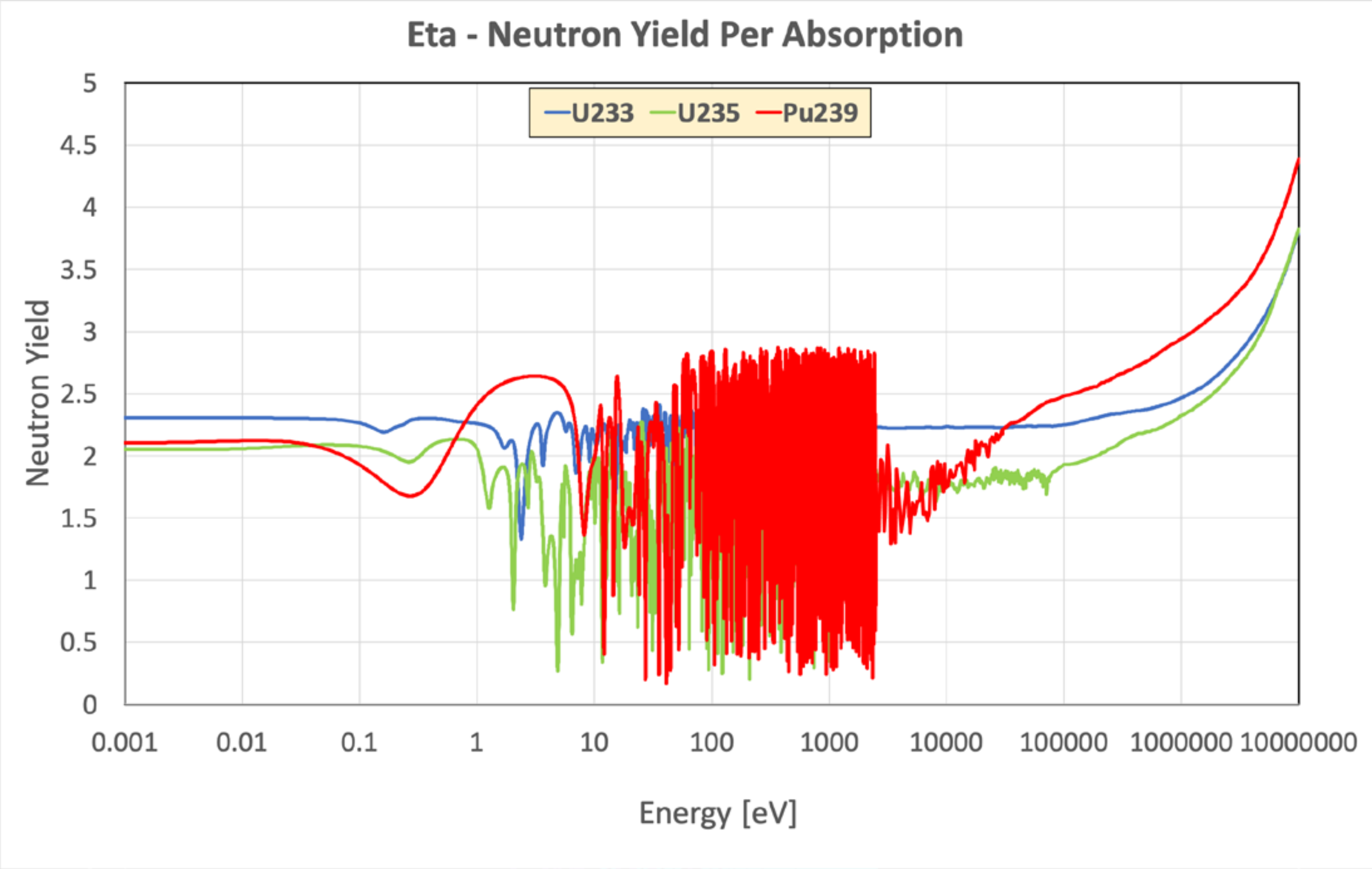
- Key consideration is avoiding technologies that would enable creating a separated stream of fissile material more attractive than LEU
  - US currently lacks a definition of LEU that includes isotopes other than ^{235}U and ^{238}U
  - Section 103 b of the AEA indicates that the NRC shall issue commercial licenses to persons whose proposed activities *will serve a useful purpose proportionate to the quantities of special nuclear material or source material to be utilized*
  - Properties of the uranium isotopes directly impact quantities of special nuclear material and source material necessary to achieve useful purposes

- Actinide separation technologies for MSR fuel salts that do not enable creation of attractive material have been demonstrated at low maturity levels

> …the previous emphasis has been on breeding performance and low fissile inventory to help limit the demand on nonrenewable natural resources (uranium) in an expanding nuclear economy; little or no thought has been given to alternative uses of nuclear fuels such as proliferation of nuclear explosives. - ORNL/TM-6413 J.R. Engel et al.

Fast Spectrum MSRs Requires Less Intensive Fuel Salt Processing for Neutronic Efficiency

- Neutron yield per absorption increases rapidly with neutron energy above 100 keV
  - Key design objective is to harden the neutron spectrum
- Designs balance salt melting temperature against actinide contents
  - Fast spectrum fuel salts tend to have higher melting temperatures
- Parasitic neutron absorption is primarily at thermal energies
- Fast spectrum MSRs have few thermal energy neutrons



Eta for ^{239}Pu is above 2.5 from ~1-7 eV
Epithermal U/Pu MSR breeder is also possible

Data from ENDF/B-VIII.0

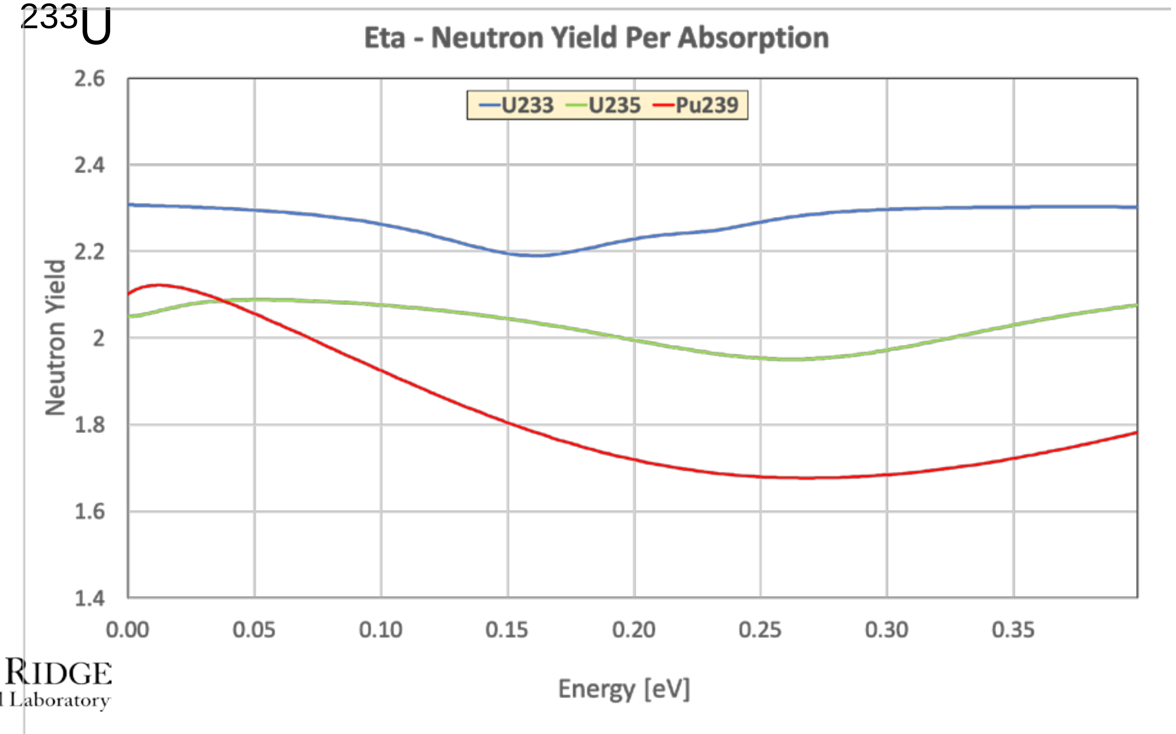
OAK RIDGE National Laboratory

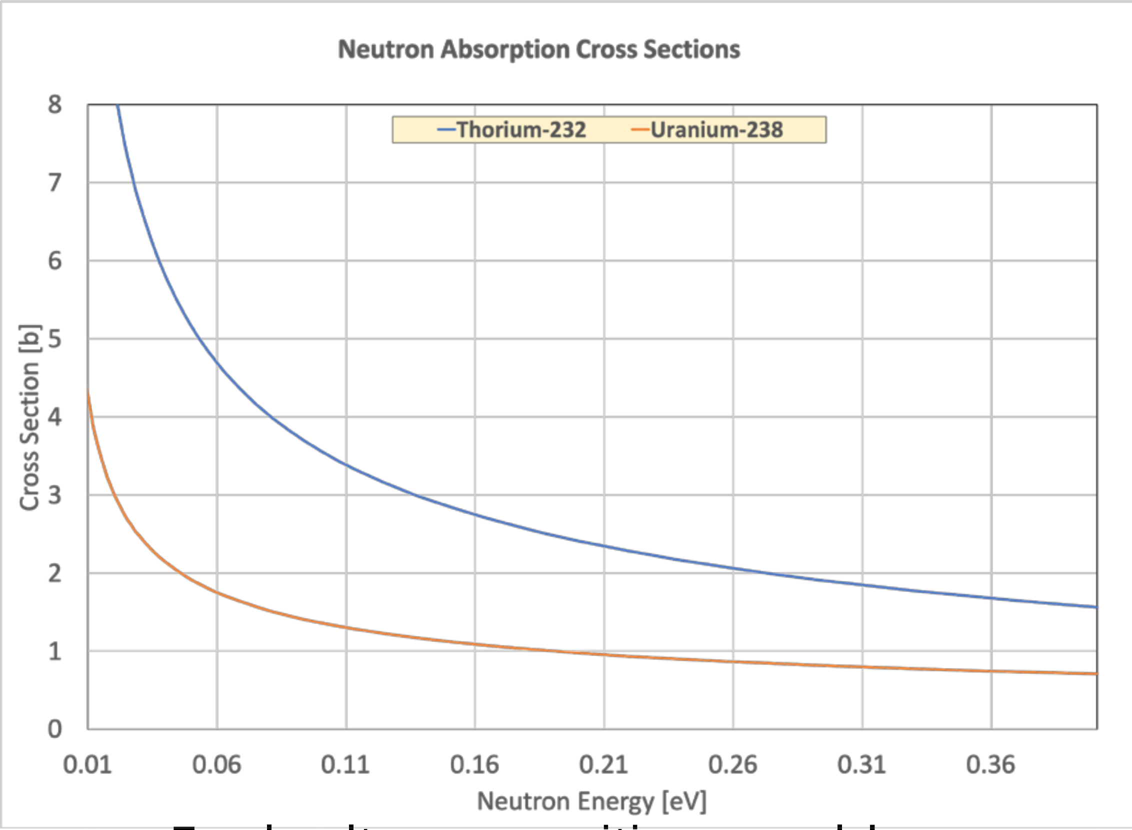
Denaturing and Co-separation Are Key Elements to Avoiding Creation of Attractive Material

- Denaturing (i.e., adding sufficient non-fissile isotopes (e.g., ^{238}U) such that the fissile material would remain LEU) is an element in avoiding attractive material
  - Technique employed by nearly all thermal spectrum reactors
  - Not compatible with a pure Th/U fuel cycle
- Co-separation of all the actinides avoids unacceptably increasing material attractiveness during processing
  - Thermal spectrum MSRs efficiently fission fissile materials resulting in development of high burnup isotope distributions
  - Co-separation has previously been proposed (e.g., in aqueous processing) as a useful means to limit material attractiveness

Blended Th/U and U/Pu Fuel Cycle Can Result in Breeding Gain With Th and U_{nat} as Fertile Feeds

- ^{232}Th absorption cross section is larger than ^{238}U absorption cross section at low energies
  - Requires effective moderation and core heterogeneity to result in ~300 meV flux peak in the fuel salt
- Neutron yield per absorption is ~2.3 at 300 meV in ^{233}U





- Fuel salt composition would include several times as much ThF_4 as UF_4 (e.g., 15 versus 0.75 mol%)

Cross Sections from ENDF/B-VIII.0

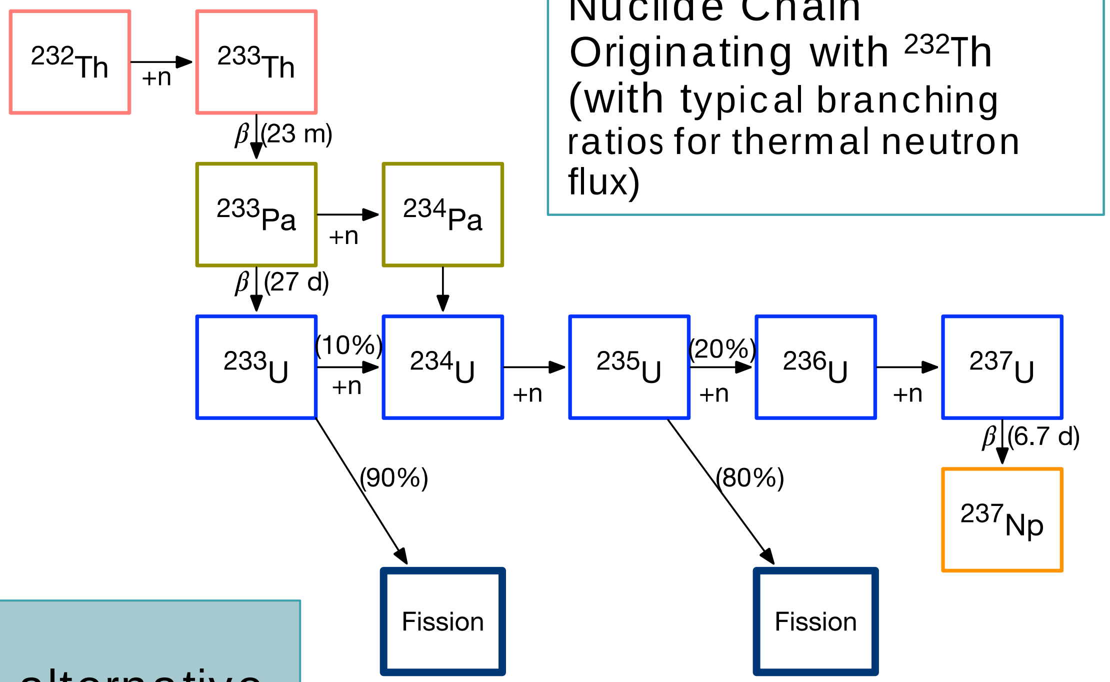
Aluminum Has Been Shown to be a Reductant and Solvent for Actinides in Fluoride Salts

- Co-separation demonstration from fluoride fuel salt performed by French fuel cycle program (Conocar, et al, 2005)
- Contacting fluoride fuel salt with liquid aluminum was demonstrated to efficiently separate actinides into a metallic aluminum phase
  - Thermodynamics shows that aluminum has the highest metallic phase distribution of likely metallic reductants
- Single stage reductive extraction via contacting with liquid aluminum transferred more than 99.3% of Pu and Am to the metallic phase
- Separation factors above 1000 between Pu and lanthanides were demonstrated
- Technique remains at low maturity with many unknowns

Protactinium-233 Needs to Decay Outside of a Neutron Flux to Efficiently Generate Uranium-233

- Protactinium-233 has a large thermal neutron absorption cross-section
  - Origin of need for substantial fuel salt processing to achieve breeding gain
- Accessible material with ^{233}U (or ^{235}U) content above LEU is unacceptably attractive
  - Cannot meet the useful purpose proportional to the quantities and forms of SNM test from AEA or Presidential directive to avoid fuel cycles that provide access to attractive materials

Nuclide Chain Originating with ^{232}Th (with typical branching ratios for thermal neutron flux)

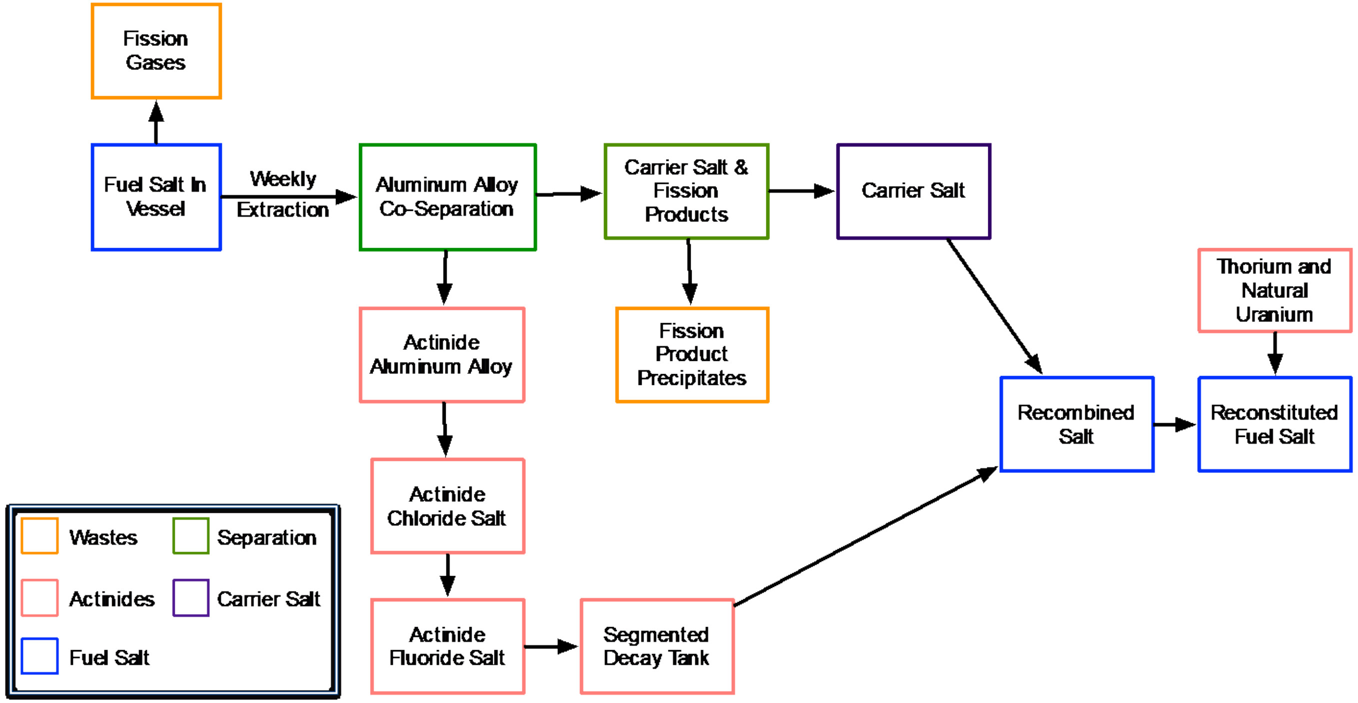


> ...we will redirect funding of U.S. nuclear research and development programs to accelerate our research into alternative nuclear fuel cycles which do not involve direct access to materials usable in nuclear weapons. – President Carter April 7, 1977

- Historic MSR program developed denatured MSR design without separations
  - ORNL/TM-6413 *Molten Salt Reactors for Efficient Nuclear Fuel Utilization Without Plutonium Separation* – J. R. Engel, et. al., 1978

Multiple Batches of Fuel Salt, Co-Separation, Denaturing, and Efficient Core Design Must Be Combined to Obtain Breeding Gain While Maintaining Low Attractiveness

- Fuel salt in tubes minimizes fuel salt volume and facilitates frequent transfers
  - Multiple historic MSR designs employed fuel salt in tubes (e.g., ARE, MSBR (prior to 1967), and MOSEL)
- Radiation damage to fuel salt tubes becomes critical technology element
  - Similar to cladding in sodium cooled fast reactors
- Aqueous homogeneous reactor used bottom goose neck to facilitate frequent fuel transfers



Fuel Process Diagram for Low-Attractiveness, Thermal-Spectrum Molten Salt Breeder Reactor

Halide Salts Have Advantageous Characteristics for Fissile Resource Utilization and Heat Transfer

- The advantageous fuel salt characteristics enable a wide set of design and processing options depending on performance objectives
- High temperature (and high exergy) and accessibility of the fission products substantially impact the potential products
  - First deployments are more likely to focus on market needs that cannot easily be met by competing technologies (e.g., high quality process heat)
- Fast spectrum designs are likely to have higher power outputs due to the lower cross sections and consequent need for more fissile material for criticality
  - Fast spectrum designs do not optimize well at small sizes
- Once-through LEU, thermal-spectrum MSR has substantially higher TRL than either a fast-spectrum chloride salt or intensively processed Th/U breeding MSR
  - Diverse, more complex systems are likely to follow if the initial deployments are successful

Après moi, le deluge - Louis XV of France