Molten Salt Reactor PROGRAM

Update for Chlorine Isotopes Separation by TDIS Why Establish a Volatility Capability

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Chlorine Isotopes Separation by TDIS

- The Chlorine Isotopes Project was granted to PNNL by DOE-NE in late FY2022.
- The effort seeks to provide a credible separation of natural abundance $^{35,37}Cl$ to enriched ^{37}Cl.
- A credible partitioning of ^{35}Cl /^{37}Cl requires a good first pass enrichment, but additionally at a scale that will accommodate the prodigious amount of chloride salt and fertile/fissionable metal chlorides required in the core of a MCSR.
- The 1st phase was completed on time and under budget and the project was extended to FY25.
- The project funds were spent as of 4/30/25 and the project is currently on hiatus

Why Enrich Chlorine from its Natural Abundance $^{35}Cl/^{37}Cl$ to High Purity ^{37}Cl?

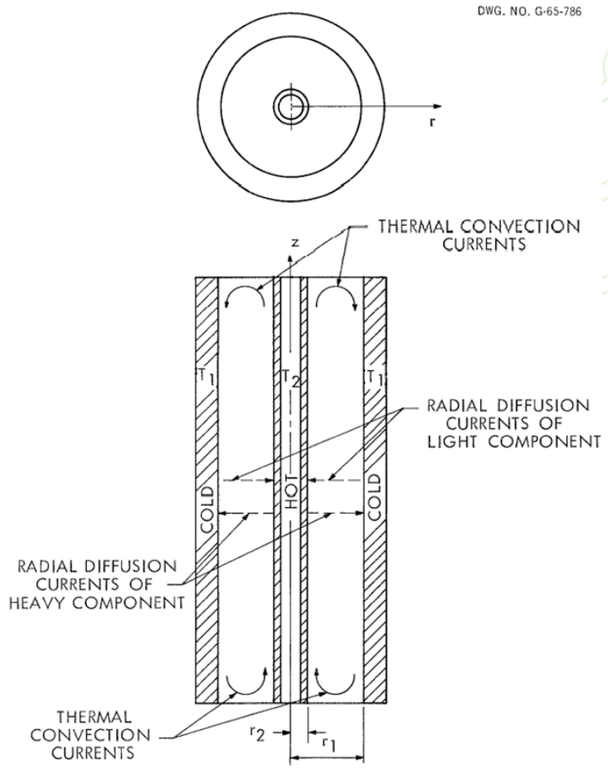
- ^{35}Cl has higher abundance than ^{37}Cl (76% ^{35}Cl and 24% ^{37}Cl)
- Thermal neutron irradiation of ^{35}Cl produces ^{36}Cl ($^{35}Cl(n,\gamma)^{36}Cl$) with a relatively large neutron cross section of ~42 barns
- The half-life of ^{36}Cl is 301,000 years and its decay produces a 98% beta emission (716 keV) to stable ^{36}Ar
- the cross section of ^{35}Cl in combination with other high neutron cross section poisons reduce the neutron economy of the reactor

Why Enrich Chlorine from its Natural Abundance $^{35}Cl/^{37}Cl$ to High Purity ^{37}Cl?

- Secondly, the $^{35}Cl(n,p)^{35}S$ reaction, which decays back to ^{35}Cl. Accordingly, yields of sulfur will accumulate in the salt. For a properly reduced fuel salt, the likely form of the sulfur would be S^{2-}. A few thousand ppm S (as S^{2-}, S^0) are corrosive to Ni, Mo and react with fertiles. $UCl_3 + S = U_xS_{y\,(ppt)}$, $PuCl_3 + S = Pu_xS_{y\,(ppt)}$
- The $^{35}Cl(n,\alpha)^{32}P$ produces radio-phosphorus ($t_{1/2}$= 14d) that also decays to more sulfur. P can interact with these MOCs as PCl_3 or more reduced forms of phosphorous
- ^{36}Cl production can be reduced by isotopically separating natural ^{35}Cl from ^{37}Cl

An Optimized Protype for the Thermal Diffusion of $H^{35,37}Cl$

- Clusius and Dickel. 1939. “Das Trennrohr. II. Trennung der Chlorisotope.” Zeitschrift fur Physikalische Chemie. 44B(1):451-473 (in German)
- Kennedy and Seaborg. 1940. “Isotopic Identification of Induced Radioactivity by Bombardment of Separated Isotopes; 37-Minute ^{38}Cl. Phys. Rev. **57**:843-844.
- Akabori et al. 1941. “Separation of Isotopes by Thermal Diffusion, II. Separation of Chlorine Isotopes.” *Osaka Nuclear Physics Laboratory.* **23**:500-604.
- Shrader. 1946. “Partial Separation of the Isotopes of Chlorine by Thermal Diffusion.” Phys. Rev. **69**:439-442
- Kranz and Watson. 1953. “Chlorine Isotope Separation by Thermal Diffusion.” Phys. Rev. 91(6):1469-1472.
- Greene, Hoglund, and Von Halle. 1966. “Thermal Diffusion Column Shape Factors: Part I. Shape Factors Based on an Inverse Power Repulsion Model. Report No. K1469. Union Carbide Corp., Oak Ridge, TN



The separation column for TDIS is a tube inside of a tube, where thermal convection currents and radial diffusion work to provide the isotope separation.

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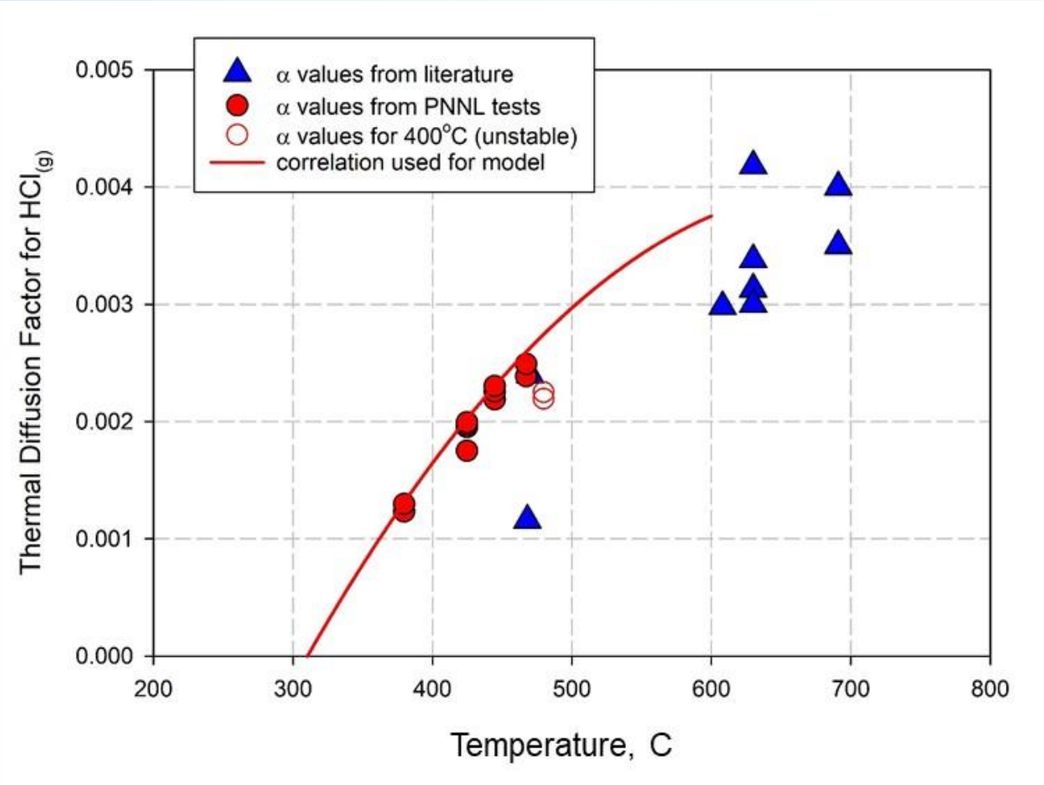
The Relevance of the Thermal Diffusion Constant, α, for HCl



Comparison of PNNL and literature value measurements of the thermal diffusion constant, α, for $HCl_{(g)}$. The temperature plotted is the T_{avg} of the column.

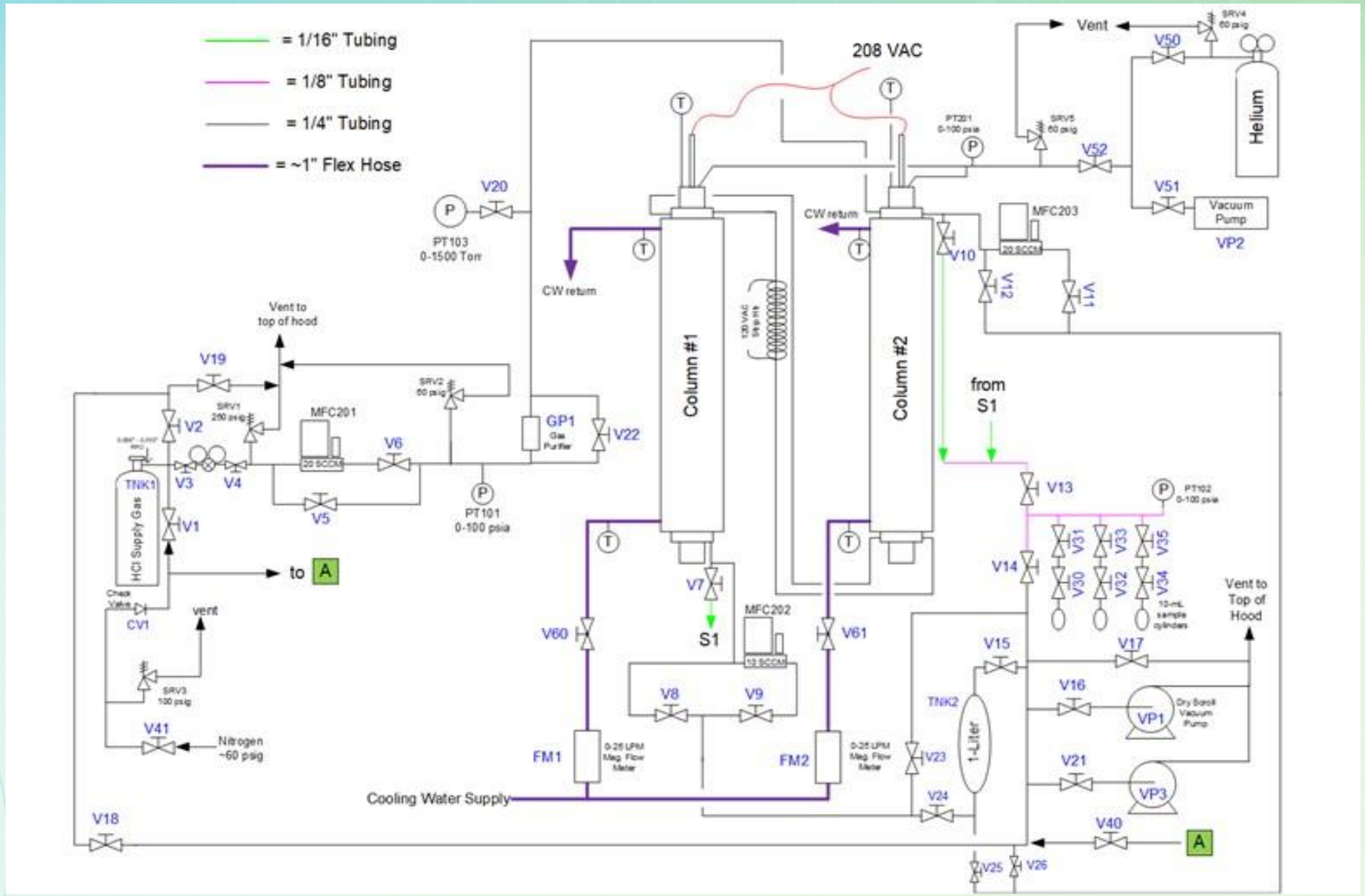
1st phase prototype

P&ID for the two, 6-foot serial columns and associated apparatus

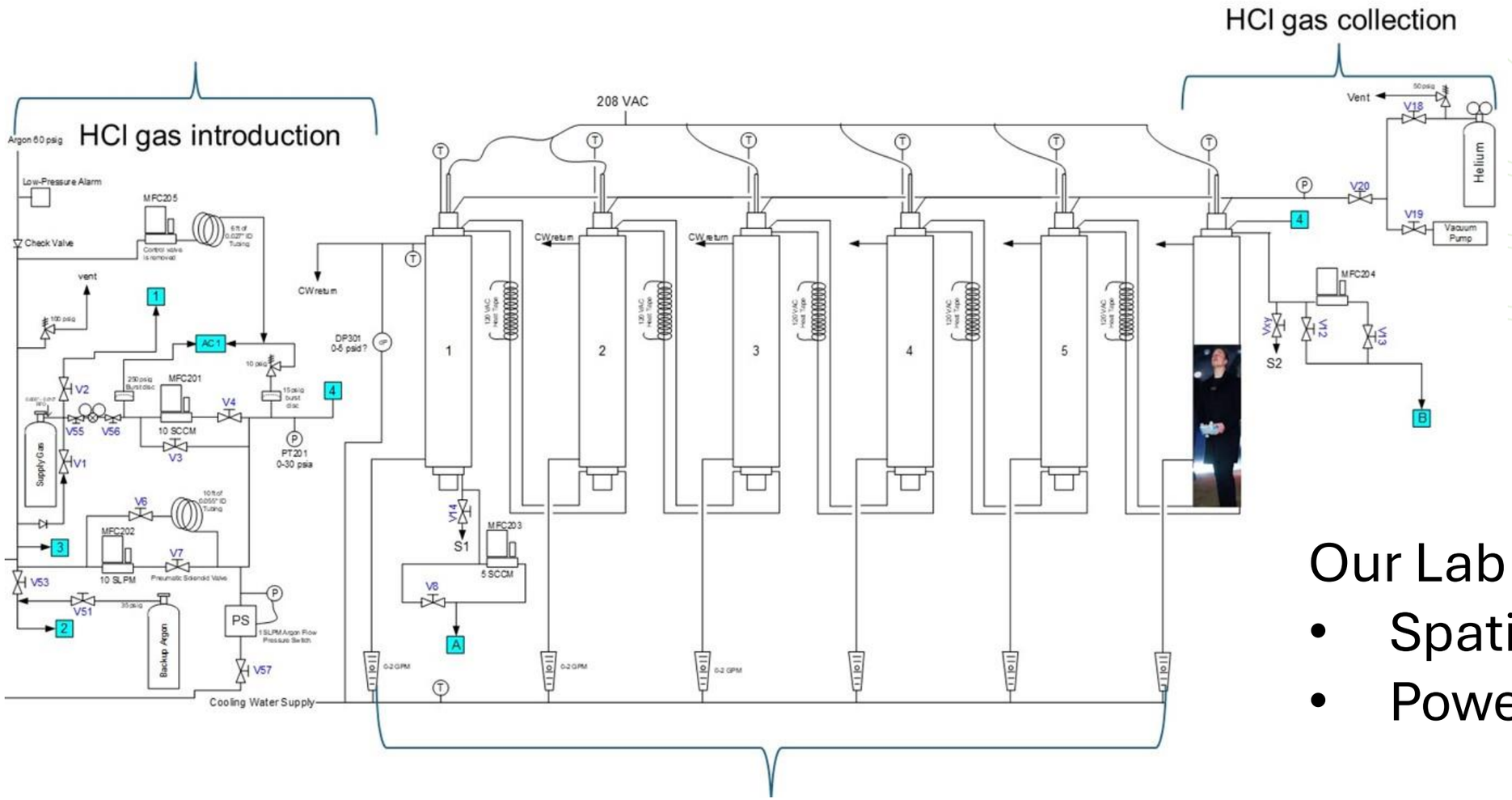
Infinitely tall column
Five nines+ purity

Initial guesses based on literature data

Validated model



FY 2025:2nd Phase Extended TDIS System



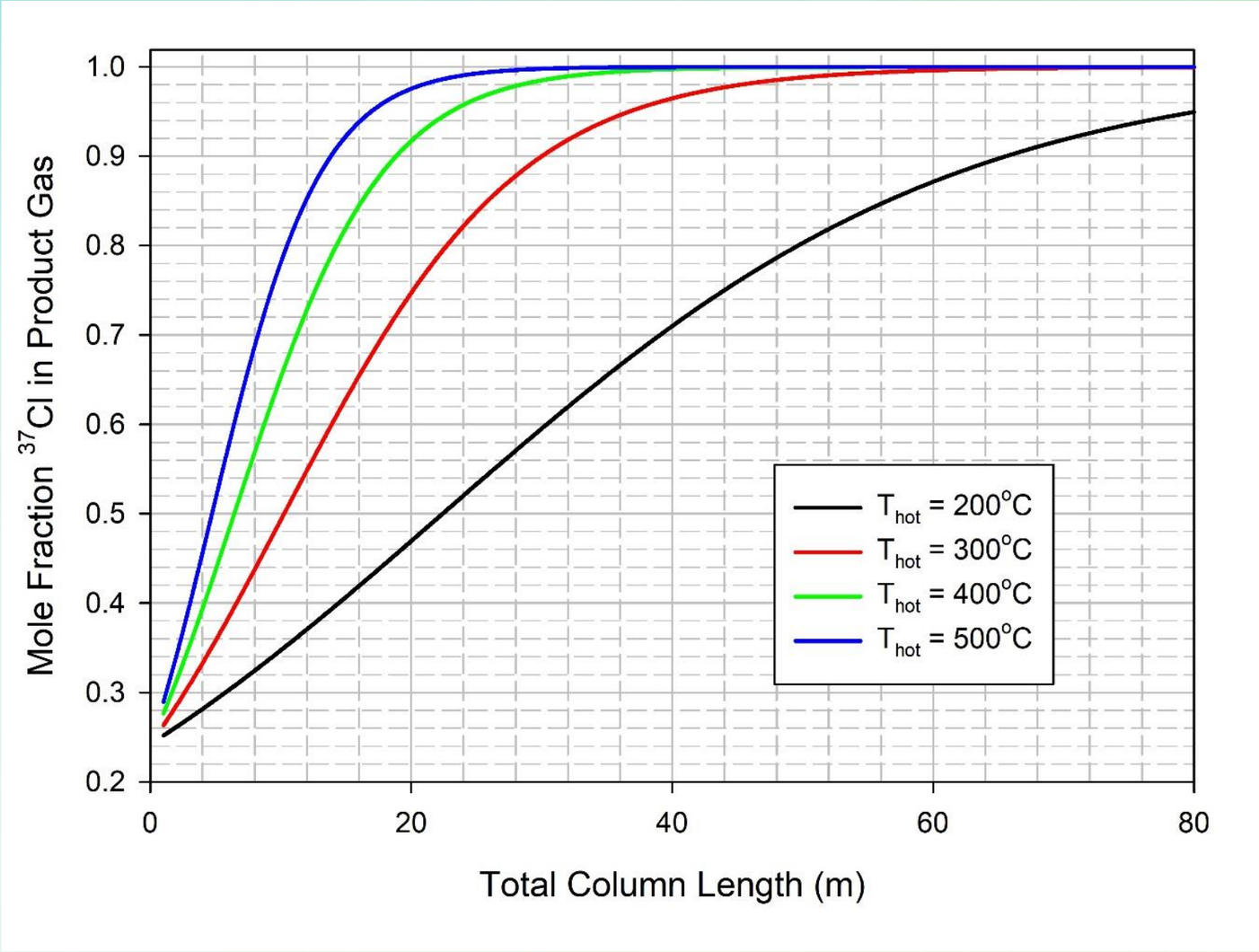
P&ID for the extended TDIS system designed at PNNL in FY25.

Our Lab is:

- Spatially restricted
- Power restricted

Enrichment Predictions of the Extended TDIS System – A Data Validated Model

- The validated COMSOL MPP model provides design predictions for larger scale TDIS systems
- 6 columns total serial length 18-20 m
- First pass separation 0.9 enrichment
- For instance, an irradiation experiment would require 2nd pass

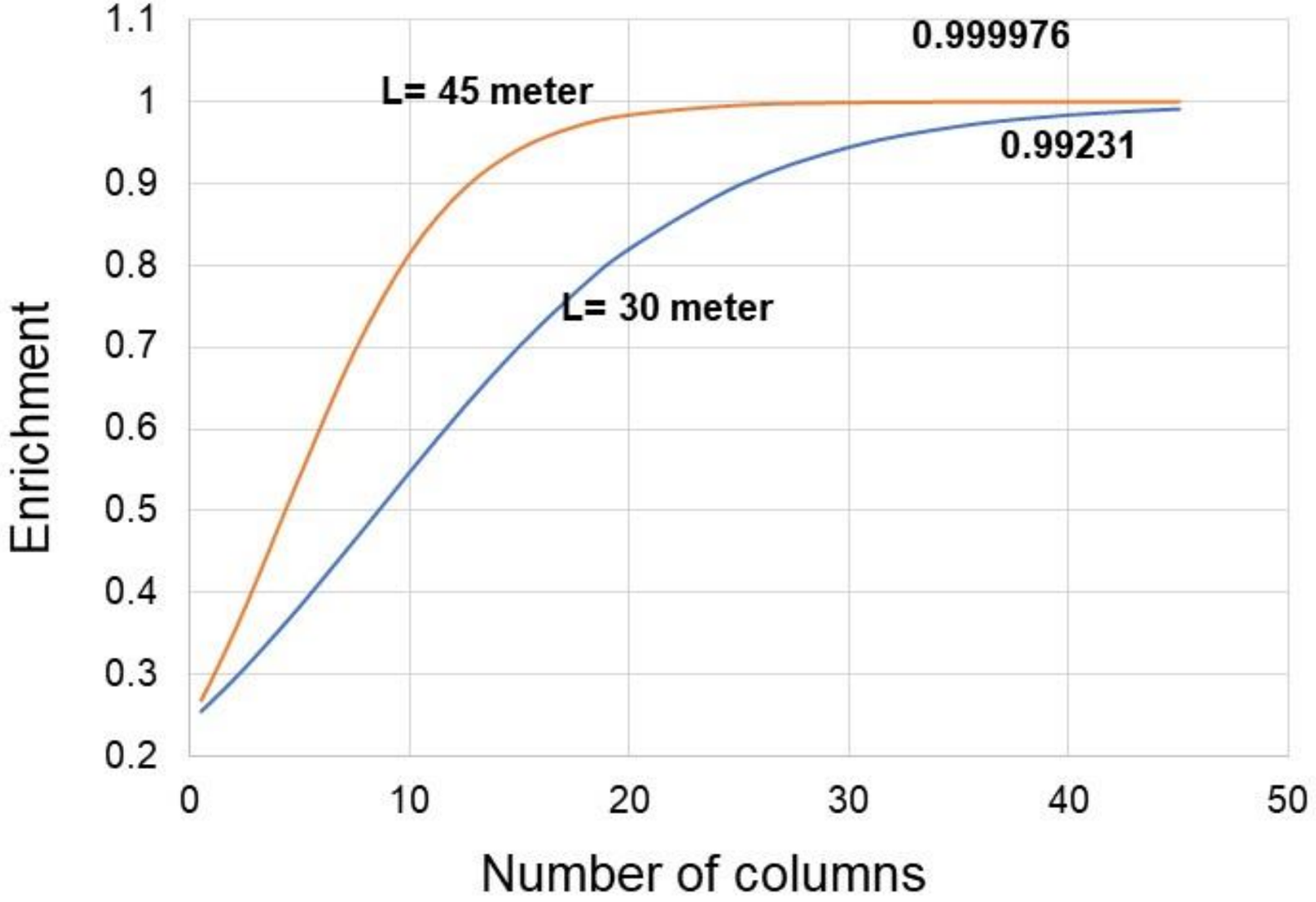


A Case for Establishing a Fuel Salt a Volatility Capability

Fission product loading of a designed fuel salt will produce cases of solvent -nonvolatile solutes, solvent –volatile solutes, and cases of solvent- insoluble solutes. Alteration of the volatility profile of a well-prepared parent fuel salt may allow assessment of short and long-term impacts of problematic solute loadings.

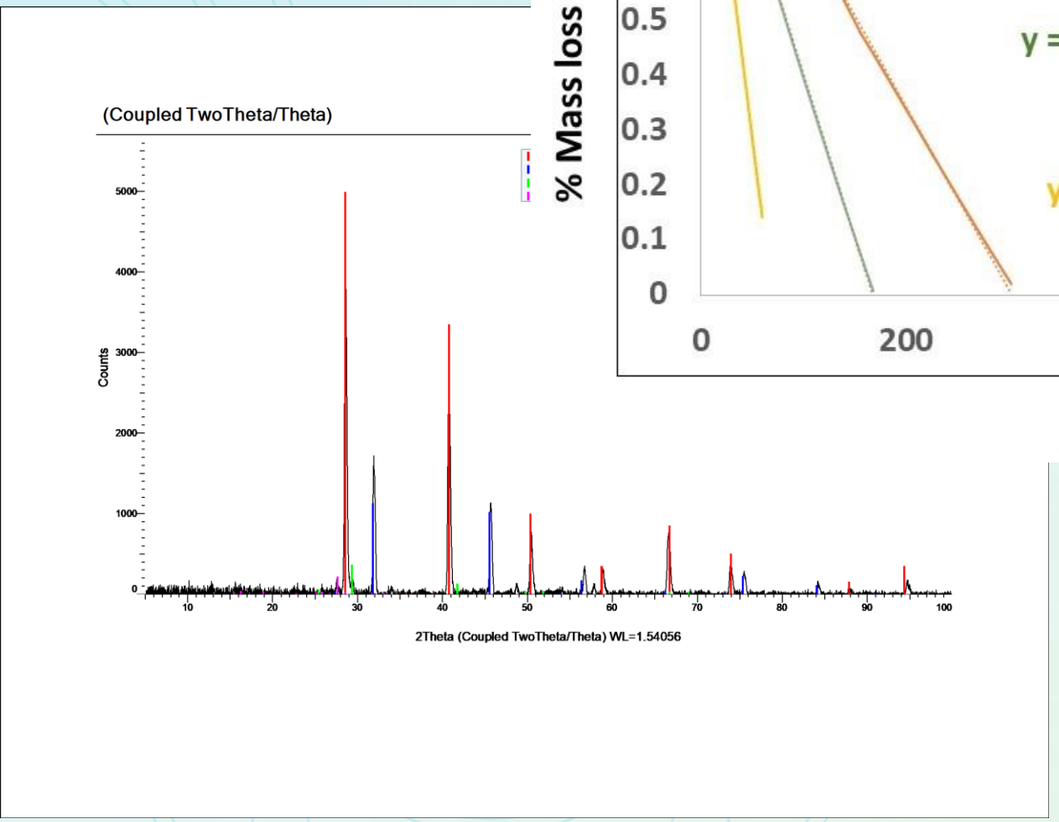
What does the volatility profile look like? A characteristic temperature range will allow very low to high vapor pressures to be measured for most substances or mixtures, the vapor phase speciation may consist of congruent or incongruent vaporization (all or fractional species) from a mixture.

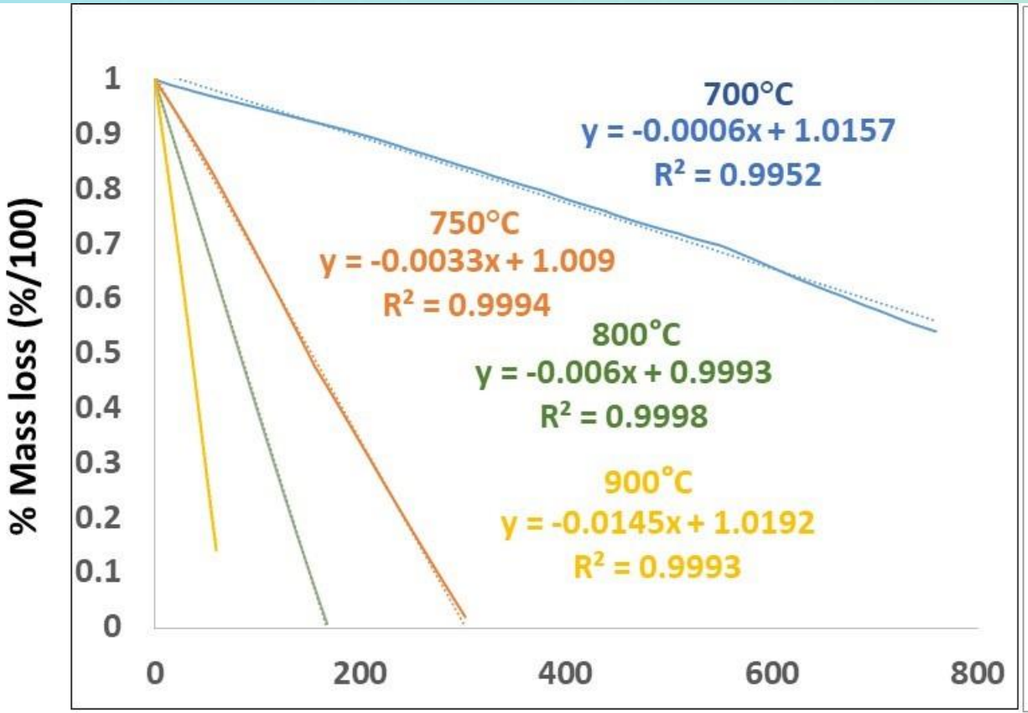
Enrichment Predictions of the Extended TDIS System –A Data Validated Model

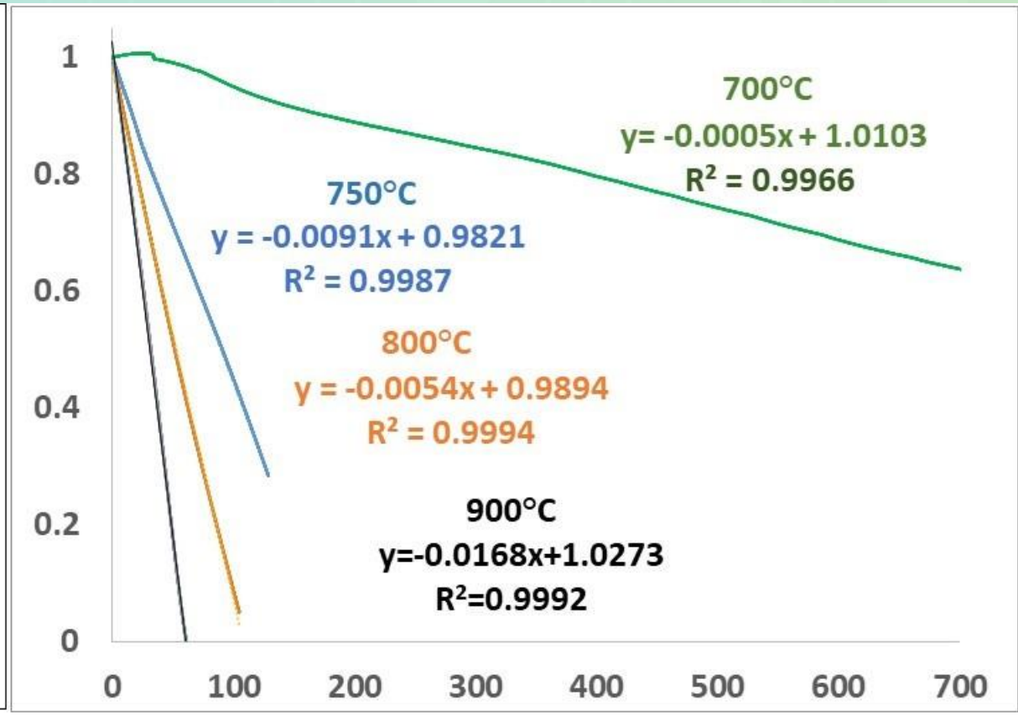


Enrichment in ^{37}Cl for 30-m and 45-m columns using α and L (the column length) as chosen and transport constant H and K values as calculated from data acquired on the test system described above

Temperature dependence of 25/75 and 75/25 ClNaK







Time, min

Do's and Don'ts

Do confirm water content

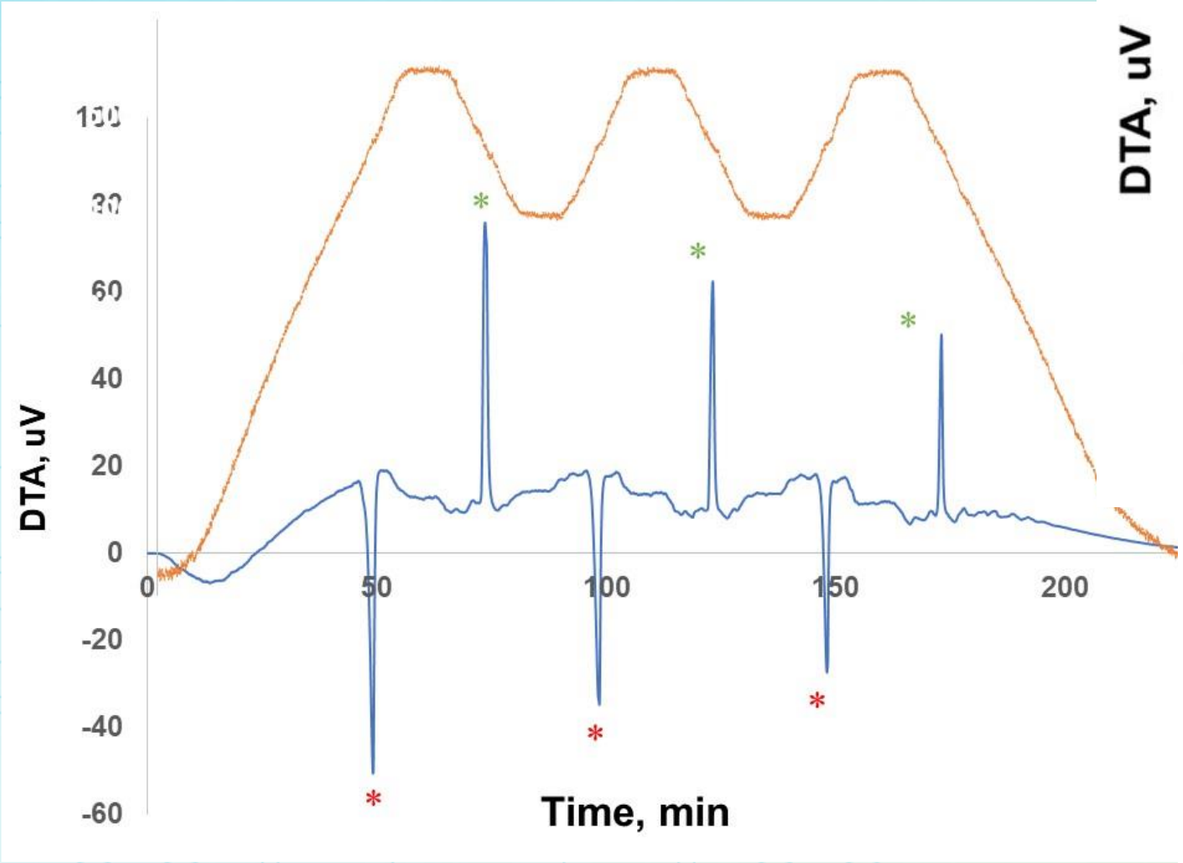
Do confirm structural compliance with literature

Do rigorously closed experiments *or analyses*

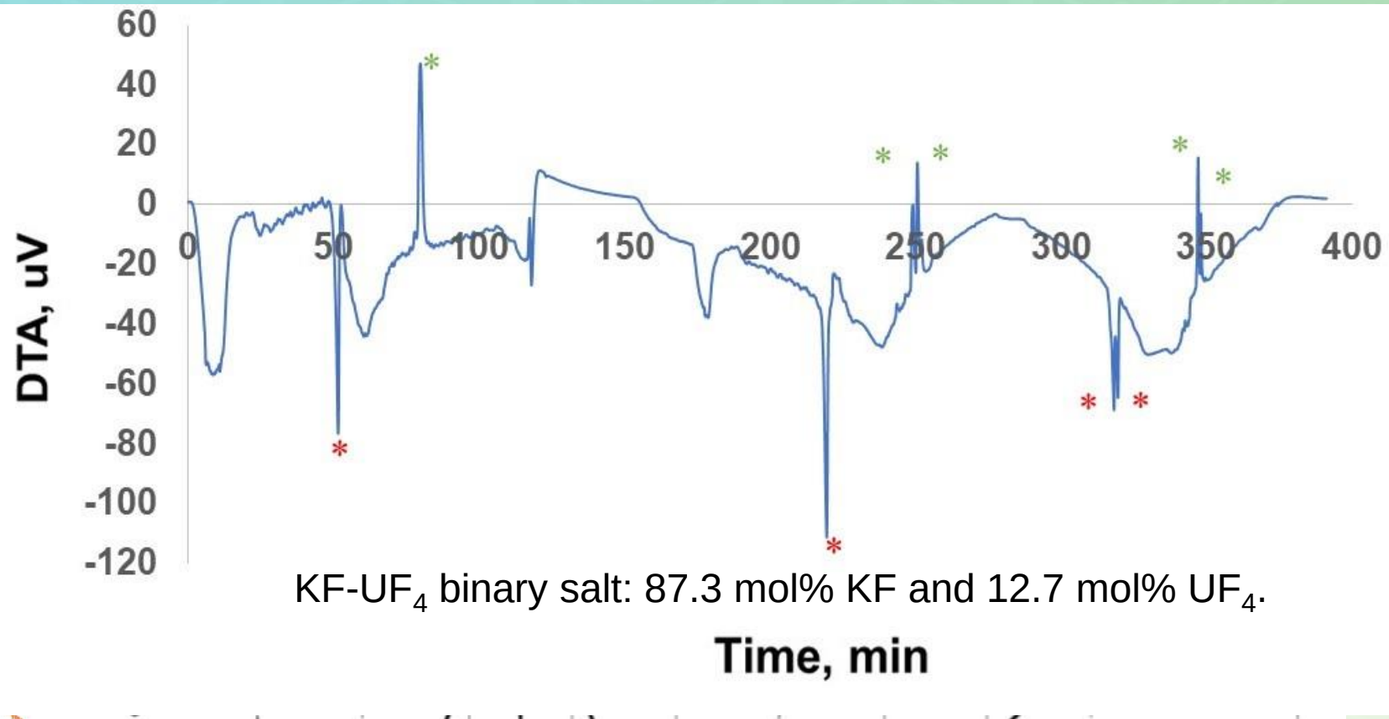
Don't use inferior precursor materials, Na, K, $MgCl_2$, etc., NU, DU

1. **$LiF\text{-}UF_4$ (73.0 mol%, LiF and 27.0 mol% UF_4)**
2. **$KF\text{-}UF_4$ (87. 3 mol%, KF and 12.7 mol% UF_4)**
3. **$NaF\text{-}ZrF_4\text{-}UF_4$ (53.1 mol% NaF, 40.7 mol% ZrF_4, and 22.2 mol% UF_4)**
4. **$LiF\text{-}ThF_4\text{-}UF_4\text{-}PuF_3$ (77.5 mol% LiF, 12.3 mol% ThF_4 6.6 mol%, UF_4, 3.6 mol% PuF_3)**
5. **$LiF\text{-}ThF_4\text{-}UF_4$ (72.3 mol% LiF, 1.8 mol% ThF_4, and 25.9 mol% UF_4)**
6. **FLiNa-U (19 mol% U)**
7. **ClNaK-U (0.2 mol% U)**
8. **ClNa-Pu (10- ~50 mol% Pu)**

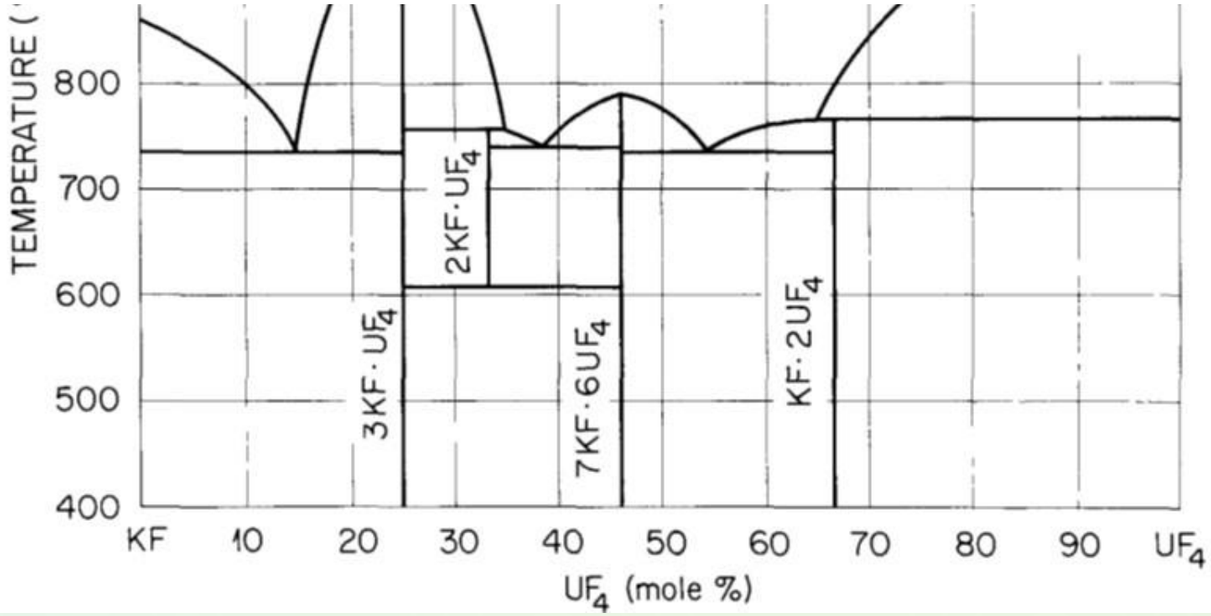
Temperature Dependence of 25/75 and 75/25 ClNaK



Thermogravimetric data for the LiF-UF_4 salt at the composition o 73.0 mol%, LiF and 27.0 mol% UF_4. Barton says 490°C Observed 485°C



KF-UF_4 binary salt: 87.3 mol% KF and 12.7 mol% UF_4.



Chlorine Isotopes Separation for Fast Spectrum MSRs

PNNL TEAM

Mike Powell	*Engineering Computational (COMSOL) Design*
Zach Huber	*Mech Engineer (PM)*
Bruce McNamara	*Physical Chemist (PI)*
Tyler Schlieder	*Mass spectrometry*

Colligative Properties Measurements, Volatility, Radio volatility

PNNL TEAM

Benjamin Scheibe	*PM, synthesis/ structure*
Bruce McNamara	*Physical Chemist (PI)*
Suhee Choi	*dewatering and residual water measurement*
Parker Okabe	*volatility measurements*
Michaella Harris	*volatility measurements*

Thank you!