Overview of the Recovery and Processing of ^{233}U and other Activities

G. D. Del Cul,

Oak Ridge National Laboratory

Center for International Security Affairs (CISA)
Los Alamos
May 19-20, 2002

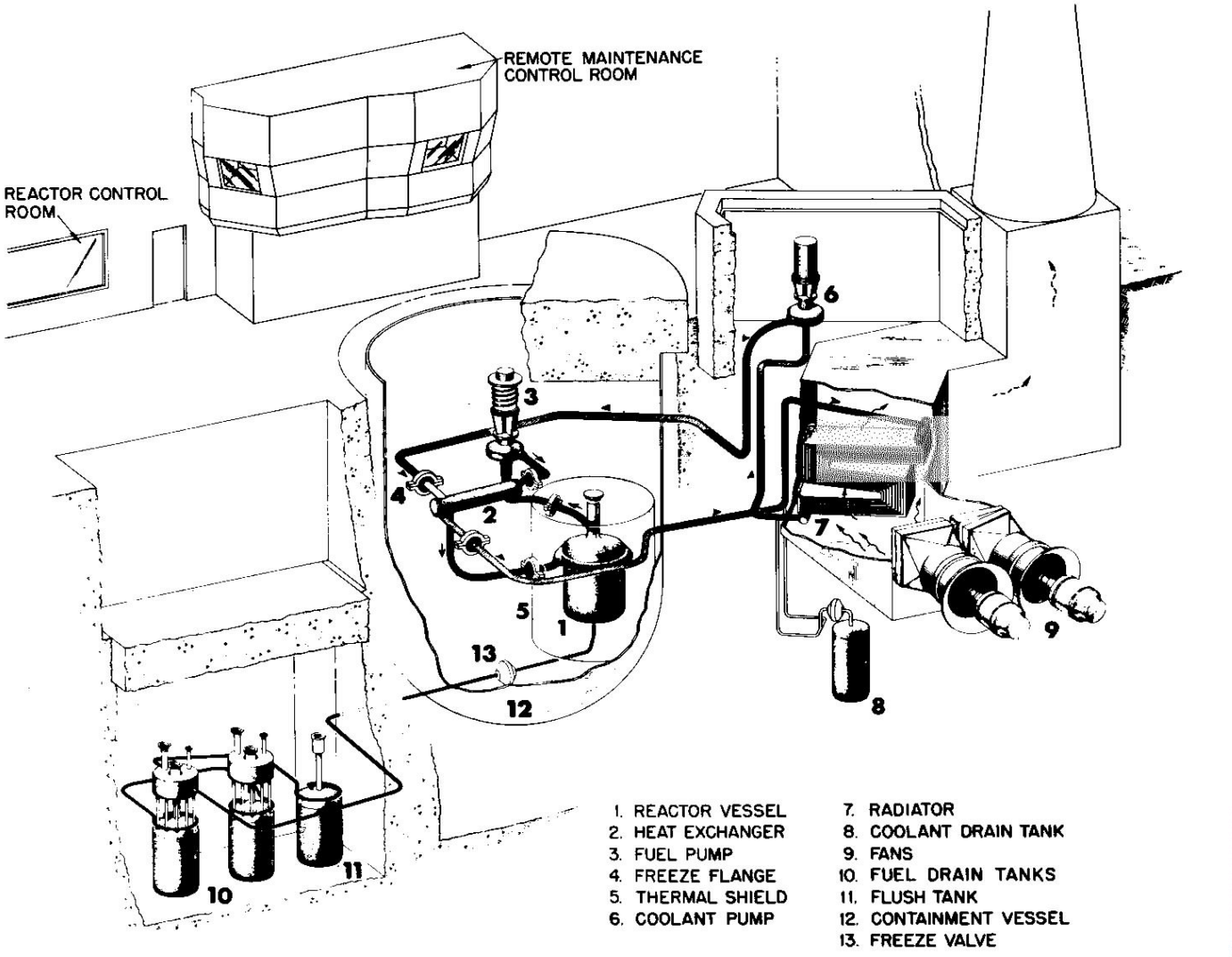
Removal and Recovery of ^{233}U from the MSRE

- The ORNL-Molten Salt Reactor Experiment (MSRE) operated from 1965 to 1969 to test a high-temperature homogeneous fluid–fueled reactor
- Originally fueled with $LiF/BeF_2/ZrF_4/^{235}UF_4$ (64.1-30.0-5.0-0.81 mol%)
- These MSRE salts melt at ~450ºC
- After successful operation (72441 MW-h) the ^{235}U was removed and recovered as the volatile UF_6 by fluorination

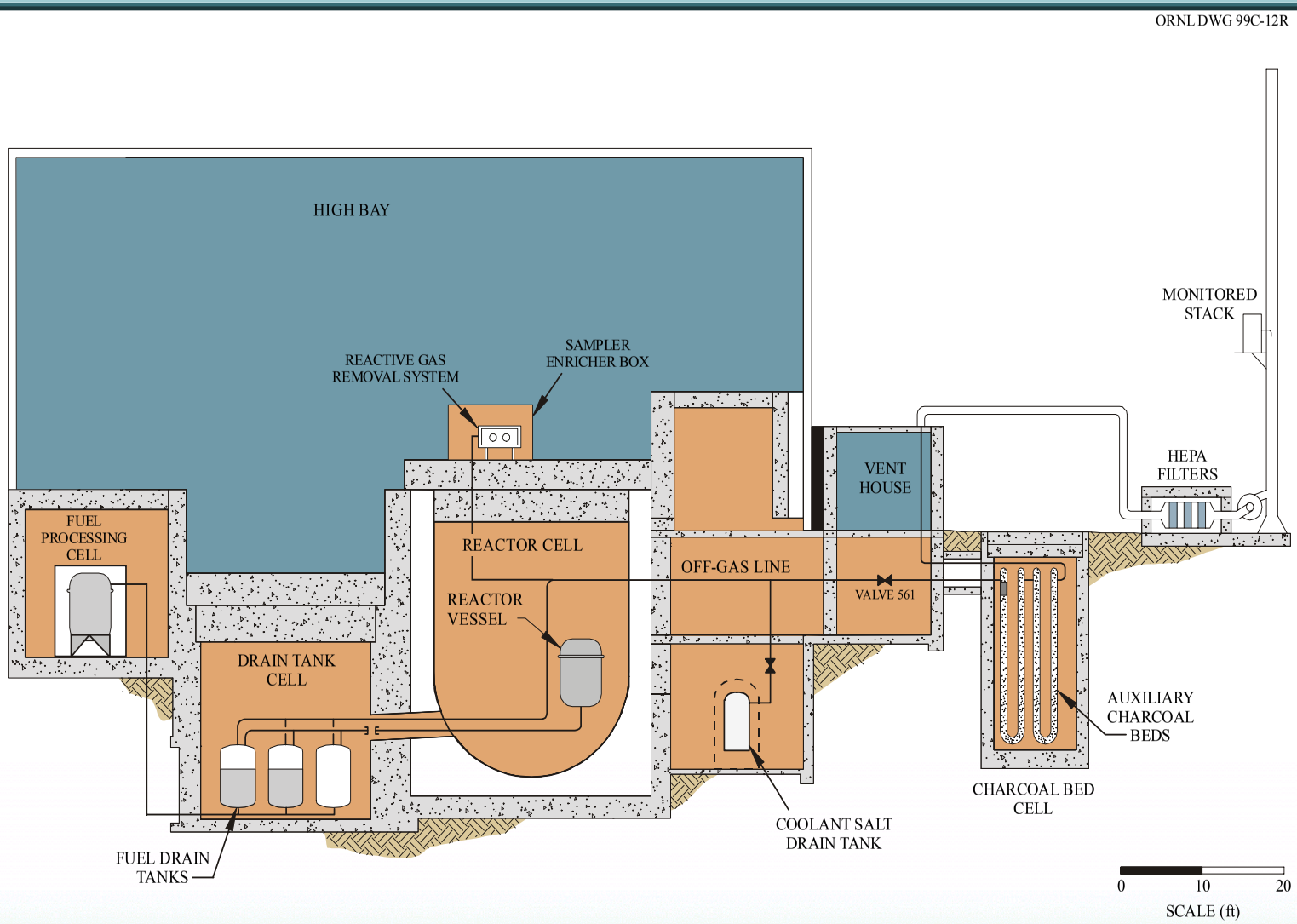
Background

- The reactor was then refueled with $LiF/BeF_2/ZrF_4/^{233}UF_4$ (64.5- 30.4-4.9-0.14 mol%) to test the Th breeding cycle
- About 4,350 kg (~2 m^3) of salt in the fuel salt circuit
- After the successful completion of the ^{233}U campaign (33296 MW- h), the salt was drained into two storage tanks
- The fuel salt still remains in these tanks since Dec.1969

Overview of the MSRE Reactor



Overview of the MSRE System



Gas analysis of two samples from off-gas system showed significant concentrations of F_2 and UF_6

Samples taken because of increased radiation levels

Species	Gas composition (Torr)	
	First sample	Second sample
UF_6	70	68
HF	1200 ppm	1000 ppm
MoF_6	10	10
CF_4	5	*5*
F_2	*a*	350
He, Ar, N_2, O_2 [b]	305	305

[a] Not determined analytically but assumed the same as second sample

[b] Quantity determined by difference from total sample pressure. Qualitative identification by mass spectroscopy.

MSRE ^{233}U contains 160 ppm ^{232}U

Medically beneficial chain

^{233}U(159,200 y) → ^{229}Th(7,340 y) → ^{225}Ra(14.8 d) → ^{225}Ac(10.0 d) → ^{221}Fr(4.8 m) →

^{217}At(32.3 ms) → ^{213}Bi(45.6 m) → ^{213}Po(~4.2 ms) → ^{209}Pb(3.28 h) → ^{209}Bi(stable)

Undesirable chain

^{232}U(72 y) → ^{228}Th(1.913 yr) → ^{224}Ra(3.66 d) → **^{220}Rn(55.6 s)** → ^{216}Po(0.15 s)

→ ^{212}Pb(10.64 h) → ^{212}Bi(60.6 m) → ^{212}Po(45 s) → ^{208}Pb(stable)

↓

^{208}Tl(3.053 m, 2.6 Mev ϒ) → ^{208}Pb(stable)

Because of ^{208}Tl, shielding is required

Radiolysis generated F_2 and low temperature fluorination of salt produced UF_6

Radiolysis and recombination produces fluorine

$LiF + h\upsilon \rightarrow Li^{\bullet} + F^{\bullet}$ $BeF_2 + h\upsilon \rightarrow Be^{\bullet} + 2\,F^{\bullet}$ $F^{\bullet} + F^{\bullet} \rightarrow F_2$

Annealing at ~200 °C was intended to restore the reduced sites back to LiF and BeF_2

but actually generated UF_6 by low-temperature fluorination of UF_4

$$F_2 + UF_4 \rightarrow UF_6$$

MSRE remediation project established to remove and stabilize the ^{233}U

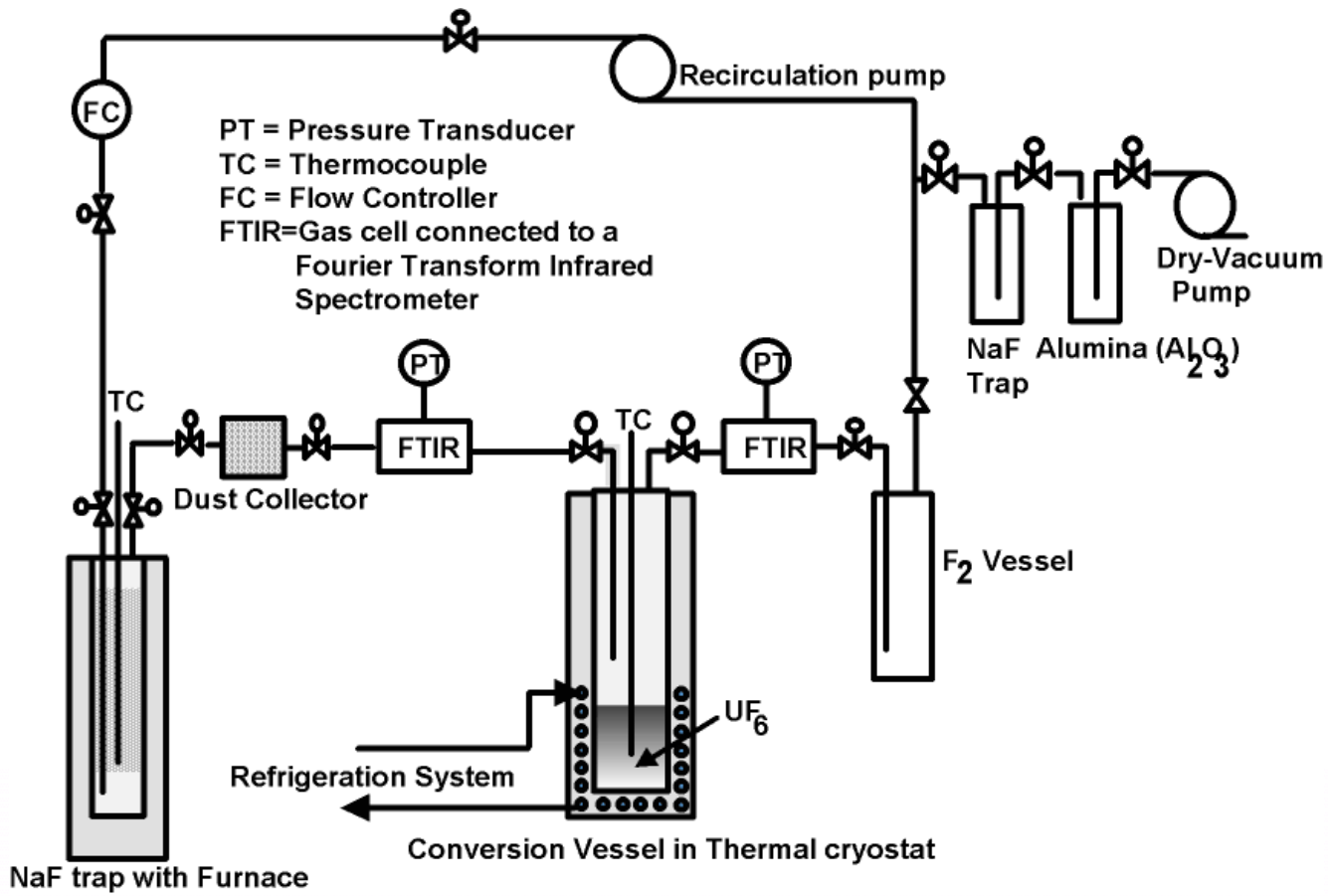
- The MSRE remediation includes removing about 37 kg of U
- 23 kg have been already removed from the piping system and chemisorbed in 25 NaF traps
- The recovery of ~11kg of uranium from the fuel salt will generate another 15 to 19 NaF traps
- About 3 kg of uranium laden into activated charcoal beds were also removed
- The NaF traps and the uranium-laden charcoal are not suitable for long-term storage and they will be converted to a stable U_3O_8

Passivation of the C_xF formed at the top of the ACB

- The top portion of the ACB had trapped F_2 and UF_6
- Activated charcoal fluorinated at low temperature can, if provoked, deflagrate (deflagration = low grade explosion)
- Uranium removal methods could potentially provoke deflagration
- A process was developed, termed "passivation", which converted the reactive carbon fluoride to unreactive products, removing the threat of deflagration

$$C_xF\,(s) + 4/3\,NH_3\,(ads) \longrightarrow x\,C(s) + NH_4F(s) + 1/6\,N_2\,(gas) + heat$$

Uranium Recovery Closed-loop System



Conversion System

Initially water vapor is condensed as ice on top of the frozen UF_6 and then allowed to warm to room temperature

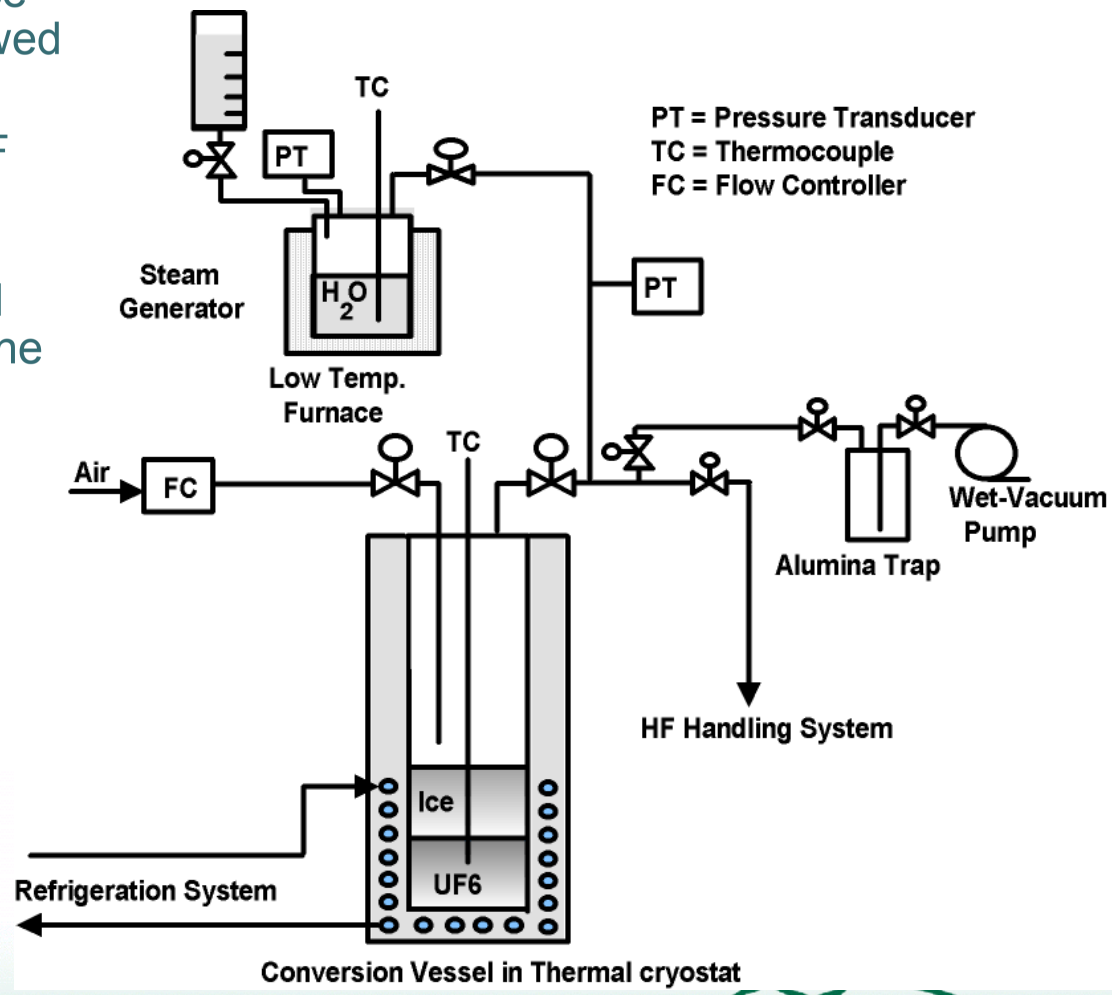
$UF_6 + (2 + x)H_2O \rightarrow UO_2F_2 \bullet xH_2O + 4HF$

The resulting solid cake is step-wise heated and contacted with pressurized steam (~200 psi) that penetrates into the cake, gradually reacting with the oxyfluoride-oxide mixture

Upon heating, the UO_2F_2 slowly decomposes forming U_3O_8 and UF_6

$9\ UO_2F_2 \rightarrow 3\ UF_6 + 2\ U_3O_8 + O_2$

The UF_6 reacts with water to produce more UO_2F_2 that again decomposes producing UF_6 and U_3O_8 and the cycle repeats until completion



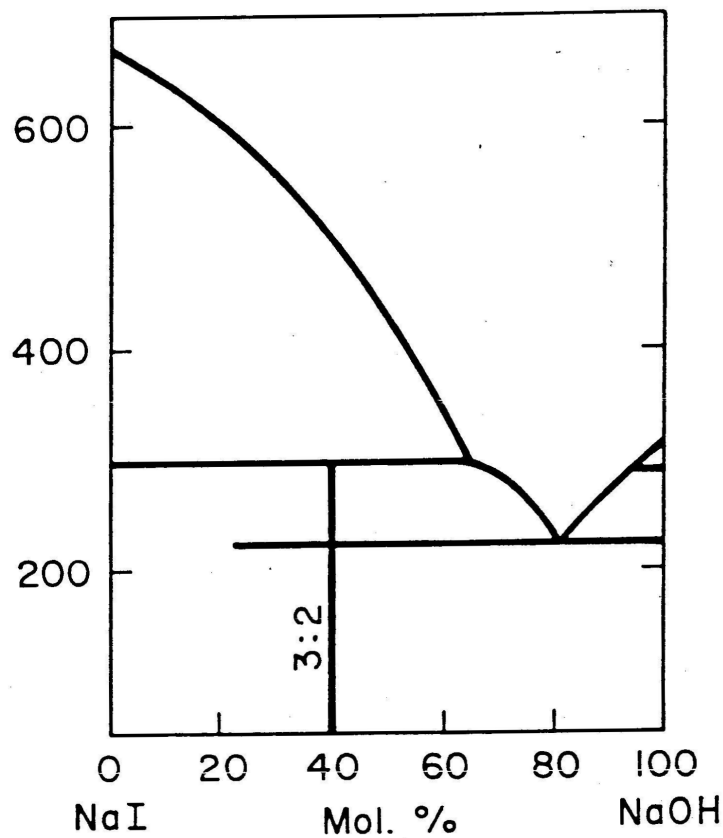
Sodium Iodide Production from Molten Salts

L. M. Toth and L.D.Trowbridge

Purpose

- Scrubbing iodine (e.g. I_2, HI, or CH_3I) from fuel processing off-gas streams via reaction and dissolution in molten salts
- Prepare NaI targets.

The phase diagram indicates that at high iodine concentration, NaI precipitates as the primary phase component as the melt is cooled.



Giuseppe scarpa, Atti reale accad. Lincei, Sez. I, 24, 961 (1915)

Developmental Work To Date

- A few scoping experiments conducted on the KI/KOH and NaOH/NaI system. After freezing, salt showed two distinct phases.
- Upcoming experimental efforts will be directed at the trapping of iodine from the incoming vapor stream.
- A thermochemical data set was developed to calculate the phase behavior in molten NaOH/NaI of impurity species such as $CO3^{=}$,$O^{=}$ and NO_x^{-}.

Flex Process

Main Idea: Some metal oxides will dissolve in a molten fluoride salt that contains zirconium tetrafluoride and others will not.

$$MO_y(s) + y/2\ ZrF_4\ (salt)$$

$$\Updownarrow$$

$$y/2\ ZrO_2\ (salt) + MF_{2y}\ (salt)$$

Possible Separation of Transuranic Elements from U, Th and Fission Products.

- Simple thermodynamic calculations predict:
  - Oxides of U, Th, Alkali, Alkali earth, rare earth and other trivalent metals should dissolve.
  - Np, Pu, Am and Cm tetravalent oxides and noble metals should not dissolve.

Planned Proof-of-Principle Experiments

- Experimentally determine solubility and dissolution rates for actinides and fission products
- Determine filterability of the undissolved solids