Molten Salt Reactor PROGRAM

Reckoning of Salt Precursors, Volatility and Vapor Pressure on an Engineered Salt Design its Operational and Reprocessing Motifs

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04/22/2026

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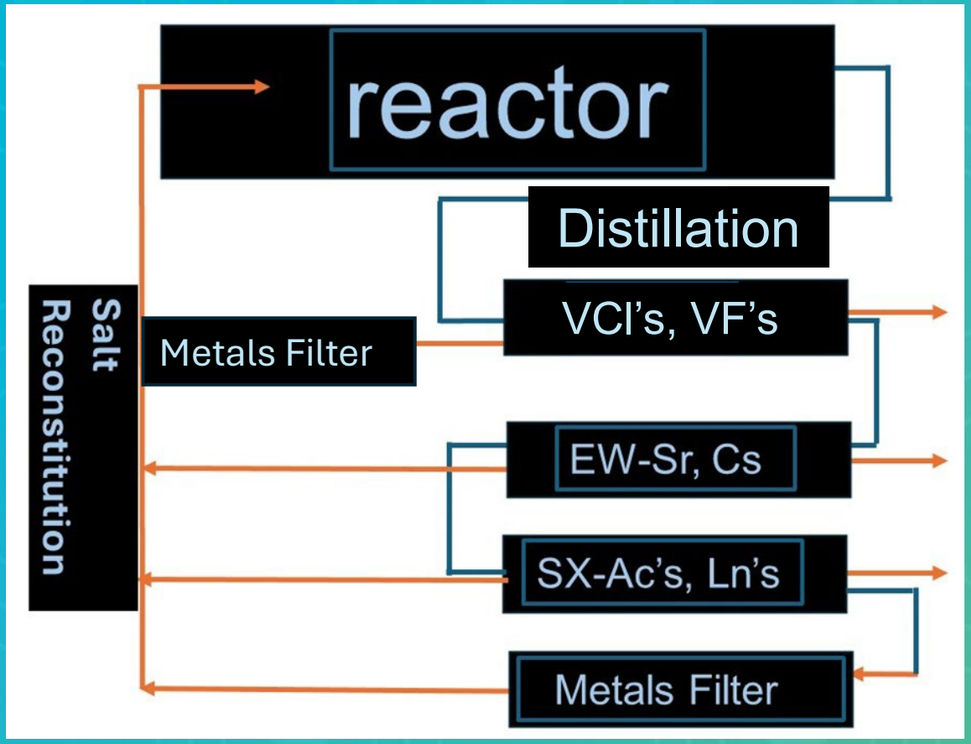
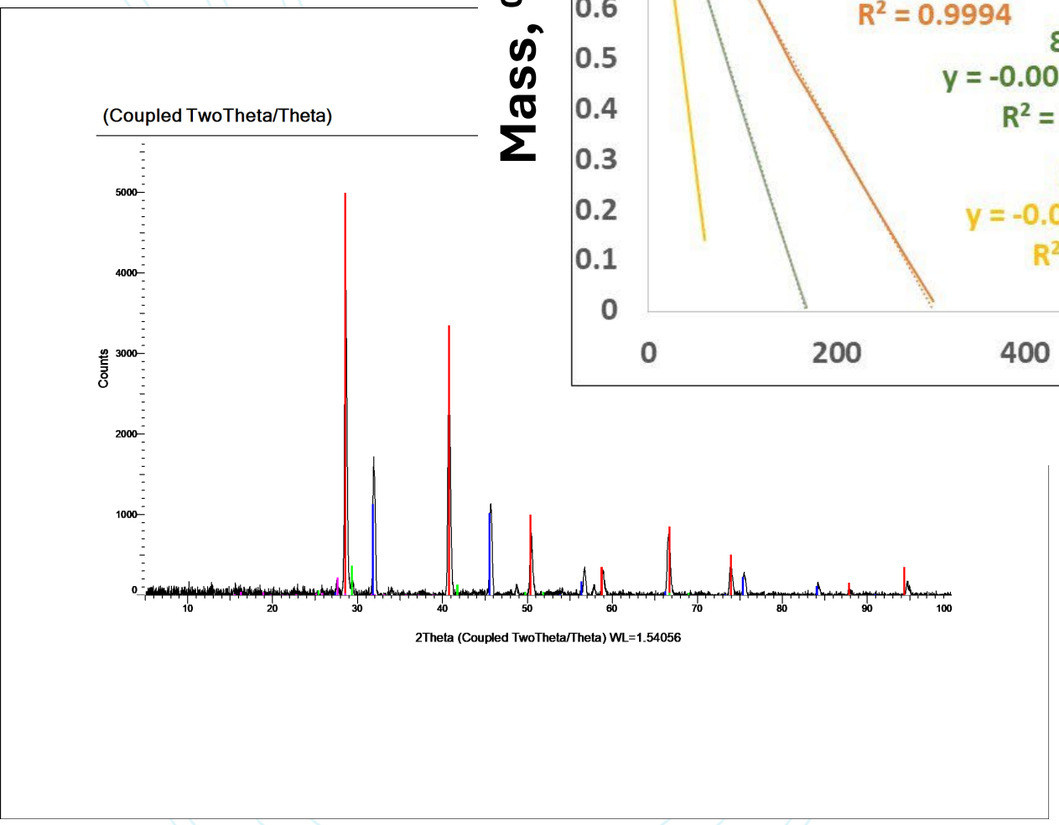
Salt Reprocessing of a Molten Salt Reactor

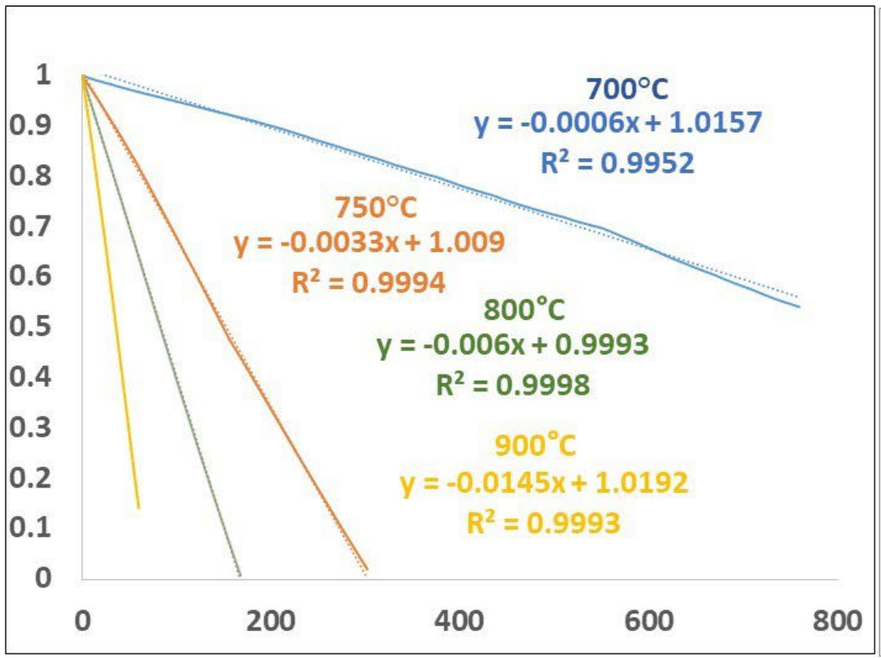


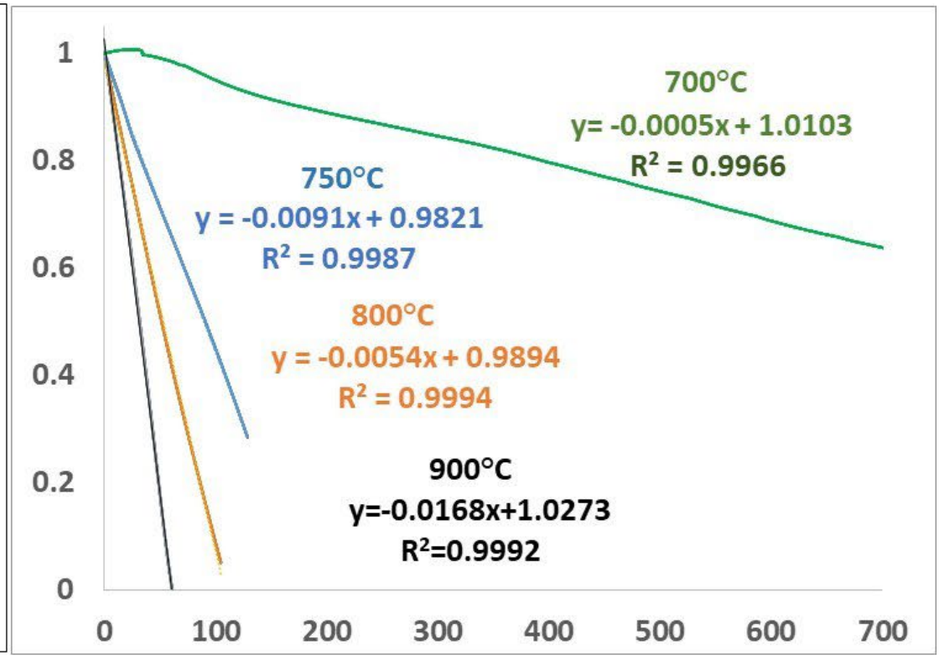
- Reprocessing specific to reactor, salt
- Distillation versus F-V / Cl-V
- High vapor pressure additives
- Throw it out!!! The salt -and the reactor!
- Advanced materials of construction

Vapor Phase Recovery of Chloride and Fluoride Base Salt, Fertiles, and Useful FP's

Temperature Dependence of ClNaK Removal 25/75 and 75/25 End Members







Time, min

- $PuCl_3$ might sublime, U's
- PuF_3 827-1200°C, might sublime, U's

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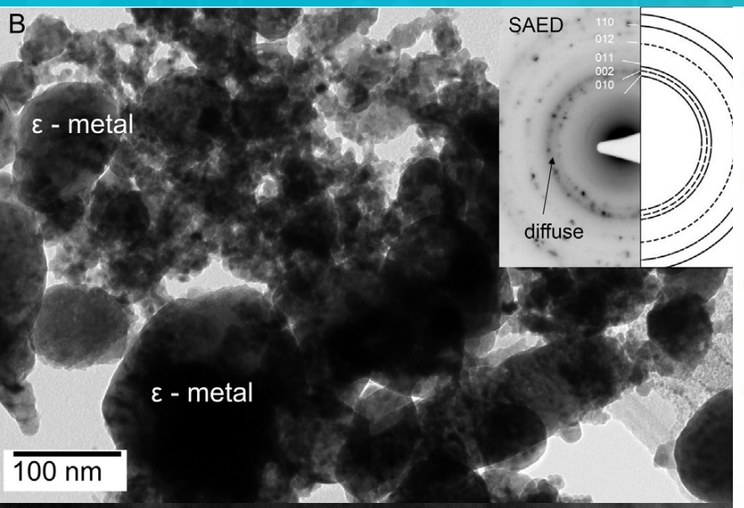
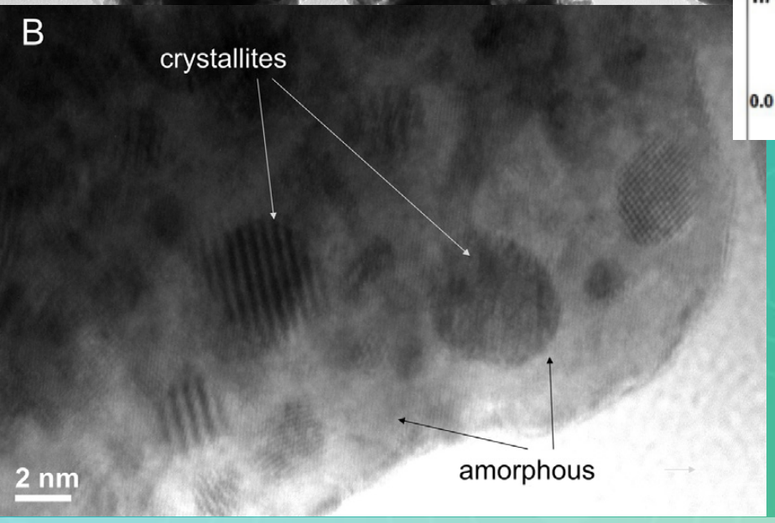
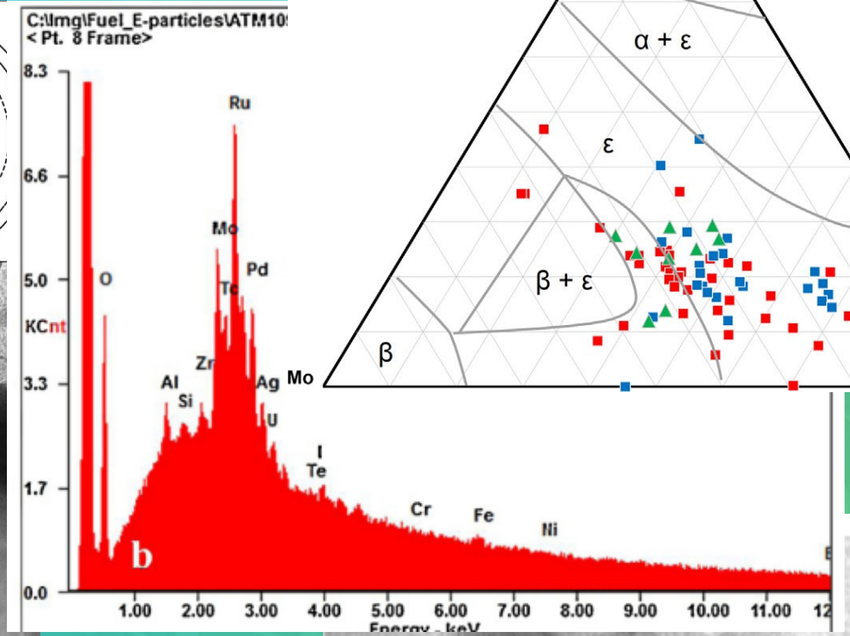
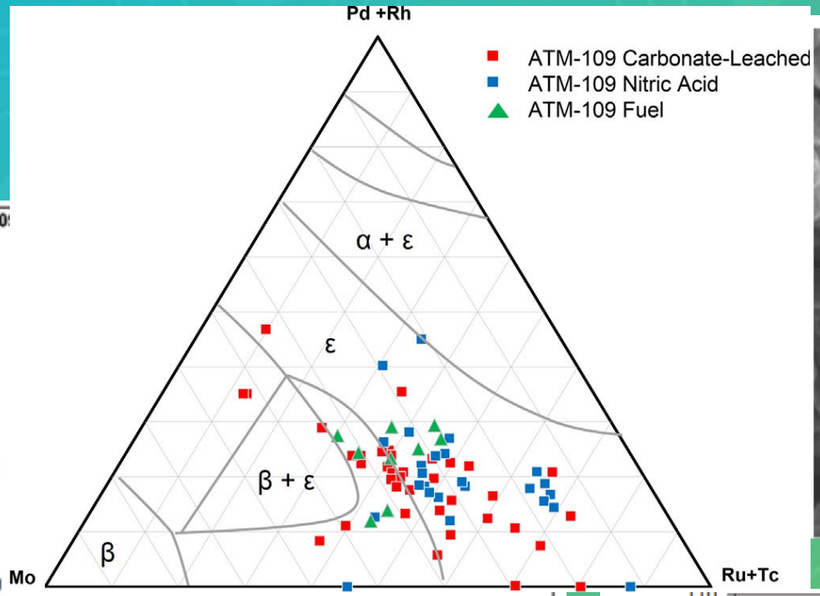
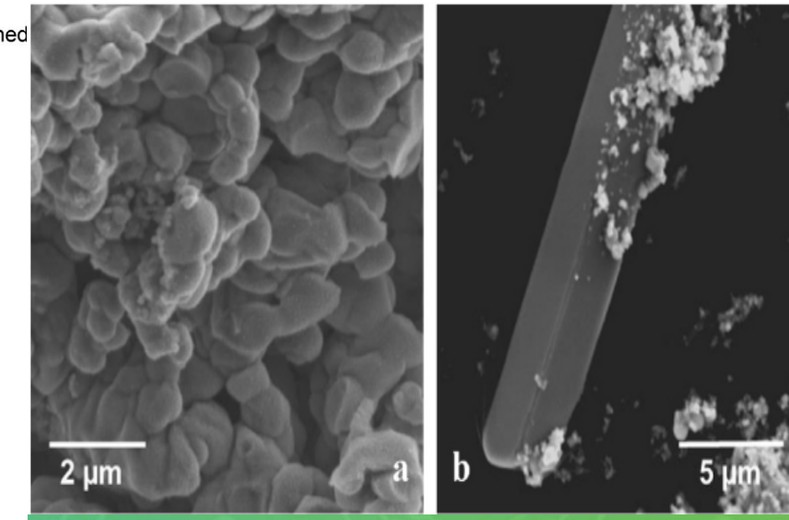
FV Recovery of ε phase constituents

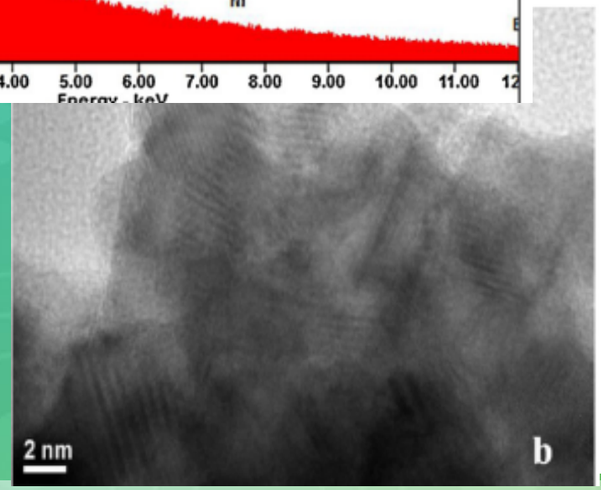


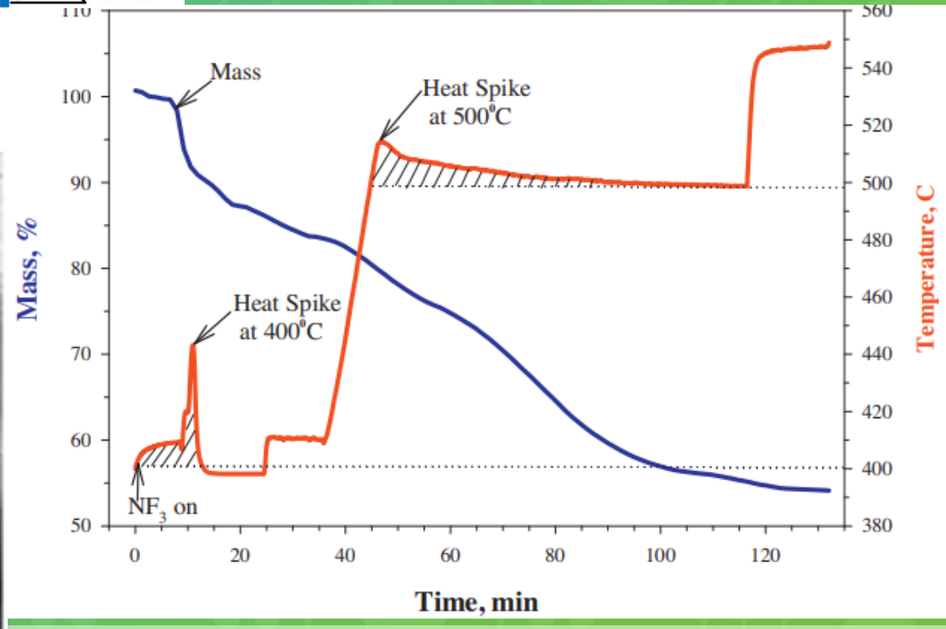






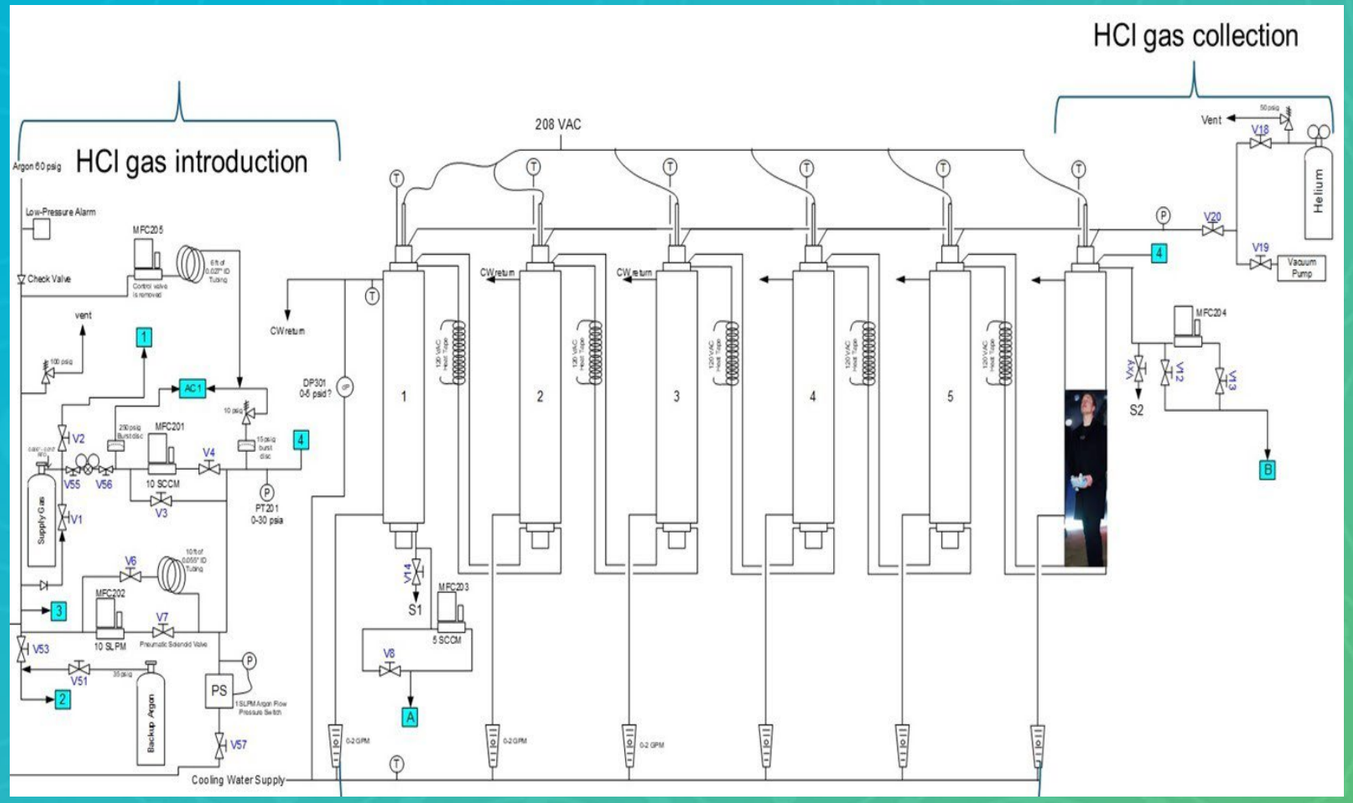






https://doi.org/10.1016/j.jfluchem.2014.02.010

Ongoing $^{35}Cl/^{37}Cl$ Separations at PNNL



Volatility for Recovery of Chloride Salt

Recovery of chloride base salt, especially enriched Cl^{37} from fertiles, and useful fission products.

Radiolytic corrosion (S, P) of MOC's and precipitation of Pu, U as sulfides, phosphides

Cl-37 Enriched Salt Precursors for Fast Spectrum (FS) Power or TRU Burner MSRs

$(NH_4)_2CO_{3(s)} + 2H^{37}Cl_{(g)} \rightarrow 2NH_4{}^{37}Cl_{(s)} + CO_{2(g)} + H_2O_{(g)}$ NH_4Cl sub=338°C

$Na_2CO_{3(s)} + 2H^{37}Cl_{(g)} \rightarrow 2Na^{37}Cl_{(s)} + CO_{2(g)} + H_2O_{(g)}$

$K_2CO_{3(s)} + 2H^{37}Cl_{(g)} \rightarrow 2K^{37}Cl_{(s)} + CO_{2(g)} + H_2O_{(g)}$

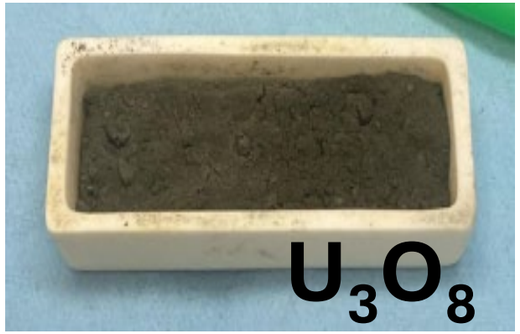
FS MSR Power: Fertiles from hydride/ dihydride of high purity metal powders, e.g., U, Pu, Am, and powders reacted with chlorinating reagents 1MWth to 3000 MWth -500 kg to 1000's kg metal. ***JNFCWT Vol.21 No.1 pp.55-64, March 2023***

$Pu + 3NH_4{}^{37}Cl \rightarrow Pu^{37}Cl_3 + 3NH_3 + 1.5H_2$

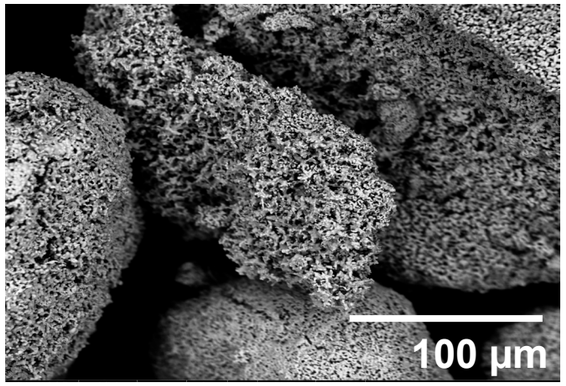
$Pu + 3H^{37}Cl \rightarrow Pu^{37}Cl_3 + 1.5H_2$

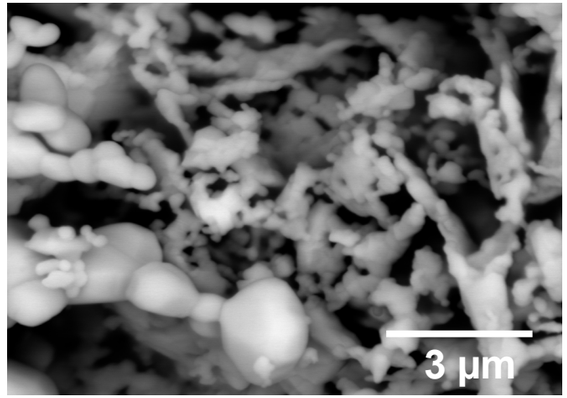
Where do you get your UF_4?

- Purity requirements depend on use
- AEC period UF_4 synthesis was a 20y problem
- Y12-U-metal derby
- Ammonium Diuranate (ADU)
- Industrial scale methods
  1. Standard deconversion UF_6 to UF_4
  2. UF_6 sparge into the molten salt



ρ= 6.7 g/cm^3

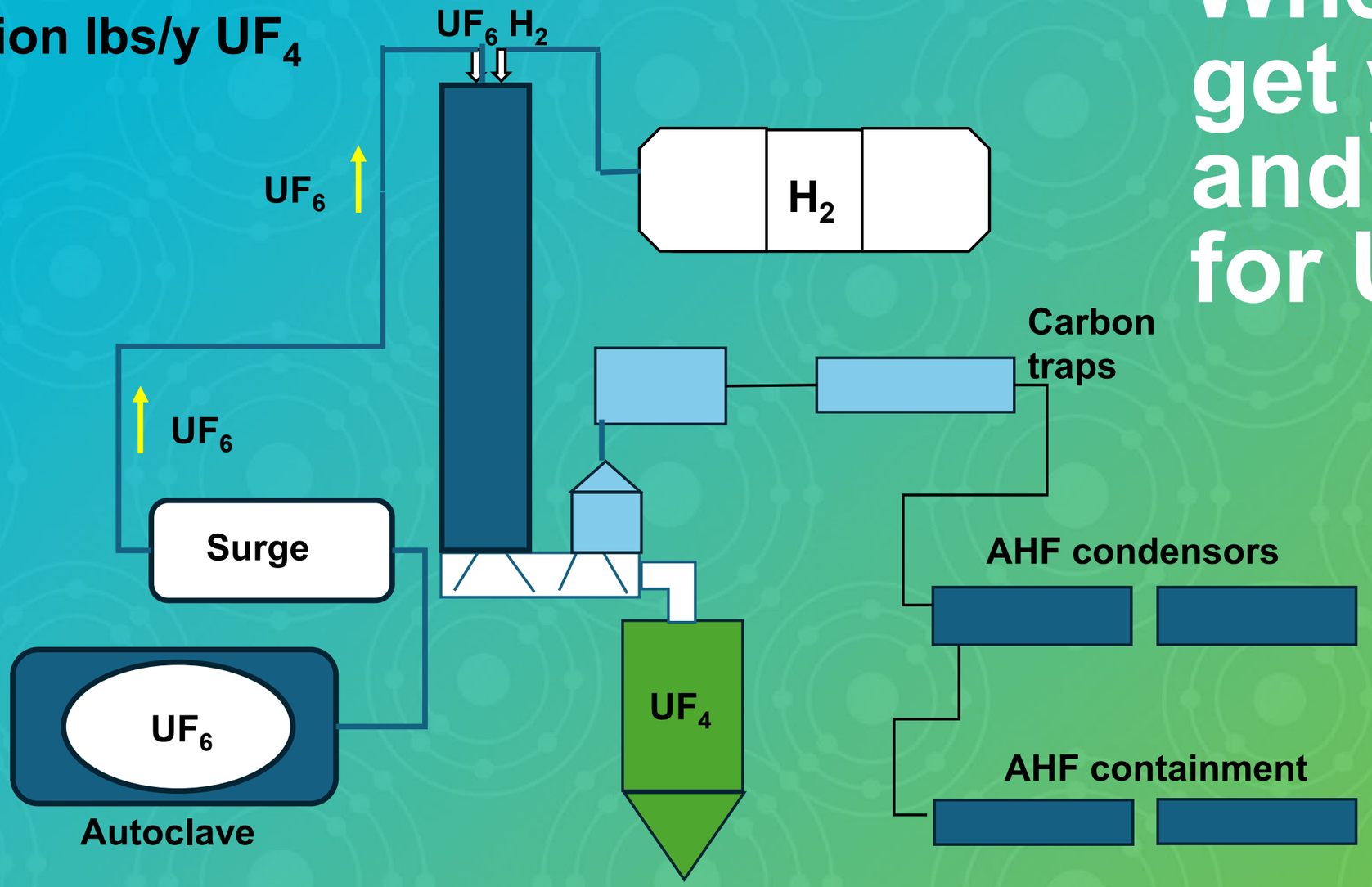




Where do you get your UF_4 and will it work for UCl_4 ?

$H_2 + DUF_6 = DUF_4 + 2HF$

9 million lbs/y UF_4



Where do you get your UF_4?

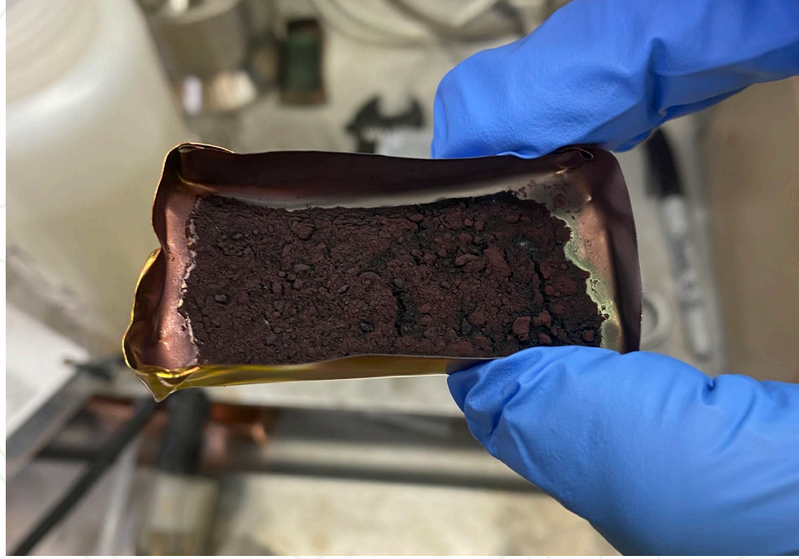
Furnace Tube Synthesis of UF_4 and UF_3

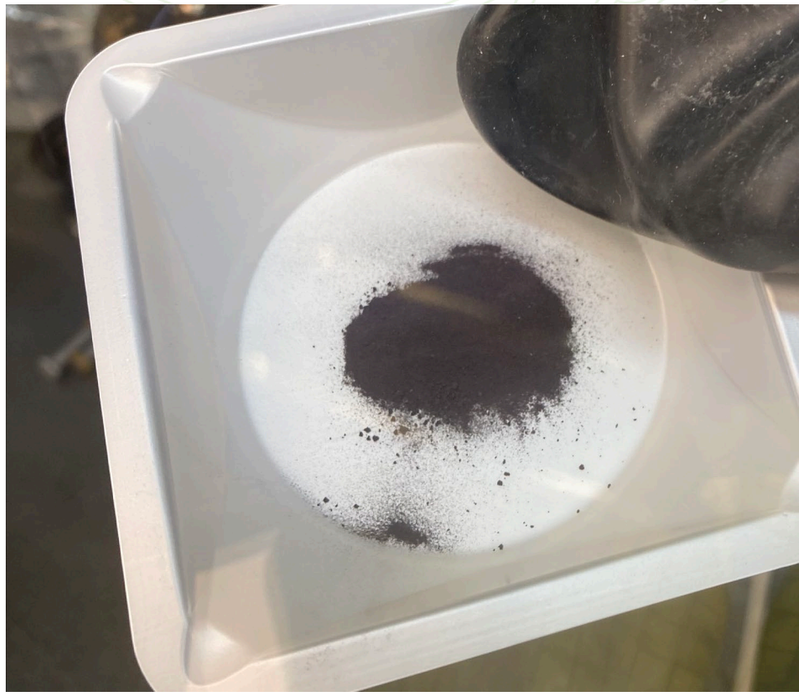
Thermochimica Acta, 43 (1981) *333-338*

$$UF_4 + 1/2H_2 \xrightarrow{800\text{-}852^\circ C} UF_3 + HF\uparrow$$

$$UF_4 \xrightarrow[H_2O,\ O_2]{300^\circ C} UO_{(2+x)} \longrightarrow U_3O_8$$

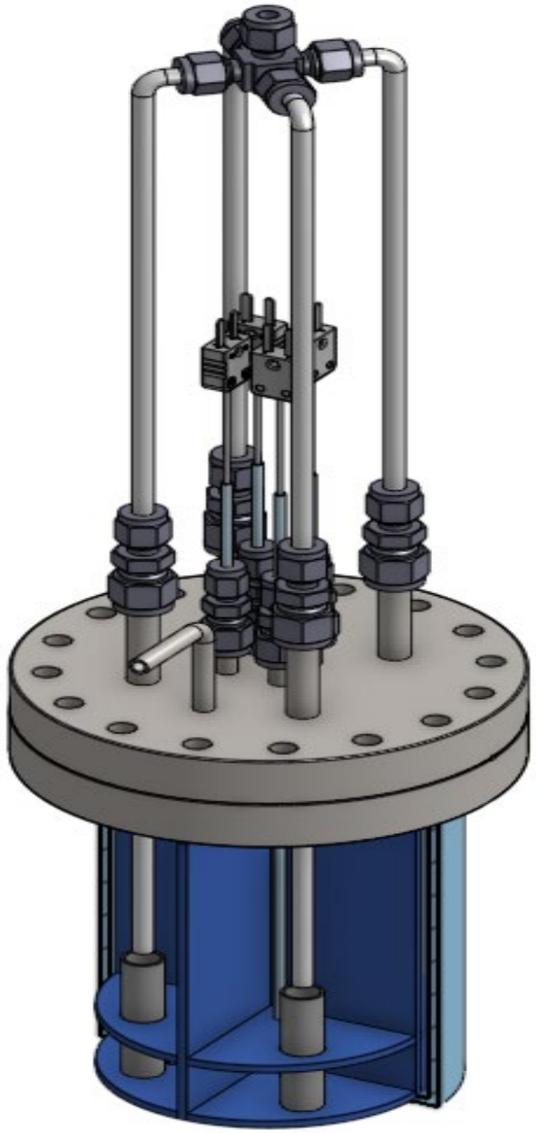
$$4UF_3 \xrightarrow{>1000^\circ C} 3UF_4 + U$$





Thermochimica Acta,Volume 43, Issue 3, 1981, 333-338

Molten Salt Synthesis: Multiport Capability



$NaF\text{-}KF\text{-}UF_4$

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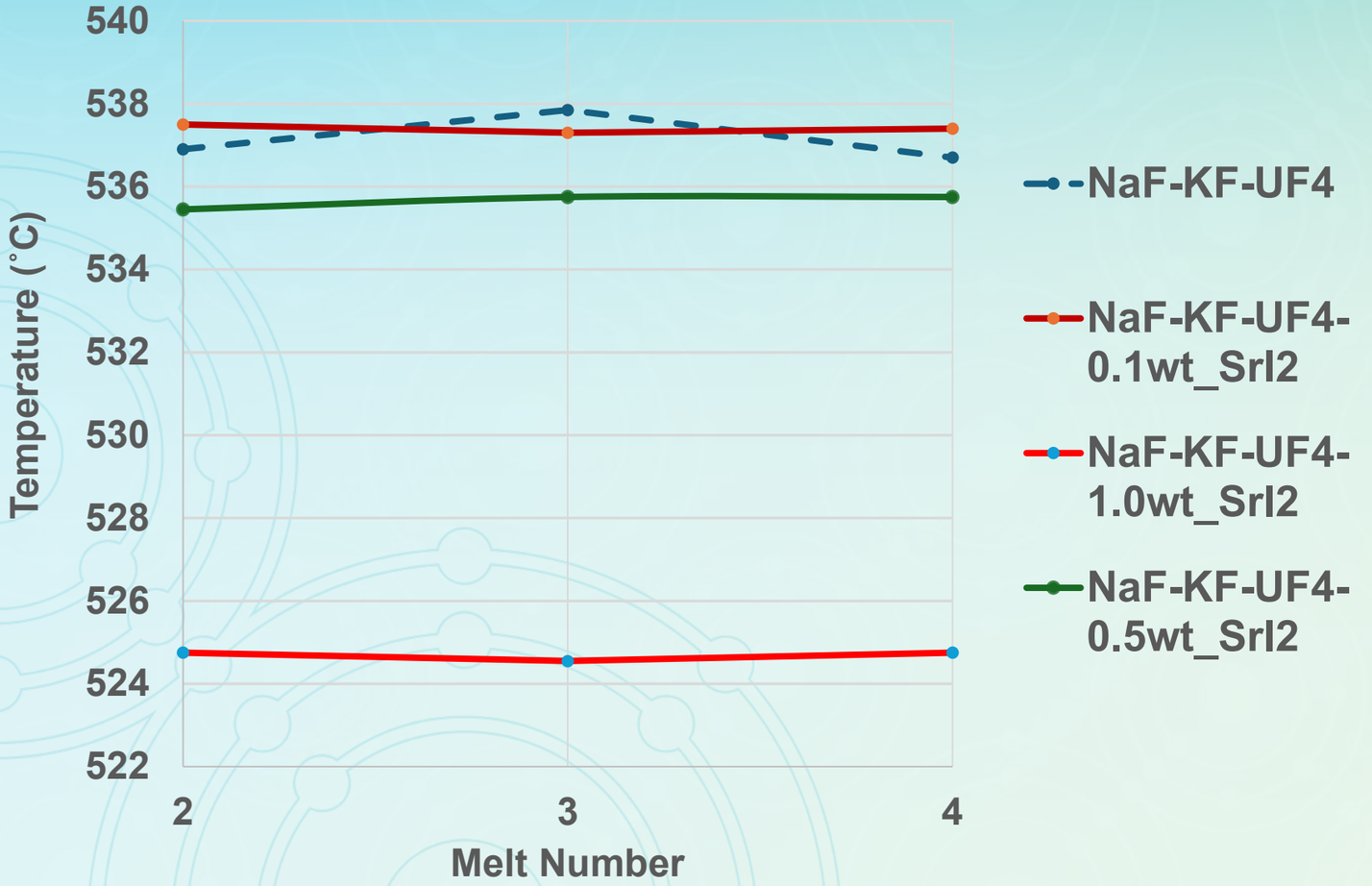
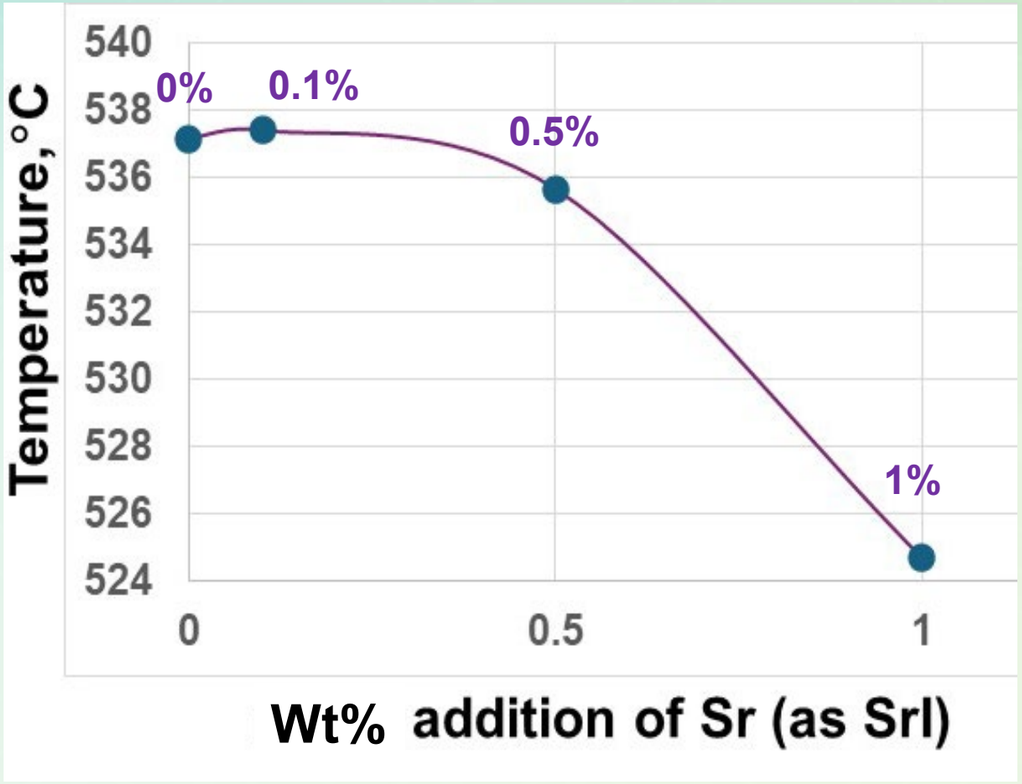
Melting Point Depression for Sr additions to the Ternary Fluoride Salt





Why Think About Salt Volatility

How to do the measurement

- Effusion low pressure <5-10 Pa
- Transpiration > 10 Pa
- Boiling point
- Static

} non absolute methods
depends on mwt of the vapor species

} absolute methods
Independent on mwt of the vapor species

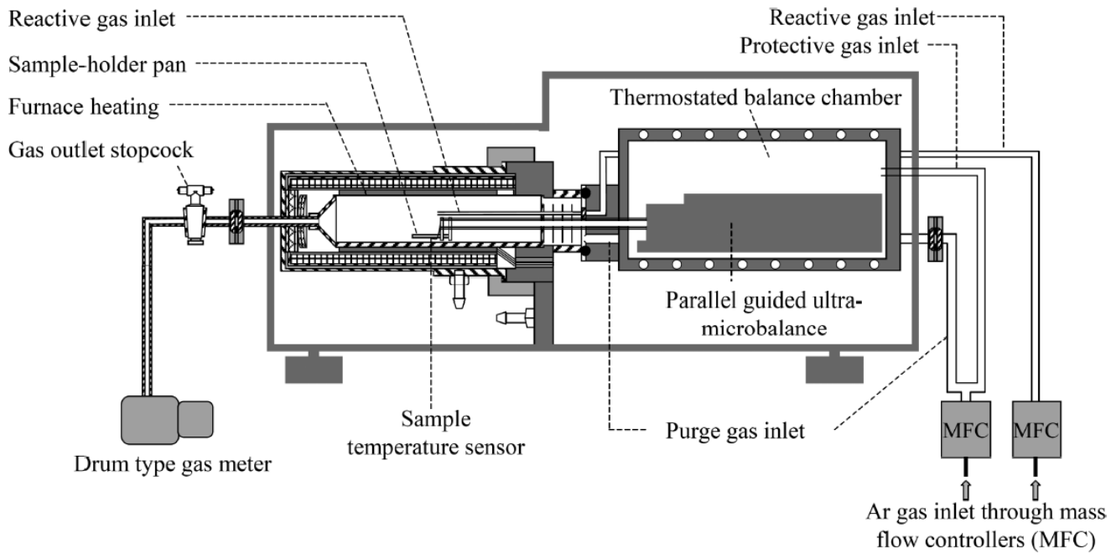
K. Sense 1954-1956: (Transpiration) Pure NaF, pure BeF_2, pure ZrF_4

For the binary, propose NaF + ZrF_4 = $NaZrF_5$

And also, proposed the existence in the liquid phase of Na_3ZrF_7

K. Sense et al, BMI-1199, 1957

Mass Loss Transpiration



$$P(\text{apparent}) = \{[(dm/dt)/(dV/dt)](RT_c/M)\}P^{\text{total}}$$

P^{total} = total pressure in the transpiration cell (typically 1 atm)

(d*m*/d*t*) = rate of mass loss at temperature *T*

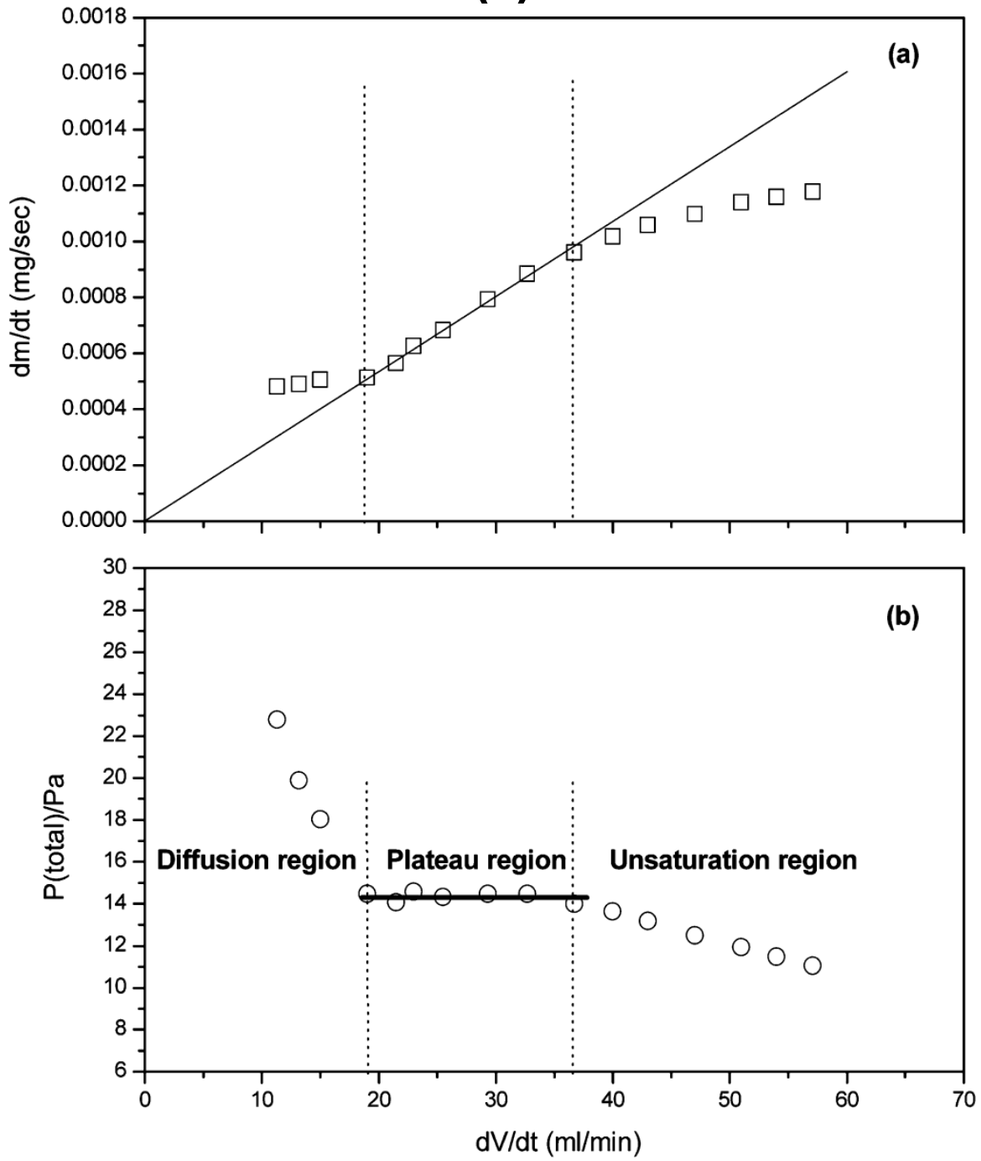
(d*V*/d*t*) = volume rate of the carrier gas transporting vapor out

R = universal gas constant

T_c = temperature of the carrier gas

M = mean molecular weight of the vapor

CsI (s) at 885 K



R. Viswanathan, et al, Thermochimica Acta 427 (2005) 137-147

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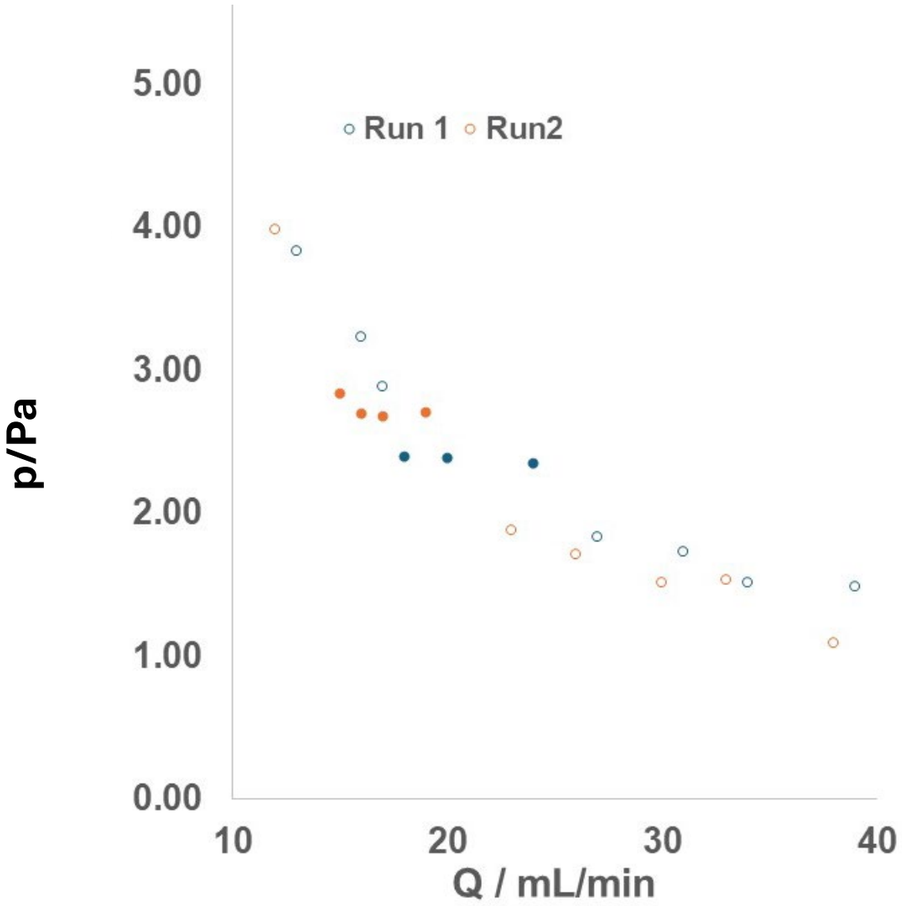
Mass Loss Transpiration: TeO_2



p/Pa	St.Dev
2.42	0.25
2.60	0.21
2.38	0.03

$$\log p(Pa) = \left\{14.2 - \frac{13321}{T(K)}\right\} \pm 0.03(884 - 987\ K)$$

Thermochimica Acta Volume 467, Issues 1–2, 30 , 2008, 80-85

T/K	p/Pa
971	3.03
970	2.93

doi/abs/10.1021/j150524a009

$$\log p(Pa) = \left\{13 - \frac{12000}{T(K)}\right\})$$

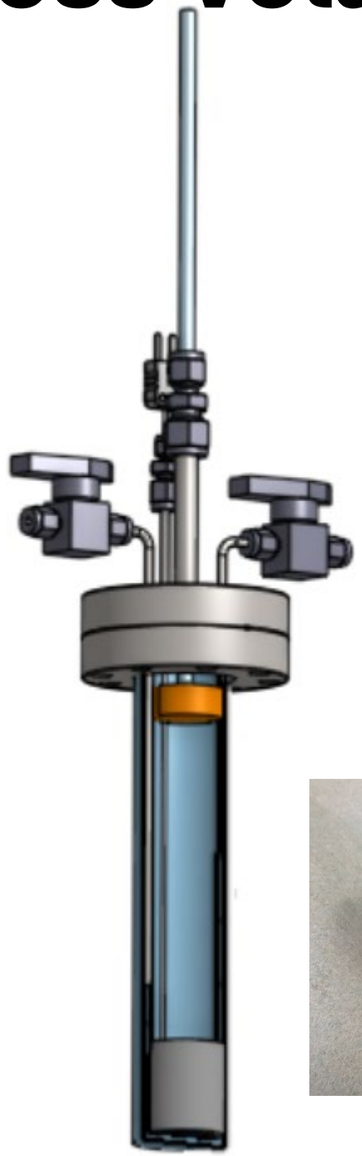
T/K	p/Pa
971	4.38
970	4.25

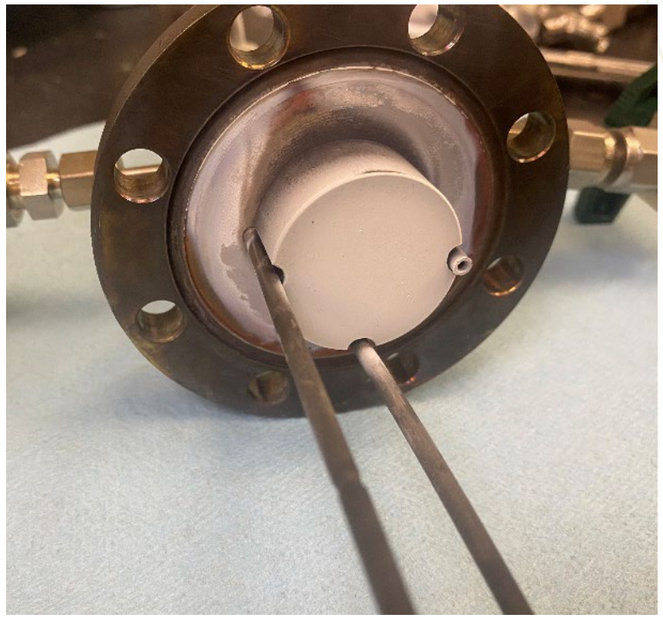
$$\log p(Pa) = \left\{13.78 - \frac{12650}{T(K)}\right\})$$

T/K	p/Pa
971	5.65
970	5.48

O. Glemser, R.V. Haeseler, A. Muller, Z. Anorg.Allg.Chem., 329 (1964), 352

Gross Volatility Approach

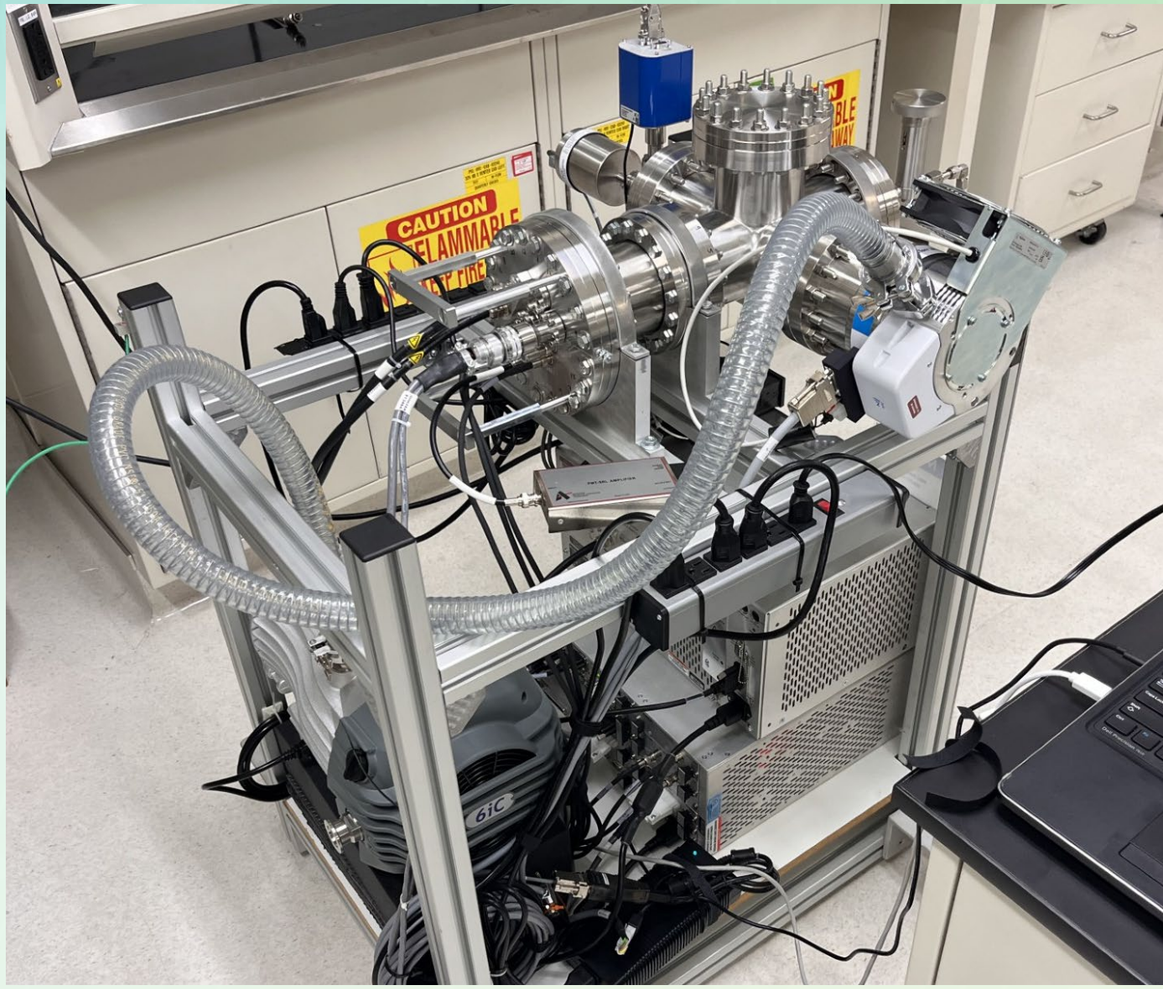




Net mass on condensation plate = 0.02 g

Working Toward the KEMs Experient Mass Spectrometry

- **Extrel MAX500 HT Mass Spectrometer** (MS) for real-time evolved gas analysis (EGA) during thermogravimetric analyzer (TGA) ramps, enabling identification of sublimated species and vapor pressure measurements
- Requires a fully heated transfer path (up to 600°C) with a fixed, heated capillary that meters a small, steady leak into the Electron Impact (EI) ionization source
- Tunable EI source, capable of supporting Knudsen-effusion mass spectrometry (KEMS) to quantify appearance potentials of volatilized molecules



Team at PNNL

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