U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Molten Salt Reactor PROGRAM

Chlorine Isotopes Separation for Fast Spectrum MSR

Bruce McNamara
Pacific Northwest National Laboratory

MOLTEN SALT REACTOR CAMPAIGN REVIEW MEETING

Chlorine Isotopes Separation for Fast Spectrum MSRs

PNNL TEAM

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

- **The Chlorine Isotopes Project was granted to PNNL by DOE-NE in 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.**

Why enrich $^{35}Cl/^{37}Cl$ from its natural abundance: $^{35}Cl(75.77\%)$, ^{37}Cl (24.23%)

- **Amongst the issues prejudicial to the success of the MCSR reactor is the (n,γ) cross section of the natural abundance ^{35}Cl isotope in the range of energies of interest.**
- **^{35}Cl (about 76% of natural chlorine) features a relatively large (n,γ) cross section (44 b) at thermal energies**
- **The ^{36}Cl activation product, is a long-lived (301,000 years) energetic (709 keV) beta emitter that is highly soluble in water.**
- **^{36}Cl production can be reduced by isotopically separating natural ^{35}Cl from ^{37}Cl.**

References from the Pioneers

The existence of isotopes among the heaviest or radioactive elements was initially described in 1903 by E. Rutherford and F. Soddy . A decade later, in a short letter to the editor of Nature in 1913, Soddy proposed the term "isotope"; and suggested "the chemical elements are not really homogeneous, but merely chemically homogeneous, that their atoms have identical outsides but different insides"

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.

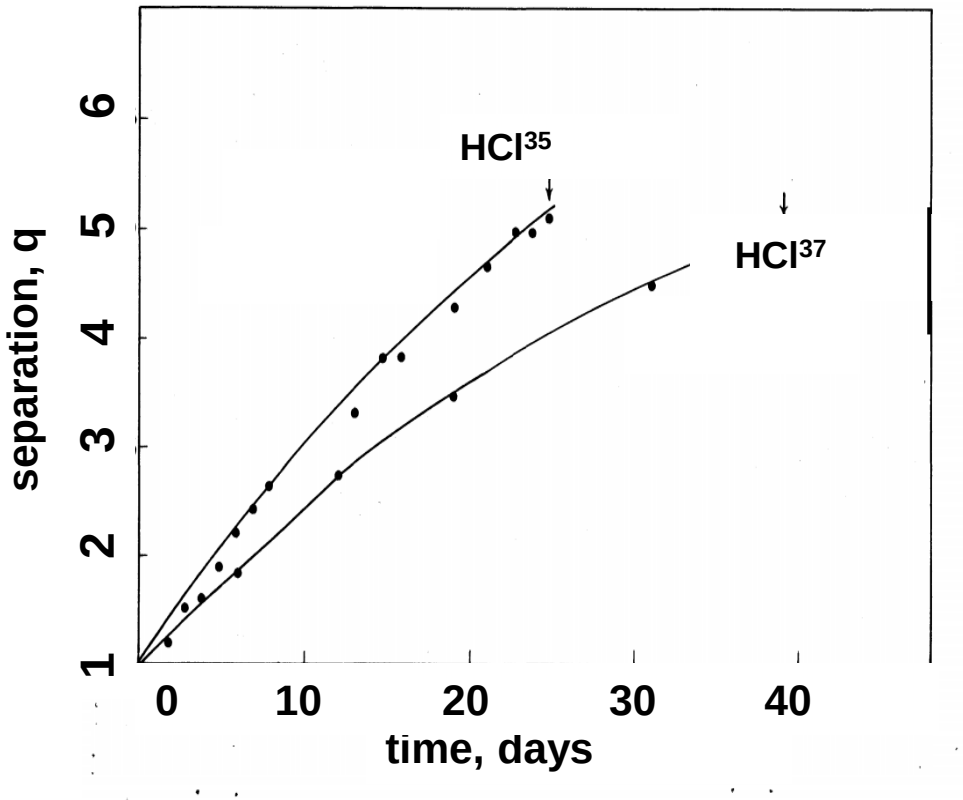
Shrader. 1946. "Partial Separation of the Isotopes of Chlorine by Thermal Diffusion." Phys. Rev. **69**:439-442

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

1st Apparatus

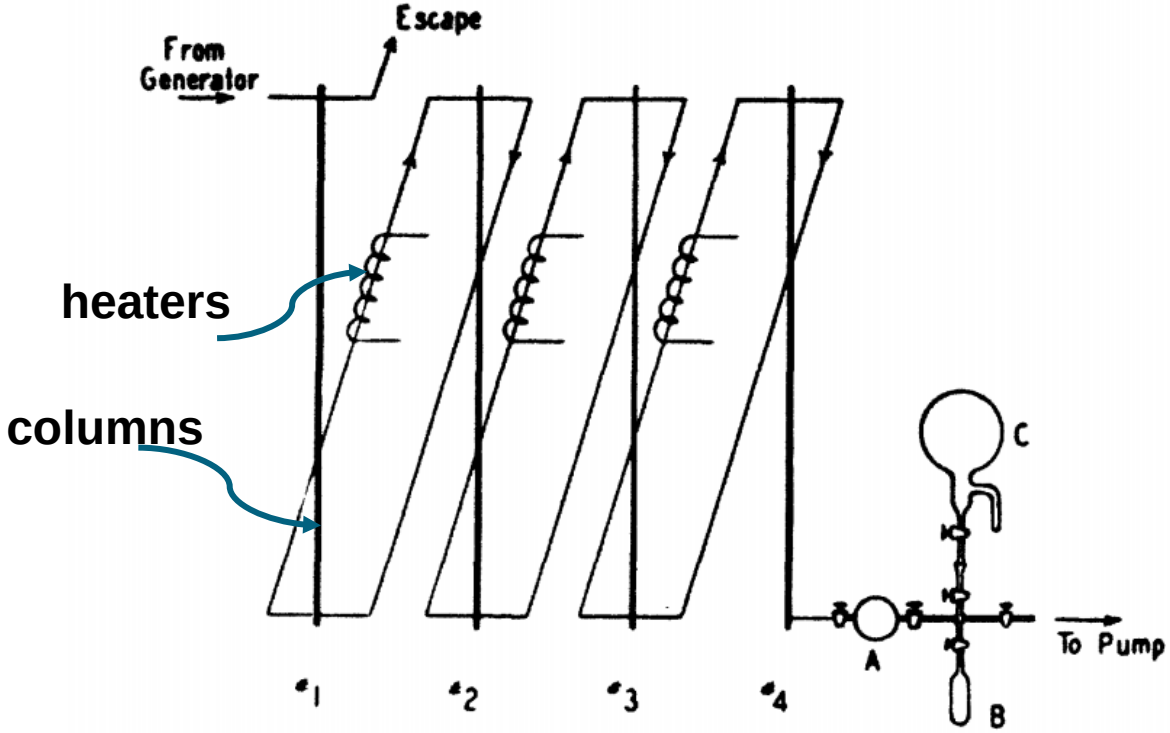
First apparatus (Clusius) using one column took longer than 40 days to reach equilibrium achieved 94 % separation



K. Clusius and G. Dickel, Zeits. f. physik. chemic 344, 1939

Four consecutive columns for diffusion of HCl isotopes in about 1000 cm^3 of dry HCl gas

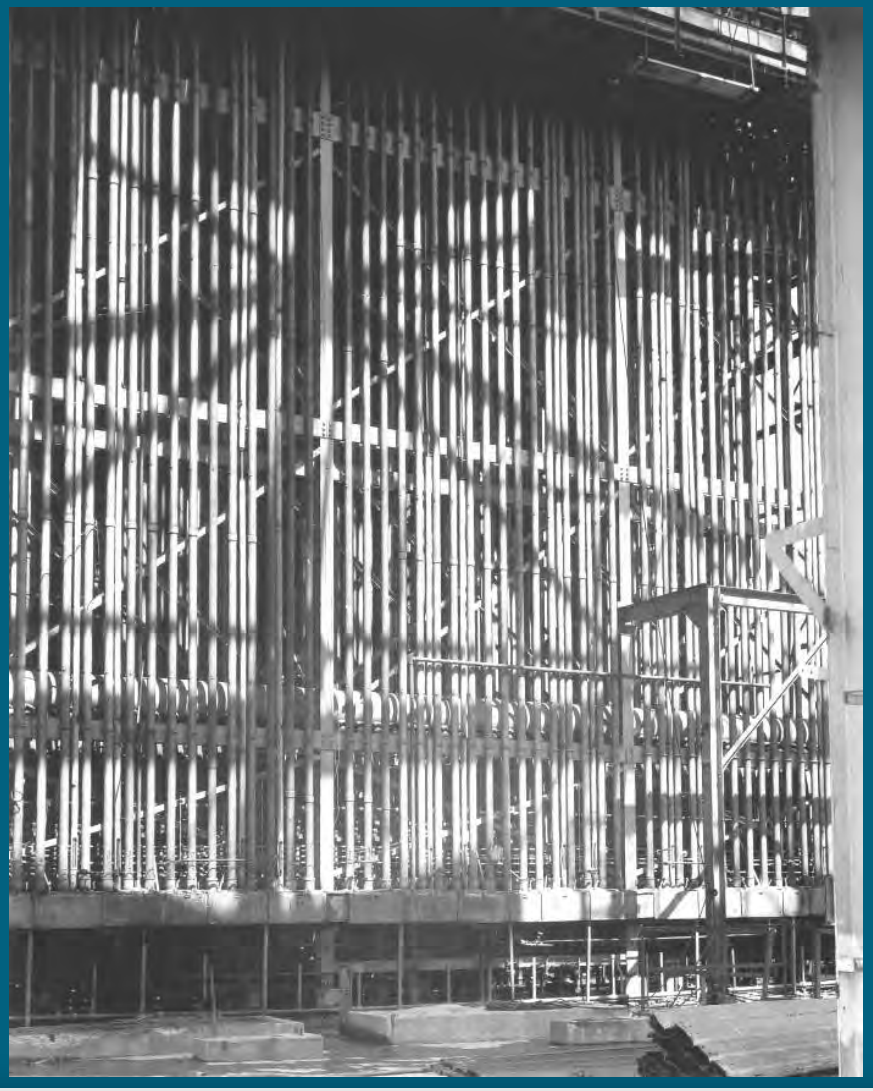
Equilibrium isotope concentrations Cl^{37}/Cl^{35} in this apparatus took about 20 days



E.F. Shrader, Partial Separation of the Isotopes of Chlorine by Thermal Diffusion, Physical Reviews, Vol 69(9,10) 1946

TD of Liquid UF_6 (S-50 Plant) Clinch River

- **The S-50 Project was part of the Manhattan Project's effort to select an enrichment method for uranium**
- **2,142 columns, each 48 ft (14.6 m) long**
- **Serial connection**



FY23-24 Project Milestones

1. Develop a model that allows best guess design / construction of a prototype thermal diffusion separations apparatus

2. Build the separations columns and associated hardware

3. Establish analytical method for rapid measurements of the $^{35}Cl/^{37}Cl$ ratio

4. Vary temperature and pressure with measurement of the $^{35}Cl/^{37}Cl$ ratio

5. Separate measure of the parameter α with parametric variation of T and P

6. Iterate improved column design for high enrichments, optimized separations arrangements for increased throughputs

7. Validate to understand efficiency and economics of scale up

A Key Parameter for Design

For a thermal separation column with two isotopes, the equilibrium separation (q_e) is given by

$$q_e = \exp\left(\frac{HL}{K}\right) = \frac{c_L(1 - c_0)}{c_0(1 - c_L)}$$

where:

- ***L*** **= total column length, cm; 680 cm for Kranz and Watson's apparatus**
- c_0 **= concentration of light product gas at top of column**
- c_L **= concentration of light product gas at bottom of column**

Transport Equation

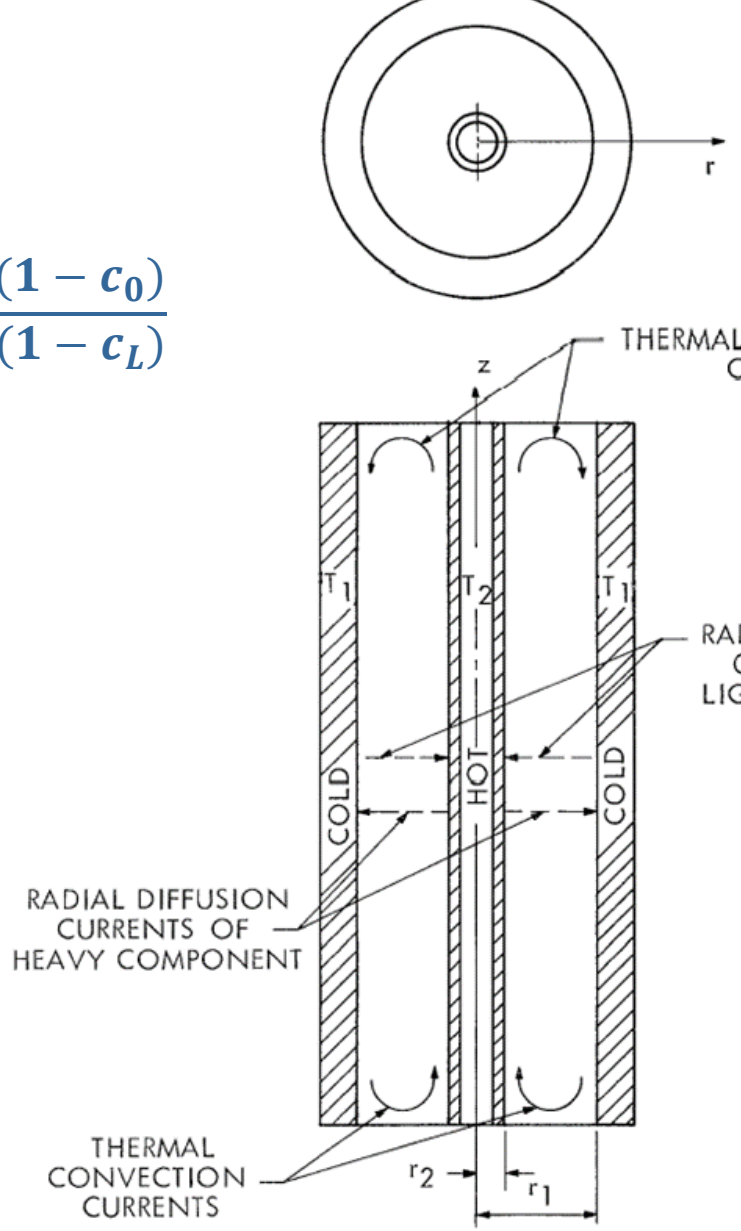
Greene et al., Thermal Diffusion Column Shape Factors, K-1469 (1966)

$$\tau = Hx(1 - x) - (K_c + K_d)\frac{dx}{dz},$$

$$q_e = \exp\left(\frac{HL}{K}\right) = \frac{c_L(1 - c_0)}{c_0(1 - c_L)}$$

where

τ	is the net transport of light component toward the top of the column,
x	is the mole fraction of the light component in the mixture,
z	is the axial column coordinate, and
H, K_c, and K_d	are the transport coefficients.



$q_e = \exp\left(\frac{HL}{K}\right)$ The transport coefficients H, K = K_c + K_d can be calculated for any gaseous mixture of isotopes which obeys an inverse power repulsion law

Calculation of Column Transport Coefficients

Use "shape" factors from Greene et al., Thermal Diffusion Column Shape Factors K-1469 (1966)

values for h_m, k_c and k_d are determined by interpolation of tabulated values

inputs for table are *n*, R, and θ

$$q_e = \exp\left(\frac{HL}{K}\right) = \frac{c_L(1-c_0)}{c_0(1-c_L)}$$

for HCl, *n* = 0.8747 (based on plot of power-law fit of viscosity vs. Temp.)

$$H = \frac{2\pi}{6!}\frac{\theta\bar{\rho}^2 g}{\bar{\mu}} r_{avg}(r_1 - r_2)^3 \left(\frac{T_2 - T_1}{T_{avg}}\right)^2 \bar{h}_m(\theta, R, n) \quad \text{(g of HCl}^{35}\text{ /s)}$$

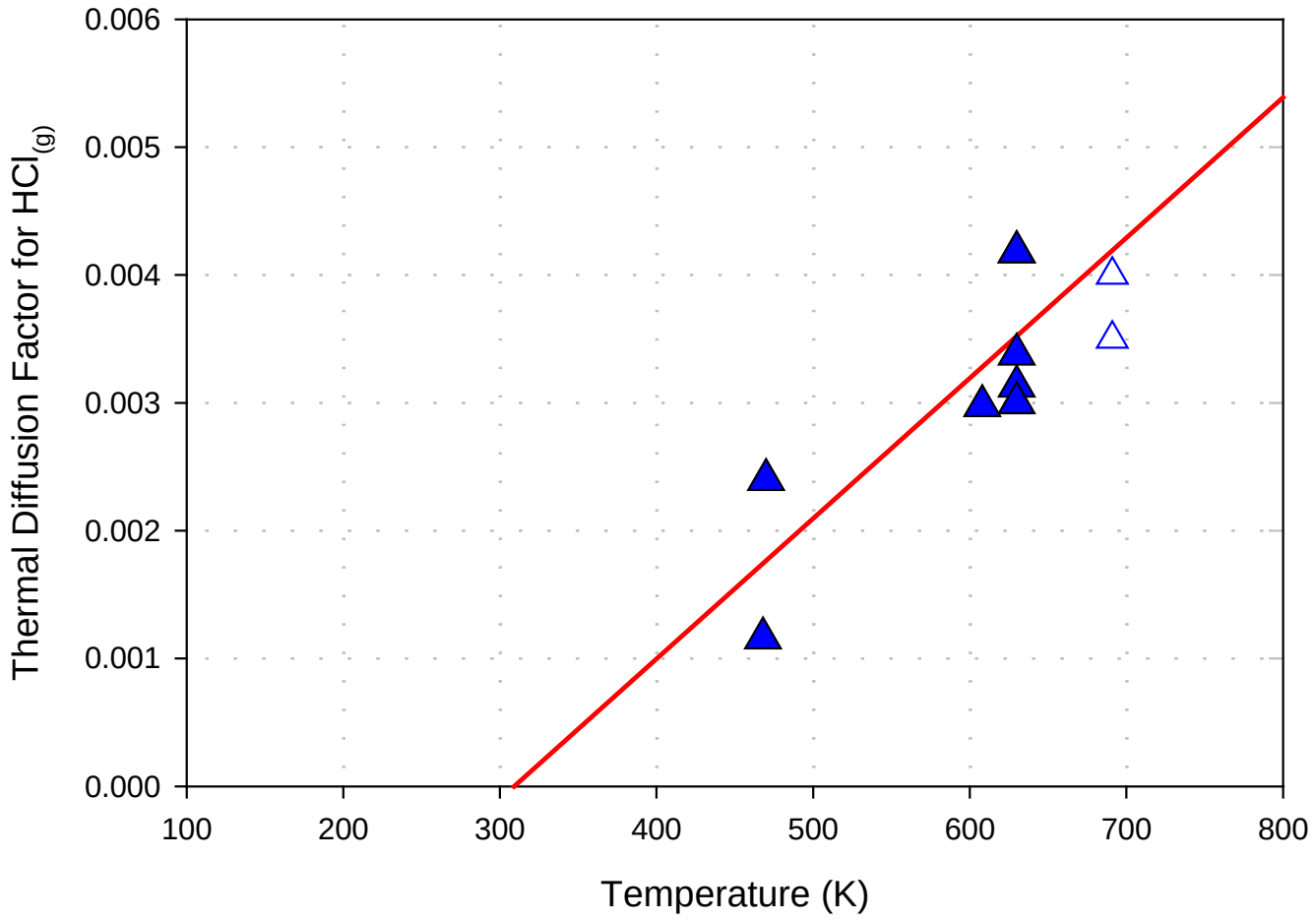
$$K_c = \frac{2\pi}{9!}\frac{\bar{\rho}^3 g^2}{\bar{\mu}^2 \bar{D}} r_{avg}(r_1 - r_2)^7 \left(\frac{T_2 - T_1}{T_{avg}}\right)^2 \bar{k}_c(\theta, R, n) \quad \text{(g of HCl}^{35}\text{ /cm/sec)}$$

$$K_d = 2\pi\bar{\rho}\bar{D} r_{avg}(r_1 - r_2) \bar{k}_d(\theta, R, n) \quad \text{(g of HCl}^{35}\text{ /cm/sec)}$$

r_1	is the radius of the cold (outer) wall,
r_2	is the radius of the hot (inner) wall,
r_{avg}	is the arithmetic average of r_1 and r_2,
T_1	is the temperature of the cold wall,
T_2	is the temperature of the hot wall,
T_{av}	is the arithmetic average of T_1 and T_2.
g	is the acceleration of gravity,
$\bar{\rho}$	is the density of the process gas evaluated at the average temperature, $\bar{T}$,
$\bar{\mu}$	is the viscosity of the process gas evaluated at $\bar{T}$,
$\bar{D}$	is the coefficient of ordinary diffusion of the process gas evaluated at $\bar{T}$,
$\bar{\alpha}$	is the thermal diffusion constant for the process gas evaluated at $\bar{T}$,
$R = r_1/r_2$	is the ratio of the radius of the cold wall to that of the hot wall,
$\theta = T_2/T_1$	is the ratio of the temperature of the hot wall to that of the cold wall,
n	is a function of the force law index, and
$\bar{h}_m$, $\bar{k}_c$ and $\bar{k}_d$	are the values of the shape factors.

Values of α from literature sources

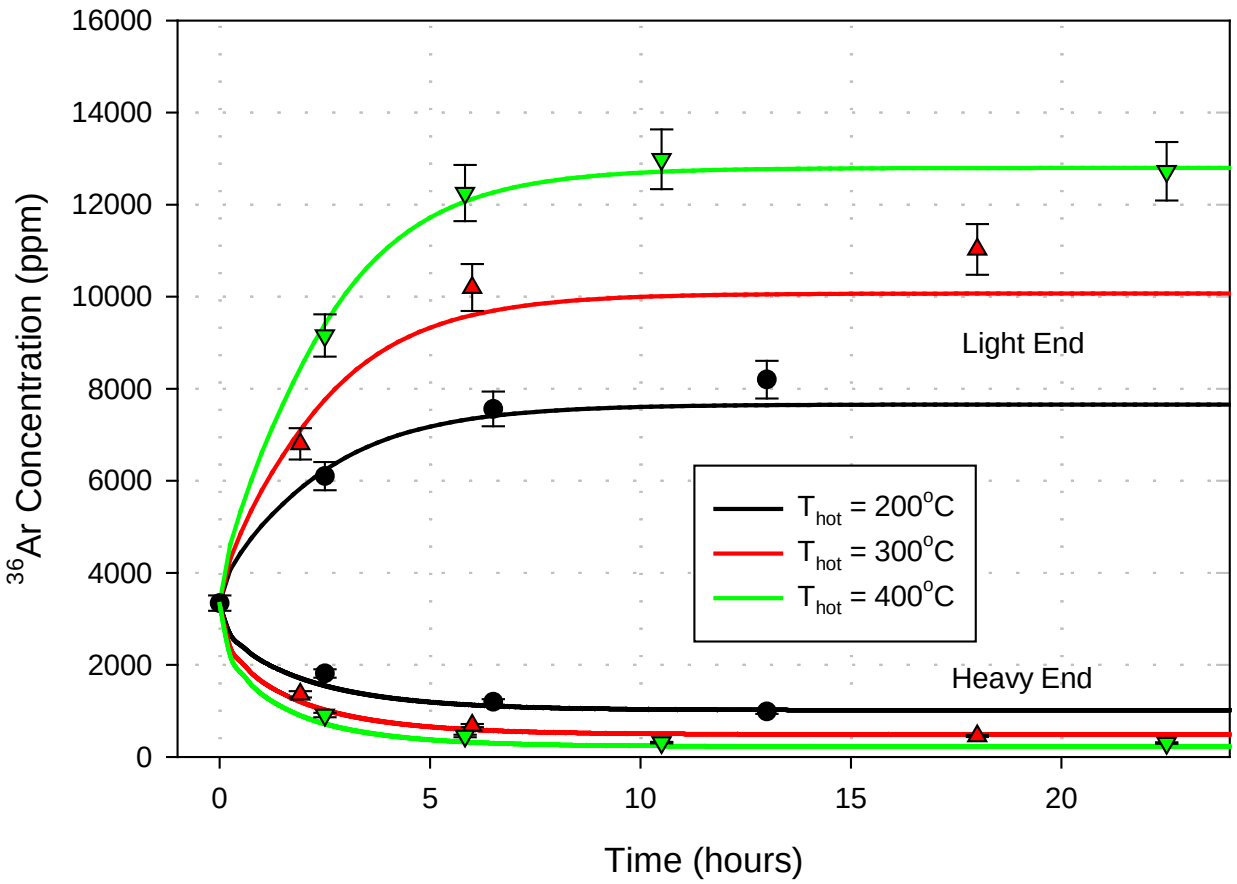
- **Graph shows a values from literature sources**
- **Data is fit with a line that implies:**
  α = 9.64E-6*T – 2.67E-3
- **The predicted temperature where α = 0 is about 310K**
- **Determining this zero-crossing point is important for setting the minimum value for T_{cold}**



Recommended Column Design (based on analysis targeting 4-5 mm gap)

- **Use 3.0-inch Tube (Tube Gauge 7) for innermost tube**
  - ID = 2.624”, OD = 2.975” (after OD grinding)
- **Use 3.5-inch Tube (Tube Gauge 16) for cold wall between HCl and cooling water**
  - ID = 3.37” (after honing), OD = 3.50”
- **Outer cooling jacket formed by wrapping a spiral of ¼-inch SS tube around the 3.5-inch tube and then adding a sheet-metal outer jacket**
- **Divots are machined into the innermost pipe and ¼-inch ball bearings (SS) are placed in the divots during assembly; these maintain the pipe well centered and allow for axial movement due to thermal expansion**
- **Overall length is ~6 ft.; cartridge heaters will stick out about 6 inches farther from the top, so total length will be about 6’6”**
- **Resulting channel gap is ~4.8 mm at operating temperature of T_{hot} = 350-400°C**

Shakedown testing of the columns using ^{38}Ar and ^{36}Ar



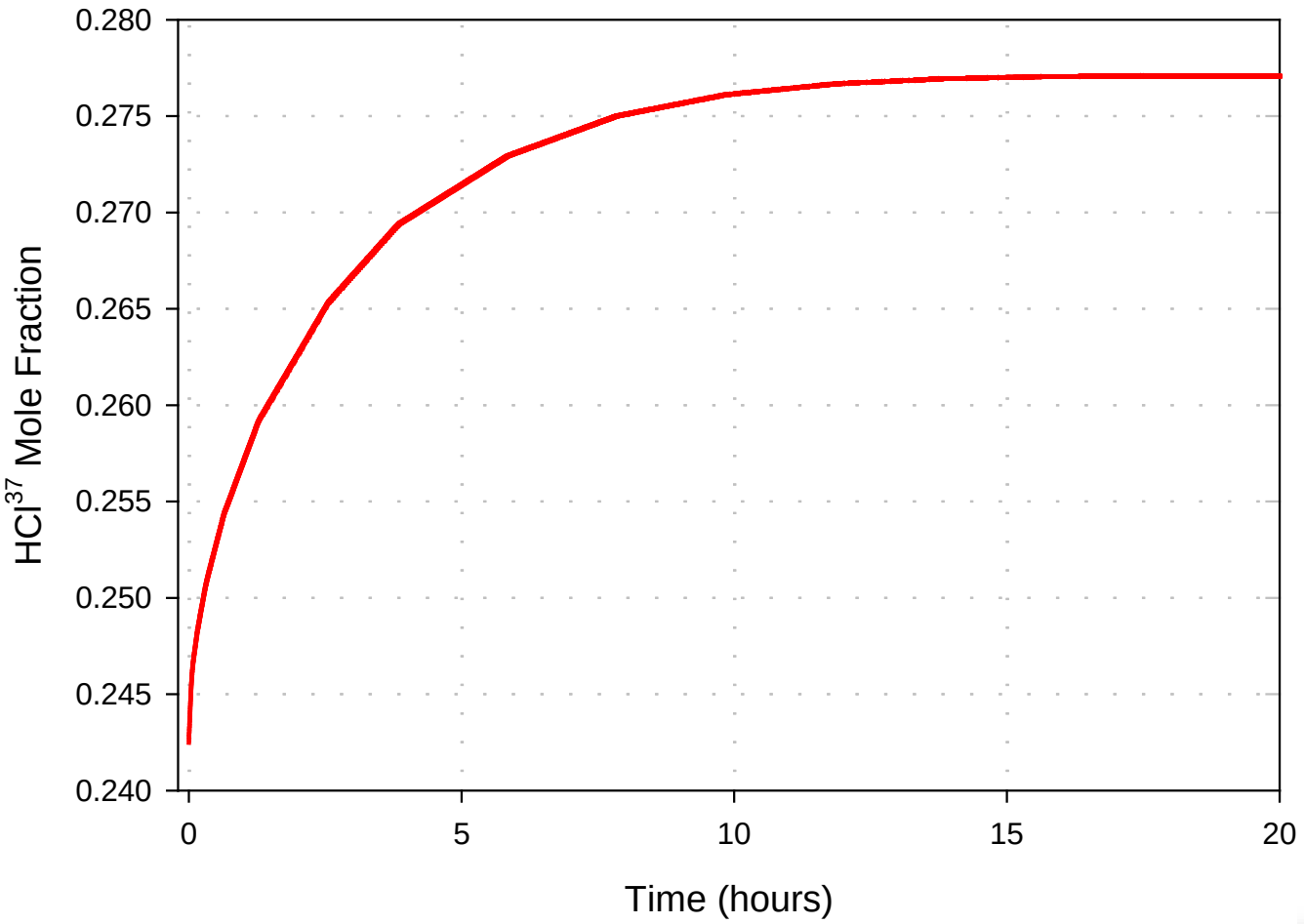
The separation is asymptotic in time. This flattening out of the separation factor is a function of the tube length, if all other features of the tube geometry are optimized.

The result demonstrates the tubes are working at least for Ar 36/38 separations and that increases in the column length will increase the separation factor.

$$q_e = \exp\left(\frac{HL}{K}\right) = \frac{c_L(1-c_0)}{c_0(1-c_L)}$$

Predicted Concentration of $H^{37}Cl$ at the Heavyside of the PNNL TDIS System using the Model at 0.84 atm and T_{hot} = 400°C

- Plot shows predicted concentration of ^{37}Cl
- These predictions are for 0.84 atm and T_{hot} = 400°C
- Approximately 15 hours of operation is required to reach a steady-state concentration



. Each individual column has an internal volume of approximately 1.72L giving a total internal gas volume of 4L 3.4L available for

Current Operations of the TDIS system

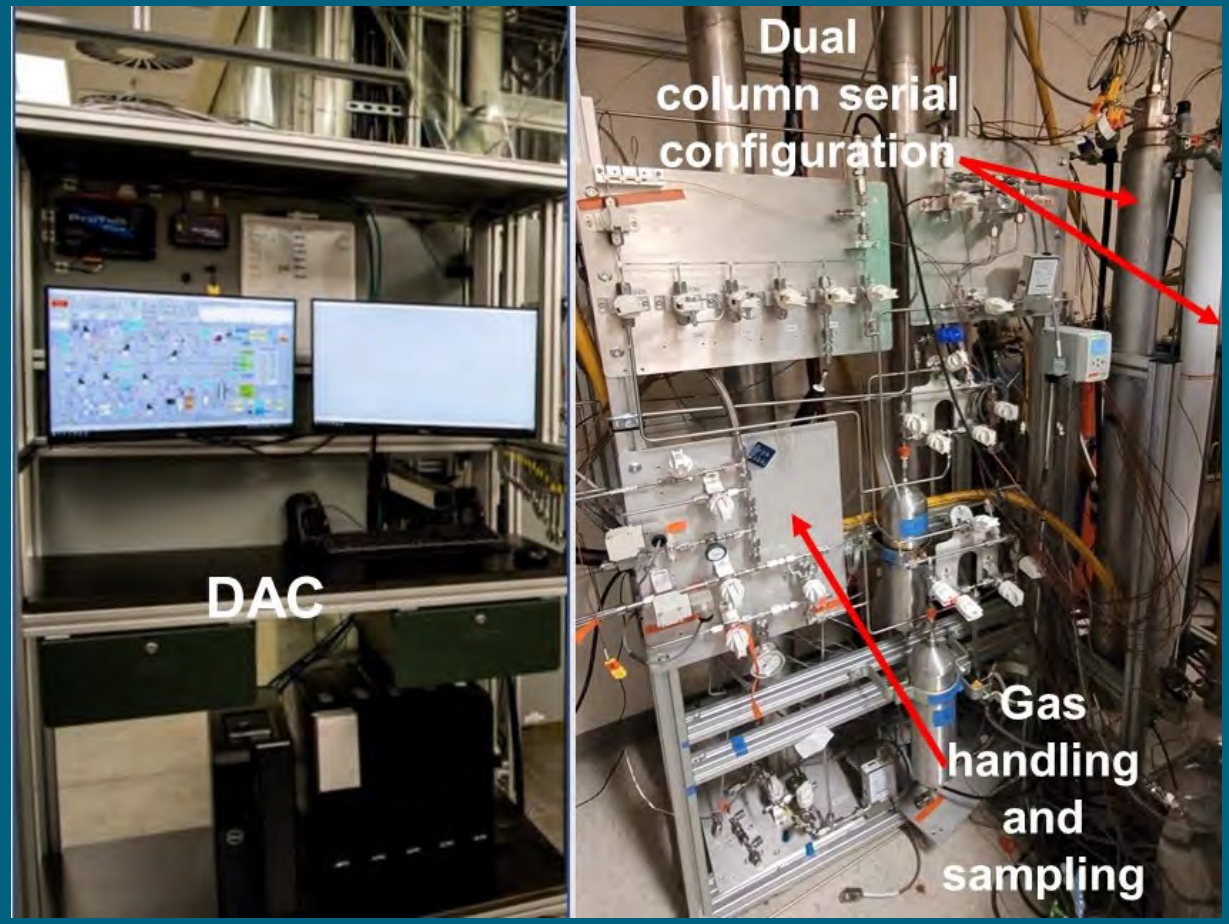
Apparatus built in the 1st quarter of 2023

Completed shakedown testing in July of 2023

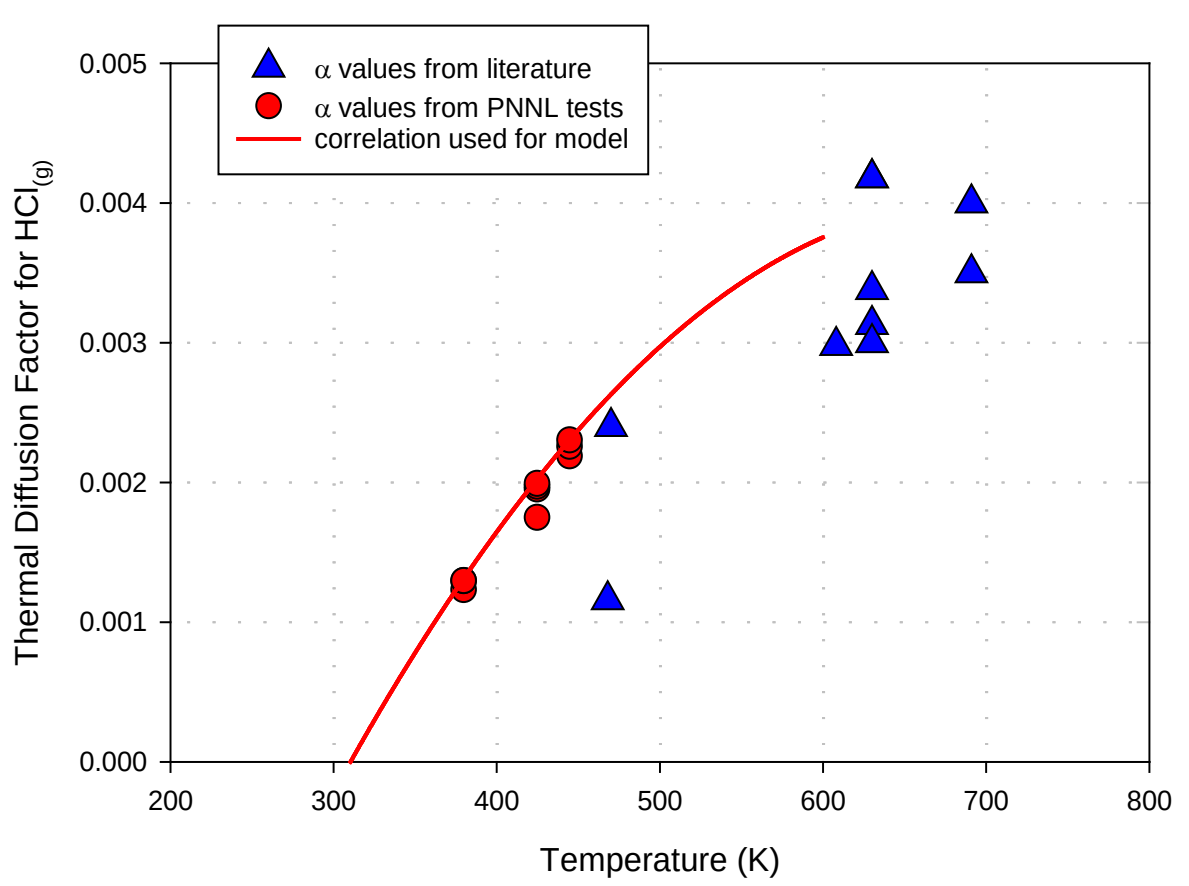
Two serially connected column system

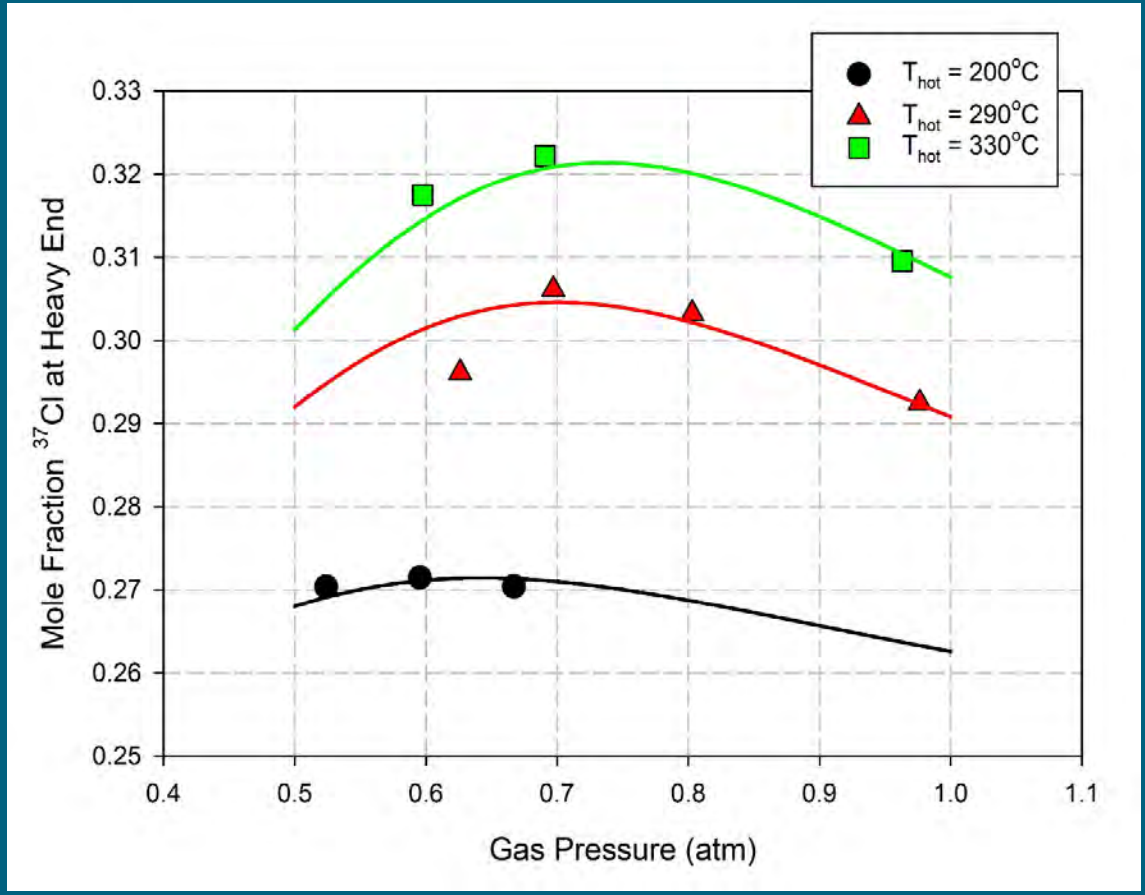
Each column has an internal volume of ~3.7 L for HCl

-



New measurements of the Thermal Diffusion Constant, α, for HCl

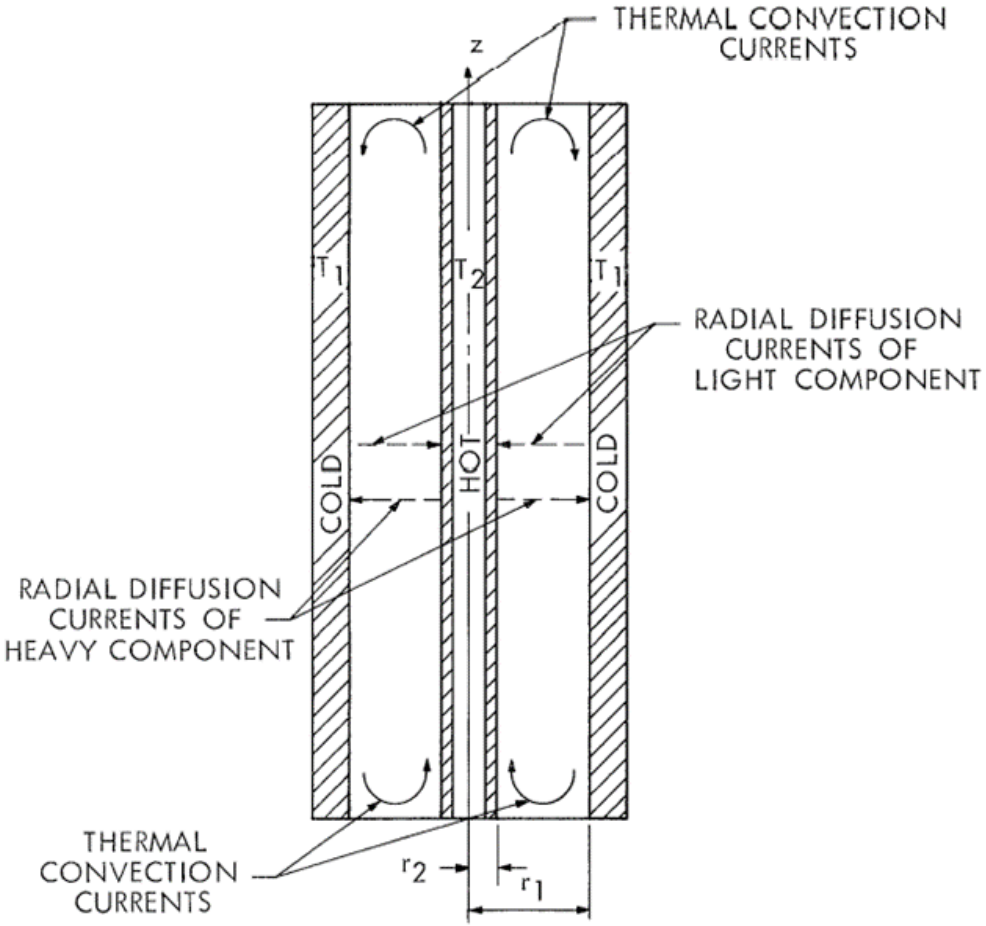




Measured and modeled pressure dependence of isotope separation for multiple temperatures.

Materials of Construction: The One Tube Experiment in Quest of α at Higher Temperature

- Used tube was disassembled and cleaned and reassembled
- Tube was sent to vendor for Silica –type coating applied internally to the intact device
- The coated tube will be sent back to PNNL
- Tested from 400 to 800°C for durability and measurement of α



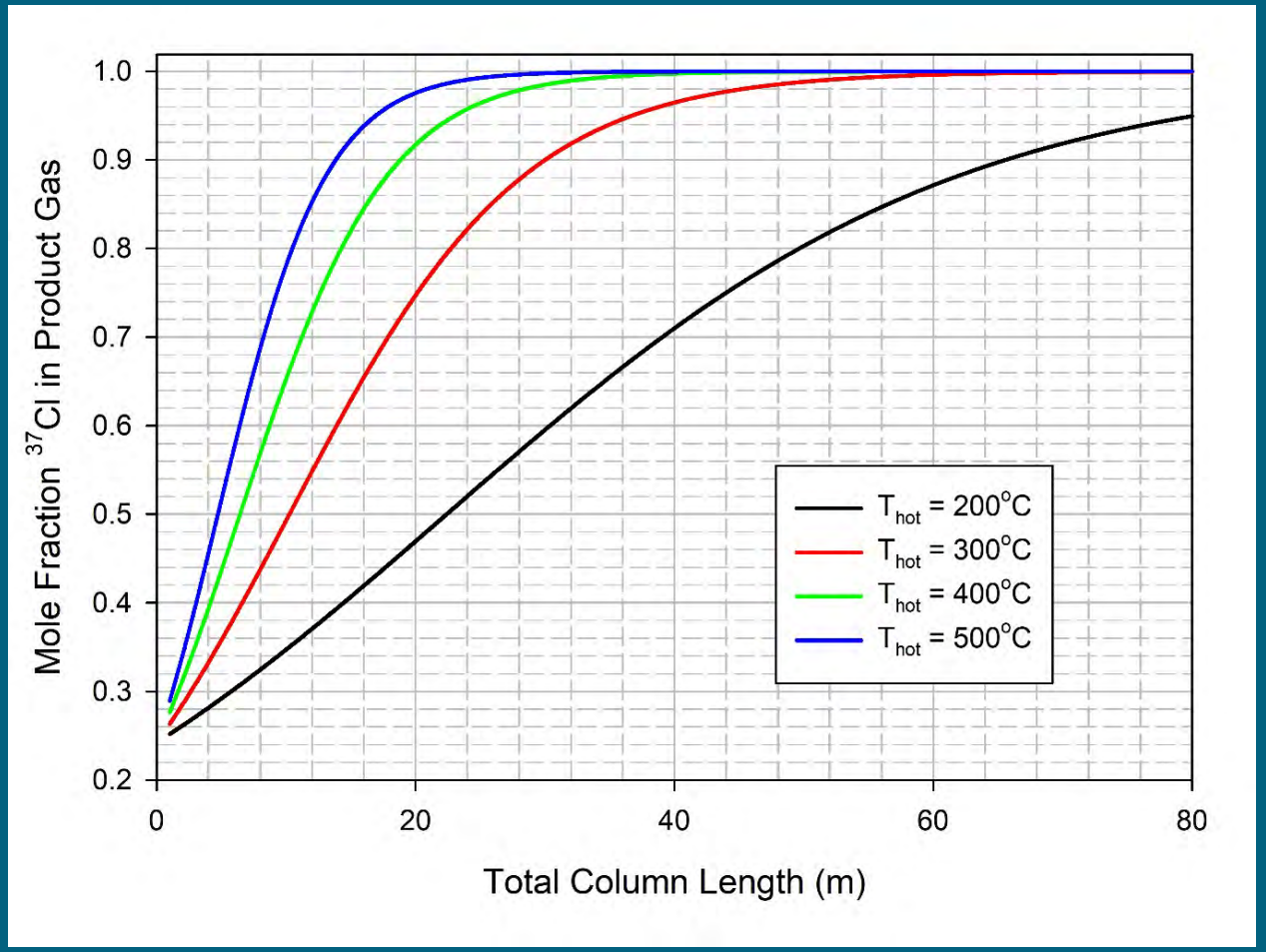
Production Versus Enrichment

For the purpose of production of lower enriched Cl^{37}:

6 tubes at 9’ (3m) each – so 18m of columns operated at 400C ~85% enriched

The plot provides the design data needed for reaching higher enrichments than the small scale TDIS column used in the present work

20 meter of total tube length with a hot side temperature of 500 °C will yield 98% ^{37}Cl under no flow (infinite reflux)

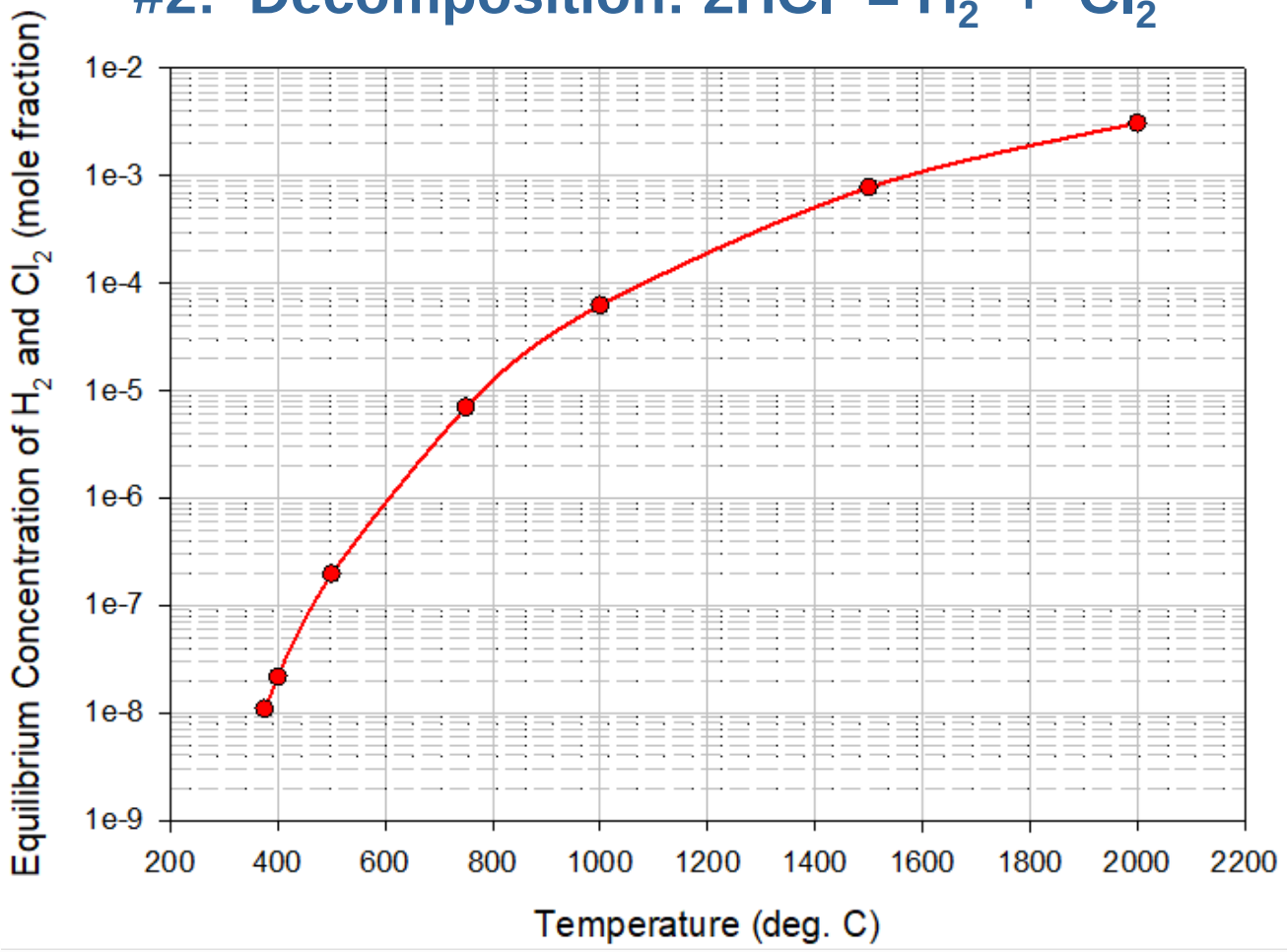


The Bad Stuff: Temperature Dependent Decomposition of HCl

#1: Metal Tubes

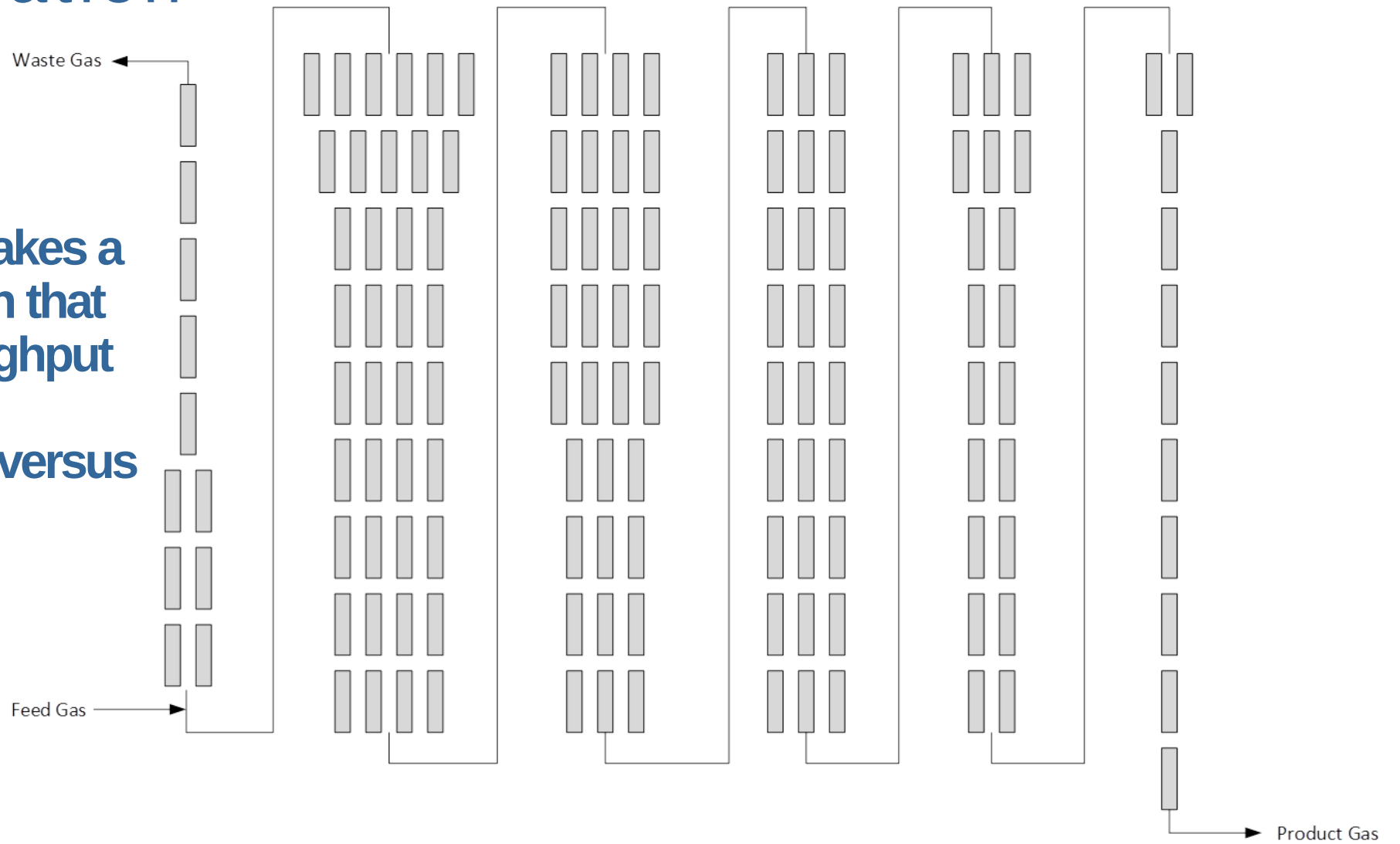
- Cold wall is honed stainless steel (SS)
- Cold wall is maintained near room temperature by active cooling
- Hot wall is fine ground Inconel
- Ball bearings (Dimples) along gap were fine ground SS

#2: Decomposition: $2HCl = H_2 + Cl_2$



Cascade Separation

- **In contrast to the serial connectivity, a cascade arrangement of tubes makes a 3-dimensional separation that leads to increased throughput**
- **“Bleed and feed mode ” versus the “static mode”**



Ongoing and Future Work

- The validated model will be used to inform further design improvements for both production (quantity) and enrichment levels.

The One Tube Experiment. Enrichment level improvements should increase perhaps dramatically with measurement of the thermal diffusion constant, α at higher temperature

The project will work towards a tool that enables facility design. It is envisioned that a manufacturer would be able to provide operational and product criteria, and the team would be able to help in the design of a facility.

Serial and Cascade Tube Arrangements

Access to higher enrichments and rates of ^{37}Cl production using the metal columns developed at PNNL will initially come from a strategic numerical design of the number of columns and their serial or cascade arrangement.

Operational criteria will drive entry location of feed gas, the production rate, storage of gas in cylinders, and the needed enrichment.

The validated TDIS model in COMSOL MPP will greatly increase the ability to predict and design the serially aligned tubing cascades envisioned for meeting a product demand.

Thank you

bruce.mcnamara@PNNL.gov

U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY