

NE 591: Advanced Reactor Materials

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Last Time

- Intro to molten salts
- Salt reactor designs and general benefits
- Fluorides and chlorides salts for different applications
- Requirements for fuel salts
- Control of oxygen and redox conditions is critical to limit precipitation of the fuel and corrosion of the cladding

Changes During Fission

- The fission process continuously alters the fuel salt redox conditions
- When a U or Pu ion fissions, the available electrons will rearrange on each fission product to satisfy its valence requirements and produce either net oxidizing or reducing conditions in the melt
- For UF₄, four F ions are released; often fission products require less than four and thus there will be an excess of F ions with net oxidizing conditions

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

Fission Products

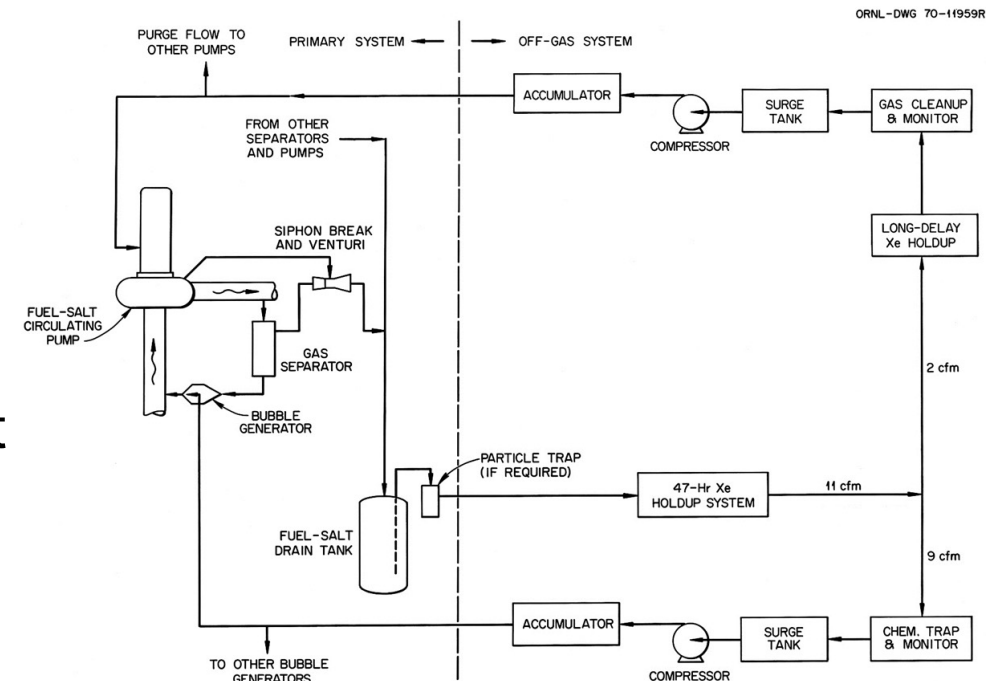
- Distribution of fission products is a central safety issue
- Fission products may be gaseous, solid, or dissolved
- Alkali and alkaline earth fission products form stable salts – Rb, Cs, Sr, Ba
- Lanthanides and some transition metals can form stable salts
- Semi-noble fission products plate out on metal surfaces – Nb, Mo, Tc
- A few elements are very sensitive to redox changes
- May elect to actively remove gaseous fission products
 - Lowers the in-core accident source term
 - Requires cooling fission product traps
 - Bubble formation and collapse results in reactivity jumps

Fission Product Plating

- Noble metals are insoluble in the fluoride salt and can be found in helium sparge gas, on the graphite, or deposited on the metallic surfaces of the primary circuit
- The deposited material contributes to the heat generation from its decay even after the reactor shutdown, decreasing the overall safety of the MSR
- The deposits on the graphite specimens in the case of thermal reactors absorb neutrons during the operation and lead to lower efficiency of the reactor
- One way of avoiding this detrimental precipitation is to remove the insoluble fission products by helium bubbling before they interact with the structural materials

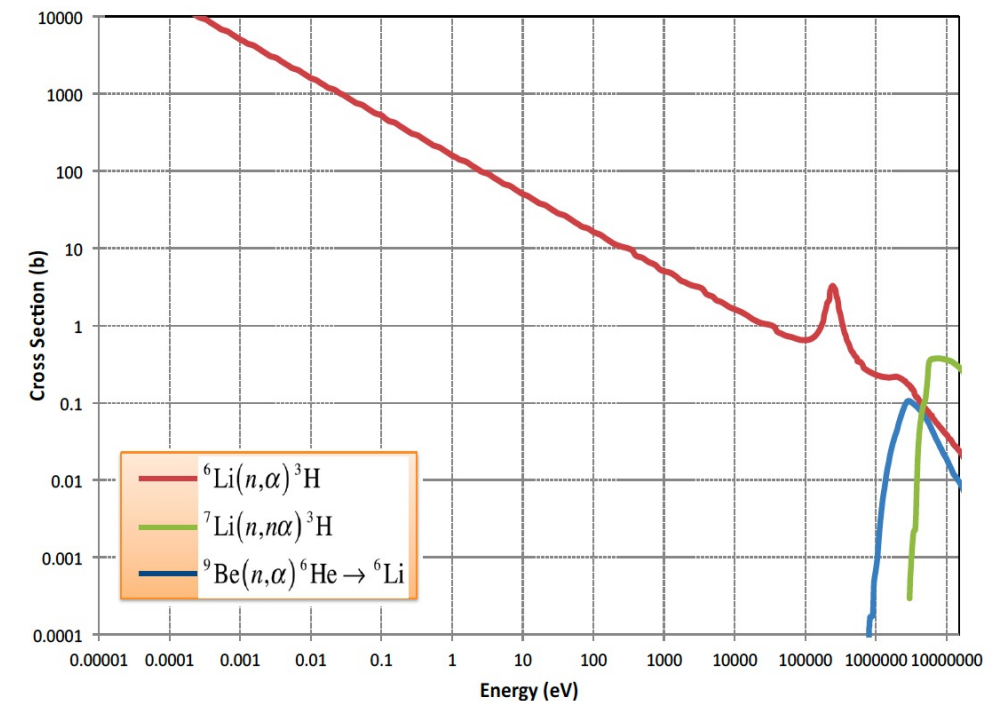
Cover Gas

- The cover gas (off-gas) handling system is a key element of any MSR
- Fission gases such as xenon and krypton will readily escape the salt
- Acidic gases may accumulate as a result of radiolysis
- Tritium is formed by neutron interactions with light elements in the salt
- The cover gas system will contain the radionuclides emerging from the free surface above the fuel salt as well as any sweep or sparging gases used



Tritium

- Tritium production and control is an issue for Li-bearing salts
- Tritium is produced by neutron reactions with lithium, beryllium, and fluorine as well as being a ternary fission product
- Tritium can exist as ions or as TF, depending on redox conditions
- Above 300C tritium will diffuse through structural materials



Radiolytic Stability

- Radiolysis is the dissociation of molecules by ionizing radiation
- Molten salts are highly radiolytically stable
- Salts are combinations of strongly electronegative elements with strongly electropositive metals with very high bond energies
- Formation energy of salts is more negative than metal fluorides
- MSRE graphite and Hastelloy N exposed to coolant salt was clean after ~3 years of operation

Table 1 Thermodynamic properties of fluorides

<i>Compound (solid state)</i>	<i>$-\Delta G_{f,1000}$ (kJ mol⁻¹)</i>	<i>Compound (solid state)</i>	<i>$-\Delta G_{f,1000}$ (kJ mol⁻¹)</i>
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

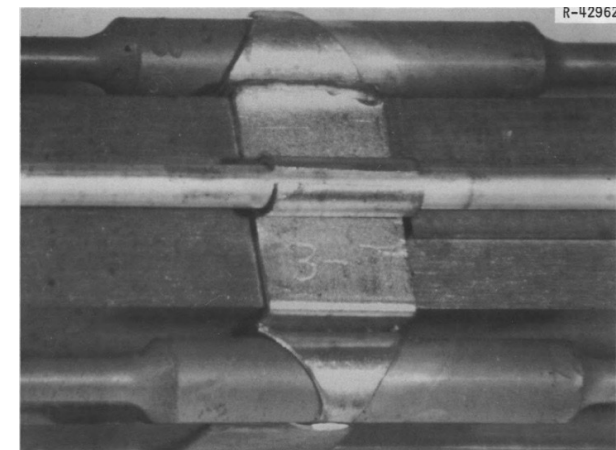


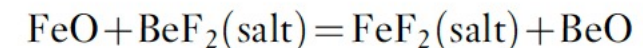
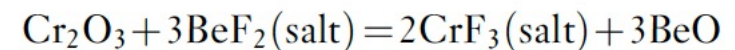
Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

Three principal corrosion processes

- Reactions due to oxides on the metal
- Reactions with dissolved impurities
- Reactions with necessary constituents of the melt

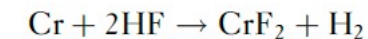
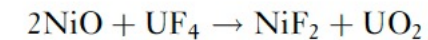
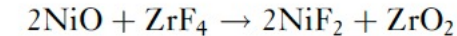
Protective coatings?

- It is not useful to apply a protective coating of, for example, an oxide layer on the structural material for the two following reasons:
 - although some oxides are relatively insoluble in the fluoride melt, most are readily dissolved
 - all oxides rapidly recrystallize
- Oxide films on the surface of the alloy can be attacked by the fluoride melt
- The formed oxides (BeO below) typically don't matter as long as they do not contain fissile elements
- The formed fluorides are more important as they will act as oxidants of Cr in the alloy



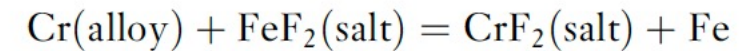
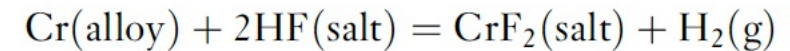
Oxides and Impurities

- Oxide films on the metal are dissolved, leading to cladding constituent fluorides
- Other corrosion reactions are possible with solvent components
- Such reactions can lead to rapid initial corrosion
- These impurity reactions can be minimized by maintaining low impurity concentrations in the salt and on the alloy surfaces



Dissolved Impurities

- In addition to impurities generated by reactions with oxides, impurities may result from incomplete removal of HF or of easily reducible fluorides during the salt purification
- This is done by successive reactions with HF–H₂ and H₂

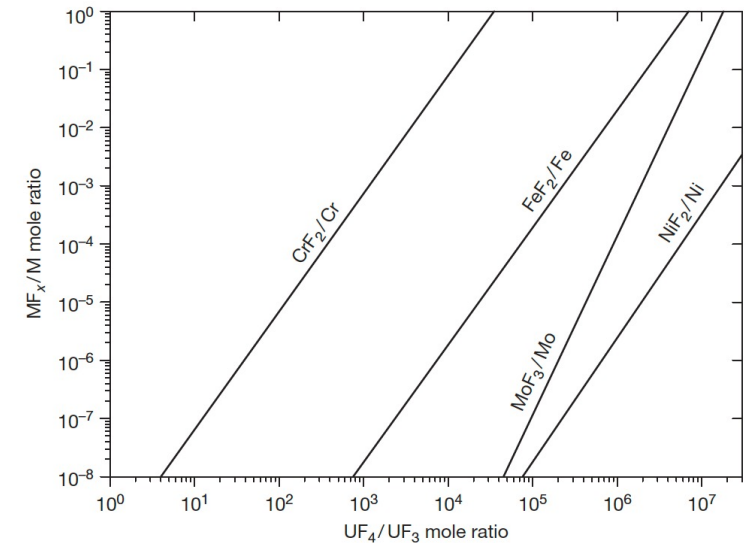
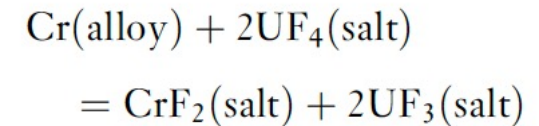


Graphite Compatibility

- Graphite does not react with molten fluoride mixtures of the type to be used in the MSR concepts
- After carbon, borides and nitrides appear to be the most compatible nonmetallic materials
- Thermodynamic data suggest that the most likely reaction is:
$$4\text{UF}_4 + \text{C} \leftrightarrow \text{CF}_4 + 4\text{UF}_3$$
- but this should come to equilibrium at very low CF₄ pressures
- CF₄ concentrations over graphite–salt systems maintained for long periods at elevated temperatures have been shown to be below the limit of detection

Constituents of the Melt

- The oxidation reaction of alloy components with UF₄ has been suggested to play an important role in corrosion
- The equation will define/buffer the electrochemical potential of the salt via the UF₄/UF₃ ratio
- Based on reasonable estimations of the activity coefficients for the above reaction, the equilibrium concentration of CrF₂ is of the order of 130–300 ppm for a fuel with 1% UF₃ contained in Hastelloy-N



Tellurium

- When Te is present in the metallic form in the fuel, it corrodes Ni-based alloys and embrittles its surface grain boundaries
- Embrittlement is a vital issue to consider because it can result in cracking of the structural materials
- This intergranular embrittlement produced in Hastelloy-N can be significantly reduced by adding 1–2 wt% of niobium into the Hastelloy-N
- Another way to suppress the corrosion rate is by increasing the reducing conditions of the fuel, which is done by the increasing the UF₃/UF₄ ratio
- This allows Te to be present as Te⁻² rather than in an 'oxidized' metallic form, and this is less aggressive against the nickel-based alloys

Materials for MSR systems

- The materials required fall into three main categories: (1) metallic components for primary and secondary circuits, (2) graphite (or other structural steels) in the core, and (3) materials for molten-salt fuel reprocessing systems
- The metallic material used in constructing the primary circuit of an MSR will operate at temperatures up to 700–750C
- Nitrogen can oxidize the outside of the material due to exposure to air
- Operating lifetime of 30-50 yrs, with fluences of up to 8×10^{21} n/cm²
- The metal must have moderate oxidation resistance, must resist corrosion by the salt, and must not be subject to severe embrittlement by neutrons
- The material must shapeable, with wall thicknesses from >1cm to less than 1mm, and weldable

Metallic Materials for MSR systems

- Fairly extensive literature exists on corrosion of metal alloys by molten fluorides in convection or forced flow loops
- Limited experimental efforts on irradiation-combined corrosion effects
- Nickel-based and austenitic stainless steels were primarily investigated
- General knowledge:
- Corrosion is associated with outward diffusion of Cr through the alloy
- Corrosion rate is marked by initial rapid attack associated with dissolution of Cr and is largely driven by impurities in the salt
- This is followed by a linear corrosion rate which is controlled by mass transfer

Metallic Materials for MSR systems

- General knowledge:
- Minor impurities in the salt can enhance corrosion by several orders of magnitude
- Dissolution can be mitigated by a chemical control of the redox conditions in the salts
- Stainless steels, Inconel 600, Hastelloy-B, and Hastelloy-W were explored, but either excessively corroded or had poor aging properties
- Hastelloy N was developed with a composition of Ni–16%Mo–7%Cr–5%Fe–0.05%C
- Limited Cr is included to impart moderate oxidation resistance in air, but not high enough to lead to high corrosion rates in salt
- Hastelloy N has excellent corrosion resistance to molten fluoride salts at temperatures considerably above those expected in MSR service

Metallic Materials for MSR systems

- Problems with Hastelloy-N
- Is subject to irradiation hardening due to accumulation of He at grain boundaries
- This is potentially mitigated through alloys with fine carbide precipitates to trap He
- Tiny cracks formed on the inside surface of Hastelloy-N piping for the MSRE
- Intergranular cracks were due to Te, which can likely be controlled with appropriate redox conditions
- Additions of Ti can aide in fine carbide precipitates, and additions of Nb can limit Te cracking
- No alloys with both additions have been studied, but it is supposed to additions of 1% Ti and 1% Nb can sufficiently solve both problems

Materials for MSR systems

- Focus on graphite core
- Graphite is the principal material other than salt in the core of the reference breeder reactor design with a thermal spectrum, or used as a reflector in fast designs
- The graphite structures will operate in a fuel salt environment over a range of temperatures from 500 up to 800C
- There are two main requirements in the graphite in MSRs: that both molten salt and xenon be excluded from open pore volume
- Significant penetration of the graphite by the fuel salt would generate a local spot, leading to enhanced radiation damage to the graphite and perhaps local boiling of the salt

Graphite for MSR systems

- Extensive experimental work has demonstrated the compatibility of graphite with molten salts
- Graphite undergoes the same shrinkage/turnaround processes during irradiation
- For molten salts, post-turnaround graphite is of concern, due to the increased porosity allowing for salt ingress
- This puts a cap on fast neutron fluence in graphite for salt systems at about $3E22$ n/cm², which translates into about 3-4 years as a moderator in the MSBR
- Graphite needs to be surface-sealed to prevent Xe penetration
- ¹³⁵Xe can diffuse into the graphite and function as a neutron poison
- Pyrocarbon sealing was explored, but led to more rapid turnaround

Materials for MSR systems

- Reprocessing materials
- The key operations in fuel reprocessing are (1) removal of uranium from the fuel stream for immediate return to the reactor, and (2) removal fission products from the fuel solvent
- One severe corrosive environment in this process includes salt at 550C with F₂ and UF₆, and so that an average valence of 4.5 exists
- Other severe corrosive environment is at 650C with salt containing molten alloys of Bi, Li, Th, etc. with HF-F₂ gases
- The environment must be an inert gas or a vacuum to prevent deterioration of the reactive species of structural material to ensure long-term service
- Typically, Ni or Ni-based alloys have been used for containment

Other Salt Reactor Concepts

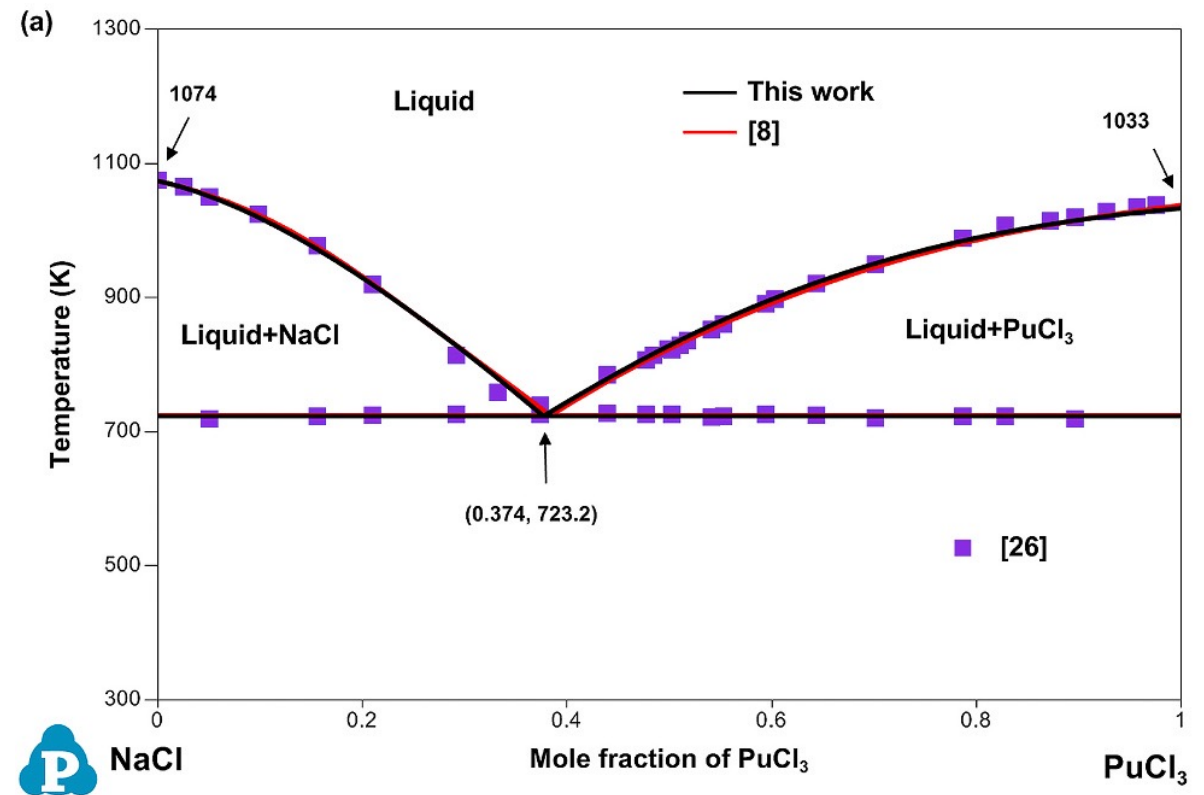
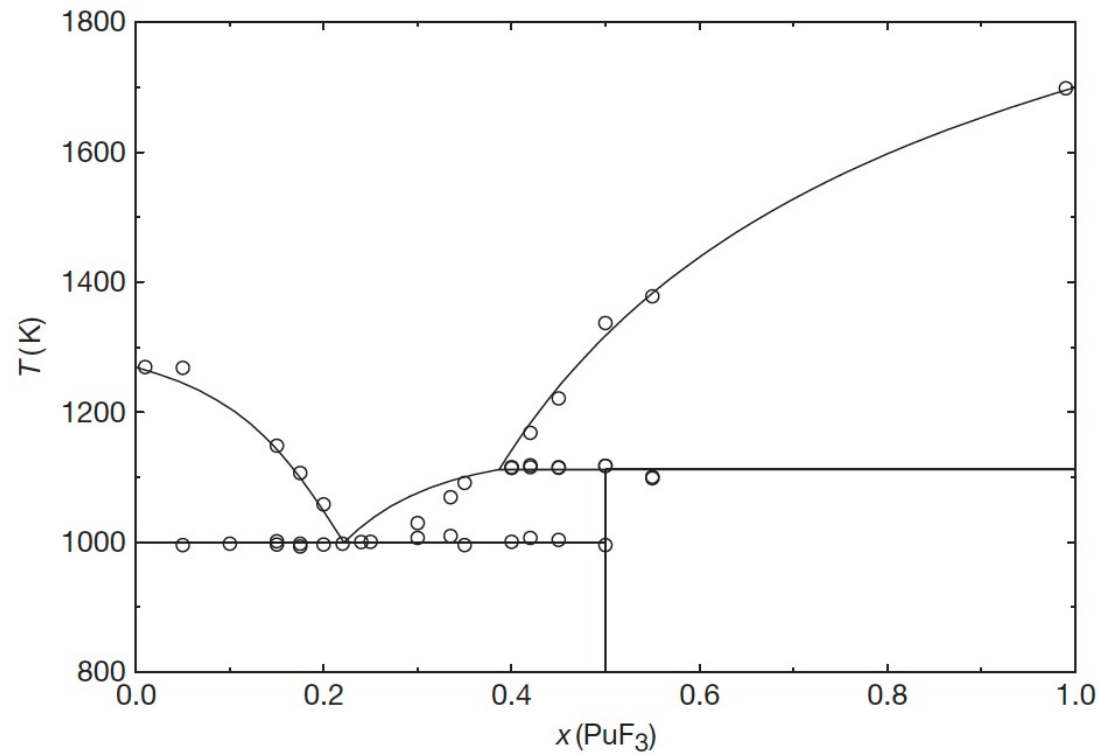
- AHTR: TRISO particles in graphite compact prismatic core with molten salt coolant
- LSFR: solid fueled fast reactor with molten salt coolant
- SSR: liquid fueled, non-flowing
- Secondary Coolant Loop: may use nitrate, chloride, or fluoroborate salts, with different corrosion
- Materials for these systems either experience higher temperatures or higher flux/fluence requirements, and thus Hastelloy-N type materials may not be applicable
- Potential options are 9Cr-1MoV coated in Ni, ODS Ni alloys, Ni-based superalloys, ODS Fe alloys, and Mo alloys
- Stainless steels can be options for secondary loop

Chloride Salt Corrosion

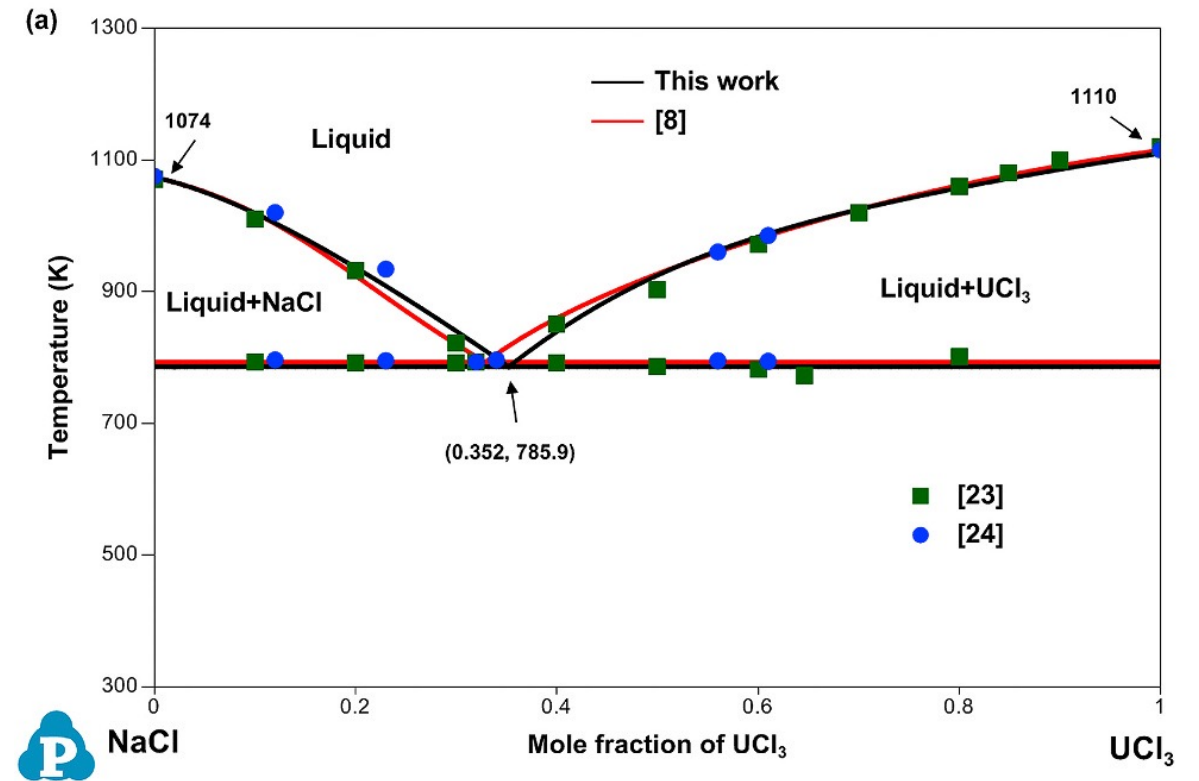
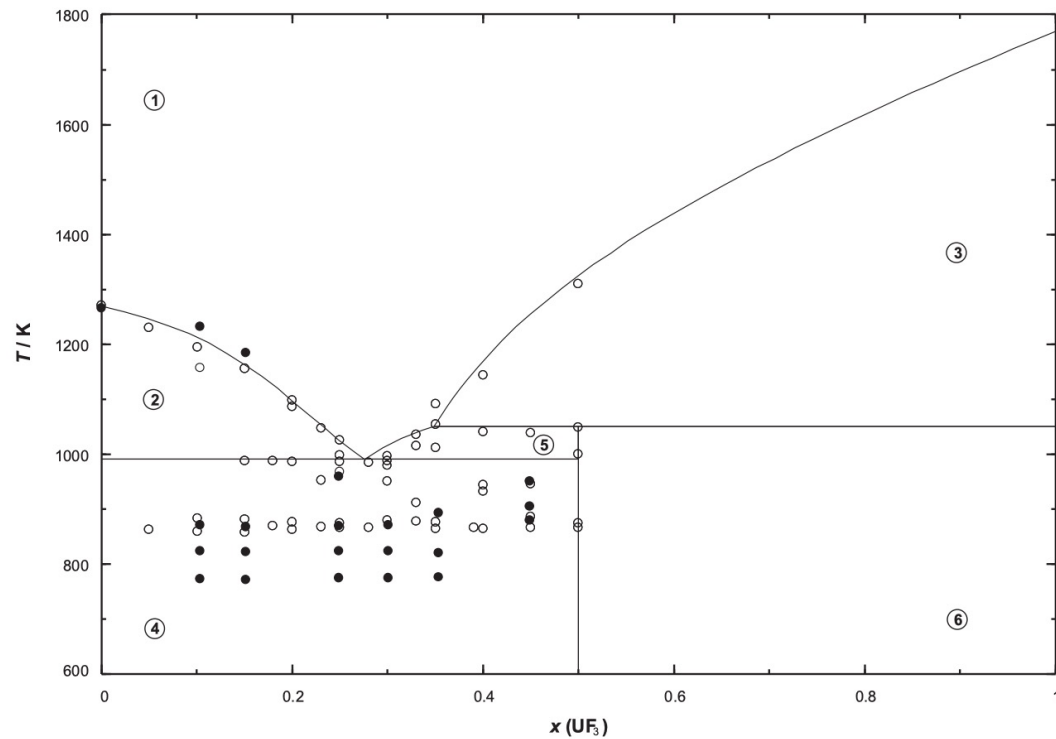
- Very little corrosion data is present for chloride salt systems
- The existing data does not conform to expected trends
- The effect of chromium content in the alloy does not seem to be an important factor, and the effect of temperature is not clear
- These corrosion rates are comparable to fluoride salts with stainless steel, and are considerably higher than corrosion rates with Hastelloy-N

<i>Loop^a</i>	<i>Loop material</i>	<i>%Cr–Ni–Mo in Fe alloy</i>	<i>Duration (h)</i>	<i>T_{max} (°C)</i>	<i>ΔT (°C)</i>	<i>Corrosion rate (μm year⁻¹)</i>
Tests with LiCl–KCl eutectic salt						
TCL-F	347SS	17.5–1.4–0.2	5500	575	155	12
TCL-L1	410SS	12.4–0.2–0.1	2200	570	160	50
TCL-L3	2.25Cr–1Mo	2.25–0–1	697	550	150	High ^b
Tests with 30NaCl–20KCl–50MgCl ₂ eutectic salt (mol%)						
TCL-L5	347SS	17.5–11.4–0.2	2467	500	45	93
TCL-L6	410SS	12.4–0.2–0.1	3971	494	42	79
FCL-M1	347SS	17.5–11.4–0.2	1034	520	0	31
FCL-M2	347SS	17.5–11.4–0.2	656	515	0	256

Na(ha)-Pu(ha)₃



Na(ha)-U(ha)3



Summary

- Distribution of fission products is a central safety issue, and fission products may be gaseous, solid, or dissolved
- Gaseous species can be collected in the cover gas or sparge gas
- The materials required fall into three main categories: (1) metallic components for primary and secondary circuits, (2) graphite (or other structural steels) in the core, and (3) materials for molten-salt fuel reprocessing systems
- Primary focus on Ni-based alloys for a wide variety of salt-facing components
- Graphite can be readily used and has experience in the core
- Corrosion challenges change depending upon the reactor type/design
- We still know relatively little about molten salts, especially regarding their fundamental thermophysical properties and their long-term corrosion behavior under irradiation