

# **NE 795-014: Advanced Reactor Materials**

Fall 2023

Dr. Benjamin Beeler

# Exam Graded

- Average: 81.4
- Curved exams by 8 points

# 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

# 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<sub>2</sub> 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  $U^{4+}/U^{3+}$  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  $UF_4/UF_3$  ratio in a molten salt reactor fuel

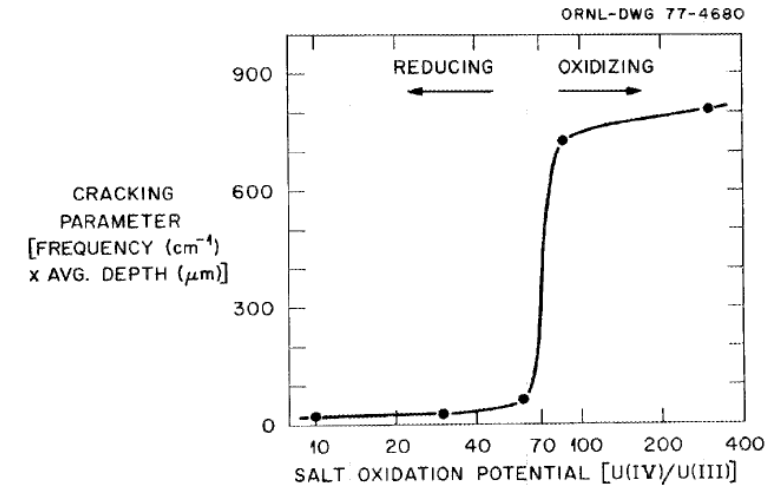
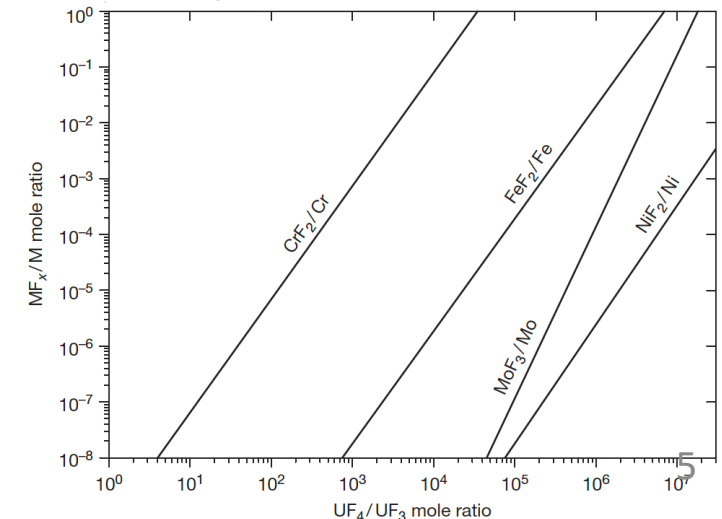


Fig. 12. Cracking Behavior of Hastelloy N Exposed 260 hr at 700°C to MSBR Fuel Salt Containing  $CrTe_{1.266}$ .



# Changes During Fission

- The redox potential is a measure of the tendency of a chemical species to acquire electrons from or lose electrons and thereby be reduced or oxidized
- 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 UF<sub>4</sub>, 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 <sub>3</sub> )	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 <sub>4</sub> )	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

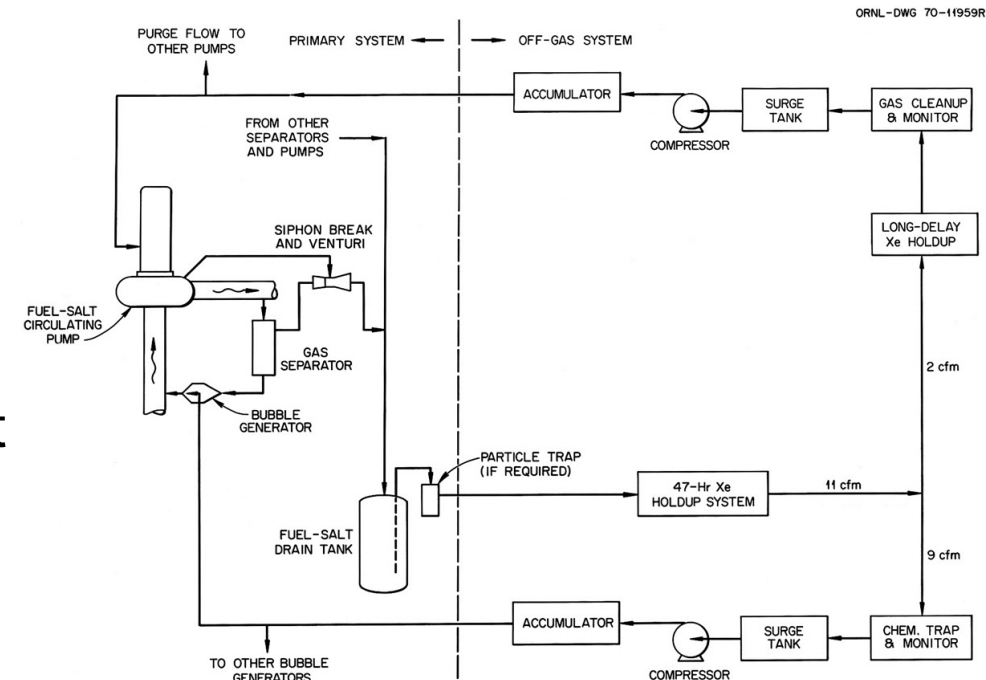
# Fission Product Plating

- 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



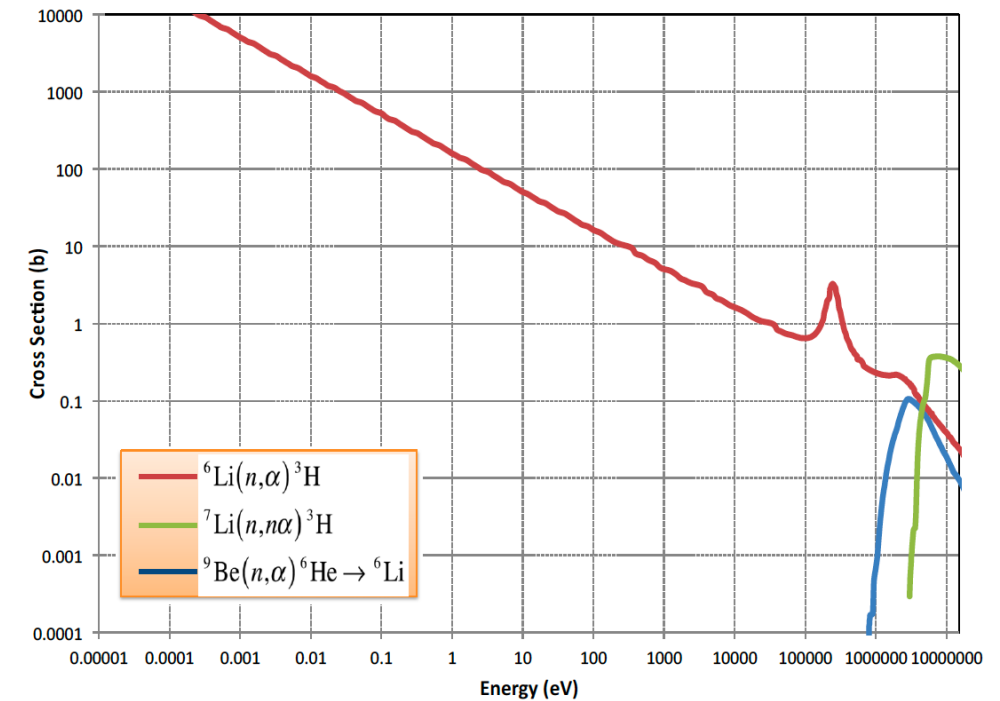
# Cover Gas

- 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><math>-\Delta G_f^{\circ}</math> (kJ mol<sup>-1</sup>)</i>	<i>Compound (solid state)</i>	<i><math>-\Delta G_f^{\circ}</math> (kJ mol<sup>-1</sup>)</i>
LiF	522	AlF <sub>3</sub>	372
NaF	468	VF <sub>2</sub>	347
KF	460	TiF <sub>2</sub>	339
BeF <sub>2</sub>	447	CrF <sub>2</sub>	314
ThF <sub>4</sub>	422	FeF <sub>2</sub>	280
UF <sub>3</sub>	397	HF	276
ZrF <sub>4</sub>	393	NiF <sub>2</sub>	230
UF <sub>4</sub>	389	CF <sub>4</sub>	130

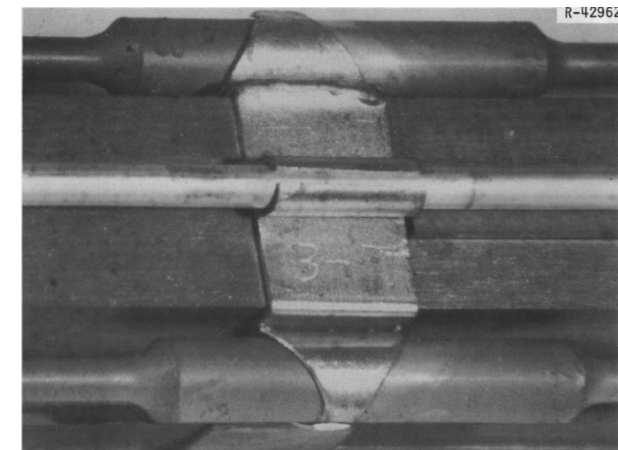


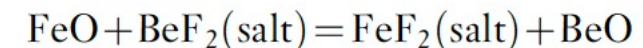
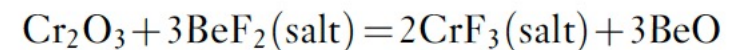
Fig. 1. Graphite and Hastelloy N Surveillance Assembly Removed from the Core of the MSRE After 72,400 Mwhr of Operation. Exposed to flowing salt for 15,300 hr at 650°C.

# 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

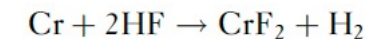
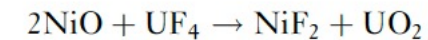
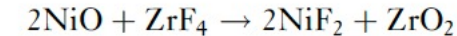


# Cr 'Oxidation'

- 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  $\text{UF}_4$  with structural metals (M) is strongly temperature dependent, and when the salt is circulated, a mechanism exists for mass transfer and continued attack
$$2\text{UF}_4 + \text{M} \leftrightarrow 2\text{UF}_3 + \text{MF}_2$$
- This reaction is of significance mainly in the case of alloys containing relatively large amounts of chromium

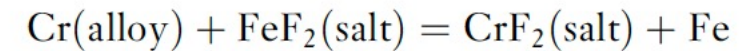
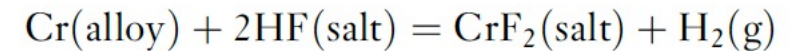
# Oxides and Impurities

- 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–H<sub>2</sub> and H<sub>2</sub>



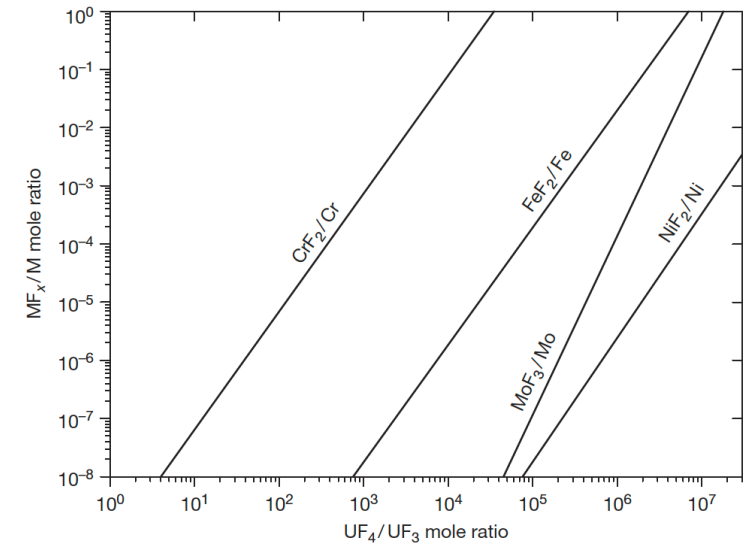
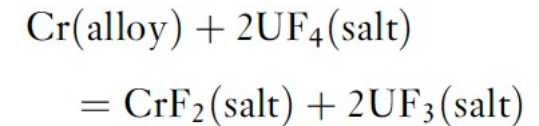


# Graphite Compatibility

- 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 CF<sub>4</sub> pressures
- CF<sub>4</sub> 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 UF<sub>4</sub> has been suggested to play an important role in corrosion
- The equation will define/buffer the electrochemical potential of the salt via the UF<sub>4</sub>/UF<sub>3</sub> ratio
- Excess fluorine liberated via fission reacts with UF<sub>3</sub> to form more UF<sub>4</sub>, increasing corrosion rates
- Based on reasonable estimations of the activity coefficients for the above reaction, the equilibrium concentration of CrF<sub>2</sub> is of the order of 130–300 ppm for a fuel with 1% UF<sub>3</sub> 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 UF<sub>3</sub>/UF<sub>4</sub> ratio
- This allows Te to be present as Te<sup>-2</sup> 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
- Operating lifetime of 30-50 yrs, with fluences of up to  $8 \times 10^{21}$  n/cm<sup>2</sup>
- 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 aid 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 hot 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  $3\text{E}22 \text{ n/cm}^2$ , which translates into about 3-4 years as a moderator in the MSBR
- Graphite needs to be surface-sealed to prevent Xe penetration
- $^{135}\text{Xe}$  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 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<sup>a</sup></i>	<i>Loop material</i>	<i>%Cr–Ni–Mo in Fe alloy</i>	<i>Duration (h)</i>	<i>T<sub>max</sub> (°C)</i>	<i>ΔT (°C)</i>	<i>Corrosion rate (μm year<sup>-1</sup>)</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 <sup>b</sup>
Tests with 30NaCl–20KCl–50MgCl <sub>2</sub> 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

# 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