NE 795-014: Advanced Reactor Materials

Fall 2023

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Housekeeping

- Reminder, test on Thursday on SFRs

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

Alkali Metals	Alkaline Earths	Halogens
3 Li Lithium 6.94	4 Be Beryllium 9.0122	9 F Fluorine 18.998
11 Na Sodium 22.990	12 Mg Magnesium 24.305	17 Cl Chlorine 35.45
19 K Potassium 39.098	20 Ca Calcium 40.078	35 Br Bromine 79.904
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	53 I Iodine 126.90
55 Cs Caesium 132.91	56 Ba Barium 137.33	85 At Astatine (210)
87 Fr Francium (223)	88 Ra Radium (226)	117 Ts Tennessine (294)

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

Thermal and Fast

- Often salt reactors are further subdivided into fast and thermal spectrum reactors
- List of examples of reactor systems with solid fuel, thermal liquid fuel, and fast liquid fuel

Solid Fuel MSRs (all thermal spectrum)			
Molten-Salt Reactor with Micro-Particle Fuel (MARS)	Kurchatov Institute, Russia	16	TRISO-coated LEU/FLiBe/Graphite pebble bed
Advanced High Temperature Reactor (AHTR)	ORNL, United States	3 400	Coated U particles in blocks or plates/FLiBe/Graphite
Small Advanced High Temperature Reactors (SmAHTR)	ORNL, United States	125	Coated U particles in blocks or plates/FLiBe/Graphite
Pebble Bed – Fluoride Salt-Cooled High Temperature Reactors (PB-FHR)	UC Berkeley, MIT and UW, United States	242	TRISO-coated LEU/FLiBe/Graphite pebble bed
Thorium Molten Salt Reactor, Solid Fuel (TMSR-SF)	SINAP, China	395	TRISO-coated U-Th/FLiBe/Graphite pebble bed
Indian High Temperature Reactor (IHTR)	BARC, India	600	TRISO-coated U-Th/FLiBe/Graphite pebble bed

Thermal Spectrum Liquid Fuel MSRs			
Thorium Molten Salt Reactor, Liquid Fuel (TMSR-LF)	Shanghai Institute of Applied Physics (SINAP), China	395	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
Integral Molten Salt Reactor (IMSR)	Terrestrial Energy, Canada and the United States	400	UF_4/fluorides/graphite
ThorCon Reactor	ThorCon International, Singapore	557x2	UF_4/NaF-BeF_2/graphite
Liquid-Fluoride Thorium Reactor (LFTR)	Flibe Energy, United States	600	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
FUJI-U3	Japan	450	ThF_4-$^{233}UF_4$/^7LiF-BeF_2/graphite
Advanced Molten-salt Break-even Inherently-safe Dual-mission Experimental and Test Reactor (AMBIDEXTER)	Ajou University, Korea	250	$^{233}UF_4$-ThF_4/^7LiF-BeF_2
Transatomic Power MSR (TAP)	Transatomic Power, United States	1 250	UF_4/FLiNaK/SiC clad $ZrH_{1.6}$
Compact Used fuel BurnEr (CUBE)	Seaborg Technologies, Denmark	250	SNF/fluorides/graphite
Process Heat Reactor	Thorenco, United States	50	UF_4/NaF-BeF_2/Be rods
Stable Salt Thermal Reactor (SSR-U)	Moltex Energy, United Kingdom	300-2 500	UF_4/fluorides/graphite
Fast/Epithermal Spectrum Liquid Fuel MSRs			
Molten Salt Fast Reactor (MSFR)	SAMOFAR, France – EU – Switzerland	3 000	ThF_4-UF_4/^7LiF-
Molten Salt Actinide Recycler and Transformer (MOSART)	Kurchatov Institute, Russia	2 400	$TRUF_3$ or ThF_4-UF_4/^7LiF-BeF_2 or NaF-^7LiF-BeF_2
U-Pu Fast Molten Salt Reactor (U-Pu FMSR)	VNIINM, Russia	3 200	UF_4-PuF_3/^7LiF-NaF-KF
Indian Molten Salt Breeder Reactor (IMSBR)	BARC, India	1 900	ThF_4-UF_4/LiF-
Stable Salt Fast Reactor (SSR-W)	Moltex Energy, United Kingdom	750-2 500	PuF_3/Fluorides
Molten Chloride Fast spectrum Reactor (MCFR)	TerraPower, United States		U-Pu/Chlorides
Molten Chloride Salt Fast Reactor (MCSFR)	Elysium Industries, United States and Canada	100-5 000	U-Pu/Chlorides
Dual Fluid Reactor (DFR)	Dual Fluid Reactor, Germany	3 000	U-Pu/Chlorides

Benefits of MSRs

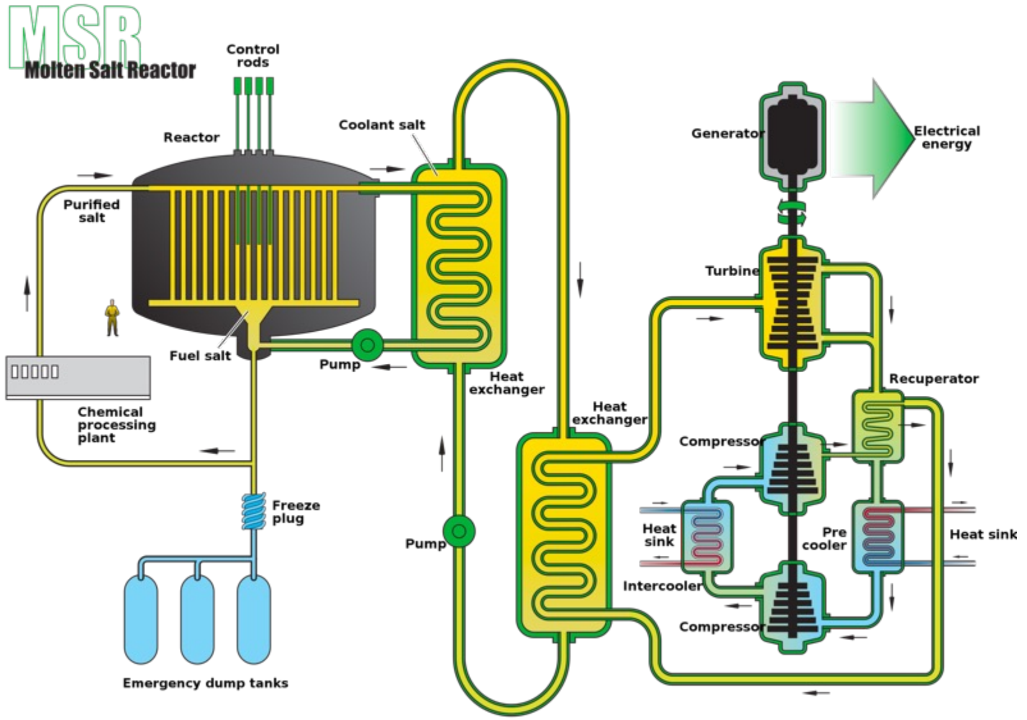
- MSRs operate at or close to atmospheric pressure, rather than the 75-150 times atmospheric pressure of typical light-water reactors (LWR)
- This reduces the large, expensive containment structures used for LWRs
- Radioactive fission gases can be naturally absorbed into the molten salt
- MSRs can have 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.
- MSRs have a strong negative reactivity feedback coefficient induced by the thermal expansion of the fluid
- Backup safety measure of dump tanks for rapid removal of fuel
- Possibility of online refueling and waste removal, plus benefits of reprocessing

Table 1 Typical fuel salt inlet temperatures of selected MSR concepts

MSR concept	T_{inlet}	T_{outlet}	*Reference*
MSRE	908K	936K	2
MSBR	839K	977K	3
MSFR	903K	923K	4
MOSART	873K	988K	5
TMSR	873K	923K	

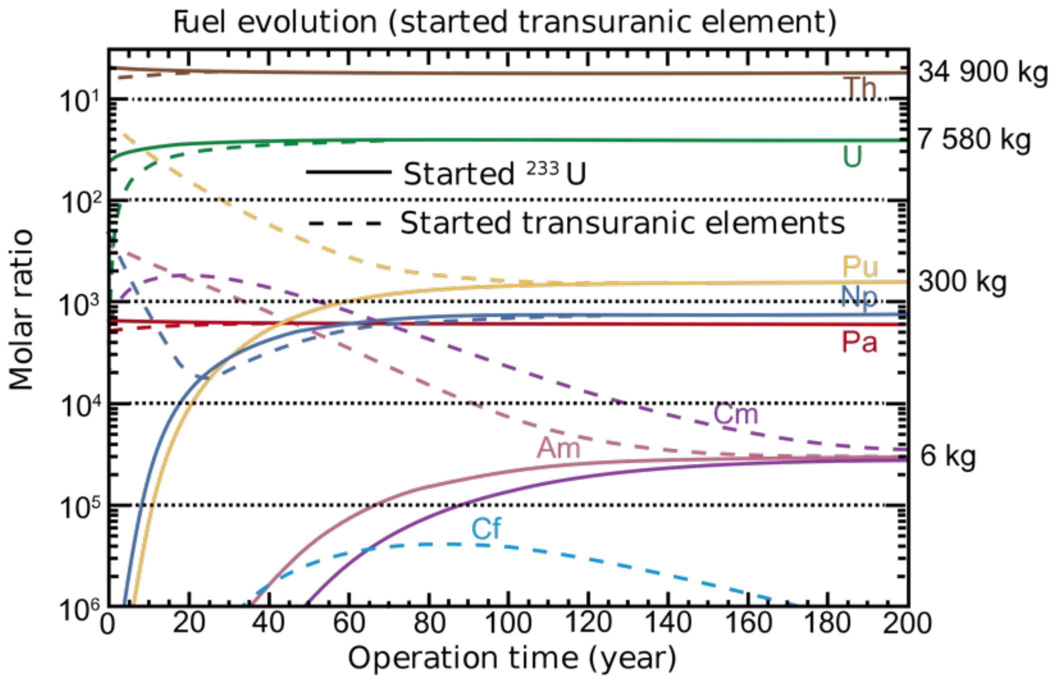
Design/Nomenclature

- When people usually refer to an MSR, they mean a thermal, fluoride-fueled, flowing loop reactor
- This is due to historical reasons, as we will discuss
- Thus, we have, unless otherwise specified: a liquid fuel with fission species dissolved in the salt; the fuel being pumped through and out of the reactor to a primary HX; secondary loop is typically also a molten salt and goes to a heat exchanger; tertiary loop is your steam turbine loop



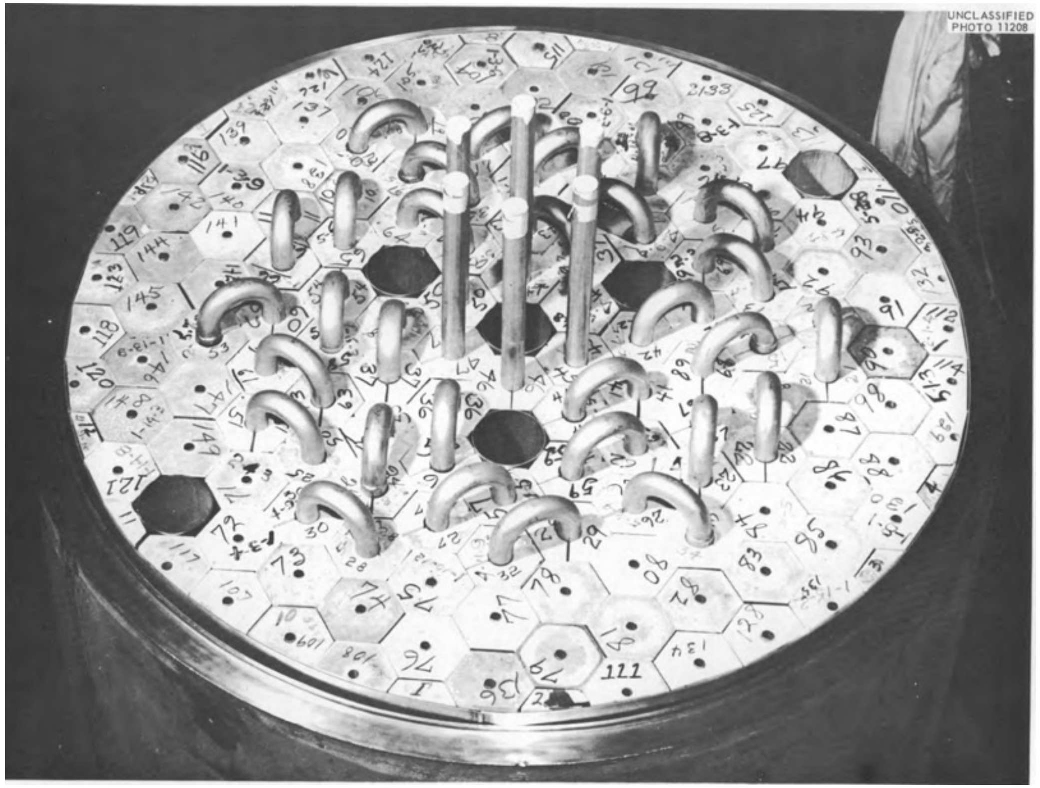
Challenges of MSRs

- 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



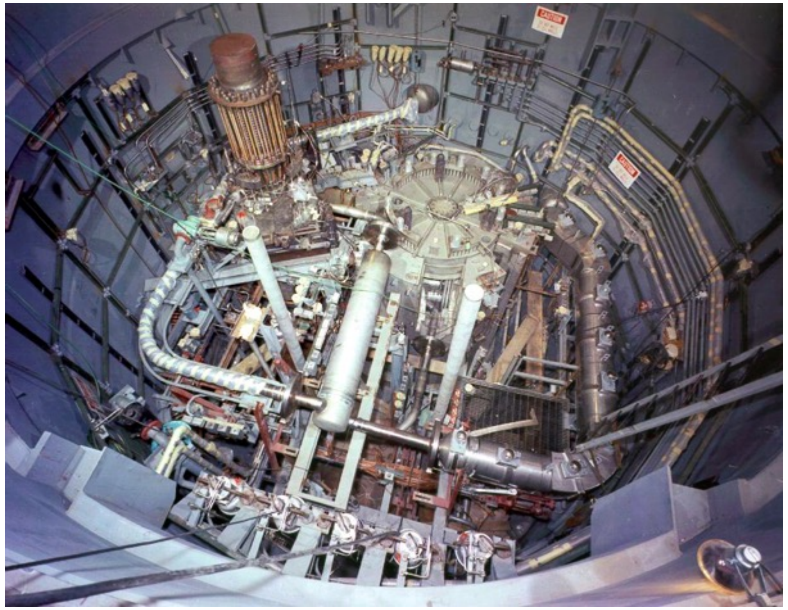
Beginning of MSRs

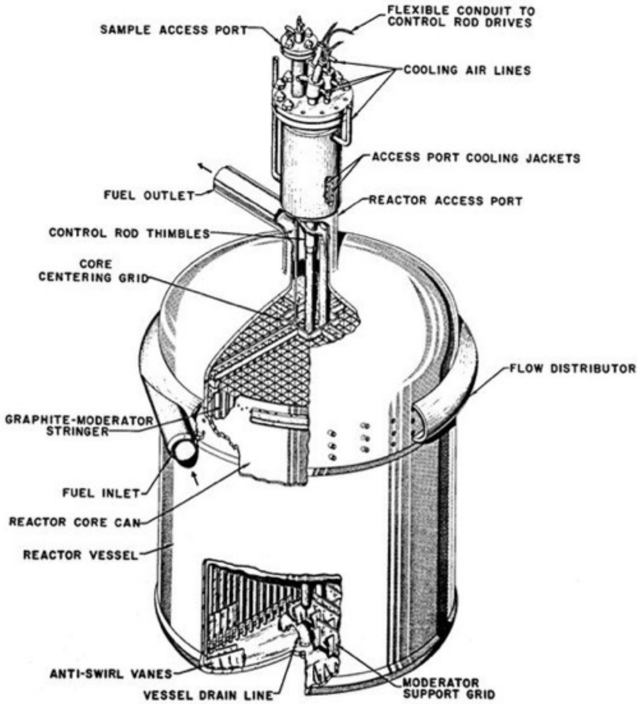
- Aircraft Reactor Experiment (1954) was a 2.5 MWth thermal-spectrum nuclear reactor experiment designed to attain a high power density and high output temperature for use as an engine in a nuclear-powered bomber aircraft
- It used the molten fluoride salt NaF-ZrF4-UF4 (53-41-6 mol%) as fuel, was moderated by a hexagonal-configuration beryllium oxide (BeO), and had a peak temperature of 860C



MSRE

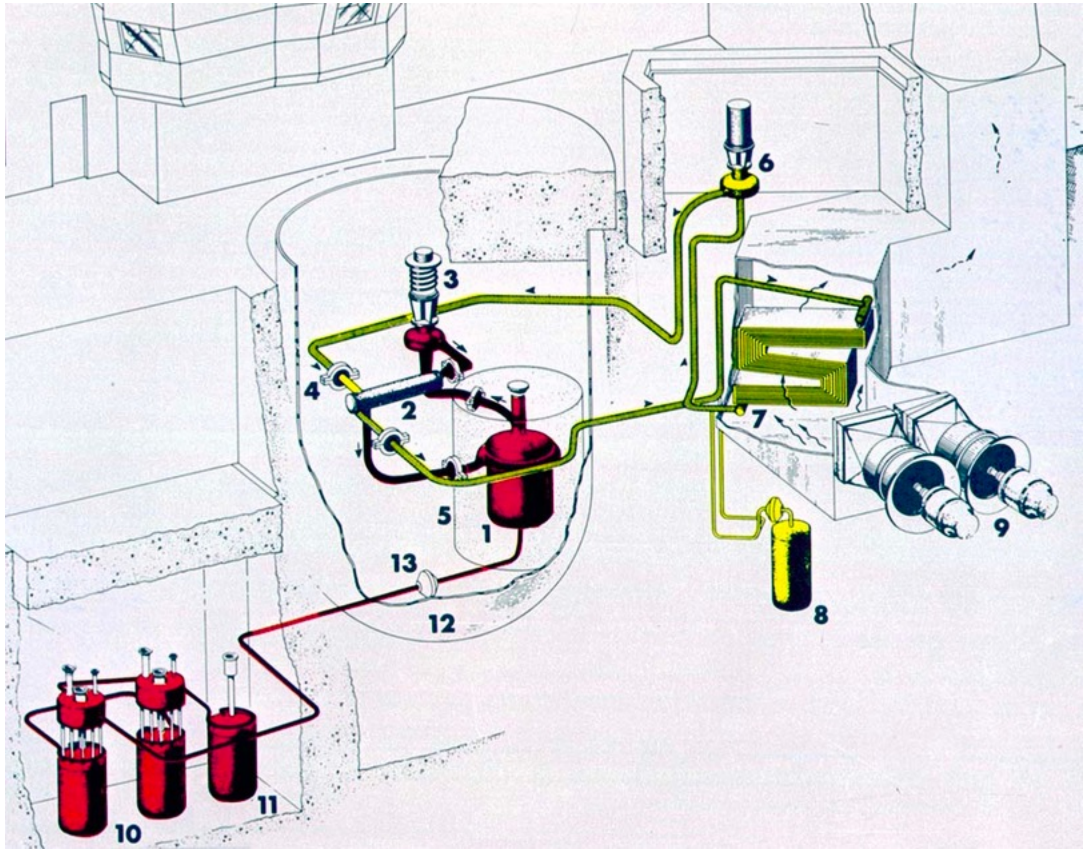
- The Molten-Salt Reactor Experiment (MSRE) was an experimental molten salt reactor at the Oak Ridge National Laboratory (ORNL); it went critical in 1965 and was operated until 1969





MSRE

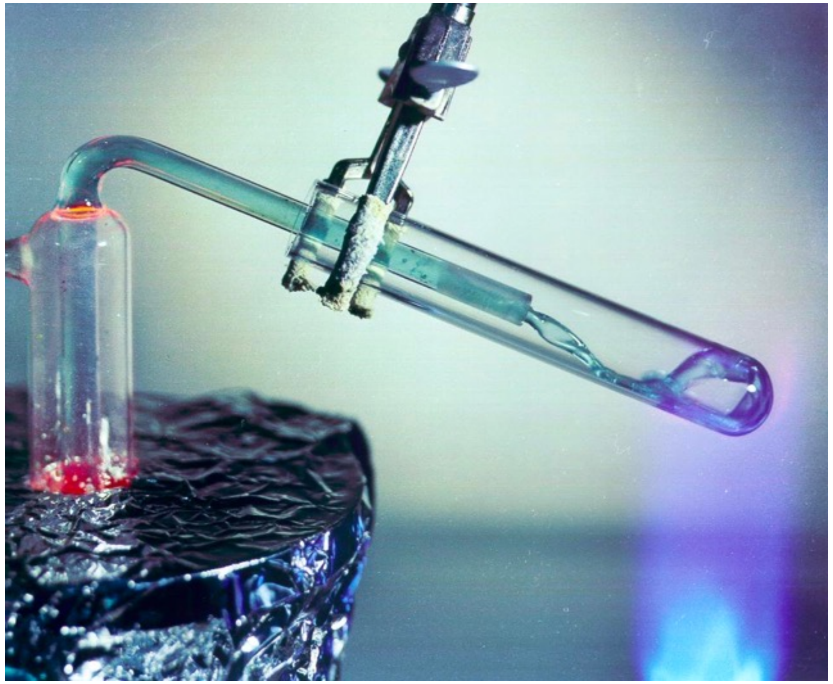
- MSRE was a circulating fuel type, utilizing LiF-BeF_2-ZrF_4-UF_4
- The secondary coolant salt was LiF-BeF_2 (FLiBe), and the moderator was graphite
- Salt-facing component were made of Hastelloy-N, which is a low chromium, nickel–molybdenum alloy



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)
  - Oxidation prevention material
  - Fission products

- Coolant salts are molten salts with advantageous heat transfer properties



Fuel Salt Requirements

- Low neutron absorption of non-fissile species
- Radiolytic/thermal stability under in-core conditions
- Dissolve fissile materials
- High heat capacity, high boiling point, high thermal conductivity fluids
- Melting point below ~525C
- Low vapor pressure
- Relatively insensitive to fission products
- Both fluoride and chloride salts, under mildly reducing conditions, are reasonably compatible with high temperature structural alloys and graphite

Table 1 Thermodynamic properties of fluorides

Compound (solid state)	$-\Delta G_{f,1000}$ ($kJ\,mol^{-1}$)	Compound (solid state)	$-\Delta G_{f,1000}$ ($kJ\,mol^{-1}$)
LiF	522	AlF_3	372
NaF	468	VF_2	347
KF	460	TiF_2	339
BeF_2	447	CrF_2	314
ThF_4	422	FeF_2	280
UF_3	397	HF	276
ZrF_4	393	NiF_2	230
UF_4	389	CF_4	130

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

Solution Species

- Solute species serve to lower the melting point, and can dually serve as an oxygen getter
- Must have low neutron absorption cross section and be chemically compatible with cladding
- BeF2, LiF, ZrF, and NaF are commonly utilized due to the combination of these properties

Fluoride compounds in solid state	ΔG_f, 1000K[a,b] (kJ/mol of F)	(kcal/mol of F)	Melting point (°C)	Thermal neutron cross-section (barns)
Diluents				
CaF_2	–523	–125	1418	0.43
LiF	–523	–125	910	0.18
BaF_2	–519	–124	1368	1.17
SrF_2	–515	–123	824	0.17
YF_3	–473	–113	1290	0.23
MgF_2	–473	–113	848	0.033
NaF	–469	–112	727	0.032
KF	–456	–109	1387	1.27
BeF_2	–435	–104	1263	0.063
ZrF_4	–393	–94	995	0.53
AlF_3	–377	–90	858	1.97
PbF_2	–259	–62	554	0.01
BiF_3	–209	–50	649	0.032
Structural metals				
CrF_2	–310	–74[a]	1100	3.1
FeF_2	–278	–67[a]	930	2.5
NiF_2	–243	–58[a]	1330	4.6

Fuel Salt Classes

- Thermal spectrum reprocessing optimized fluoride salts
  - FLiBe (^{7}LiF-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

Coolant Salts

- Coolants have the same requirements as fuel salts, but without the consideration of fission product solubility, and a higher focus on chemical compatibility and thermal properties
- Some secondary systems also consider nitrate salts, such as NaNO3 and KNO3 or a mixture of the two, often referred to as solar nitrate; or fluoroborates such as NaF-NaBF3

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)	1.81 exp (1912.2/T (K))	0.0877 exp (2240/T (K))	0.0248 exp (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)

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
- Chlorides typically have lower melting points, which is preferable

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 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

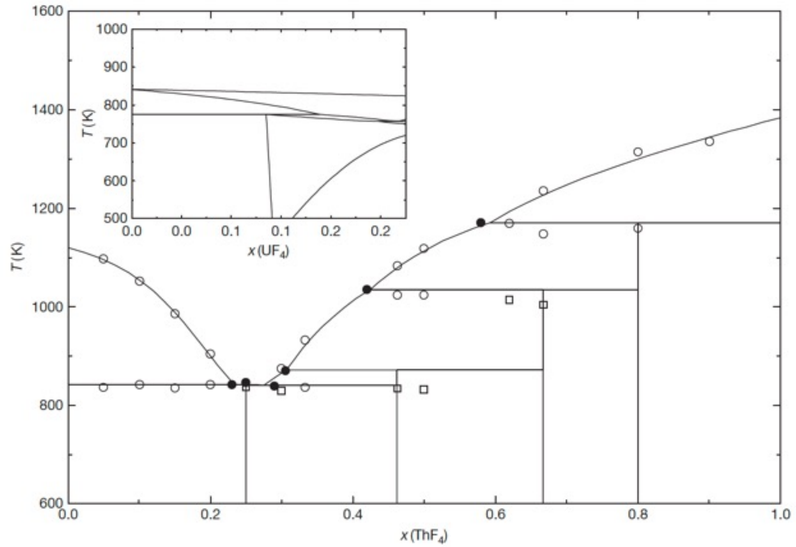
- Thermal spectrum molten salt fuels were identified as candidates for breeding (converting fertile into fissile), specifically in the thorium fuel cycle
- Li-Be-F salts were selected because of the low thermal neutron cross sections of ^{7}Li (σ_{th} = 0.045 b) and Be (σ_{th} =0.0088 b)
- Natural lithium 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
- Tritium production can become a problem without enrichment

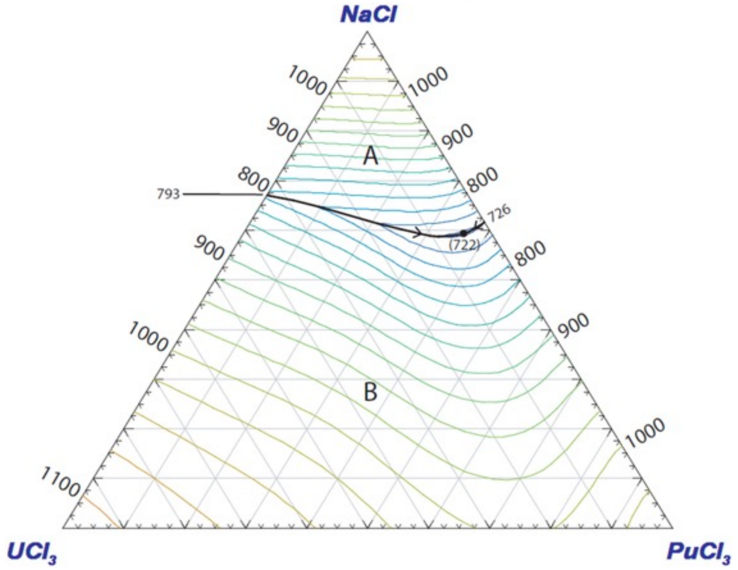
Fast Spectrum MSRs

- 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

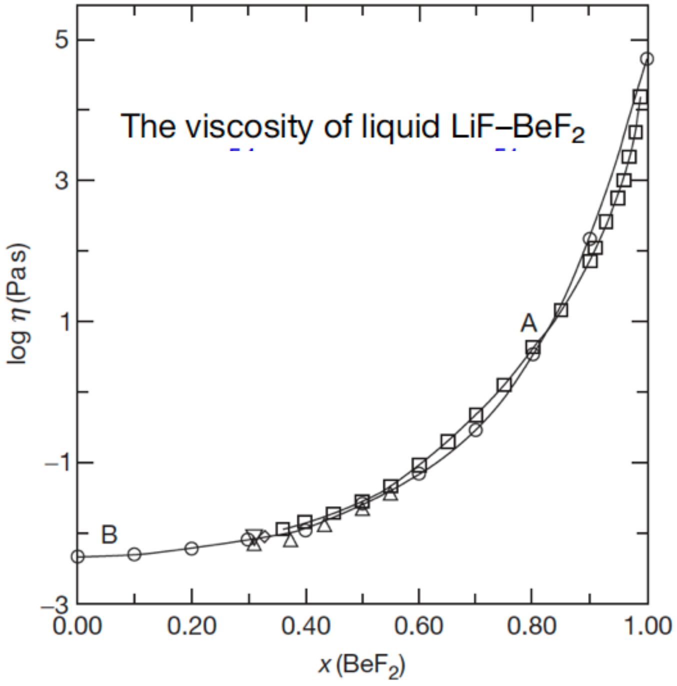
- The solubility of ThF_4 in a matrix of LiF can be deduced from the binary phase diagram
- For example, the solubility of ThF_4 in a melt of LiF for T 903K (inlet temperature of the MSFR) is between 20.0 and 32.3 mol%
- Compositions in this range are, thus, of interest as fuel for MSRs
- Similarly, eutectic composition and melting temperature are key factors that govern the utilization of specific salts
- Many fission products will form some kind of salt species, with varying degrees of solubility

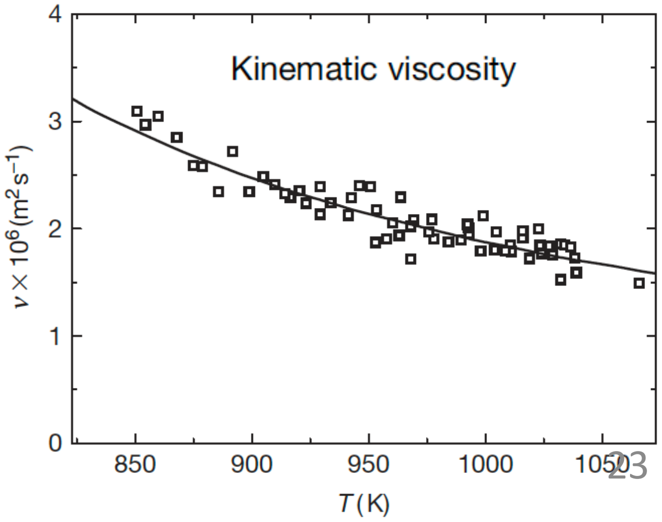




Low Viscosity

- 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 dynamic 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

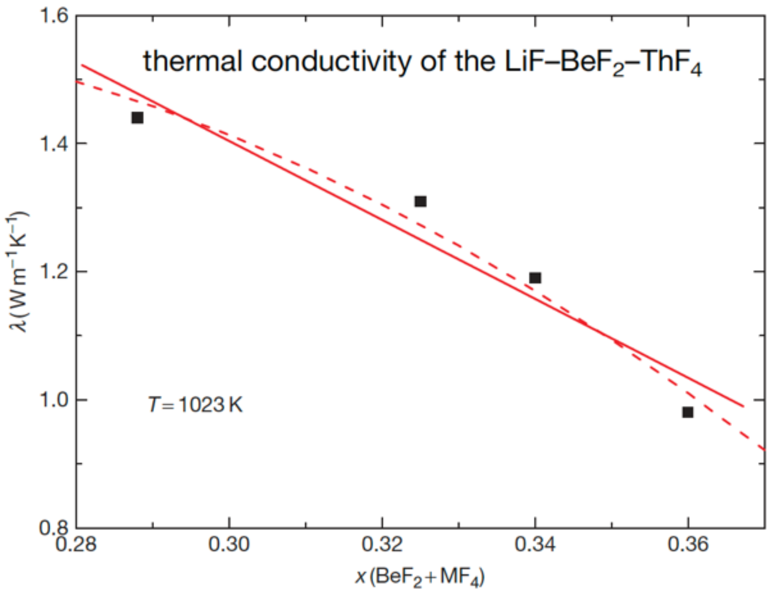




Heat Capacity and Thermal Conductivity

- 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

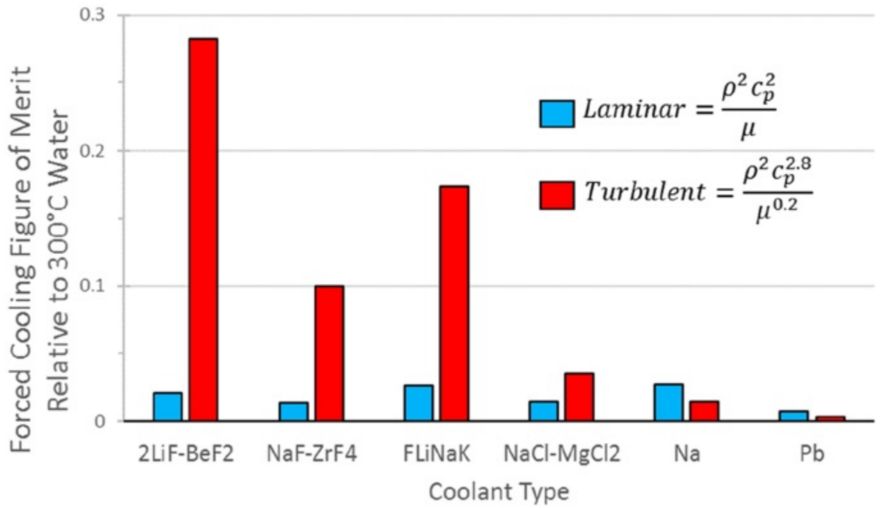


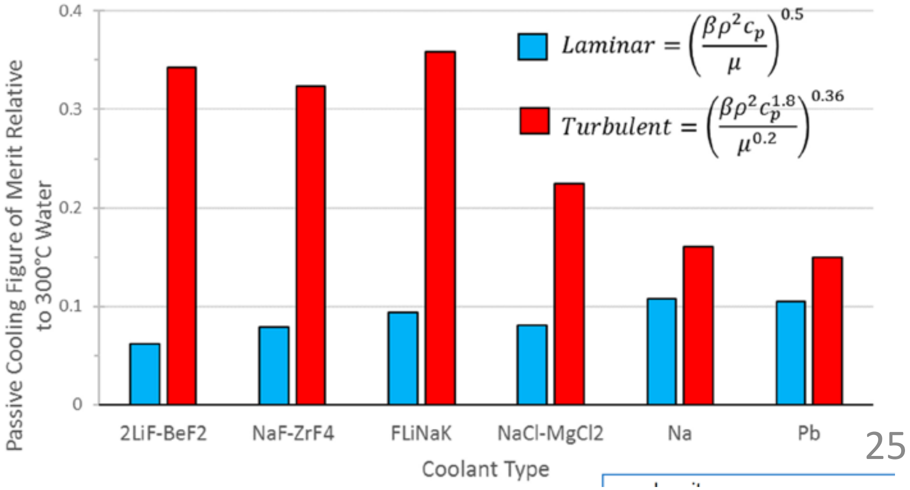
$$\alpha = \frac{k}{\rho c_p}.$$

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + Q$$

Heat Transfer

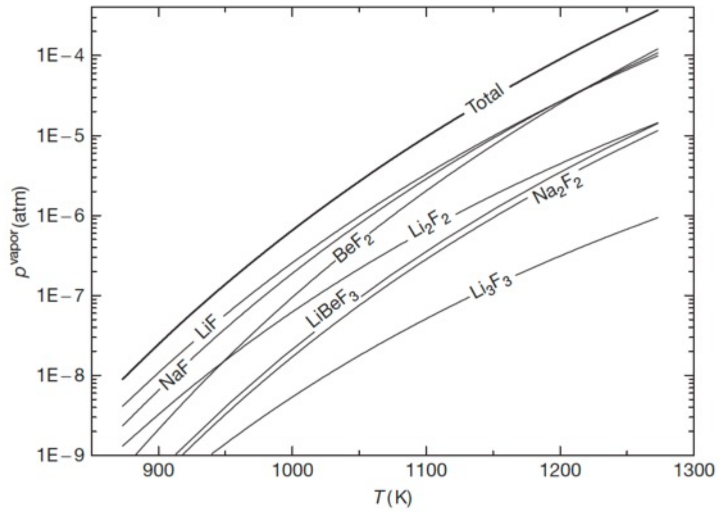
- Large heat capacity and low viscosity are key properties allowing good heat transfer in molten salts
- In both forced flow and passive cooling conditions, molten salts outperform liquid metals in turbulent flow for heat transfer
- However, experimental data for heat transfer is still significantly 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 oxygen 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
- Oxygen also plays a key role in corrosion processes

- 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

Summary

- Molten salt reactors: intro and history
- Fast and thermal; high temperatures; low pressures; flowing fuel salt with secondary salt loop
- Fluorides and chlorides salts for different applications
- Requirements for fuel salts: low melting point, good thermal conductivity, radiation/temperature stability, beneficial solution species, etc.
- Talked through the concepts of a number of the properties of salts
- Control of oxygen and redox conditions is critical to limit precipitation of the fuel and corrosion of the cladding