Li, Na, Be – lowest M.P.

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

ZrF_4 NaF

BeF_2 — least cross-section

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

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

Fuel & Blanket

UF_6 → volatile

UO_2F_2 → strong oxidant

U(VI) → not thermally stable & strong oxidants
UF_5, U_2F_9

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

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

Aircraft experiment: UF_4-NaF-ZrF_4
UF_4 & ZrF_4 – isomorphous & similar unit cell

$UF_4 - NaF - ZrF_4$

$UF_4 - NaF - BeF_2$

$UF_4 - LiF - BeF_2$

$UF_4 - LiF - NaF - BeF_2 - UF_4$

Thorium

Th (IV)

$ThF_4 - LiF - BeF_2$ < 16 - 22 % ThF_4

9 - 10 mol% BeF_2

↓

similar to

$UF_4 - LiF - BeF_2$

↓

$UF_4 - ThF_4 - LiF - BeF_2$ behaves similarly to the ternary

Plutonium

PuF_4 → possibly soluble, but an oxidant

PuF_3 → 0.25 - 0.45 mol% soluble in 25-50 mol% BeF_2 flibe

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, cp – drop calorimetry
Ni or Inconel

– ice-calorimeters & large copper-block calorimeters

Viscosity 1 capillary efflux
2) modified Brookfield rotating-cylinder

for liq. film of varying thickness

– k_{solid}: slab, steady state heat flux

Vap press PuF_3, UF_4, ThF_4 low vap press

AlF_3, BeF_2, ZrF_4 – appreciable vap. press < 700°C

Vap press

1. Rodebush & Dixon apparatus UF_4-NaF-ZrF_4 800–1000°C
2. Sense – transport method NaF-ZrF_4

↑ complex vap phase

< 2 mmHg @ 50 mol% ZrF_4, 900°C

mostly ZrF_4 ⇒ snow 918 °C MP ZrF_4

vs 542°C MP BeF_2

larger alkali size ⇒ 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 He → 1 atm press.

HF @ 700°C → remove H_2O
HF → H_2 over 1 h, 800°C

$U^{5+} \rightarrow U^{4+}$
$U^{6+} \rightarrow U^{4+}$

HF @ 800°C → volatilize H_2S, HCl

oxides, oxyfluorides of U & Zr → MF_4
& also
$2HF + Ni \rightarrow NiF_2 + H_2$

H_2 @ 800°C

$NiF_2 \rightarrow Ni$ (soluble)
$FeF_2 \rightarrow Fe$ (soluble)

Radiation Stability

100 exposures in Inconel capsules, w/ UF_4

$10^{11} - 10^{14}$ n/cm²-s $UF_4 + NaF + \{KF, BeF_2, ZrF_4\}$

80 — 8000 W/cm³ = 80 — 8000 MW/m³

600 — 800 hr ≈ 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. → Ref 16

@ 1093°C → 12 mils & Inconel grain growth

due to overheating, probably, not irradiation

Loop tests

Aircraft reactor Experiment ← UF_4 - NaF - ZrF_4

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 eql. among components

lacking: valence state of all FP fluorides

⇓

unknown if fission results in oxidation of container material

M°_{walls} + (FP)F ⇄ FP° + $M_{walls}F$

sufficiently stable? — more noble?

Noble Gases — Kr, Xe

NaF–ZrF4; UF4 NaF ZrF4; LiF NaF KF } Henry's law solubilities

ΔHsol'n > 0

⇓

sparging in low-temp won't lead to bubble-formation @ high temp — due to dec solb.

solubility ↑ w/ T↑

↓ w/ AW noble gas ↑

He, Ne, Ar

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

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

1 atm Ar → 0.05 mol / m^3 Ar.

2LiF = 52
BeF2 + 47
= 99

100g/mol
0.1 kg/mol

$$\frac{2000\ kg/m^3}{0.1\ kg/mol} = 20\,000\ mol/m^3\ flibe$$

(2.5 appm Ar)

Small-scale in-pile tests

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

ΔH = heat of solution →
solubility ↑ w/ T↑ → ok to sparge @ low temp.

solubility will ↑ w/ temp ↑ → gas will remain dissolved → won't form bubbles.

~~ARE~~ – less Xe poisoning than expected
no system for Xe removal

<u>Other FP</u> Gr I, II, III, IV

Rb, Cs, Sr, Ba, Zr, Y, Lanthanides
→ very <u>stable fluorides</u>

Conclusion: can tolerate high BU

@600°C
LiF – NaF – KF
0.5% { LiF-BeF₂
2-3% { NaF – ZrF₄
} will dissolve high concentrations of Zr, I, II @ 600°C

↓
RE & Y fluorides
RE = 15 Lanthanides + Yttrium + Scandium

solubility ↑ 0.5% / °C
Lanthanides: solub ↑ w/ A↑

Se, Te, Br, I → depends on oxidation potential

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

→ probably reduced to M^0 by Cr in Inconel

fluorides of some of these may be stabilized in the melt

deposited on walls of ARE

RuF_5: some was volatized

detected in ARE

Fission Process

$FP^+ \rightarrow FP^0$

$U^{4+} \rightarrow U^{3+}$

} to maintain charge ballance

number of cation equivalents: **4** (starting from UF_4)

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

⇒ 3.2+ cation equ ⇒ something else needs to oxidize

OR

some of the FP oxidize

UF_3 fraction ⇒ oxidize UF_3

Fuel Reprocessing

1. Solvent extraction
2. Selective precipitation
3. preferential ion exchange

} aq. sol'n of SF

---

1. UF_6 volatization by HF treatment ⇒
   - 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

@ 100°C $UF_6\,(g) + 3\,NaF \rightleftarrows 3NaF \cdot UF_6$

- Nb & particulate matter activ. also absb. on NaF bed
- Ru remains in vap.

@ 400°C UF_6 desorption & sep from Nb.

Pu or Th recovery – not possible this way

1. Selective sorption
2. Selective absb. on oxide beds