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Molten Salt Reactor PROGRAM

Chlorine Isotopes Separation for Fast Spectrum MSR

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Chlorine Isotopes Separation for Fast Spectrum MSR

PNNL TEAM

Bruce McNamara	*Physical Chemist (PI)*
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Tyler Schlieder	*Mass spectrometry*

Why enrich $^{35}Cl/^{37}Cl$ from natural its 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.

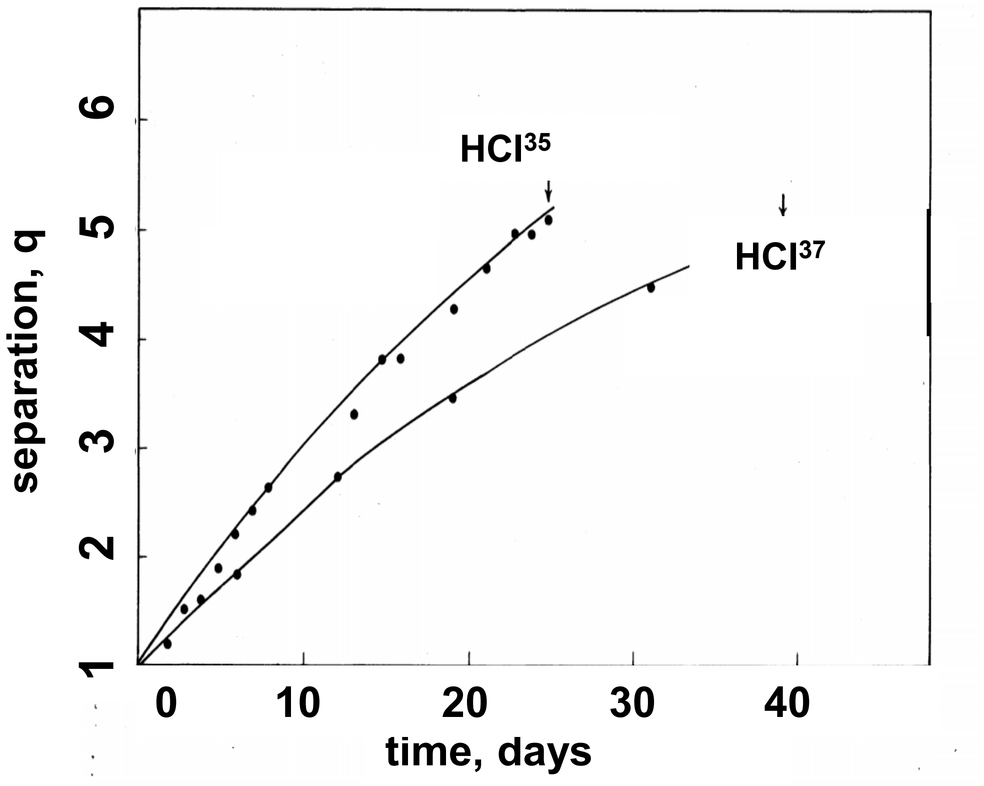
^{36}Cl production can be reduced by isotopically separating natural ^{35}Cl from ^{37}Cl.

References for Consideration

- 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

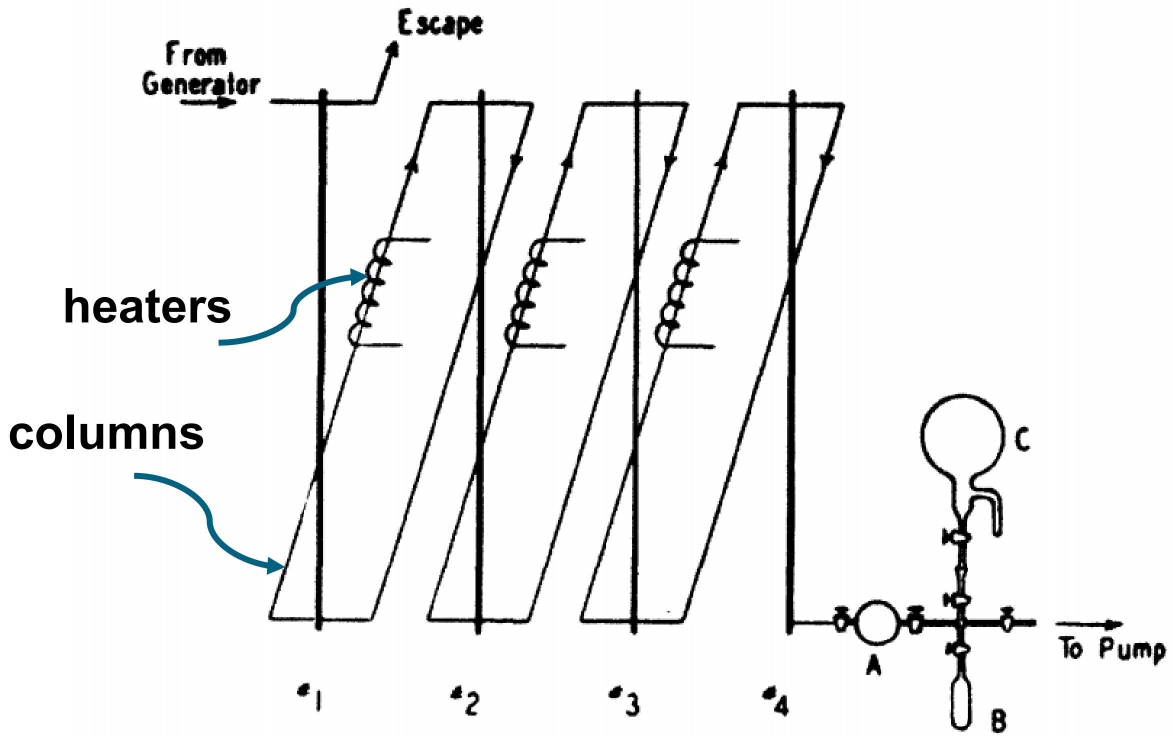
First apparatus (Clusius) using one column took longer than 40 days to reach equilibrium achieved 94 % separation



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

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Project Goal Posts

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

Build the separations columns and associated hardware

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

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

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

Iterate towards improved column design, optimized separation parameters

Validate to understand efficiency and economics of scale up

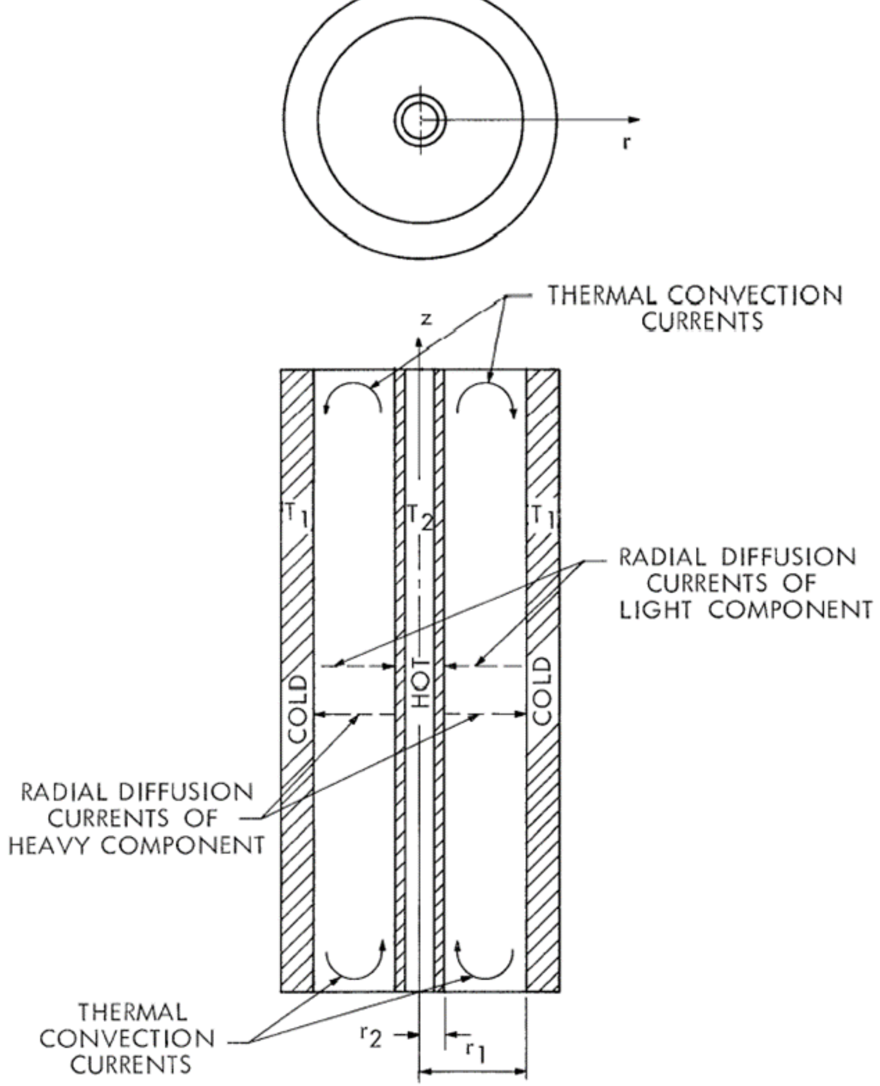
The Transport Equation

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

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

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.



The transport coefficients H, K_c, and 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

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

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

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

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

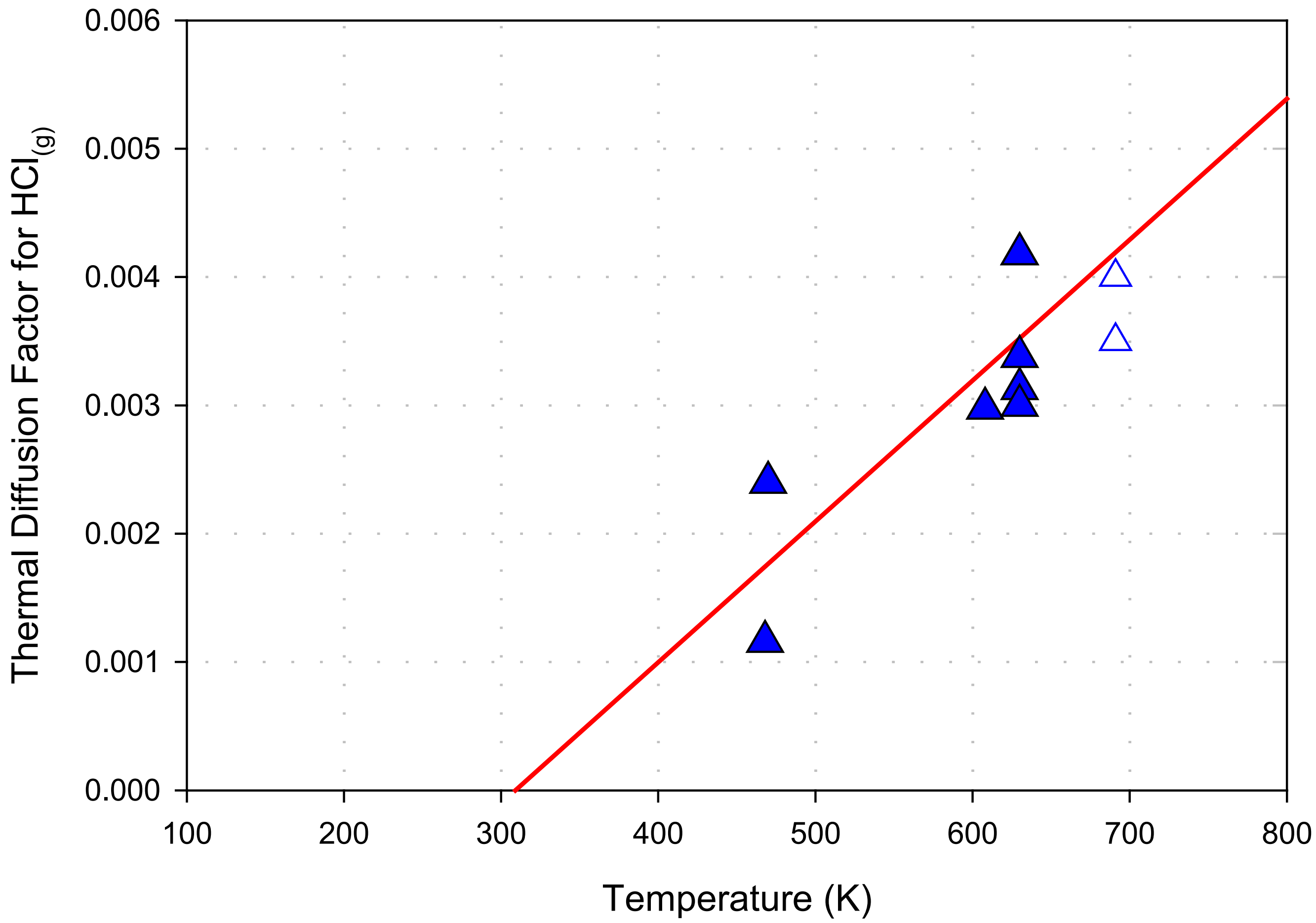
$\theta = T_2/T_1$ is the ratio of the temperature of the hot wall to that of the cold wall,

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.

α Values 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}**



Preliminary Column Sizing Calculations

- **Assume hot wall temperature of 400°C**
  - this temperature is driven by a combination of ease of use and the corrosion rate of 316SS at higher temperatures
- **Assume *α* goes to zero at around 110°C (385K; based on lit. data)**
  - Assume cold wall is operated at ~110°C by circulation of pressurized PGW solution
  - Want to operate cold wall at a temperature no colder than the point at which *α* goes to zero (otherwise the separation is working against itself in the lower-temperature regions)
  - Use *α* vs. T correlation from previous slide, at T_{avg} $\alpha \sim 0.0023$
- **Assume inside diameter of cooling jacket is 7.5 cm (radius = 3.75 cm) and then vary diameter of heated tube to find maximum predicted separation**
  - vary pressure over the range of 0.5 to 4 atm
  - vary inside radius from 0.03 cm to 3.5 cm; gaps of less than 2.5 mm likely challenging to maintain
  - assume no decomposition of HCl at temperatures less than 400°C
- **Assume column length of 2.0 meters**
- **Assume concentration of HCl^{37} is maintained at 0.246 at light end of column by high feed/exit flow**

Prediction of Column Performance

- Assuming literature values for α vs. temperature, α for T_{avg} = 745K is α = 0.0125

- Using this α value gives H = 7.51E-6 g/s

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

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

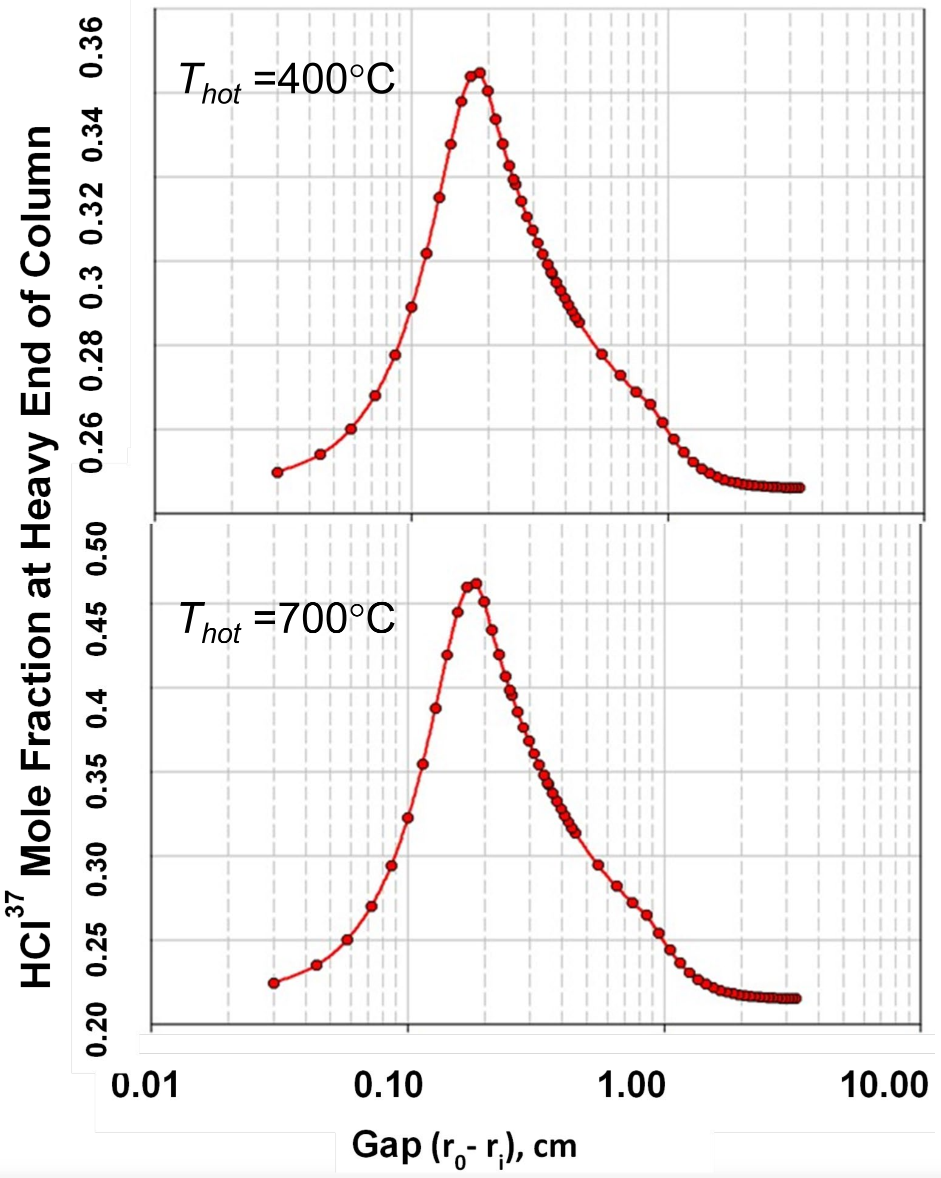
- where:
  - L = total column length, cm; 680 cm for Kranz and Watson's apparatus
  - c_0 = concentration of light product gas at top of column
  - c_L = concentration of light product gas at bottom of column

Prediction of Column Performance

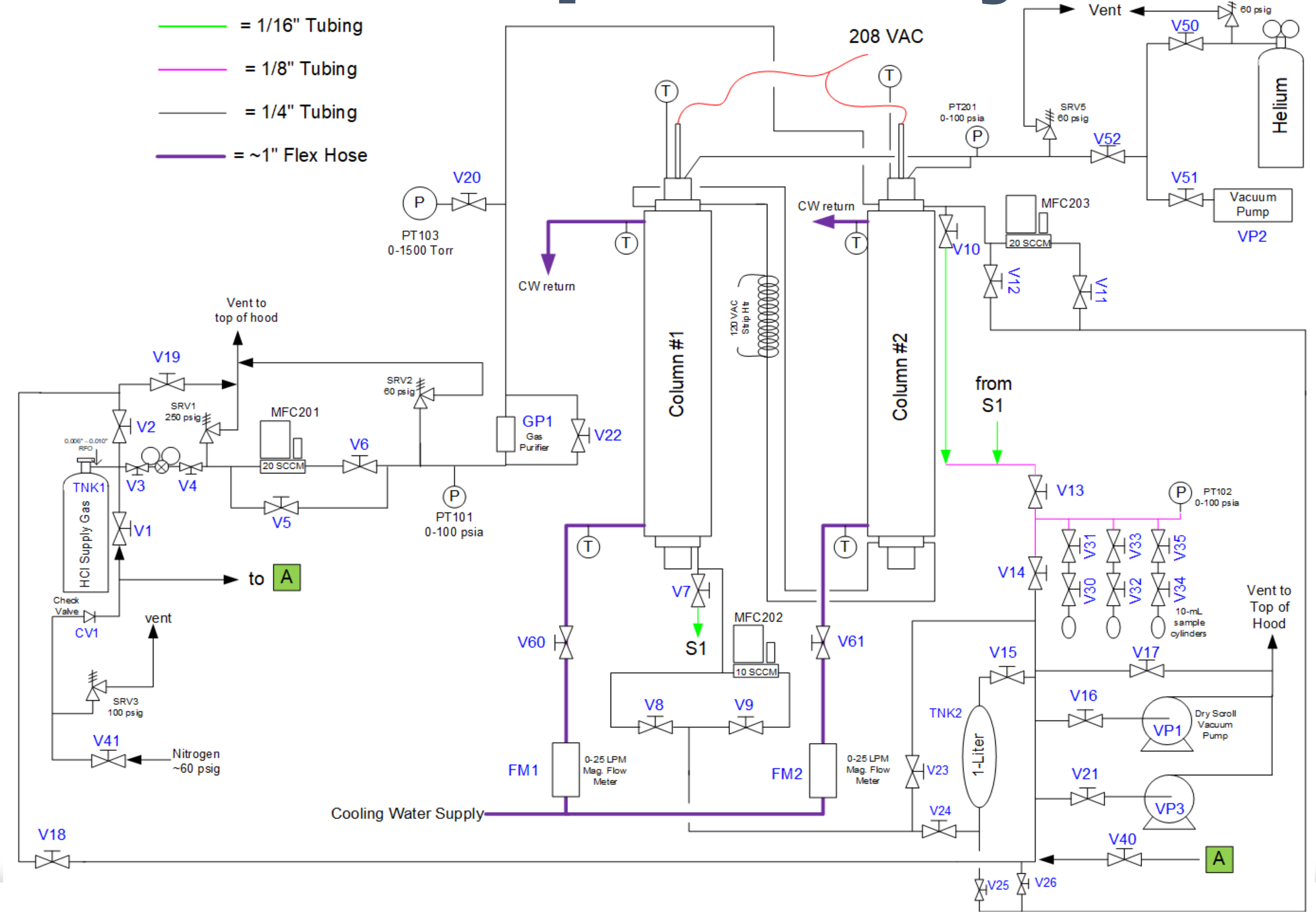
- **Substituting in the values for H, L, and K gives:**
  - $q_e = \exp(HL/K) = 291 = c_L(1\text{-}c_0)/(c_0(1\text{-}c_L))$
- **For the case where HCl^{35} is being produced, $c_0 = 0.75$**
  - solving for c_L gives $c_L = 0.9989$ (99.89% pure HCl^{35})
  - observed equilibrium purity was about 95%
- **For the case where HCl^{37} is being produced, $c_0 = 0.25$**
  - solving for c_L gives $c_L = 0.9896$ (98.96% pure HCl^{37})
  - observed equilibrium purity was about 62%
- **If α is adjusted by a factor of 0.3X ($\alpha = 0.0125*0.3 = 0.00375$), predicted c_L values become:**
  - c_L for HCl^{35} = 94.4%
  - c_L for HCl^{37} = 64.2%

Column Sizing Calculations

- The expected HCl^{37} mole fraction at bottom of column as function of gap at T_{hot} = 400, 700°C
- Peak performance is predicted near 2-mm gap for both conditions
- α = 0.0036 at T_{avg} = 550°C
- Going to higher pressures shifts optimal gap to smaller values; if operating pressure is allowed to go to greater than 4 atm, then optimal gap will be less than 2 mm; note that heater power increases significantly for smaller gaps
- For 2-mm gap, 400 and 700°C, T_{hot}, expected vessel heater power is about 2.3, 7.5 kW, respectively



PID for the Separation Systems



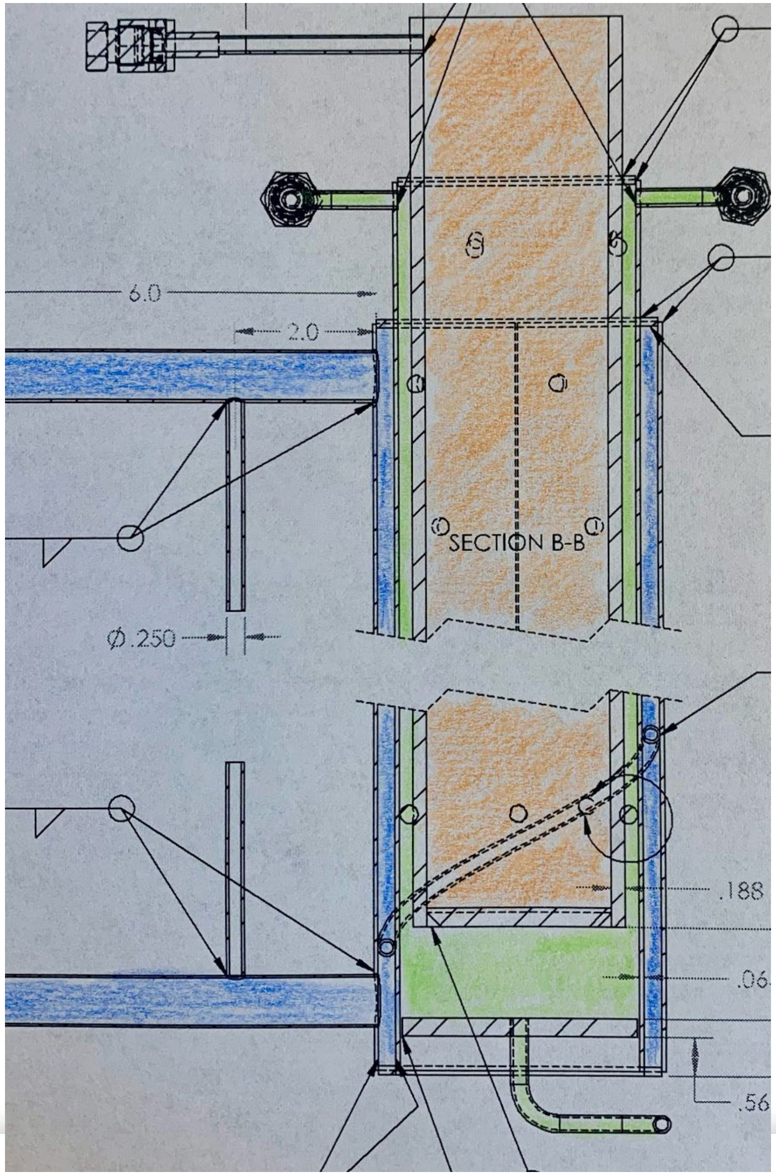
LHS: Fill Section, purging activities

Center: 2 Separation Columns

RHS: Sampling Section, He backfill, purging activities

Design of the Separations Columns

- Centermost tube contains the heater cartridge and some heat-transfer-enhancing material (copper foam and helium)
- Spiral ¼-inch tube in cooling jacket promotes good distribution of cooling water
- Top ~5 inches of column is not heated and is used to reduce thermal stresses due to high temperature gradients



Heated region (orange): copper foam and cartridge heater, T_{hot} ~ 350-400°C

HCl gas (green), in thin, annular space, T_{avg} ~ 200°C

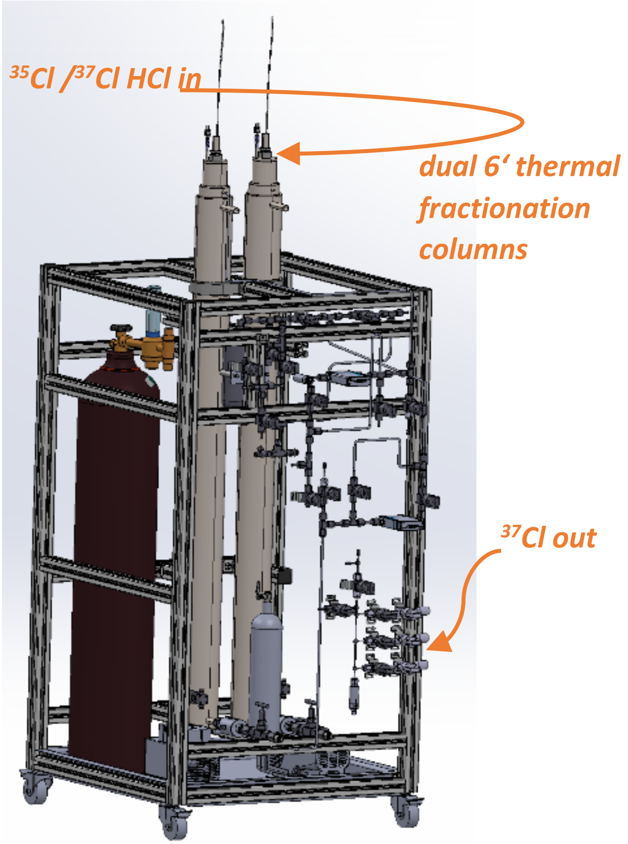
Cooling water (blue) flows through outer annular region, T ~ 25°C

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**

Hold up on Experiments

- All equipment will be in house except for the separations columns
- These were purchased and cut to length at PNNL
- Then the tubes were sent to two different shops in Texas and ground and honed and then returned to PNNL
- At PNNL the outer walls were "dimpled" for placement of ball bearings that maintain the gap distance precisely
- Assembly and welding of the columns was continued at PNNL

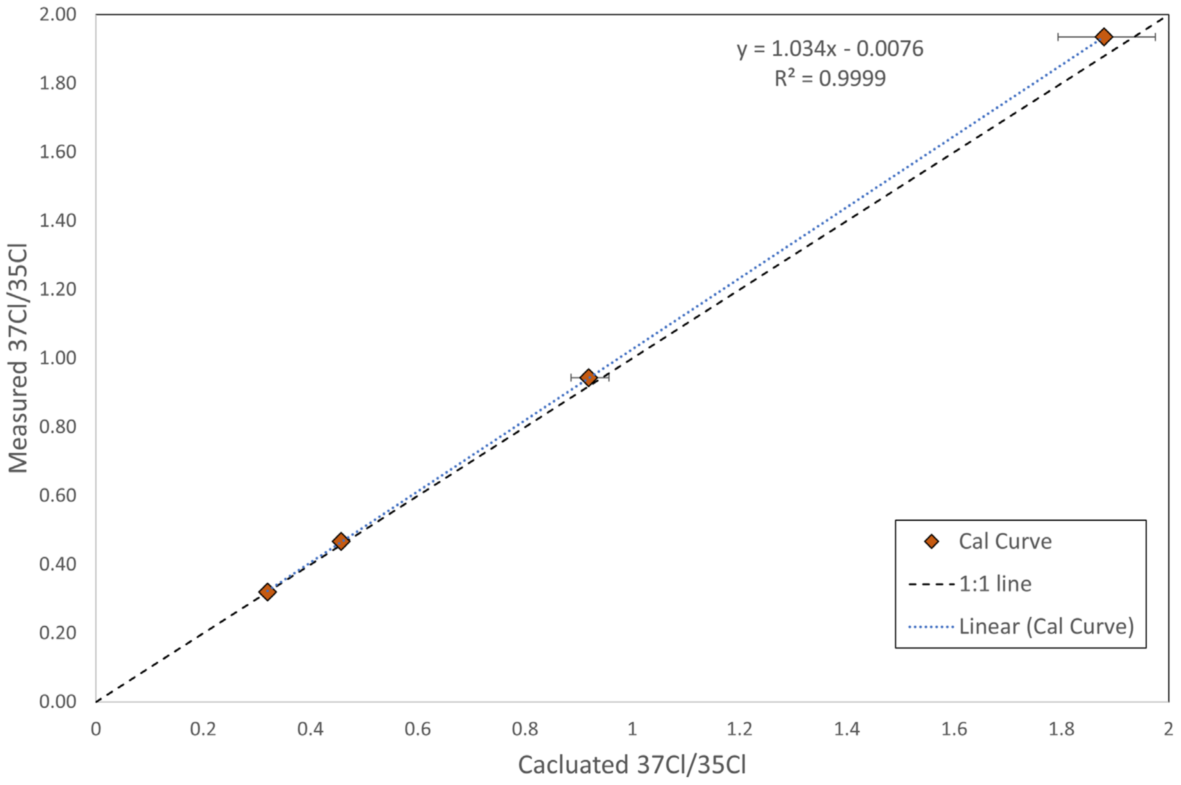


CAD work by team member Dustin Clelland

Analysis of the $^{35}Cl/^{37}Cl$ Ratio

Cl isotopic ratio measurements by triple quadrupole (QQQ)-ICP-MS

- **All measurements are made using an Agilent 8900 QQQ-ICP-MS**
- **We use O_2 in the collision reaction cell (CRC) to eliminate polyatomic interferences**
- **Accuracy is typically better than 1%**
- **Validated for $^{37}Cl/^{35}Cl$ from 0.3197 (natural) to 1.879**
- **High sample throughput – runtime of ~3-4 minutes/sample.**



Progress /Conclusions

- Administrative and safety documentation, HCl release ★ permitting, SOP ί, ∞
- Procurement ί, ∞
- Model the apparatus from various literature accounts ί, ∞
- Established an analytical method for rapid measurements of the $^{35}Cl/^{37}Cl$ ratio ί
- The separations columns and associated hardware are completed ί

Future Work

Administrative controls will be instituted on final completion of the apparatus.

- Specific activities for use of the system, e.g., valve lineups, etc., are included in a Standard Operating Procedure.

Trainings for operators are underway. Initial measurements should commence near the end of 5/2023.

Subsequent to exhaustive drying of the apparatus, measurements will include:

- Temperature and pressure variation with measurement of the $^{35}Cl/^{37}Cl$ ratio
- Validate parameter α for our design, and improve separations for the existing apparatus
- Iterate towards better column design and scale up to commercial scale apparatus

Thank you

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