

Li, Na, Be - lowest m.p.

KF-LiF
RbF-LiF + NaF tertiary + <10% UF_4

ZrF_4 NaF

BeF_2

$LiF \cdot BeF_2 \rightleftharpoons BeF_2(s) + 2LiF \cdot BeF_2$
50% mol @ <274°C

best cross-section

compounds: LiF BeF_2
 Li_2BeF_4 $LiBeF_3$
 $2LiF \cdot BeF_2$ $LiF \cdot BeF$
<274°C

Fuel & Blanket

UF_6 → volatile

UO_2F_2 → strong oxidant

$U(V)$ → not thermally stable & strong oxidants

UF_6 , U_2F_9

UF_3 → stable even above 1000°C, when pure & in inert atm

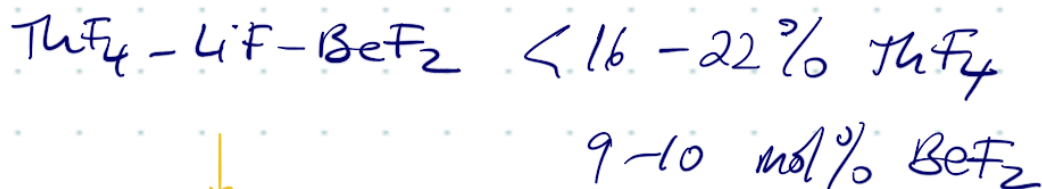
in fluoride melts $4UF_3 \rightleftharpoons 3UF_4 + U^0$ @ $T < 800^\circ C$

Aircraft experiment: UF_4 -NaF- ZrF_4

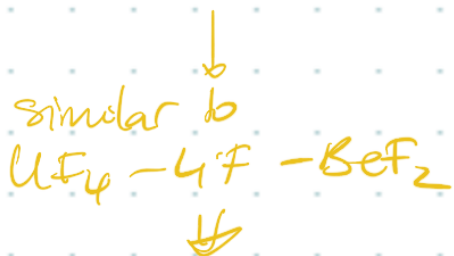
UF_4 & ZrF_4 - isomorphous & similar unit cell



Thorium



9-10 mol% BeF_2



$\text{UF}_4 - \text{ThF}_4 - \text{LiF} - \text{BeF}_2$ behaves similarly to the ternary

Plutonium

$\text{PuF}_4 \rightarrow$ possibly stable, but an oxidant

$\text{PuF}_3 \rightarrow$ 0.25 - 0.45 mol% stable in 20-50 mol% BeF_2 flux
should be sufficient for a Pu burner

Liquid state temperatures - methods:

- 1 thermal analysis
- 2 differential-thermal analysis
- 3 quenching from high-temp. eq. states
- 4 visual observation of melting
- 5 phase separation, by filtration @ high temp.

Density - buoyancy method

Enthalpy, heat of fusion, eq - drop calorimetry
Ni or Inconel

- ice-calorimeters & large copper-black
calorimeters

Viscosity 1 capillary efflux

2) modified Brookfield rotating-cylinder

for liq. film of varying thickness

- Kassel: slab, steady state heat flux

vap press

RuF_3 , UF_4 , ThF_4 low vap press

AlF_3 , BeF_2 , ZrF_4 - appreciable vap. press $< 700^\circ\text{C}$

Vap press

1. Robbush & Dixon apparatus $LiF-NaF-ZrF_4$ 800-1000°C

2. Sense - transport method

$NaF-ZrF_4$
↑
complex vap phase

< 2 mmHg @ 50 mol% ZrF_4 , 300°C

mostly ZrF_4 ⇒ snow 918°C MP ZrF_4
vs 542°C MP BeF_2

larger alkali site ⇒ vap. press ↓

large negative deviation from Raoult's law

large $\Delta S_i > 0$ partial molar entropies of solution

↑

substituting nonbridging F for bridging F

when alkali F mol% ↑ w.r.t. ZrF_4 mol%

Conclusions

adequate thermophysical properties

non-ideal solutions

complex structures in the melts

Purification

1. Minimize corrosion
2. Remove oxides, oxyfluorides & sulfur

High temp treatment with H_2 , HF

Stored in Ni, under $H_2 \rightarrow$ 1 atm press.

$HF @ 700^\circ C \rightarrow$ remove H_2O

$HF \rightarrow H_2$ over 1 h, $800^\circ C$



$HF @ 800^\circ C \rightarrow$ volatile H_2S , HCl

oxides, oxyfluorides of U & Zr $\rightarrow MF_4$
& also



$H_2 @ 800^\circ C$



Radiation Stability

100 exposures in Inconel capsules, w/ U_2F_6

$10^{11} - 10^{14}$ n/cm²-s $U_2F_6 + Na_2F + \begin{cases} KF \\ BeF_2 \\ ZrF_4 \end{cases}$

80 - 8000 W/cm³ = 80 - 8000 MW/m³

600 - 800 hr \approx 1 month

Post-irradiation studies

1. freezing point
2. chemical analysis
3. shielded petrographic microscope
4. mass spectroscopy assay
5. γ -spectroscopy
6. container condition - shielded metallograph
 corrosion < 4 mils @ 300 hr - comparable to no irr. p. 16
 @ 1093°C \rightarrow 12 mils & Inconel grain growth
 due to overheating, probably, not irradiation

Loop tests

Aircraft reactor Experiment



3 types of forced-circulation loops

1. Large loop, pump outside reactor shield

in horizontal beam hole of LiTR ("low-intensity test reactor" at ORNL)

2. Smaller loop - LiTR lattice - pump outside of lattice

3. Within a beam hole of MTR ("materials testing reactor" in Idaho)

Short duration

Small ΔT

< 4 mils corrosion

same as capsules

same as non-irradiation

↓

Conclusions

No irradiation effect on fuel corrosion

Fission Products

valence state & redox egl. among components

lacking: valence state of all FP fluorides

unknown if fission results in oxidation of container material



Noble gases

Kr
Xe



diffusion > 0

↓
sparging in low-temp
won't lead to
bubble formation
① high temp

solubility ↑ w/ T ↑

↓ w/ AX noble gas ↑

due to dec solb.

He
Ne
Ar

$$(5)10^{-8} \text{ mol/cm}^3\text{-atm} \quad 0.05 \text{ mol/m}^3\text{-atm}$$

$$(5)10^{-7} \text{ mol/m}^3\text{-Pa}$$

$$1 \text{ atm Kr} \rightarrow 0.05 \text{ mol/m}^3 \text{ Ar.}$$

$$\begin{array}{r} 2\text{LiF} = 52 \\ + \\ \text{BF}_2 = 47 \\ \hline 99 \\ \text{100 g/mol} \\ 0.1 \text{ kg/mol} \end{array}$$

$$\frac{2000 \text{ kg/m}^3}{0.1 \text{ kg/mol}} = 20000 \text{ mol/m}^3 \text{ fluoride}$$

(25 appm Kr)

Small-scale in-pile tests

Xe: retained in stagnant melt @ low conc.
removed by Helium sparging

ΔH = heat of solution \Rightarrow

solubility \uparrow w/ $T \uparrow \rightarrow$ OK to sparge @ low temp.

solubility will \uparrow w/ temp \uparrow \Rightarrow
gas will remain dissolved \Rightarrow
won't form bubbles.

~~APC~~ - less Xe poisoning than expected
no system for Xe removal

Other FP Gr I, II, III, IV

Rb, Cs, Sr, Ba, Zr, Y, Lanthanides

\hookrightarrow very stable fluorides

Conclusion
can tolerate
high flu

@ 600°C
2.5% } LiF - NaF - KF

LiF - BeF₂

2-3% } NaF - ZrF₄

} will dissolve high concentrations
of Zr, I, II @ 600°C

\downarrow
RE & Y fluorides

RE = 15 Lanthanides + Yttrium + Scandium

solubility \uparrow 0.5% / °C
Lanthanides solb \uparrow w/ $T \uparrow$

Se, Te, Br, I \rightarrow depends on oxidation potential

Ge, As, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb

\hookrightarrow probably reduced to M^0 by Br in Inconel

fluorides of some of these may be stabilised in the melt

deposited on walls of ARE

RuF₅: some was volatilised

detected in ARE

Fission Process



number of cation equivalents: 4 (starting from U₄F₉)

consider all elements of uncertain valence & assume deposited as M^0

\Rightarrow 3.2+ cation eqv \Rightarrow something else needs to oxidize

U₄F₉ fraction \Rightarrow
oxidize U₄F₉

OR
some of the FP oxidize

Fuel Reprocessing

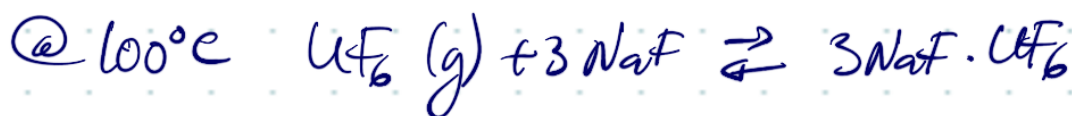
1. Solvent extraction
 2. Selective precipitation
 3. preferential ion exchange
- } ag. sol'n of SF

1. UF_6 volatilization by HF treatment \Rightarrow

- good separation from: Cs, Sr, RE
- ok sep. from Zr
- poor sep. from Nb, Ru

- I, Te, Mo - volatilize completely from the melt
- nonvolatiles - discarded in the fluoride solvent

2. Selective abs. & desorption on beds of NaF



- Nb & particulate matter a/cvt. also absb. on NaF bed

- Ru remains in vap.

@ 400°C UF_6 desorption & sep from Nb.

Ru & Th recovery - not possible this way

1. selective pptn
2. selective absb. on oxide beds