

Module 3: Reactor Perspective on Fuel and Coolant Salt Properties

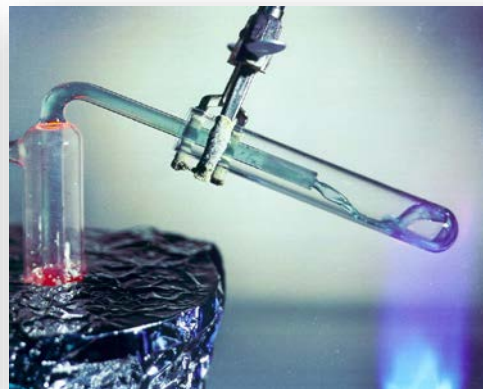
David E. Holcomb, Ph.D.
Nuclear Energy and Fuel Cycles Division

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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



(left) Solid “Frozen” and (right) Liquid “Molten”
 $2\text{LiF}-\text{BeF}_2$ salt

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
Tennesine	(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)

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)	😊	😊	😊	😊	☹️

^aHigh system working temperature desirable for high efficiency power conversion and process heat applications

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

^cLow primary system pressure reduces cost of primary vessel and piping and reduces energetics of pipe break accidents

^dLow 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 NNGNP/NHI Heat-Transfer Loop*, ORNL/TM-2006/69
 - T. M. Besmann and J. Schorne-Pinto, *Developing Practical Models of Complex Salts for Molten Salt Reactors*, *Thermo*, 2021, 1, 168-178, doi: 10.3390/thermo1020012

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 below ~550°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

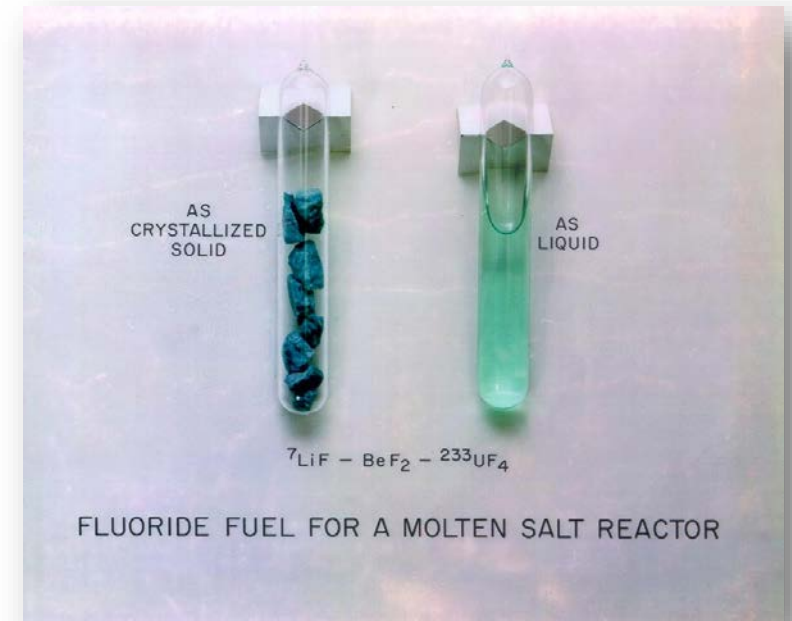
Elements or Isotopes Which may be Tolerable in High-Temperature Reactor Fuels

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.

Composition of Fuel Salts Is Tailored to Performance Objectives

- Fuel salts consist of a mixture of halide and
 - Fissile material
 - Fertile material (if used)
 - Solvent (diluent)
 - Lowers melting point
 - Moderates neutron spectrum
 - Decreases viscosity
 - Fissile oxidation prevention material
 - Preferentially oxidizes to avoid creation of fissile oxide particles due to contamination
- $$\text{ZrF}_4 + \text{UO}_2 \Leftrightarrow \text{ZrO}_2 + \text{UF}_4$$
- Fission products (upon use)
- Redox adjustment materials (e.g., Zr, Mg, Be)



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

Source: ORNL/TM-4174

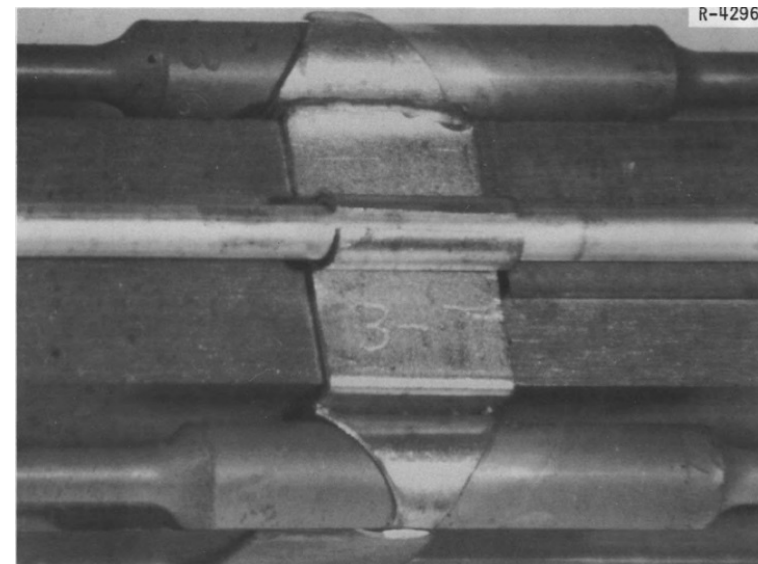


Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

Halide Salts Are Vulnerable to Radiolytic Decomposition at Low Temperatures

- Recombination ceases to dominate radiolysis as fuel salt cools
 - Fluoride fuel salt production of F_2 becomes significant below $150\text{ }^\circ\text{C}$
 - Formation of UF_6 becomes significant if fuel salt containing F_2 is subsequently reheated to $\sim 200\text{ }^\circ\text{C}$
 - Periodic reheating of fuel salt key to used MSRE fuel salt uranium migration
- Experience with chloride salts is almost nonexistent
 - Likely has similar radiolysis issues as fluoride salts
 - Would release chlorine gas including ^{36}Cl
 - No high-volatility uranium chlorides

Oxygen Contamination of Fuel Salt Can Result in Uranium Oxide Precipitation

- Oxygen substantially increases oxidative corrosion
- ZrF_4 included in MSRE fuel salt to precipitate as ZrO_2 upon oxygen contamination instead of UO_2
 - $ZrO_2(s) + UF_4(d) \rightleftharpoons ZrF_4(d) + UO_2(s)$ driven leftward by ZrF_4
- Chloride salts rely on adequate solubility of uranium oxides
 - Uranium and zirconium oxide precipitate at about same oxide activity
 - Carbochlorination can be employed to remove oxygen from melt (likely in a side stream)
 - $CCl_4 + UO_2 \rightarrow UCl_4 + CO_2$

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)
 - More volatile products can also be formed (e.g., CsI)
 - 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
²³⁵U fission yield

$^{137}\text{I} \rightarrow ^{137}\text{Xe} \rightarrow ^{137}\text{Cs}$

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

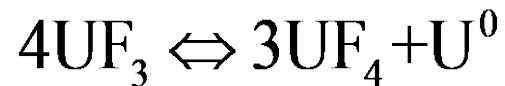
sometimes soluble

Cover Gas Handling Is a Key Element of Any MSR

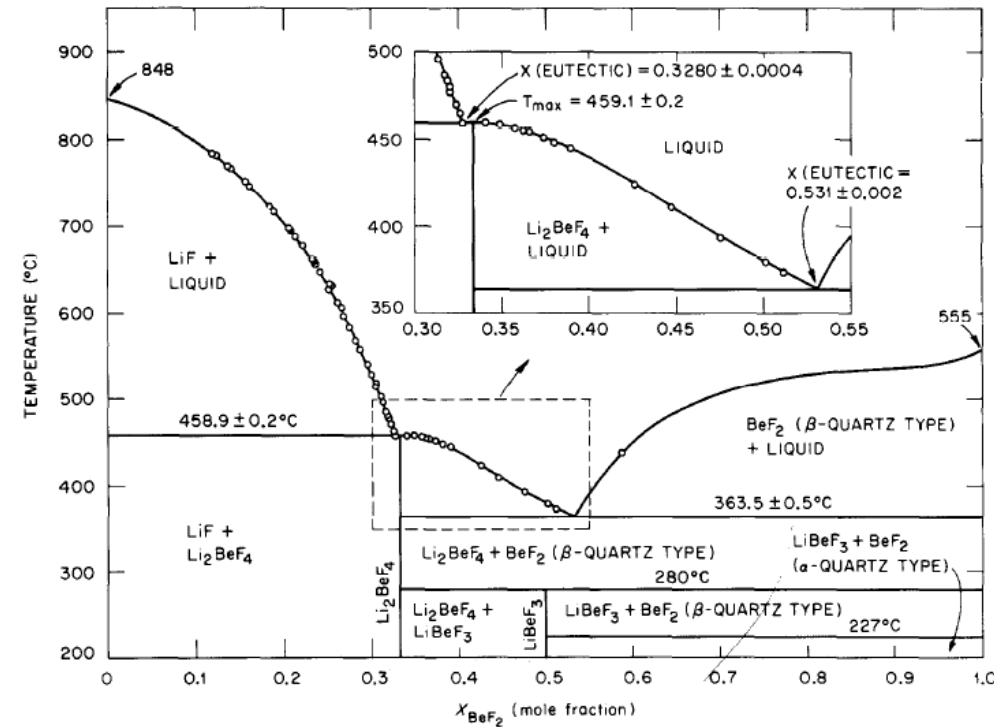
- Distribution of fission products is a central safety issue
 - Decrease in quantity of fission products in the core limits potential fuel accident source term
 - Fission products away from core change decay cooling requirements and radionuclide containment requirements
- Cover gas will inevitably contain 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 likely to be bottled
- Some fuel salt fissile components have significant vapor pressures
 - Pure UCl_4 boils at 791°C
 - Vapor pressure substantially reduced for realistic $\text{UCl}_4/\text{UCl}_3$ ratios
- Some solvents vaporize incongruently
 - ZrF_4 sublimates resulting in snow-like deposits in exhaust piping

Thermal Spectrum Fuel Salt Behaves Similarly to Solvent Salt

- MSRE nominal fuel mixture was
 - 65 LiF, 29.1 BeF₂, 5 ZrF₄, 0.9 UF₄ (mol %)
- Uranium enriched to 33%
- Uranium trifluoride disproportionates in most molten fluoride solutions



- Large UF₄/UF₃ ratio prevents disproportionation
- Isotopically pure ⁷Li - nominally 99.993% at MSRE
 - Means to limit tritium production due to large ⁶Li cross-section

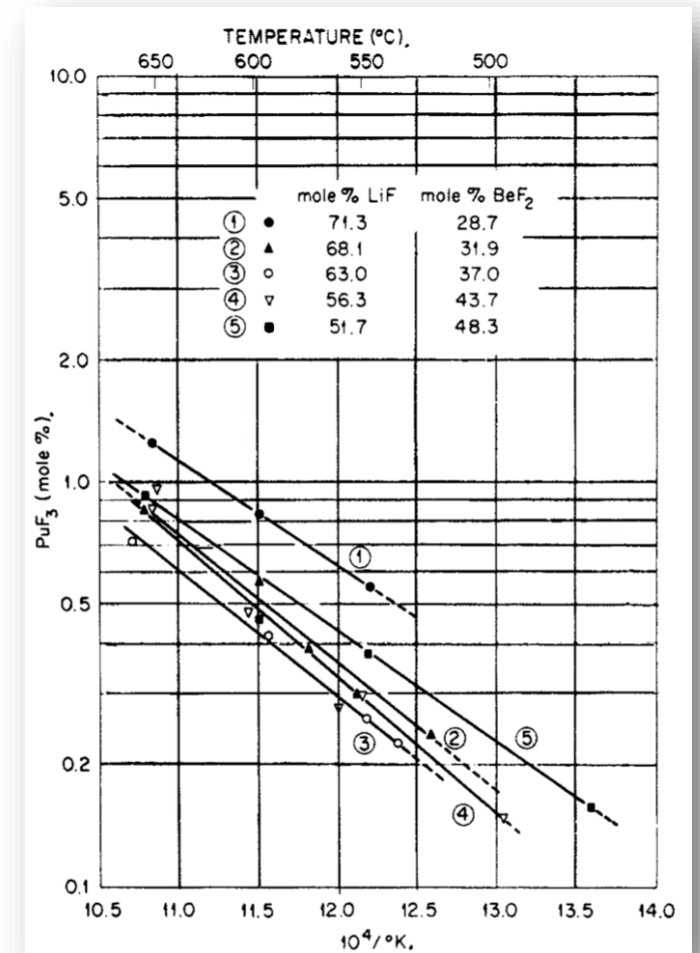


LiF-BeF₂ Phase Diagram

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

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 and 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

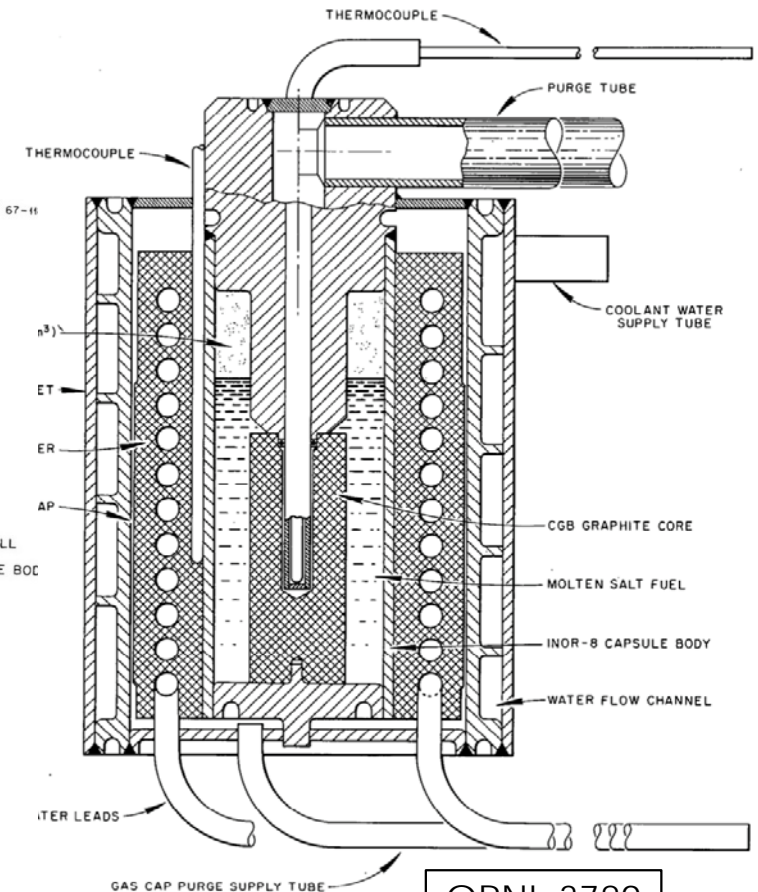
Source: C. J. Barton, "Solubility of Plutonium Trifluoride in Fused-Alkali Fluoride-Beryllium Fluoride Mixtures" *J. Phys. Chem.*, Vol. 64, 1960

Historic MSR Program Performed Capsule, Loop, and Reactor Fuel Salt Experiments

- Fuel salt capsules irradiated to assess volatility of fission products (particularly iodine, tellurium, and ruthenium) – typical experiment ORNL-MTR-47-6
 - Two sealed capsules
 - Two connected to tubing for on-line gas analysis
 - Separate purge-gas lines and sampling lines

Typical Capsule Assembly

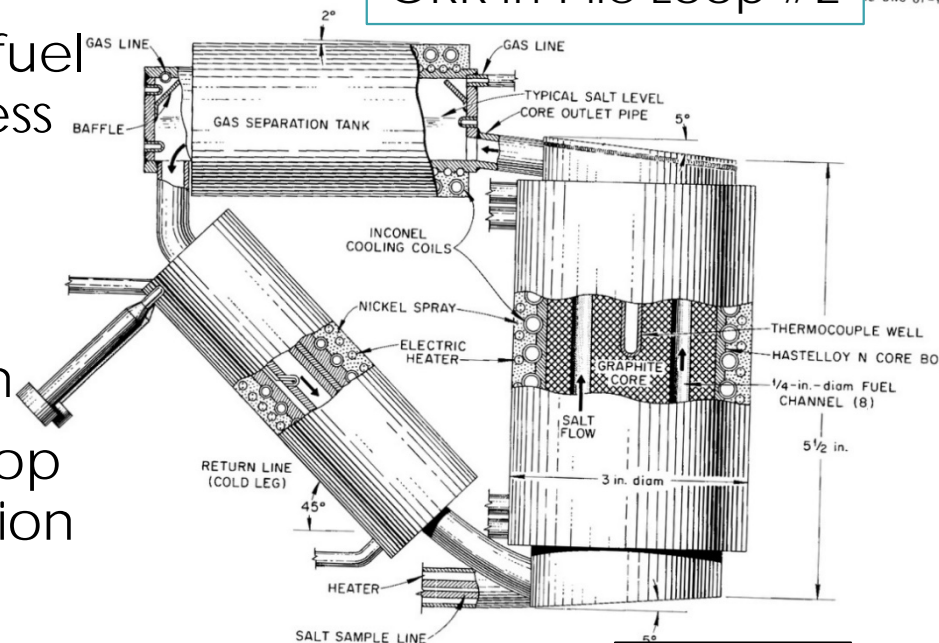
ORNL-DWG 64-4010



ORNL-3789

ORR In-Pile Loop #2

ORNL-DWG 67-11

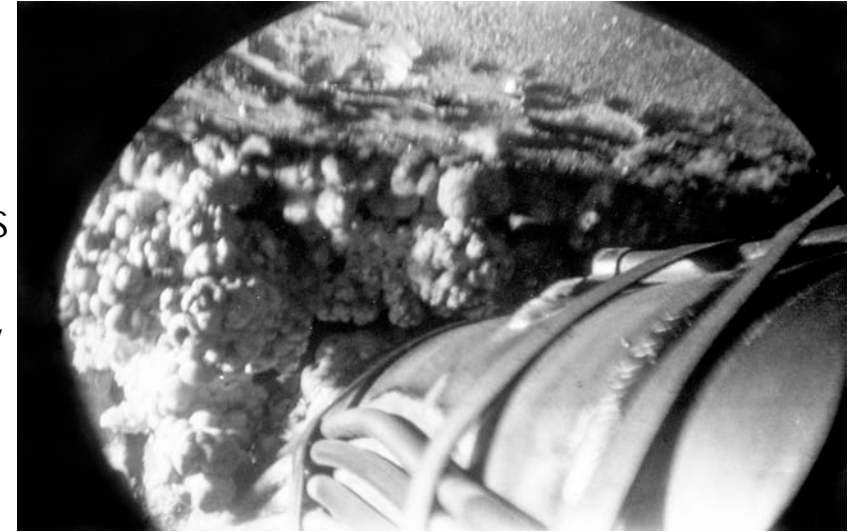


ORNL-4170

- In-pile natural circulation fuel salt loop operated to assess fission product behavior
 - Loop included free surface continuously purged with dry helium
 - Following operation loop was sectioned and fission product activities measured throughout

Fission Product Releases Into Cover Gas Were Also Evaluated at MSRE

- Direct measurements difficult
 - Only gas interface was in the pump bowl whose spray system could not be turned off. The bubbles and mists were not constant since they were affected by salt level, which varied continuously.
 - Sampler system geometry limits,
 - Lubricating oil leak from the pump bearings,
 - Flow and blowback between the pump bowl and the overflow tank
- MSRE fuel salt samples were obtained and evaluated in hot cells
 - Two different types of aerosols form in the gas phase above fuel salt and that the noble metal and fuel salt aerosols travel independently of each other
 - Molten salt must be radioactive to produce the fuel salt aerosol
- Upon final shutdown of the MSRE one of the freeze valves developed a leak
 - Gamma-spectrometric analysis was performed on samples from the containment atmosphere
 - 20 to 25 Ci of ^{133}Xe , 16 mCi of ^{131}I , and 20 mCi of ^{132}I



Leaked Fuel Salt from MSRE Freeze Valve

ORNL-4676

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

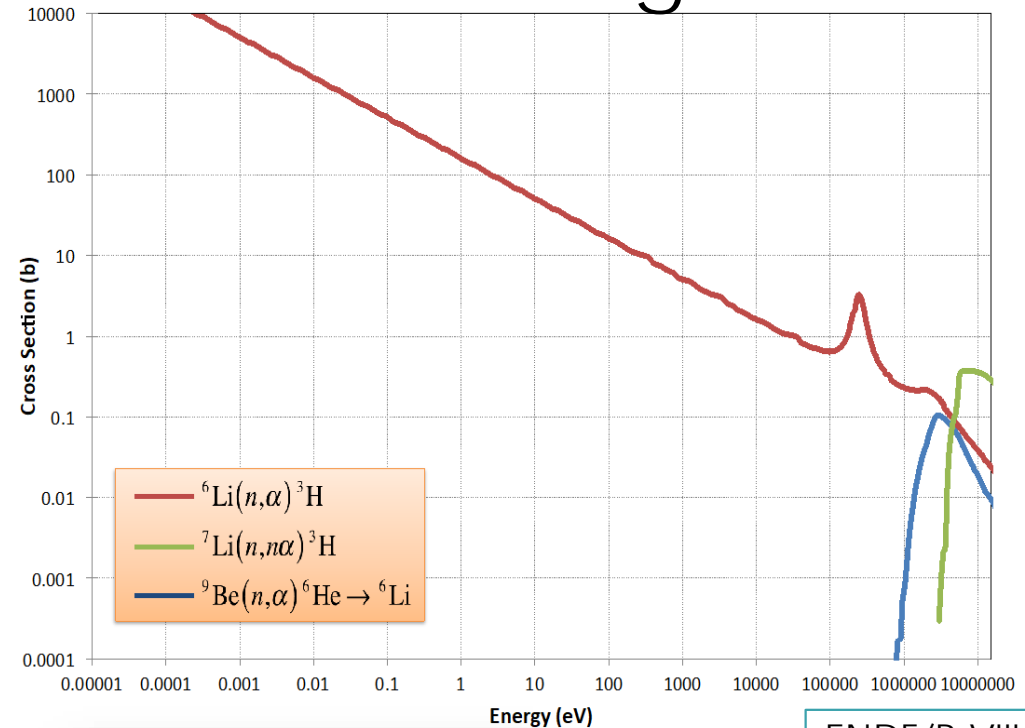
- Lithium-7 enables optimal reactor physics
 - Lithium-6 is a large cross-section thermal neutron absorber that yields tritium
 - Lithium isotope separation is also necessary for fusion and PWR chemistry control
 - Mercury amalgam-based lithium isotope separation was performed at industrial scale in the 1950s for defense purposes
- Chlorine
 - Absorption reactions in ^{35}Cl both produces ^{36}Cl (long-lived radionuclide) and results in a reactivity penalty
 - Significant uncertainty remains in ^{35}Cl isotope cross sections at relevant energies
 - Appears to be less of an issue than thought in prior decades
 - Lack of chlorine isotope separation technology was a key element in US decision in 1956 to pursue thermal breeder MSR
 - Anion exchange based separation demonstrated for chlorine decades ago
 - Not matured or commercialized because of lack of market
 - Low-temperature, liquid phase process

Substantial Fluoride Salt Fission Product Release Information Developed in Historic MSR Program

- Aircraft Reactor Program had both planned and unplanned releases
 - Copious amounts of radioactive gas evolved from the reactor and escaped into the pit from a gas leak in the fuel pump
 - ... became necessary to extemporize a gas pumping system by using compressed air jet pumps to pull a slightly negative pressure (6-10 in. H₂O) on the pits and to discharge the gas through a temporary 2-in. pipeline some 1000 ft away from the building
- Experimental demonstrations of the consequences of the failure of both the reactor and intermediate vessels
 - Irradiating fuel salt, diluting it into a larger volume of unirradiated salt, and rapidly (45-50 seconds) transferring the fuel salt into water in an open tank
 - Resulted in vigorous boiling of water but no detectable radionuclide release

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



ENDF/B-VIII.0

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

	Production rate (Ci/day)
Ternary fission	31
⁶ Li(n,α) ³ H	1210
⁷ Li(n,nα) ³ H	1170
¹⁹ F(n, ¹⁷ O) ² H	9
Total	2420

^aFrom Ref. 1.

Source: Mays, ORNL/TM-5759

Tritium Mitigation is Central to Radionuclide Containment During Normal Operation

- Multiple potential methods for restricting tritium release have been proposed
 1. Chemically trapping in secondary coolant
 - Tritium trapping in coolant salt was demonstrated in NaF-NaBF₄ (8–92 mol %) at larger scale for MSBR
 - Trapping in nitrate salt planned by prospective vendors
 2. Blocking transfer through heat exchanger tubes
 - Double walled tubes or high temperature hydride forming layer in tube wall (e.g., yttrium)
 3. High permeation windows
 4. Absorbing into high-surface-area carbon beds
 - Temperature dependent – desorbs at high temperatures
 - Nickel coating improves trapping kinetics
 5. Back diffusion of hydrogen from secondary side
 6. Conversion into hydrocarbon gas via contact with methanoid (e.g., Be₂C)
 - Not compatible with uranium bearing salts (would become uranium carbide)
- Technical difficulty of stripping tritium is increased by the small diffusion of tritium in salt
 - Necessitates turbulent flow or intimate mixing of salt and stripping media

Fuel Salts Have Multiple Subclasses

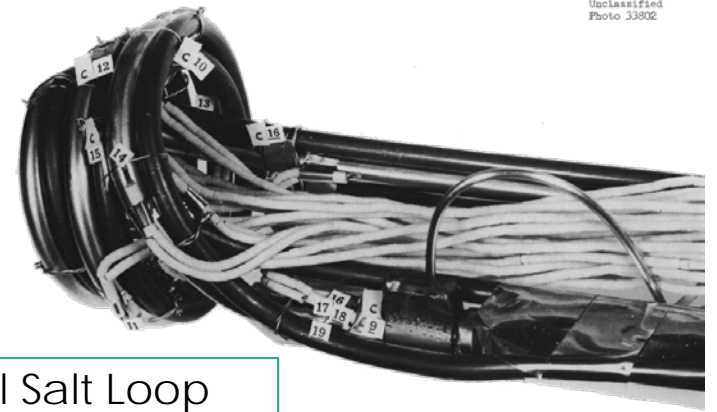
- Thermal spectrum processing optimized fluoride salts
 - Low-melt point solvent (e.g., $2^7\text{LiF}-\text{BeF}_2$ or $\text{NaF}-\text{ZrF}_4$) with lower fissile loading
 - High tritium production but optimized reactor physics for lithium and beryllium bearing salts
 - Higher vapor pressure with ZrF_4 salts
 - Lower fissile loading minimizes potential for fissile oxide precipitation
 - 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 content is a significant challenge for fast spectrum systems
- Chloride salts
 - Enables harder neutron spectrum and enhanced breeding
 - Isotopically separated chlorine preferable
 - ^{35}Cl has higher parasitic absorption and increased ^{36}Cl production
- Mixed fluoride-chloride salts
 - Highest actinide content -> hardest spectrum -> more neutrons
 - Least known properties

European Fast Spectrum
MSR starting fuel
composition
 $\text{LiF}-\text{ThF}_4-\text{UF}_4-(\text{TRU})\text{F}_3$ with
77.7-6.7-12.3-3.3 mol%

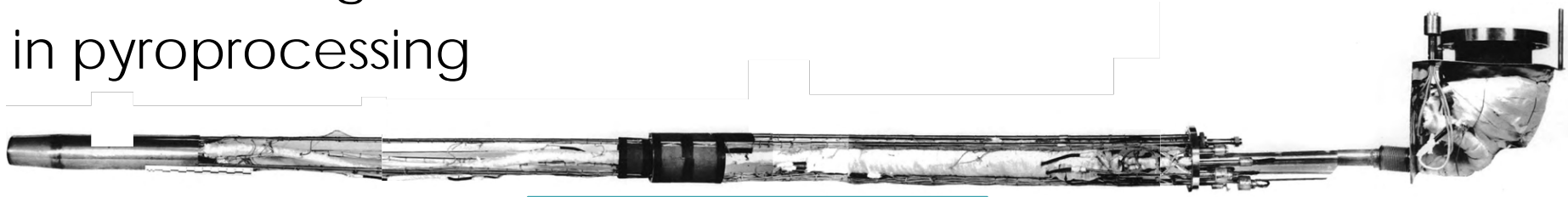
Chlorine
natural isotopic
composition
 $^{37}\text{Cl} = 24.23\%$
 $^{35}\text{Cl} = 75.77\%$

Fluoride Fuel Salts Have Substantially More Experimental Data Than Other 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



MTR In-Pile Fuel Salt Loop
Nose Coil

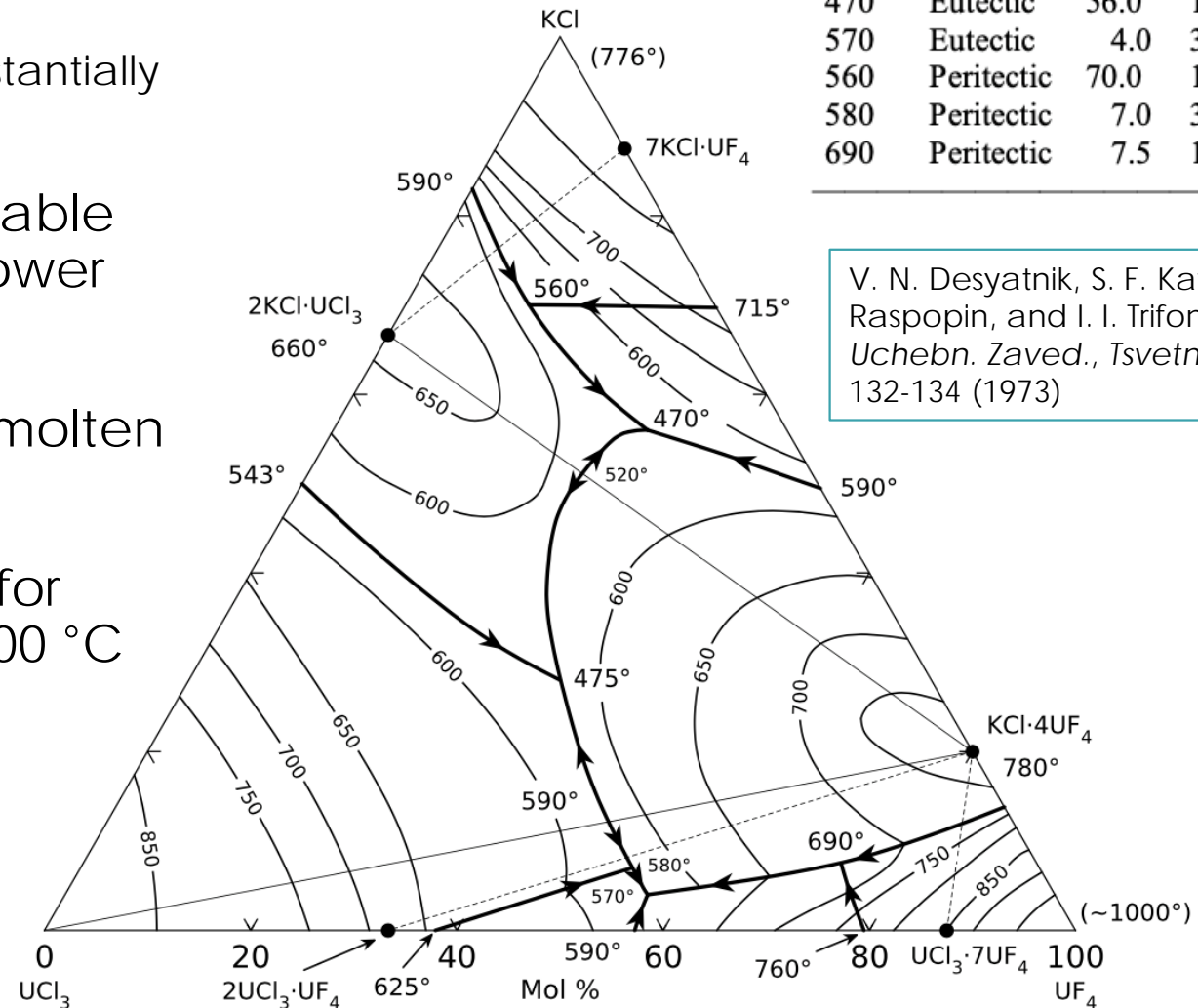


LITR Test Loop

Mixed Halide Fuel Salts Have High Potential But Almost No Experimental Data

- Increased actinide density hardens neutron spectrum
 - Neutron yield per fission increases substantially with fission energy
- High actinide fraction fuel salts enable *breed-and-burn* fuel cycles with lower quantities of fuel salt
- LANL examined mixed halides as molten blankets for fast reactors in 1960s
- Soviets published phase diagram for mixed halide fuel salt showing < 600 °C melting point in 1970s

Temp. (°C)	Type	Composition (mol%)		
		KCl	UCl ₃	UF ₄
475	Eutectic	28.0	36.0	36.0
470	Eutectic	56.0	13.5	30.5
570	Eutectic	4.0	39.5	56.5
560	Peritectic	70.0	18.0	12.0
580	Peritectic	7.0	39.5	53.5
690	Peritectic	7.5	19.0	73.5



V. N. Desyatnik, S. F. Katyshev, S. P. Raspopin, and I. I. Trifonov, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, **16** [2] 132-134 (1973)

Fission Process and Subsequent Fission Product Decays 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
- Fuel salt redox changes with decay of retained fission products and escape of gaseous fission products

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			

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

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
 - Be active metal reductant in fluorides, Mg or Zr in chlorides
- Combination of active metal redox control and cathodic protection recently demonstrated to minimize chloride salt corrosion
- Fluoride salts will likely have an ideal ratio of ~10–100
 - Uranium carbide formed when fuel salt becomes too reducing
 - Structural metal fluorides formed when too oxidizing

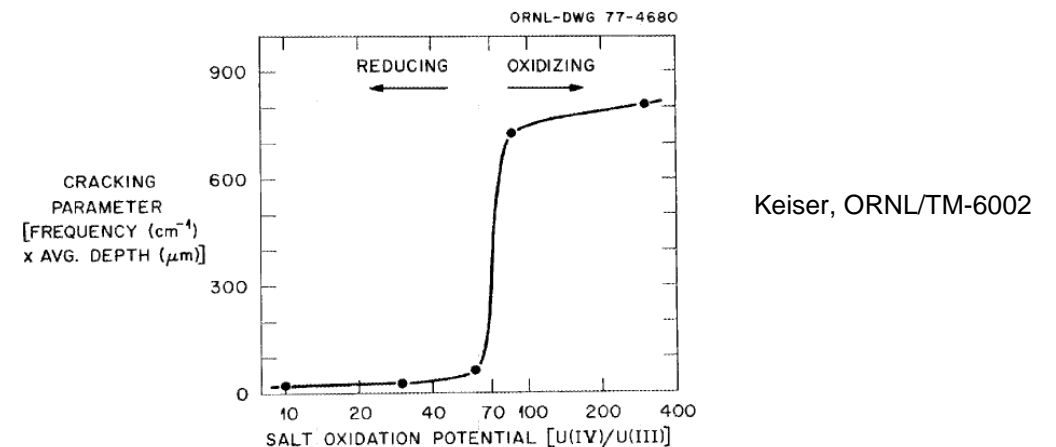
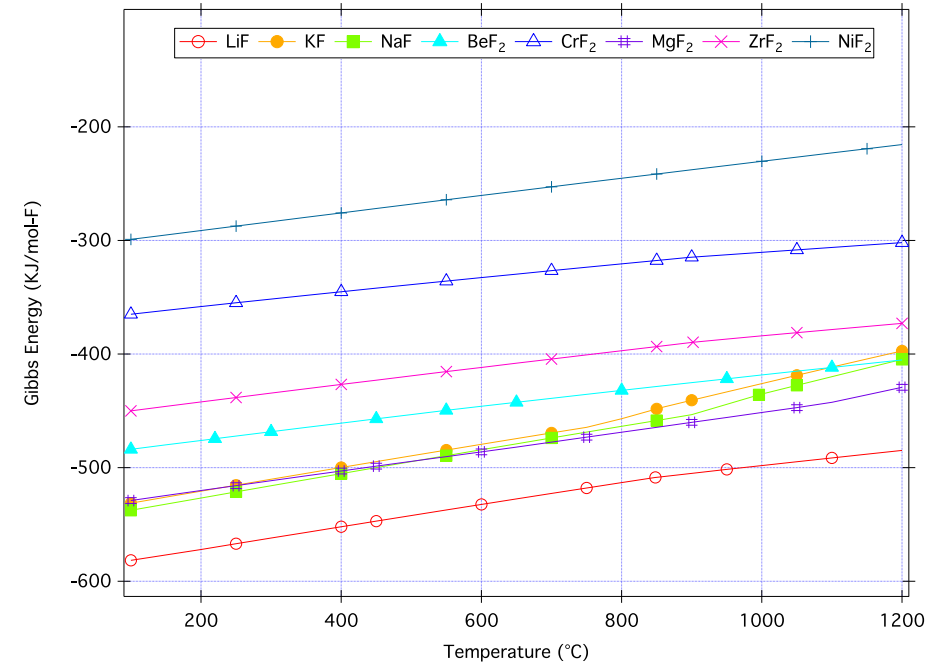
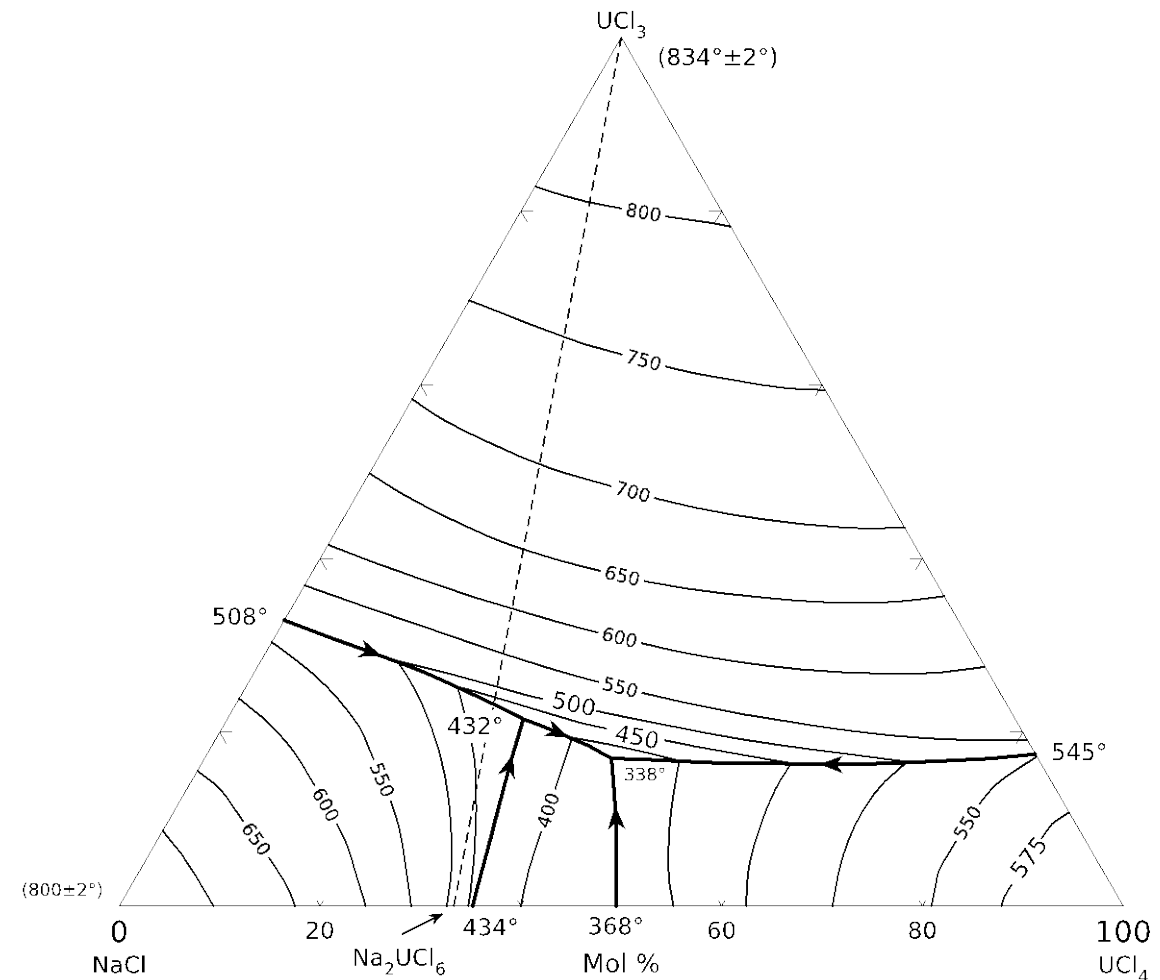


Fig. 12. Cracking Behavior of Hastelloy N Exposed 260 hr at 700°C to MSBR Fuel Salt Containing $CrTe_{1.266}$.

Phase Diagrams of Chloride Fuel Salts Show Fuel System Design Options

- A $\sim 500^\circ\text{C}$ 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)
 - Beyond the acceptable range for conventional engineering alloys

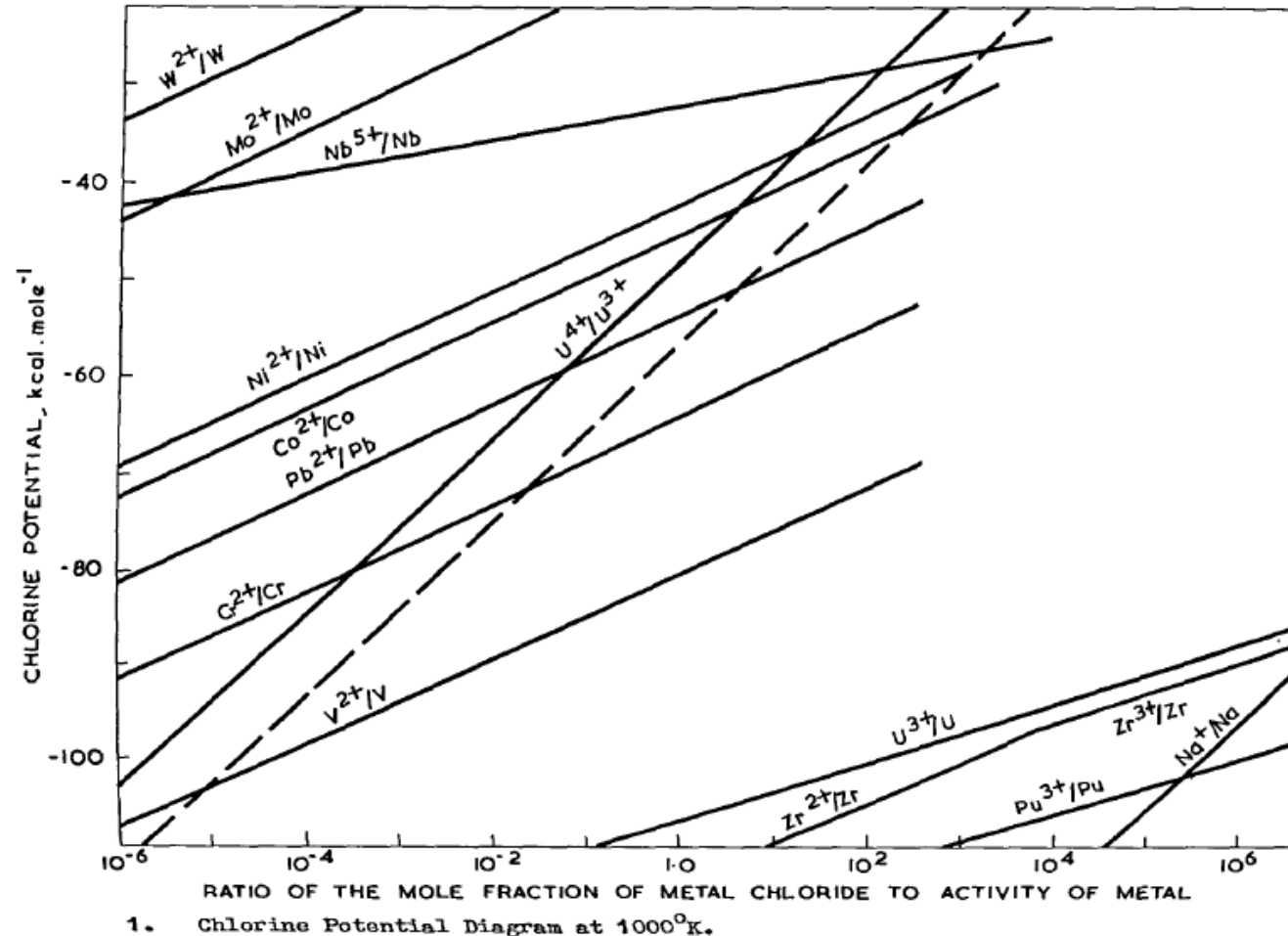


Source: V. N. Desyatnik et al. *At. Energ.*, 31 [6] 631-633 (1971); *Sov. At. Energy (Engl. Transl.)*, 31 [6] 1423-1424 (1971). Fig. 05953—System NaCl-UCl₄-UCl₃

Thermochemical Stability Drives Both Corrosion and Fissile Solubility

- Increased free chlorine results in larger amounts of dissolved structural alloy chlorides
- Increasing ratios of $\text{UCl}_4/\text{UCl}_3$ restrict acceptable choice of structural alloys
- Use of nickel-based structural alloys restricted to $\text{UCl}_4/\text{UCl}_3$ ratios of roughly 0.003 to 5%
 - Smaller amounts of UCl_4 results in disproportionation of UCl_3

$$\text{UCl}_3 \rightleftharpoons \text{UCl}_4 + \text{U}^0$$
- Refractory coatings would enable higher $\text{UCl}_4/\text{UCl}_3$ ratios

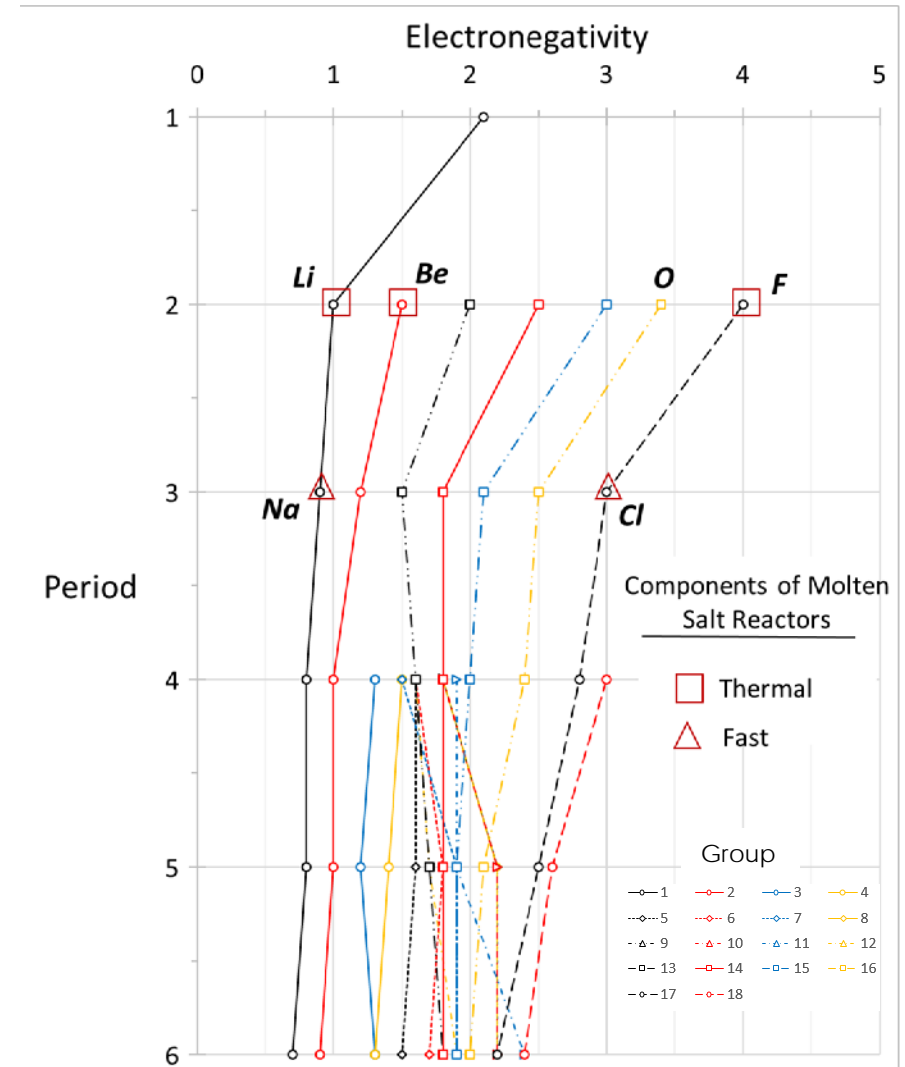


- PuCl_3 disproportionation is less favorable than that of UCl_3

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

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

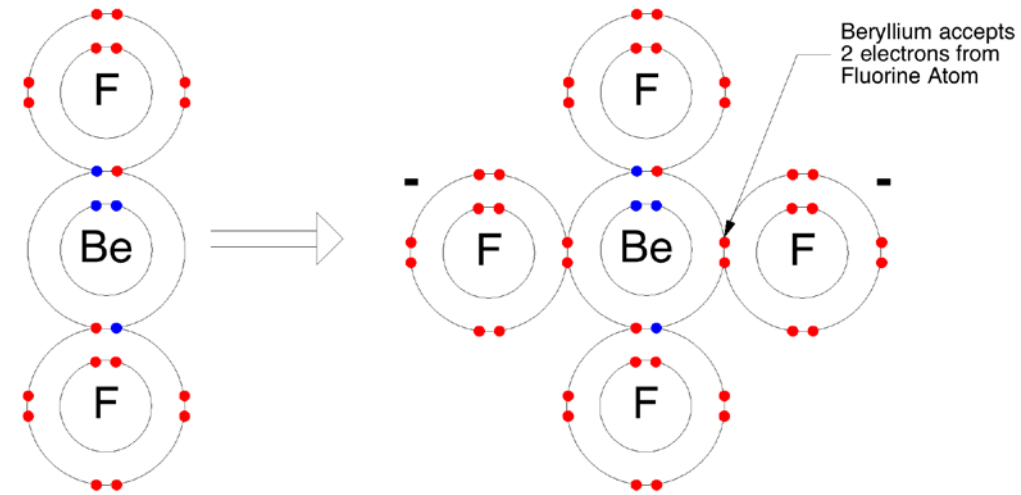
- Salts containing excess oxygen are much more corrosive
- Hydrofluorination for fluoride salts
 - HF is highly corrosive - performed offline
 - Also removes other electronegative impurities - sulfur and chlorine
 - Ammonium hydrofluoride - NH_4HF_2 alternative
- Carbochlorination for chloride salts – phosgene (COCl_2) or carbon tetrachloride used as reactant
 - $\text{MO}_2 + \text{CCl}_4 \rightarrow \text{MCl}_4 + \text{CO}_2$
- Oxygen can also be removed from some chloride melts by precipitation as aluminum oxide
 - $\text{AlCl}_3 + \text{UO}_2 \rightarrow \text{AlO}_2 + \text{UCl}_3$



Source: Taube EIR-332; p.156

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



Beryllium Fluoride Complexation

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

Characteristics of MSR 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 driving force for radionuclide dispersal
- Fluoride salts have substantially more experimental data than chloride or mixed halide salts for reactor operations
- Tritium production from lithium-bearing salts can be mitigated by stripping, blocking, and trapping

Historic MSR Program Provides Substantial Technical Basis for Salt Chemistry

It is fair to say, I think, that as a result of the supporting chemical studies which have accompanied the development of the Molten Salt Breeder Reactor concept, a sound understanding of the chemistry of such molten fluoride fueled reactors has been achieved. The most significant conclusion to be drawn is that such a reactor system -- with partially reduced UF_4 in an LiF - BeF_2 - ThF_4 solvent, contained in Hastelloy N, and moderated by graphite -- is a chemically stable system which is essentially at equilibrium and free of corrosion. Further, the equilibrium chemical behavior of the important fission products is reasonably predictable. The current successful operation of the MSRE supports these conclusions.

C. F. Baes, Jr. 1969