NE 591: Advanced Reactor Materials

Fall 2021

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Project #2

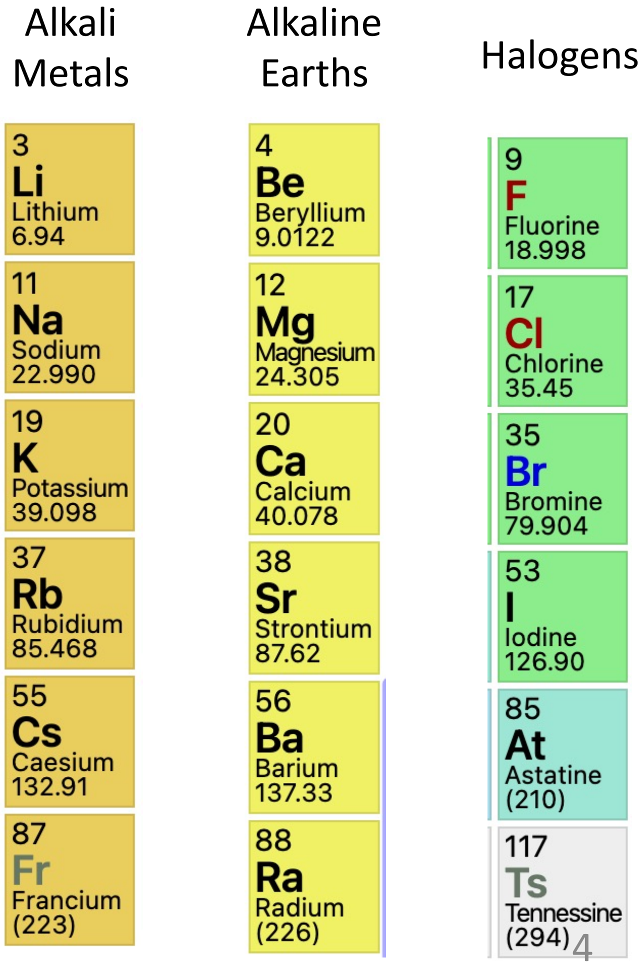
- Minor actinide bearing metallic fuels - Mahmoud
- Swelling of stainless steel under fast fluence - Hamdy
- Alternate geometries of metallic fuels (e.g., slotted) – Khadija

- 15 minute presentations + 5-10 for questions
- Due date Oct. 14

MOLTEN SALTS

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, BeF2, MgCl2, NaCl (aka table salt), ZrF4, RbF, UF4, UCl3



Molten Salt Reactors

Salt Cooled Reactor

Driven by some traditional fuel type in cladding, where the coolant is replaced with molten salt

Static Salt Fueled Reactor

The fuel itself is a liquid actinide-salt mixture contained in a cladding, often coupled with a salt coolant

Flowing Salt Fueled Reactor

The fuel itself is a liquid actinide-salt mixture which flows in a loops through the core and doubles as the coolant

Molten Salt Applications

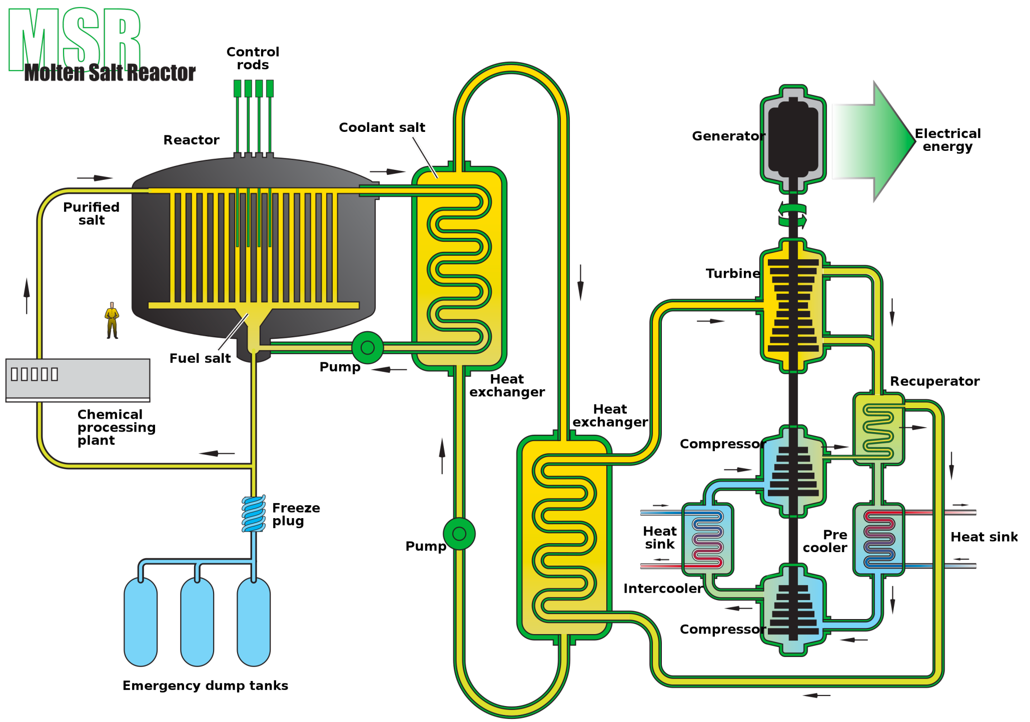
Table 2 The various applications of molten salts in nuclear reactor concepts

Reactor type	*Neutron spectrum*	*Application*	*Primary choice*	*Alternative(s)*
MSR breeder	Thermal	Fuel	$^{7}LiF–BeF_2–AnF_4$	
	Fast	Fuel	$^{7}LiF–AnF_4$	$^{7}LiF–CaF_2–AnF_4$, $NaCl–UCl_3–PuCl_3$
		Secondary coolant	$NaF–NaBF_4$	$LiF–BeF_2$, $KF–KBF_4$
MSR burner	Fast	Fuel	$LiF–NaF–BeF_2–AnF_3$	$LiF–NaF–KF–AnF_3$, $LiF–NaF–RbF–AnF_3$
AHTR[a]	Thermal	Primary coolant	$^{7}LiF–BeF_2$	
VHTR[b]	Thermal	Heat transfer[e]	LiF–NaF–KF	$LiCl–KCl–MgCl_2$
MS-FR[c]	Fast	Primary coolant	$LiCl–NaCl–MgCl_2$	
SFR[d]	Fast	Intermediate coolant[f]	$NaNO_3–KNO_3$	

[a]Advanced high-temperature reactor, graphite-moderated, thermal reactor.
[b]Very high-temperature reactor, graphite-moderated, gas cooled reactor.
[c]Molten salt cooled fast reactor, the solid fuel fast reactor with MS as a coolant.
[d]Sodium cooled fast reactor.
[e]Heat transfer salt is a medium that will be used to deliver heat from the reactor to the hydrogen production plant.
[f]To separate sodium and the steam circuits.

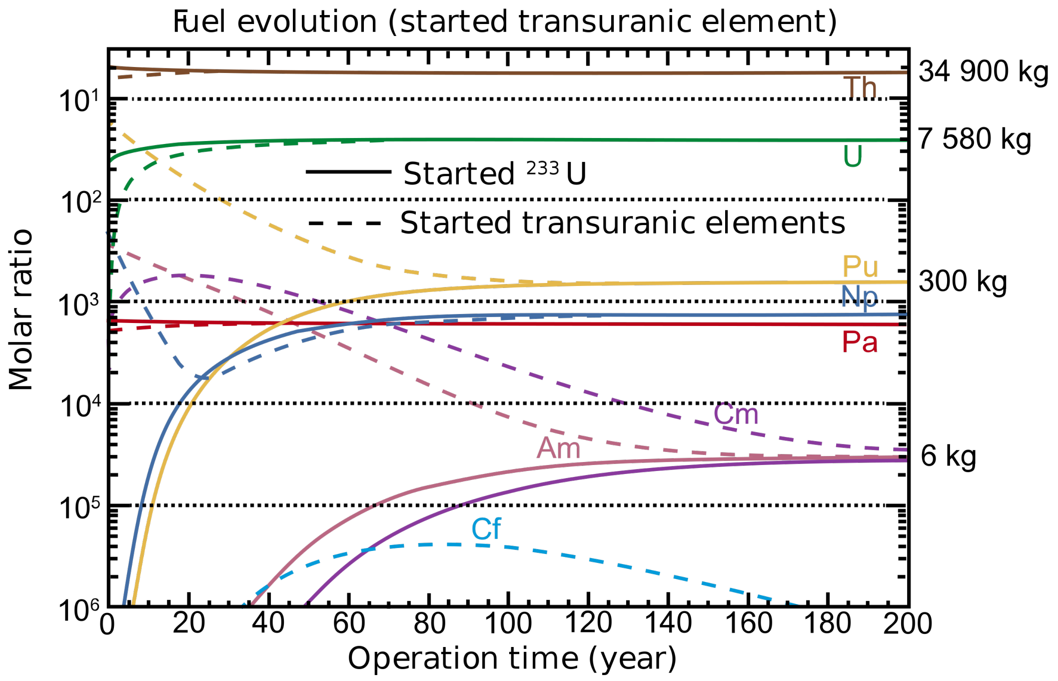
Benefits of MSRs

- MSRs operate at or close to atmospheric pressure, rather than the 75-150 times atmospheric pressure of typical light-water reactors (LWR)
- This reduces the large, expensive containment structures used for LWRs
- Radioactive fission gases can be naturally absorbed into the molten salt
- MSRs can have higher operating temperatures than a traditional LWR, providing higher electricity-generation efficiency, the possibility of grid-storage facilities, economical hydrogen production and, in some cases, process-heat opportunities.



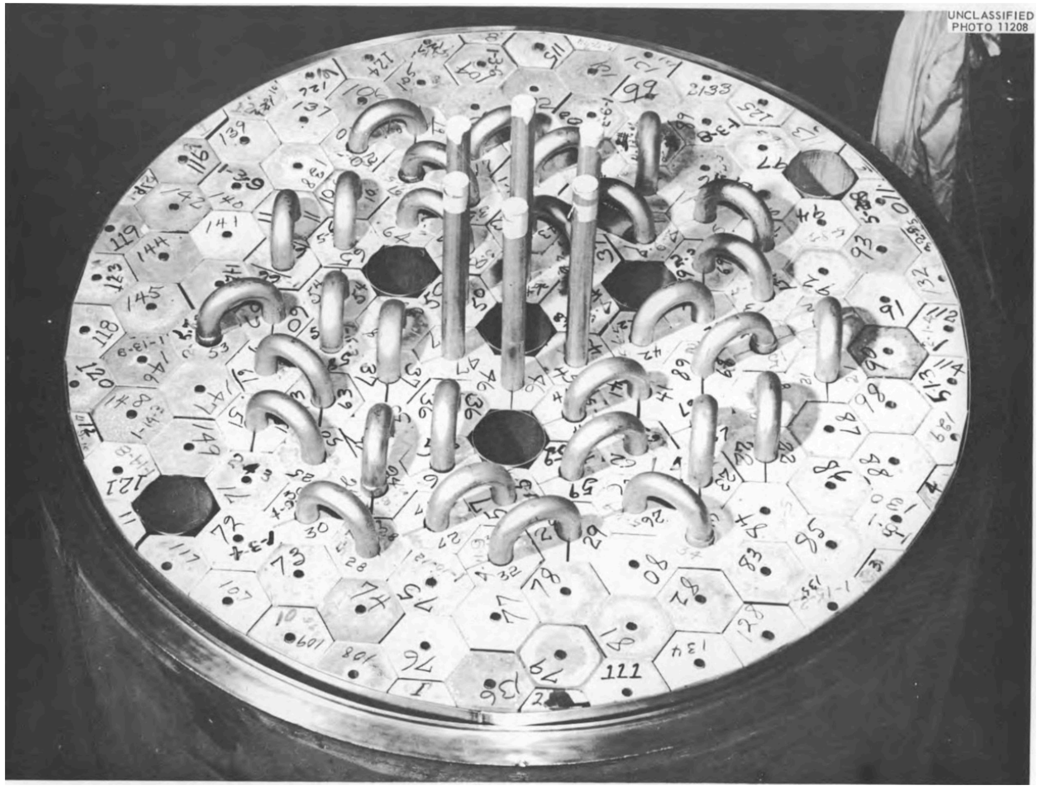
Challenges of MSRs

- The corrosivity of hot salts can break down cladding components and leech alloying elements
- The changing chemical composition of the salt as it is transmuted by reactor radiation leads to changing properties
- The processing of liquid transuranic molten salt fuel from the current spent fuel and of the on-line reprocessing of MSR fuel need to be solved



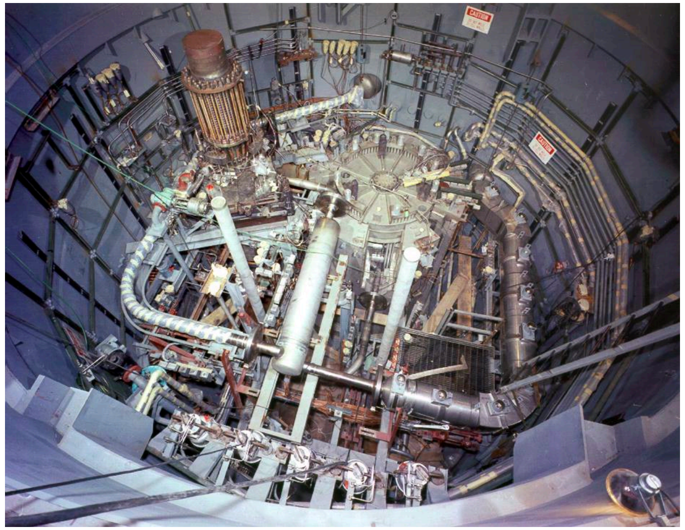
Beginning of MSRs

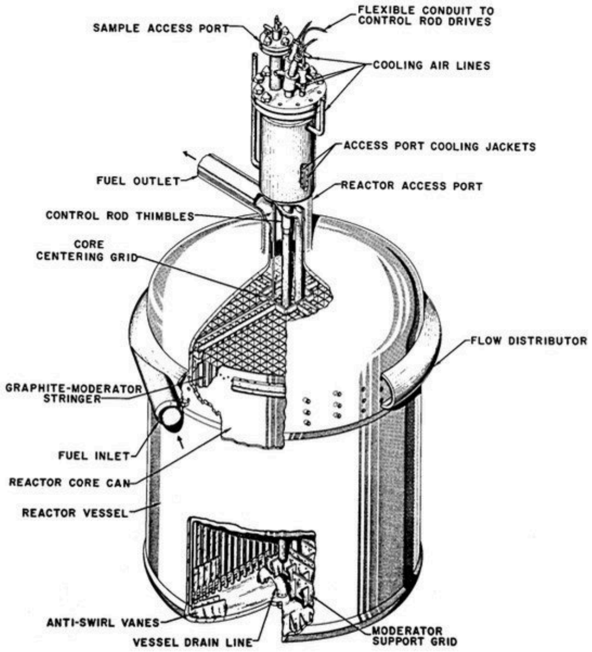
- Aircraft Reactor Experiment was a 2.5 MWth thermal-spectrum nuclear reactor experiment designed to attain a high power density and high output temperature for use as an engine in a nuclear-powered bomber aircraft
- It used the molten fluoride salt NaF-ZrF4-UF4 (53-41-6 mol%) as fuel, was moderated by a hexagonal-configuration beryllium oxide (BeO), and had a peak temperature of 860C



MSRE

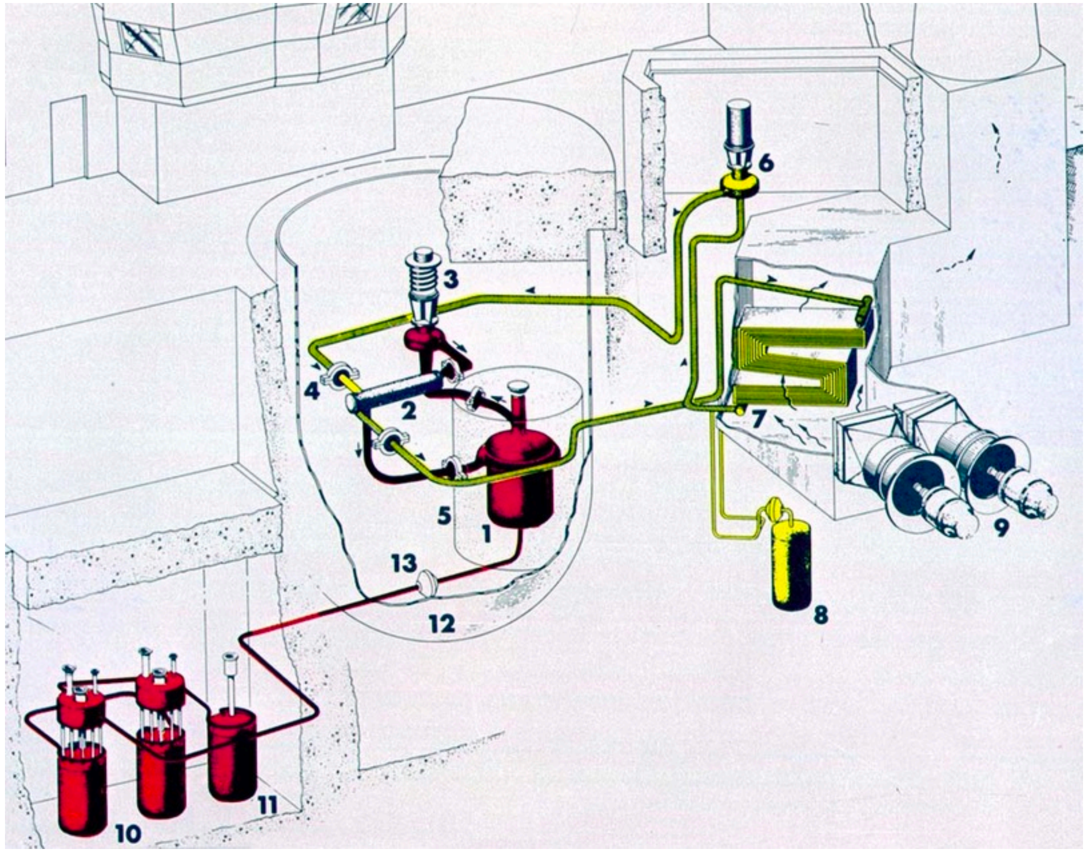
- The Molten-Salt Reactor Experiment (MSRE) was an experimental molten salt reactor at the Oak Ridge National Laboratory (ORNL); it went critical in 1965 and was operated until 1969





MSRE

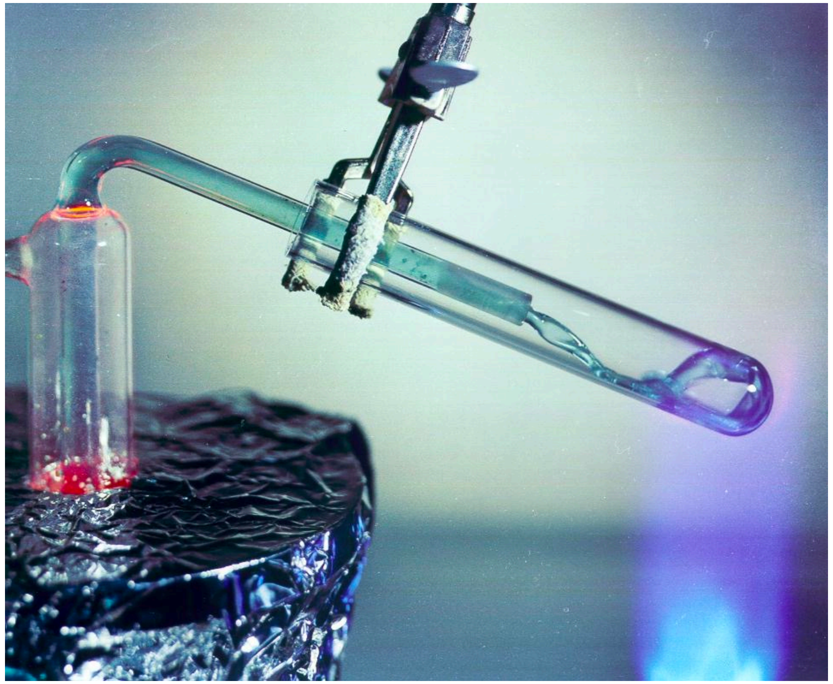
- MSRE was a circulating fuel type, utilizing LiF-BeF_2-ZrF_4-UF_4
- The secondary coolant salt was LiF-BeF_2 (FLiBe), and the moderator was graphite
- Salt-facing component were made of Hastelloy-N, which is a low chromium, nickel–molybdenum alloy



Fuel and Coolant Salts

- A fuel salt is a molten salt that contains fissile material
- Fuel salts consist of a mixture of some of all of the following:
  - Fissile material
  - Fertile material
  - Solvent (Lowers melting point, Decreases power density, Decreases viscosity)
  - Fissile oxidation prevention material
  - Fission products

- Coolant salts are molten salts with advantageous heat transfer properties



Fuel Salt Requirements

- Low neutron absorption
- Radiolytic stability under in-core conditions
- Dissolve fissile materials
- High heat capacity, high boiling point, high thermal conductivity fluids
- Melting point below ~525C
- 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

Fuel Salt Classes

- Thermal spectrum reprocessing optimized fluoride salts
  - FLiBe (^7LiF-BeF_2) and NaF-ZrF_4
  - FLiBe produces tritium, while NaF-ZrF_4 has a higher vapor pressure
- Fast spectrum and thermal spectrum, once-through fuel cycle optimized fluoride salts
  - LiF-ThF_4-UF_4-$(TRU)F_3$
  - 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, due to moderate capture cross section of ^{35}Cl

Fluorides or Chlorides

- Fluoride fuel salts have substantially more experimental data than chloride fuel salts, primarily due to history of MSRs in the thermal spectrum
- Fluorides have been operated in molten salt reactors, been tested in multiple in-pile loops, with many capsule tests
- Chloride salts have a history of laboratory measurements of physical properties, but no in-core testing of fuel salts
  – have extensive use in pyro-processing

MSR Fuels

- The fuel in the MSR must fulfill several requirements with respect to its physical and chemical properties
- These include low melting point, high solubility of relevant species, low viscosity, high heat capacity, high thermal conductivity, low volatility/vapor pressure, neutron transparency

Table 3 Selected properties of the coolant salts

Property	*LiF–BeF$_2$ (0.66–0.34)*	*NaF–NaBF$_4$ (0.08–0.92)*	*LiF–NaF–KF (0.465–0.115–0.42)*
Melting point (K)	728	657 ± 1	727
ρ(kg m^{-3})	2146.3–0.4884T (K)	2446.3–0.711T (K)	2579.3–0.6240T (K)
η(mPa s)	1.81exp(1912.2/T (K))	0.0877exp(2240/T (K))	0.0248exp(4477/T (K))
C_p(J K^{-1} g^{-1})	2.39	1.506	1.88
λ(W m^{-1} K^{-1})	1.1	$0.66–2.37 \times 10^{-4}T$ (K)	$0.36 + 5.6 \times 10^{-4}T$ (K)
log$_{10}$(p(Pa))	11.914–13003/T (K)	11.638–6550.6/T (K)	10.748–10789/T (K)

Table 4 Selected properties of the fuel salts

Property	*LiF–ThF$_4$ (0.78–0.22)*	*LiF–BeF$_2$–ThF$_4$ (0.717–0.16–0.123)*	*LiF–NaF–BeF$_2$–PuF$_3$ (0.203–0.571–0.212–0.013)*
Melting point (K)	841	771	775
ρ(kg m^{-3})	5543.0–1.2500 T (K)	4124.3–0.8690 T (K)	2759.9–0.5730 T (K)
η(mPa s)	0.365exp(2735/T (K))	0.062exp(4636/T (K))	0.100exp(3724/T (K))
C_p(J K^{-1} g^{-1})	1.0	1.55	2.15
λ(W m^{-1} K^{-1})	~1.5[a]	1.5[a]	$0.402 + 0.5 \times 10^{-3}/T$ (K)
log$_{10}$(p(Pa))	11.902–12 989/T (K)	11.158–10 790.5/T (K)	11.6509–12 827/T (K)

Neutron Economy

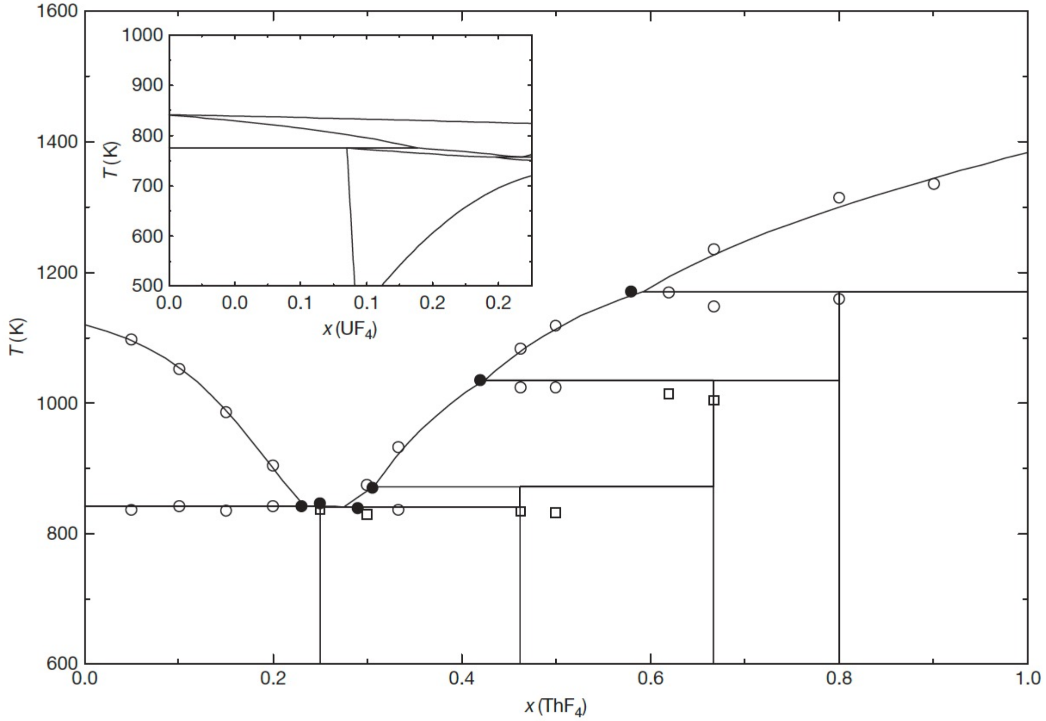
- Thermal spectrum molten salt fuels were identified as candidates for breeding (converting fertile into fissile), specifically in the thorium fuel cycle
- Li-Be-F salts were selected because of the low thermal neutron cross sections of ^{7}Li (σ_{th} = 0.045 b) and Be (σ_{th} =0.0088 b)
- Natural lithium cannot be used as part of the nuclear fuel as it contains about 7.6% of ^{6}Li (the remaining 92.4% is ^{7}Li), which has a very high parasitic neutron capture cross-section (σ_{th} = 940 b)
- Therefore, enrichment of ^{7}Li is required before it can be used in the core

Fast Spectrum MSRs

- Current MSR designs move away from thermal graphite-moderated concepts, and favor non-moderated concepts that have a fast(er) neutron spectrum and can function to burn radioactive waste
- Fuel selection for the non-moderated reactor concepts is more flexible, and elements other than ^{7}Li can be considered
- The neutron capture cross-section of the alkali halides and alkali-earth halides is generally lower in the ‘fast’ spectrum than in the thermal spectrum
- Compounds like NaF, KF, RbF, or CaF2 can be considered as part of the fuel matrix
- There are also some ‘fast’ MSR concepts which are based on chloride salts

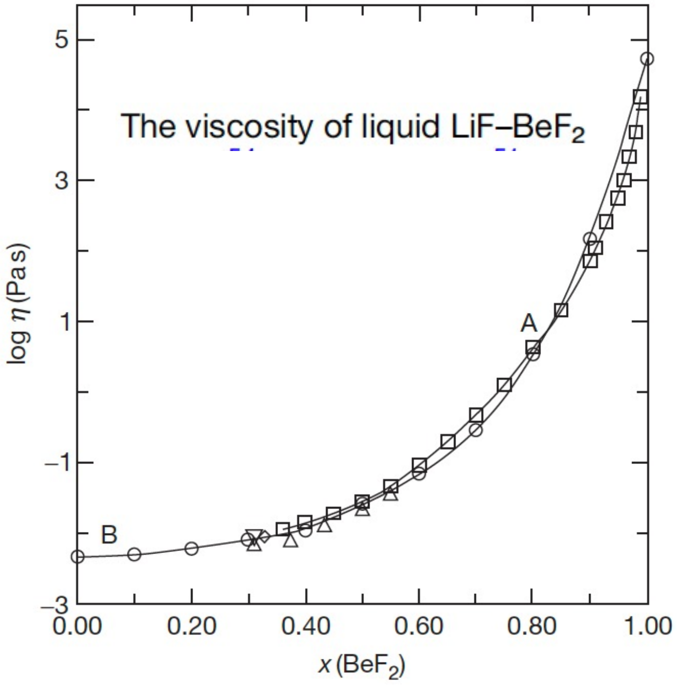
Solubility

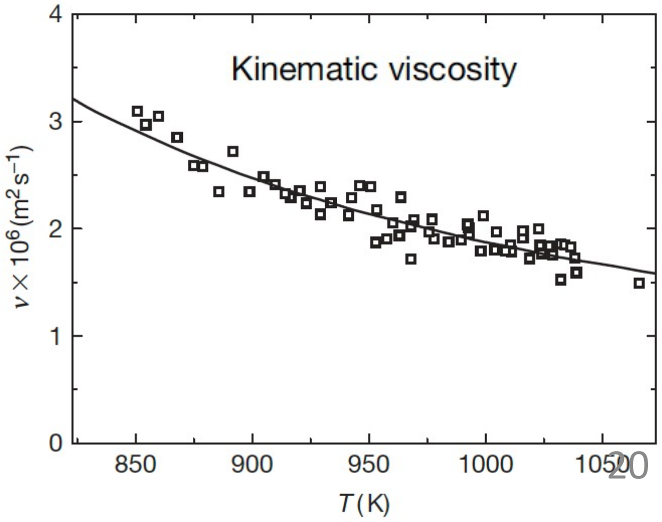
- The solubility of ThF4 in a matrix of LiF can be deduced from the binary phase diagram
- For example, the solubility of ThF4 in a melt of LiF for T 903K (inlet temperature of the MSFR) is between 20.0 and 32.3 mol%
- Compositions in this range are, thus, of interest as fuel for MSRs
- Similarly, eutectic composition and melting temperature are key factors that govern the utilization of specific salts



Low Viscosity

- The viscosity of a fluid is a measure of its resistance to deformation at a given rate; conceptualized as the internal frictional force that arises between adjacent layers of fluid that are in relative motion
- Lower viscosity results in less force to move the fluid at a given velocity
- It is sometimes more convenient to utilize the kinematic viscosity, defined as the ratio of the viscosity μ to the density of the fluid ρ
- The viscosity of fluoride systems shows significant non-ideal mixing behavior
- Thus, it is not possible to accurately estimate the viscosity of the fluoride salts from its constituents, and therefore more measurements are required

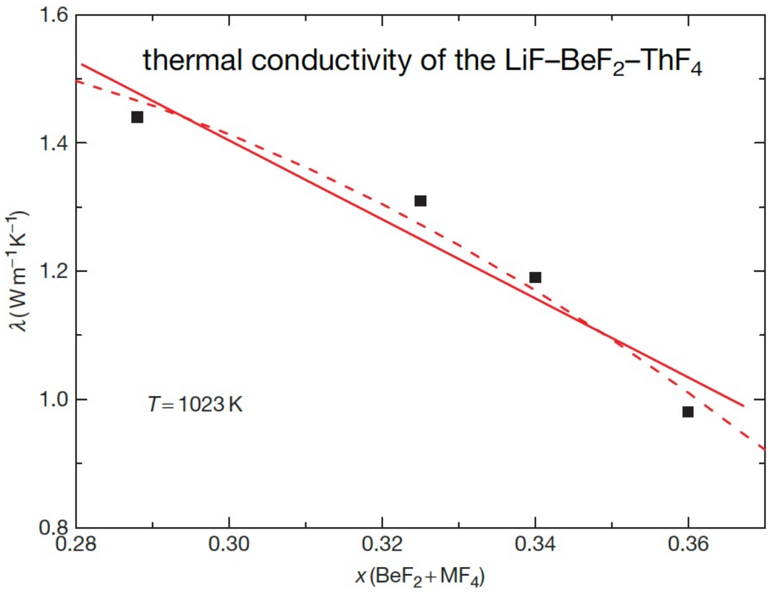




Heat Capacity and Thermal Conductivity

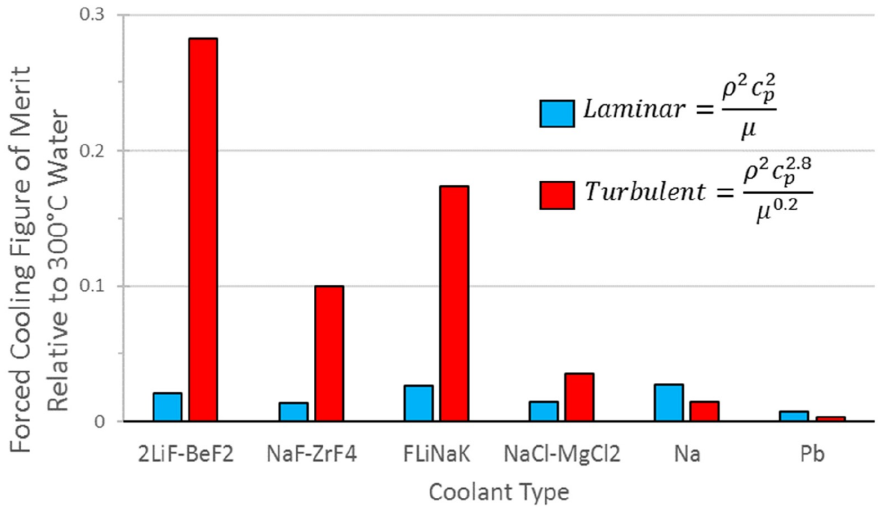
- Heat Capacity is defined as the amount of heat to be supplied to an object to produce a unit change in its temperature
- High heat capacity enables a small amount of the refrigerant to transfer a large amount of heat very efficiently
- Data on experimental heat capacity and thermal conductivity of molten fluoride systems containing actinide fluorides are generally lacking

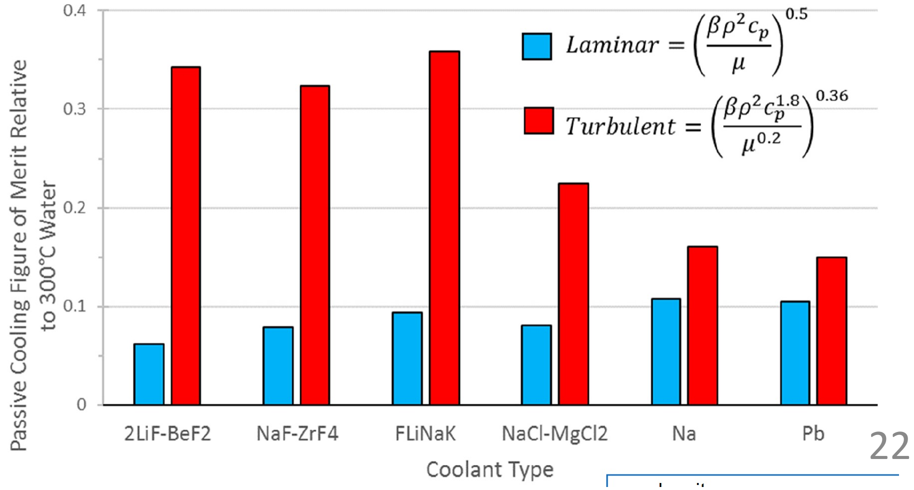
- The thermal conductivity of a material is a measure of its ability to conduct heat
- High thermal conductivity and thermal diffusivity will increase the rate of heat transfer through the fluid



Heat Transfer

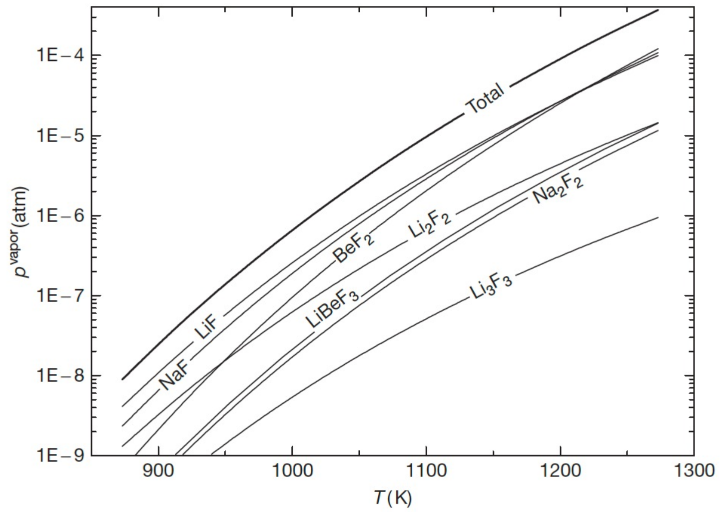
- Large heat capacity and low viscosity are key properties allowing good heat transfer in molten salts
- In both forced flow and passive cooling conditions, molten salts out perform liquid metals in turbulent flow for heat transfer
- However, experimental data for heat transfer is still significantly scattered for the range of relevant MSR conditions





Vapor Pressure (Volatility)

- Volatility is a material quality which describes how readily a substance vaporizes
- A substance with high volatility is more likely to exist as a vapor, while a substance with low volatility is more likely to be a liquid or solid
- Vapor pressure is a measurement of how readily a condensed phase forms a vapor at a given temperature
- High vapor pressures indicate a high volatility, while high boiling points indicate low volatility
- Salts should have high boiling and low freezing points, in addition to a low vapor pressure (low volatility)



Chemical Compatibility

- For any high-temperature application, corrosion of the metallic container alloy is a primary concern
- The products of oxidation of metals by molten salts tend to be completely soluble in the corroding media
- Due to this solubility, passivation is precluded and the corrosion rate depends on other factors, including oxidants, thermal gradients, salt flow rate, and galvanic coupling
- Examination of the free energies of formation for typical alloy components shows that chromium is the most active metal component
- Thus, any oxidative attachment to these alloys should be expected to show selective attack on the chromium
- Stainless steels, having more chromium than Ni-based alloys, are more susceptible to corrosion by fluoride melts

Role of Oxygen Impurities

- The behavior of these systems can be significantly affected by the presence of the oxide ion that might be resulting from contamination of the salt system
- Actinide oxides, such as UO2, can precipitate out for oxygen concentrations as low as 1E-4
- Metal oxides have much higher melting points and therefore appear as insoluble components at operating temperatures

- ZrF4 was implemented as an oxygen getter in the original MSRE fuels

$$UF_4 + 2H_2O \leftrightarrow UO_2 + 4HF$$

$$ZrF_4 + 2H_2O \leftrightarrow ZrO_2 + 4HF$$

$$ZrF_4 + UO_2 \leftrightarrow ZrO_2 + UF_4$$

- $AlCl_3$ or CCl_4 can also be used as reactants to tie up oxygen, or strip O from UO2

Role of Oxygen Impurities

- Redox processes responsible for attack by fluoride mixtures on the alloys result in selective oxidation of the contained Cr
- This removal of Cr from the alloy occurs primarily in regions of highest temperature
- The rate of corrosion has been measured and was found to be controlled by the rate at which chromium diffuses to the surfaces undergoing attack
- Reaction of UF_4 with structural metals (M) is strongly temperature dependent, and when the salt is circulated, a mechanism exists for mass transfer and continued attack

$$2UF_4 + M \leftrightarrow 2UF_3 + MF_2$$

- This reaction is of significance mainly in the case of alloys containing relatively large amounts of chromium

Control of Chemistry

- Avoiding corrosion in an MSR or in fuel-processing units with metallic components is significantly more challenging than avoiding corrosion in clean salt coolant applications
- The dissolved uranium and other such species in the fuel salt result in the presence of additional corrosion mechanisms
- In clean salt applications, these types of corrosion mechanisms can be reduced or eliminated by (1) using purified salts that do not contain chemical species that can transport chromium and other alloy constituents or (2) operating under chemically reducing conditions
- Redox control could be accomplished by including an HF/H_2 mixture

Maintaining Reducing Redox Conditions

- Maintaining mildly reducing redox conditions is the key to enabling use of engineering alloys
- Use of a circulating redox buffer provides means to maintain redox condition, while the oxidation states are changing due to fission
- The ratio of U4+/U3+ serves as a measure of the redox potential of the salt for both chlorides and fluorides
- Bottom right is the variation of equilibrium concentration of structural metal fluorides as a function of the UF4/UF3 ratio in a molten salt reactor fuel

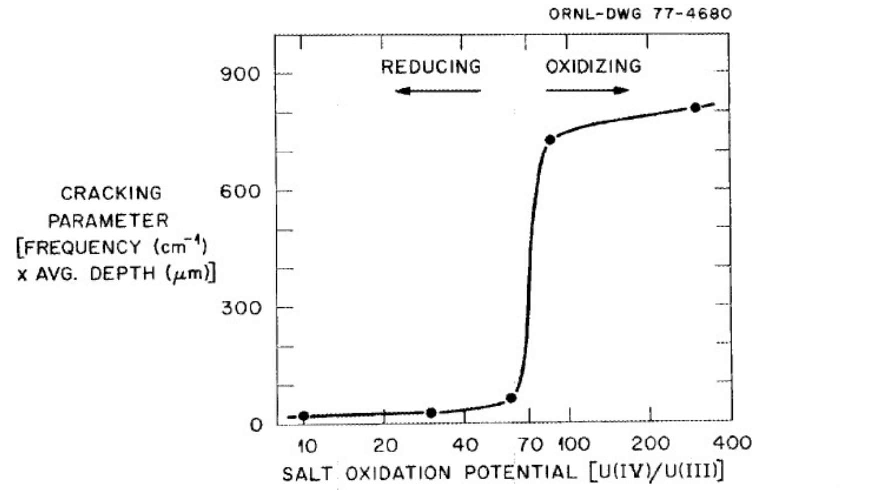


Fig. 12. Cracking Behavior of Hastelloy N Exposed 260 hr at 700°C to MSBR Fuel Salt Containing $CrTe_{1.266}$.