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PNNL-38411

Chlorine isotope separations using thermal diffusion

M2AT-25PN0705101

September 2025

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U.S. DEPARTMENT OF ENERGY
Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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operated by
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UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

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Abstract

In a chloride molten salt fast reactor (Cl-MSFR), the fuel salt might be comprised of a specific eutectic composition of alkali and alkaline earth chlorides that solubilize major and minor actinide chlorides as the fertile component(s). Each of the chloride species contain the natural abundance (^{35}Cl ~76% and ^{37}Cl ~24%) of the two stable isotopes of chlorine ^{35}Cl and ^{37}Cl. There has been an ongoing controversy for the operation of the Cl-MSFRs concerning the potential of the ^{35}Cl(n,γ)^{36}Cl, ^{35}Cl(n,p)^{35}S, ^{35}Cl(n,α)^{32}S reactions to produce ^{36}Cl, ^{32}S, and ^{32}P at relevant energies [Bulmer 1956]. The undesirable attributes of irradiated ^{35}Cl are enumerated further below.

Molten chloride salt reactors may require the use of chlorine that is enriched in the isotope ^{37}Cl so irradiation of ^{35}Cl does not interfere with neutronics, compromise reactor longevity, or promote environmentally undesirable emissions. To this end, a thermal diffusion isotope separations (TDIS) apparatus was constructed in 2023. Successful shakedown testing was achieved and enrichments of isotopic concentrations relative to natural abundance $^{35/37}$Cl were collected. Further, a multi physics model was validated and drove the timing for sampling and other critical extrapolated functions that were discussed in our M2 report, as submitted in January 2024 [Huber 2024]. Necessary data needed for extended TDIS systems, such as the thermal diffusion coefficient, were measured with high precision over our operational temperature ranges. This data had not been previously reported in literature. The data validated our TDIS model, which in turn drove accurate estimates for column lengths needed to achieve desired enrichments for varying system temperatures. They also allowed for predictive modeling of power requirements and other costs for scaled operations, e.g., serial enrichment arrangements versus cascaded ones.

Our decision to move forward in 2024 with the installation of a larger set of separation tubes and associated equipment was based on this successful development of the predictive model and demonstration of small-scale Cl enrichments that were completed in FY2024. The testing was completed prior to the end of the allotted time and under budget. Consequently, the work in FY25 was to continue, using carryover funding to initiate and finalize the fabrication of an 18-m serial separations system. After required shakedown testing, this system would produce highly enriched Cl-37 gas on its first operational run.

The FY25 work scope was an aggressive effort to build a larger separations system that would produce highly enriched ^{37}Cl gas for use by other facilities and industrial partners executed through two tasks.

The first task was to attempt to extend our earlier measurements of the thermal diffusion coefficient, α, from 400°C to about 700°C. For this reason, an internal communication that was described in our M2 [Huber 2024] that researched current activities in high-temperature coatings that might increase the operating temperature of our aparatus. An investment was made to test such a coating in a separations column at several temperatures. The task consisted of:

- Removal and cleanup of one of the existing separations columns from the existing TDIS system.
- Its shipment to a commercial special coatings group, Silco Tek, in Pensylvania.
- Coating of the column and return of the tube to PNNL
- Thermal testing of the coated apparatus.

The results of that effort are presented in this report.

The second FY25 Task was an effort to build an extended chlorine isotope separations system and use it to produce high enrichments of $H^{37}Cl$. The task consisted of:

- Removal of the two existing column arrangement built in 2023-2024.
- Procurement of materials needed for an 18-m separations system.
- Completion of the assembly of six 9.8-foot separation columns.
- Stand-up of the ~200-pound columns into the walk-in fume hood space.
- Update the existing data acquisition system to handle extra power and communications to six columns.
- Shakedown testing of the apparatus.
- Collection of enriched ^{37}Cl concentrations relative to natural abundance $H^{35/37}Cl$.
- Update of the data-validated model for facility space, power, and other costs to inform total facility costs and performance assessments.

This report updates the progress for this ongoing work.

Acronyms and Abbreviations

DAC	data acquisition and control system
FP	fission products
HCl	hydrogen chloride, gaseous
MOC	materials of construction
MPP	multi physics package
MSR	molten salt reactor
MSFR	molten salt fast reactor
Cl-MSFR	chloride molten salt fast reactor
F-MSFR	fluoride molten salt fast reactor
MSRE	molten salt reactor experiment
P&ID	process and instrumentation diagram
PNNL	Pacific Northwest National Laboratory
RGA	residual gas analyzer
TDIS	thermal diffusion isotopic separation

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1.0 Introduction

Worldwide today, there are several ongoing efforts to take advantage of the attributes of the fast spectrum molten salt chloride reactor (Cl-MSFR) concept. In the US, TerraPower is developing their Molten Chloride Fast Reactor and is working on the Molten Chloride Reactor Experiment to be deployed at INL. Exodys Energy, another US startup, has proposed a new design of Cl-MSFR for incineration of processed used nuclear fuel. In France, Stellaria, in partnership with Orano, is considering design of a 110MW Cl-MSFR. Orano has also partnered with TerraPower in the US to support in functional aspects of alternate chloride reactor fuel designs. NAAREA is interested in a 40MWe micro reactor (Cl-MSFR) design that will incinerate plutonium waste. Moltex Energy, based in New Brunswick, Canada, is considering the design of a small modular, fast spectrum Cl-MSFR fueled with spent CANDU or PWR nuclear fuel.

Accordingly, the envisioned application of the Cl-MSFR is mostly derived from the high energy neutron spectrum of these reactors that would consume existing stockpiles of plutonium and uranium. A complementary benefit includes a higher actinide solubility in chloride media that allow for higher fertile species loading than afforded by fluoride media. Further, the buildup of chloride-form fission products during irradiation should be well accommodated by their higher solubilities in the chloride salt.

The natural abundance of the stable isotopes of chlorine is 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 [Sims 1969]. The cross sections for analogous reactions with irradiation of ^{37}Cl are appreciably smaller. The half-life of ^{36}Cl is 301,000 years and its decay to stable ^{36}Ar produces an energetic, 98% beta emission (716 keV). In addition to its radioactivity, potential emission of ^{36}Cl is an unacceptable environmental hazard because of its mobility, solubility, and reactivity ($H^{36}Cl$) towards biomatter. Secondly, the $^{35}Cl(n,p)^{35}S$ reaction, which decays back to ^{35}Cl. Accordingly, yields of sulfur will accumulate in the salt. The $^{35}Cl(n,\alpha)^{32}P$ produces radio-phosphorus ($t_{1/2}$= 14d) that also decays to more sulfur. For a properly reduced fuel salt, the likely form of sulfur would be S^{2-} [Taube 1974, 1978]. S^{2-} is considered a corrosion hazard to the reactor materials of construction. Polysulfides of the alkali components are known and may be a carrier of S^{2-} in the fuel salt. Lending credence to this prediction, another chalcogenide, tellurium, was found in the fluoride-based Molten Salt Reactor Experiment (MSRE) to initiate intergranular attack on nickel-based materials of construction (MOC) [Cheng 2015, Compere 1975]. Lastly, the relatively large cross section of ^{35}Cl in combination with other high neutron cross section poisons reduce the neutron economy of the reactor. The statements above may be better informed by ^{37}Cl irradiation experiments that use relevant core geometries at energies appropriate to those encountered in a Cl-MSFR [Palmiotti, 2021].

The use of hydrogen chloride ($H^{35,37}Cl$) was chosen for enrichment testing because it is a synthetic precursor that is a readily useable reagent for generation of anhydrous alkali, alkaline earth chlorides, fertile chlorides, and precursor reagents to synthesize them, e.g., $NH_4{}^{37}Cl$ and $C^{37}Cl_4$.

The use of Cl_2 as a viable synthetic precursor to fuel salt construction is also reasonable. However, thermal diffusion isotope separations (TDIS) or centrifuge operations do not provide an ionizing mechanism, which would leave the bound Cl atoms stranded in their natural abundance. Similarly, potential reagents, such as CCl_4, are a statistical mixture of the Cl isotopes, and ones such as CH_3CH_2Cl do not provide an easy-access chlorine for the chemical requirements of the molten salt community.

Available isotope separative methodologies include electromagnetic isotope separation [Smith 2013], centrifuge techniques [Borisevich 2000, Kaliteevskny, 2023], and thermal diffusion [Jones 1946]. The timeline required for the general use of enriched ^{37}Cl for use in Cl-MSFRs might be as little as 5-10 years. The period and cost of development for the first two seem to be outside of this window by several years, although the use of a viable centrifuge concept seems to be the more cost efficient after its development.

Areas requiring timely investigation for Cl-MSFR development with unique relevance to a costly, enriched ^{37}Cl include the following

- Irradiation Studies

Neutronics evaluations that characterize the cross sections for the $^{35}Cl(n,\gamma)^{36}Cl$, $^{35}Cl(n,p)^{35}S$, $^{35}Cl(n,\alpha)^{32}S$ reactions require attention. The $^{35}Cl(n,p)^{35}S$ reaction seems important regardless of the cross section, but it would be interesting with the appropriate cross sections determined what to suspect in terms of numbers of atoms of S and P produced. There are currently no reported measurements of the $^{35}Cl(n,p)^{35}S$ cross section covering the relevant energy range, 600kev - 14 MeV, with those from Batchelder being between 2.42 and 2.74 MeV providing some experience [Batchelder 2018]. Integral/non integral measurements using appropriate geometries, relevant energies, on enriched ^{37}Cl fuel salt carriers of fertile components (e.g., UCl_3, $PuCl_3$, $AmCl_3$) would be of value

- Very High Purity Salt Synthesis

The MSRE salts were carefully made in batches but still required removal to 10 ppm levels of sulphur and phosphorus [Lindauer 1967]. Starting quantities near 1000 ppm indicated that the as-received salt had not been purified enough, requiring a removal process. Waters of hydration, occluded water, and oxides/hydroxides of the base alkali components were removed from the salt by purging the molten salt with a 10:1 mixture of HF and H_2. Use of the analogous approach, $H^{37}Cl/H_2$, seems applicable, except for the cost of the $H^{37}Cl$. Consequently, it may be preferable to produce large quantities of the salts at very low hydration using enriched $H^{37}Cl$. Synthesis of the chloride salts from gases would help to eliminate impurities from mining of the fuel salt components. Ideas that can do this at very large scale should be openly discussed and verified, as materials of construction of containments and apparatus will provide unwanted contaminants at small-scale. HCl is corrosive to most metals, and for many synthetic processes, heat is required, which exacerbates the corrosion. Accordingly, loss of $H^{37}Cl$ to containment walls will not be preventable. With the constraint as to the efficiency of use of enriched $H^{37}Cl$, its partial recovery from the metal wall might be done periodically with H_2. As an example for a divalent metal (M) chloride, hydrogen could be used to strip ^{37}Cl from the containment wall.

$$M^{37}Cl_2 + H_2 \rightarrow 2H^{37}Cl_{(g)} \ + \ M^{\circ}$$

Large scale synthesis of the required salt precursors with the added constraint of using an enriched $H^{37}Cl$ will require some thought and then a down-select of the best synthetic paths and process engineering practices. One can begin salt synthesis with addition of high purity gases or anhydrous solids to produce precursors that can incorporate ^{37}Cl into the alkali, and alkaline earths

$$NH_3 + H^{37}Cl \rightleftharpoons NH_4{}^{37}Cl$$

$$Na_2O + 2H^{37}Cl \rightleftharpoons 2Na^{37}Cl + H_2O$$

At large-scale, issues such as heat production/control and reagent recycle require special conditions but are important for complete ^{37}Cl utilization. For instance, the alkali oxides might require reaction above their sublimation or decomposition points to guarantee the anhydrous chlorides.

Carbon tetrachloride, CCl_4, has been used to produce UCl_4 from UO_2 in multi-kilogram yields [Harrison 1951]. Bench-scale quantities of the chlorides of PuO_2 and AmO_2 have been produced using this method, but upscale of these processes would be critical to synthesis of TRU-chloride fertiles that will readily dissolve in chloride carrier salts. An older industrial method for CCl_4 production can be used for strategic placement of the ^{37}Cl on carbon-[Rossberg 2006]. To do that, $H^{37}Cl$ is first decomposed to $^{37}Cl_2$. Uncatalyzed, this would require temperatures of >750°C in a metal containment.

$$2H^{37}Cl_{(g)} = {}^{37}Cl_{2(g)} + H_2$$

Reaction of the $^{37}Cl_2$ with CS_2:

$$CS_2 + 2^{37}Cl_2 \rightarrow C^{37}Cl_4 + 2S$$

The mechanism tends to leave a ^{37}Cl stranded, but industry has found some work-arounds and its recycle is possible.

- Radio Volatility

A relatively uncharted area of importance is the evolution of the chemical state of a chloride salt as neutron irradiation introduces fission products and their radiolytic effects into the salt. The physical properties of a molten salt, such as its melting point, viscosity, thermal conductivity, and heat capacity, are well documented to be closely dependent on the salt composition. The liquid salt composition also determines the colligative properties of the liquid salt. The liquid salt is in equilibrium with its vapor. It has been determined that salt components, such as dimers of KCl and NaCl, exist in the vapor over the molten salt [Wang 1996]. The concentration and speciation of these dimers increases with temperature. The addition of fission products to the liquid salt will change the compositions of the solution and the vapor phase. Irradiation of ^{35}Cl will produce radicals of ^{36}Cl via Equations 1 and 2 that are oxidants relative to the reduced form of the fuel salt. ^{36}Cl radicals may prefer to stay in the salt or may be attracted to the walls of the reactor. The radical may also visit the vapor phase of the salt with other FP volatiles, which now include $SbCl_3$, $NbCl_3$, the telerium and selenium chlorides and at higher temperatures $PuCl_3$. The mobility of these from the salt are motivated by helium or He/H_2 purging of the liquid salt. At the operating temperature of the reactor, the Cl radicals are corrosive on the MOCs of the reactor. If the MOC is molybdenum, reactions at the wall [Taube 1974] might look like $MoCl_x$ (where x = 2, 3, 4, 5). The $^{35}Cl(n,p)^{35}S$ and $^{35}Cl(n,\alpha)^{35}S$ reactions (Equations 2 and 3) produce ^{35}S and ^{32}P, respectively. Sulfur is corrosive to Ni and Mo containments [Chen 2015] and P can interact with these MOCs as PCl_3 or more reduced forms of phosphorus.

$$^{35}_{17}Cl\ (n,\gamma)\ ^{36}_{17}Cl \xrightarrow[3{,}1\cdot 10^{5}y]{\beta^-} {}^{36}_{18}Ar$$ 1.

$$^{35}_{17}Cl\ (n,p)\ ^{35}_{16}S \xrightarrow[88d]{\beta^-} {}^{35}_{17}Cl$$ 2.

$$^{35}Cl\ (n,\alpha)\ ^{32}_{15}P \xrightarrow[14.3d]{\beta^-} {}^{32}_{16}S$$ 3.

2.0 Operations of Protype TDIS Systems

The FY24 Work Scope at PNNL demonstrated the enrichment in ^{37}Cl, for use in Cl-MSFRs. The work provided a scalable technology built on existing proof of principle research. Clusius and Dickel achieved a critical success in their first separation of HCl into its isotopic components in 1939 [Clusius and Dickel 1939]. In 1940, Kennedy and Seaborg used a similar approach to separate $H^{35}Cl$ from $H^{37}Cl$ [Kennedy and Seaborg 1940]. The separation devices were made from borosilicate glass and their heights exceeded 7 meters. Experiments showed that the same efficacy of separation could be done by a series arrangement of shorter tubes [Schrader 1946]. Schrader reported 99% ^{37}Cl enrichment in his separation's first pass of $H^{35/37}Cl$. Glass is more difficult to engineer than a metal apparatus and its connectivity to metal feeds and other functional devices would be of questionable durability for a safety-conscious facility. The security of tall glass serial columns would have to be ensured by structural containments at facility scale.

By the late 1960's, the mathematical treatment of the TDIS had been well documented and coincided with existing work at PNNL that used similar and complementary systems for other isotope separations. The previous experience aided in the design and operation for an efficient multi-stage TDIS system, as was reported in our M2 deliverable for February 2024 [Huber 2024]. The concept for facility-scale production of enriched $H^{37}Cl$ is comparable in its operation to that used in centrifuge operations and can be used effectively, given a working numerical model that describes columns arrangement, feed modes, and power consumption.

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

The design of a generalized separations apparatus was based on a transport model provided by Green [Green, 1966]. Most of the information in the required equations is calculated from known physical data of HCl and the geometry of the separation apparatus. The transport equation is described in detail in our M2 deliverable for February 2024 [Huber, 2024]. In review of that, the transport of a gas up a column is determined by the geometry of the column and the thermal diffusion constant particular to the gas. A corollary to this is that an infinitely tall column provides for excellent isotopic separations. Optimization of the column geometry can significantly reduce the column height. For this work, optimization required only one parameter for a fixed column geometry, the thermal diffusion constant (α) for the gas. Fortuitously, several of these were estimated by the early TDIS work as cited. The early values for the constant were used iteratively to refine an optimized column geometry [Huber, 2024].

Specifically, the separations columns are comprised of a tube in a tube (Figure 1). In the diagram, the outer tube (T_{cold}) is jacketed and cooled to near room temperature with water. The inner tube (T_{hot}) is internally heated with cartridge heaters. The tube inside of a tube design describes a gap. The radial dimension of the gap (r_2-r_1) is maintained with high tolerance along the length of the column.

For operation of the column, the gap between the hot wall (T_{hot}) and the cold wall (T_{cold}) is filled with $H^{35,37}Cl$ gas and the hot side/cold side assembly promotes thermal convection with a radial diffusion component that together work to provide the isotope separation. The separation may be pictured as an upward movement of the gas on the hot side of the gap that raises both isotopes up the column with an increase in the concentration of the lighter isotope. This is followed by their radial diffusion to the cold side of the column, where the heavier isotope concentration is decreased.

Based on available data for *α,* modeling for the column sizing predicted that a channel gap of about 4-5 mm for a target separation value would need to be operated in the range of 1-2 atm (absolute). At higher operating pressures, the optimal channel gap is narrower, but the relatively small benefits of operating at higher pressures are negated by the difficulties associated with building columns with very narrow channel gaps. Based on these tradeoffs, a target channel gap of 4-5 mm was selected for our demonstration TDIS columns.

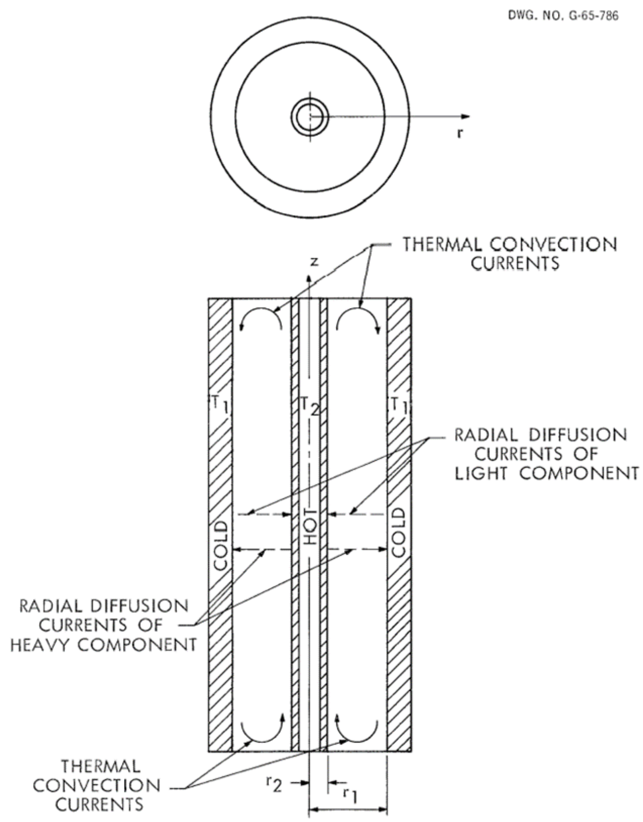

Figure 1: The separation column for TDIS is a tube inside of a tube, where thermal convection currents and radial diffusion work to provide the isotope separation.

The TDIS apparatus was built in the 1st quarter of 2023 and its shakedown testing was completed in July of 2023. For continuity, its operation is described here. Figure 2 shows the P&ID for the separation system's two, 6-foot separations columns connected in series. The column system was located inside of a walk-in fume hood. Each individual column had an internal volume of approximately 1.7 L, giving a total internal gas volume of 3.4 L available for HCl.

For ease of construction, materials that were well known and readily machinable were employed. Inconel 600 was chosen for the inner tube T_{hot} surface and a stainless steel 316L outer tube formed the T_{cold} surface.

The outer cooling jacket (providing T_{cold}) was formed by wrapping a spiral of 6.35 mm OD stainless steel tube around the 8.89 cm OD pipe and then adding a sheet-metal outer jacket. Divots were machined into the innermost pipe and 6.35 mm OD polished stainless steel ball bearings were placed in the divots during assembly. These maintained the pipe centering with a constant gap thickness and allowed for axial movement due to thermal expansion. The bearings have since been changed to Inconel 600 to reduce the corrosion potential inside the columns.

The overall length of the completed assembly was approximately 183 cm. The cartridge heaters (providing T_{hot}) extended out about 15 cm farther from the top. The total effective length for thermal diffusion separation was about 162 cm per column (i.e., *L* = 162 cm). The resulting channel gap was approximately 4.5 mm at varied operating temperature of T_{hot} = 300-400^{o}C. The piping and instrumentation diagram (P&ID) for the total apparatus is shown below in Figure 2. On the left-hand side of the P&ID is the HCl fill equipment, in the center are the two separations columns, and on the right-hand side is the sampling apparatus, vacuum pumps needed to remove and/or move gases through the system, and a helium backfill setup to increase heat transfer for the cartridge heaters inserted into the center tube of the columns.

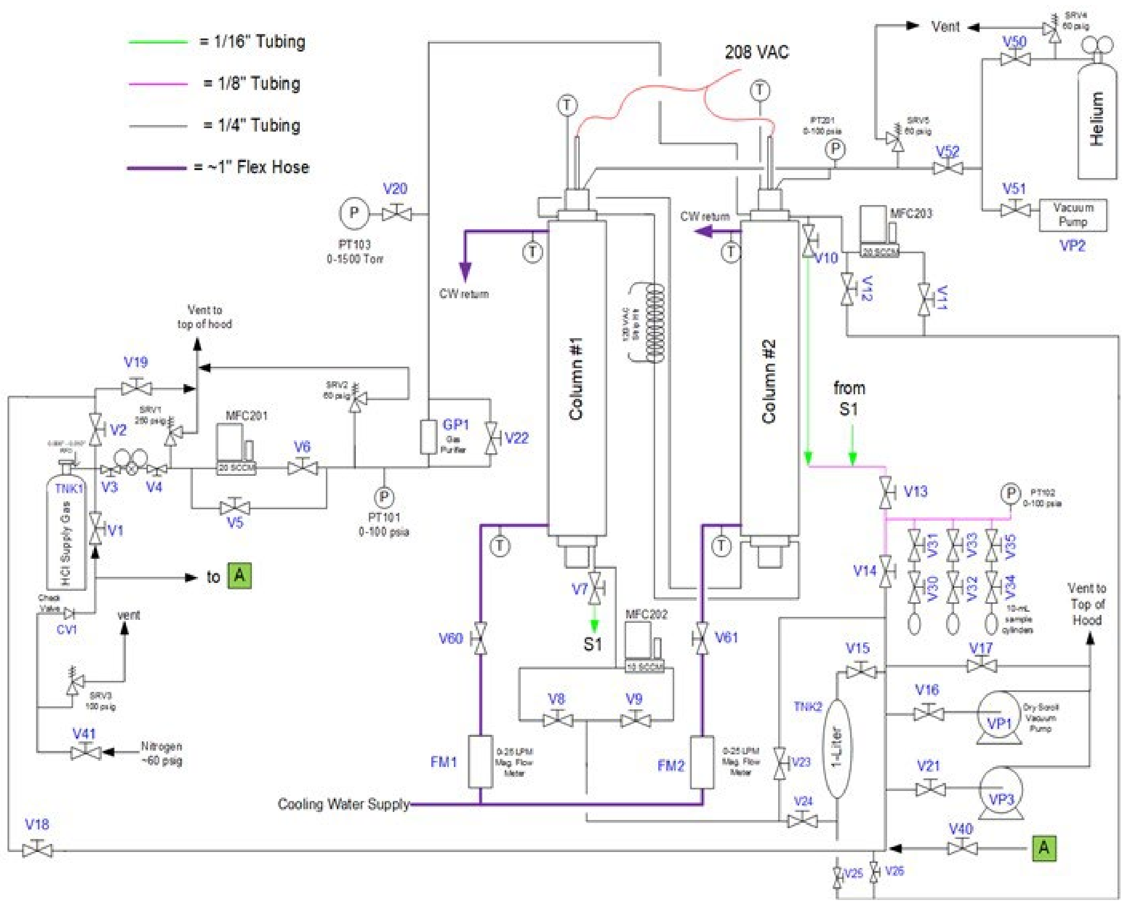

Figure 2: P&ID for the two, 6-foot columns and associated apparatus. The left-hand side provides the HCl gas feed to the system, the center is the separation columns, and the right-hand side is the sampling, vacuum, and He backfill setup.

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

Measurement of the temperature and pressure dependences in the thermal diffusion constant α was undertaken. The tests were specifically chosen to verify and bound the model predictions for pressure and temperature dependence of the thermal diffusion constant. A static (or infinite reflux) mode of operation refers to a non-flowing, static pressure of HCl gas into the system. After system thermalization has occurred, measurements can be made. The bleed and feed mode of operation refers to one where the separated product is removed from one end of the apparatus while a simultaneous feed of new HCl replenishes the total volume at the front end of the apparatus. Bleed and feed type tests are important for validating the model's use in predicting production environments where the operation would constantly separate and produce the enriched product gas.

Figure 3 shows our temperature dependent data juxtaposed with literature data that had been used in the model for the first guess at an optimized geometry for the 6-foot column geometry [Huber, 2024]. The thermal diffusion coefficient (α) markedly increases with temperature. The higher temperature literature data was acquired from the incidental use of glass separations columns. The use of glass in natural physics experiments was common to premodern times. The magnitude of the diffusion constant increases the value of the transport coefficients used in the model. Consequently, the higher temperature (>600°C) data indicate that increased enrichments can be accessed using shorter or fewer columns.

High fidelity measurements of the temperature dependence of α tightened up the precision in our model for larger column design predictions. The lower temperature data collected from the TDIS system, as plotted in Figure 3, is more precise than the scattered data set collected from literature. The open red circles were not used in the correlation, as the data was collected under unstable pressure and flow conditions and were likely biasing the data low. The literature data for α appears to underpredict column performance. Therefore, separations predictions, based on the data as plotted, will be lower than the observed values. Additional higher temperature measurements of the thermal diffusion coefficient were planned for FY25 to increase the understanding of the temperature dependence of α.

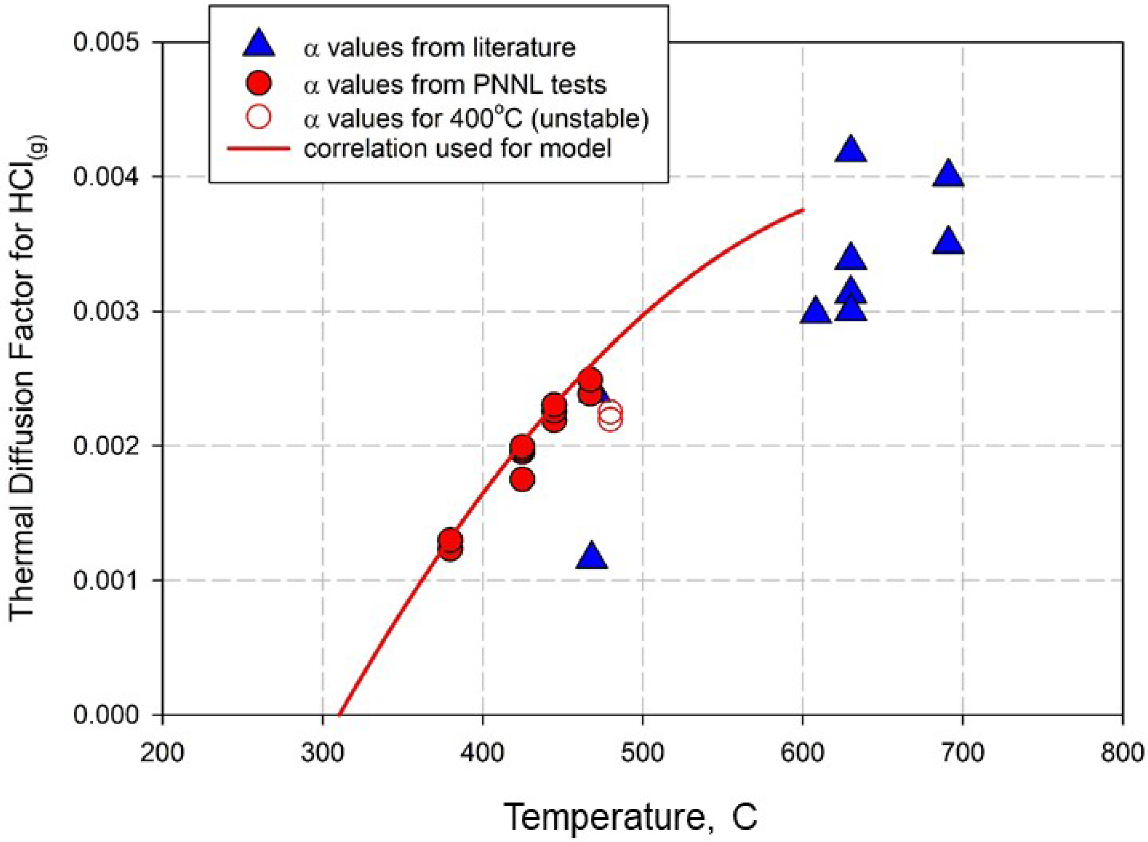

Figure 3: Comparison of PNNL and literature value measurements of the thermal diffusion constant, α, for $HCl_{(g)}$. The temperature plotted is the T_{avg} of the column. The red line is a correlation used for prediction during modeling efforts. The open red circles were not used in the correlation, as the data was obtained under pressure and flow instability issues, likely biasing the data low.

5.0 FY 2025 Work Scope: The Extended TDIS System and High Temperature Coatings Testing

The 2025 Work Scope: AT-25PN070510 [Huber, McNamara 2024] proposed to launch an extended separations system based on the two-column test design. The extended system would produce highly enriched ^{37}Cl gas for use by other facilities and industrial partners. A second task was to extend our measurements of the thermal diffusion coefficient, α, from 400 to 700°C. Extending the temperature range of the separation columns necessitated the application of high temperature coatings to the columns. For this reason, a short internal communication was assembled under the FY 24 funding. The document researched current ativities in high-temperature coatings that might increase the operating temperature of our aparatus.

A silicon nitride coating was applied to the interior of a 6-foot separations column and tested at several temperatures. The task consisted of:

- Removal of one of the existing separations columns from the existing TDIS system.
- Its shipment to a commercial special coatings group, SilcoTek, in Pensylvania.
- Coating of the intact column and its return to PNNL
- The treated column was received early in FY25 (September 2024).
- Receipt of the column was followed by its thermal testing.

Figure 4: The SilcoTek coated 6' column was received on 9/14/2024. The discoloration along the length of the column was from the coating process.

The column in Figure 4 was installed into the test system shown in Figure 2. The tests started at 325°C (hot-side temp) and were then increased to 385°C and then 415°C. The red data points in Figure 5 show the measured pressure loss rates for the uncoated column. The red line represents an Arrhenius fit of the data; the reaction rate was assumed here to be well described by an Arrhenius relationship. The pressure detection limit was around 0.02 psia/day, which means all the data points should have vertical error bars of about ±0.002 psia/hour.

The blue data points were measured on the SilcoTek separations column. There was no evidence of pressure loss below 415°C. Pressure loss (downward arrows) would indicate the onset of materials corrosion. At 435°C, some decomposition became apparent. With this pressure change, the system was left to run for another day and the decomposition rate increased. The temperature was allowed to decrease to 415°C, then 385°C, and finally to 340°C. For the last three tests, the decomposition rate (blue dots) followed reasonably close to the initial tests (red dots) we had measured previously using the uncoated separations column. The behavior was reproducible and no further damage to the column was apparent.

The column performance data indicate that the coating was deficient with respect to our anticipated high temperature operations. It was not clear if the corrosive HCl gas found a point of ingress on the Inconel surface or if the coating was itself compromised. The reproducibility of the data would suggest the former. Alternately, the coating application may not be suited for thermal expansion of the Inconel surfaces. For follow on work, aspects of the coating's adhesion properties need to be better understood to improve high temperature use of the separations columns. At this time, further work with the coatings has been suspended.

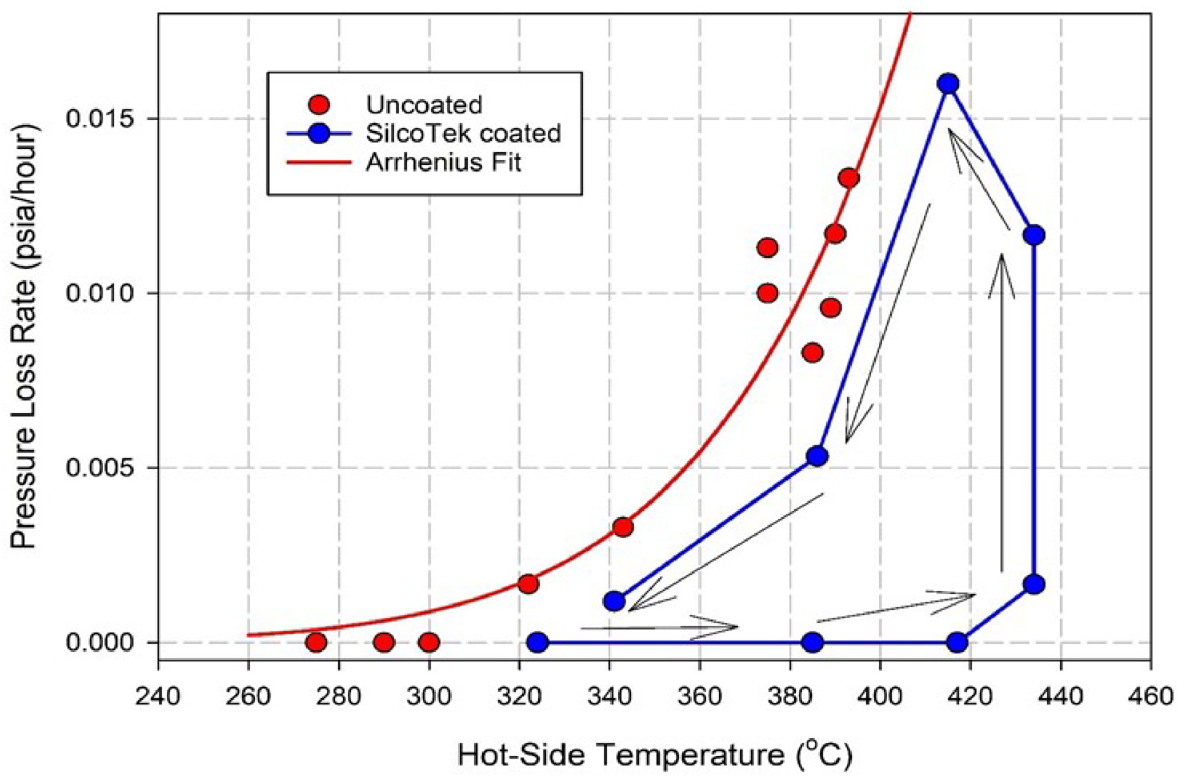

Figure 5: The SilcoTek–coated separations column performance. Onset of decomposition began near 435°C. On cooling, the pressure decrease (decomposition) ceased. No further damage was experienced at temperatures below 435°C.

The second Task in the FY25 Work scope was an ambitious effort to build and operate an extended chlorine isotope separations system. In brief, the tasks and their status are listed:

1. Removal of the 2 existing TDIS columns arrangement built in 2023-2024 — complete.
2. Procurement of materials needed for an 18-m separations system — complete.
3. Fine machining (honing, grinding) of surfaces of the six, 9.8′ separations columns — complete.
4. Welding the six, 9.8′ separations columns and associated apparatus — near complete.
5. Updating of the data acquisition system to handle communication to the six columns — complete as possible, before stand-up and securing of the columns.
6. Placement and securing of the ~200-pound columns into the walk-in fume hood space — requires 2-3 days.

7. Attachment of HCl feed and sampling systems to complete the serial assembly of six, 9.8′ separations columns — requires 1 day.
8. Shakedown testing of the apparatus collection of enriched ^{37}Cl concentrations relative to natural abundance $^{35/37}Cl$ — requires 1-2 weeks.
9. Sample collection and high-fidelity measurement of enrichment — requires 3-4 weeks.
10. Update of the data-validated model for facility space, power, and other costs to inform facility cost and performance assessments — updating is contiguous with data acquisition and assessments — upon request.

All required procurements had been received at PNNL by October 2024.

The data acquisition system was completed in January 2025 but cannot be functionally tested until the separations columns are placed in their upright condition and secured. Additional monetary and schedule concerns were encountered.

5.1 The Extended TDIS System

Concerning the functional column geometry discussed for the two-column TDIS system testing, the extended system required little change, except in its length. The overall length of a completed column assembly was increased to approximately 320 cm (10.5’). The cartridge heaters (providing T_{hot}) extended out an additional15 cm from the top. The total effective length for thermal diffusion separation is now about 300 cm (9.8’) per column. The resulting channel gap remained the same at approximately 4.5 mm (providing r_1-r_2) at operating temperatures of T_{hot} = 300-400°C. The P&ID for the total apparatus is shown below in Figure 6. On the left-hand side of the P&ID is the HCl fill equipment and in the center are the six separations columns, and the right-hand side is the sampling apparatus, the vacuum pumps needed to remove and/or move gases through the system, and a helium backfill setup to increase heat transfer for the cartridge heaters inserted into the center tube of the columns.

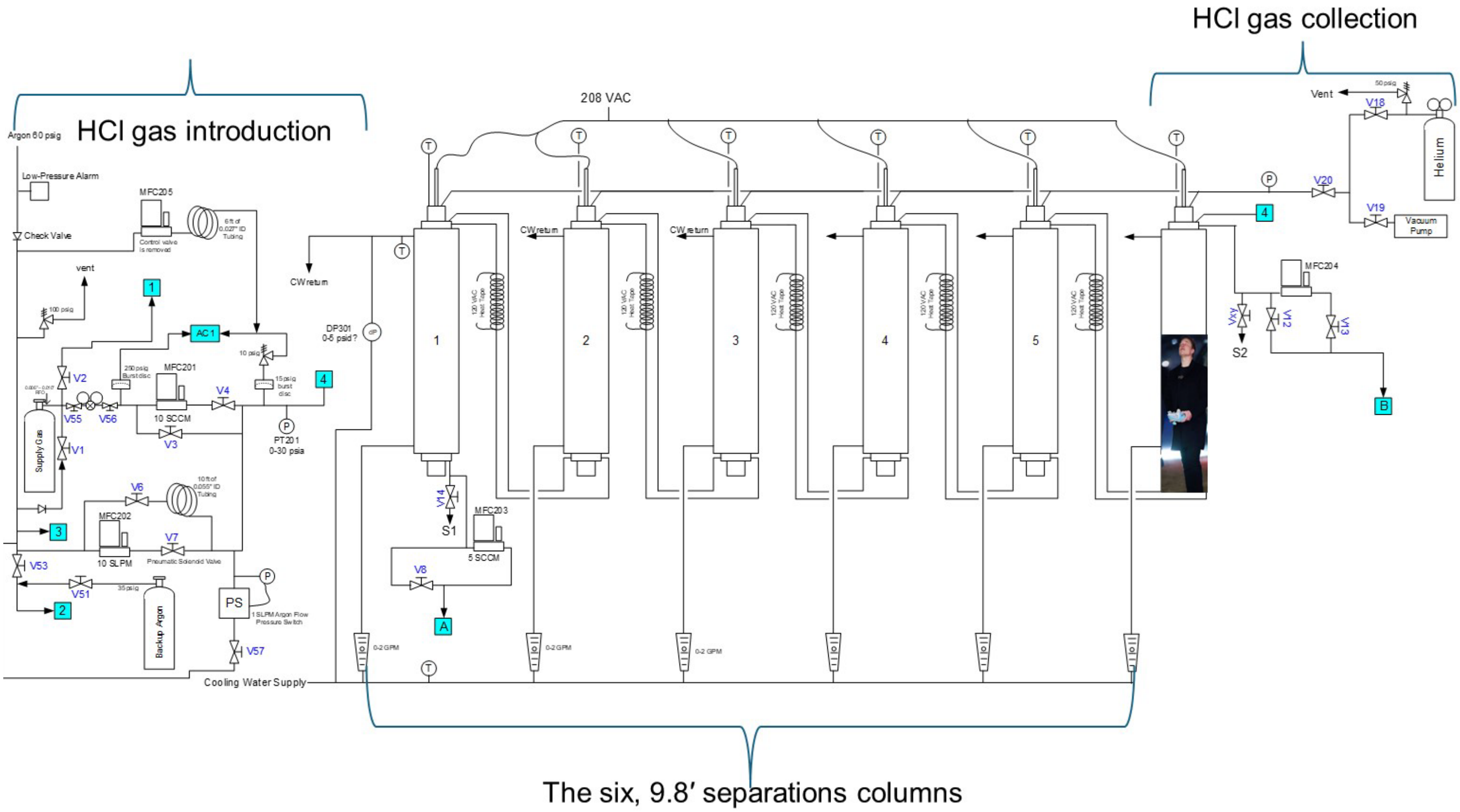

Figure 6: P&ID for the extended TDIS system designed at PNNL in FY25. The left-hand side of the image shows the HCl gas introduction apparatus, in the center are the six separations columns, and the right-hand side shows the columns and gas sampling area. An upright man located on the 6th column shows the relative scale of the apparatus.

The six columns have been machined. In Figure 7A, the interior surface of the (top) stainless tube has been polished. The inner Inconel 600 surface was ground to the polished surface. The honing and grinding shops were in Cleveland and Texas, respectively. The long tubes in particular presented problems for the honing tool. The tubes were then dimpled (divots cut into the surface) to accommodate Inconel balls that maintain the gap distance but also relieve thermal stresses over the length of the columns. Plates were welded onto the bottom and tops of the tubes as shown in Figure 7B. The next step is for crafts personnel to stand up the tubes in the walk-in fume hood.

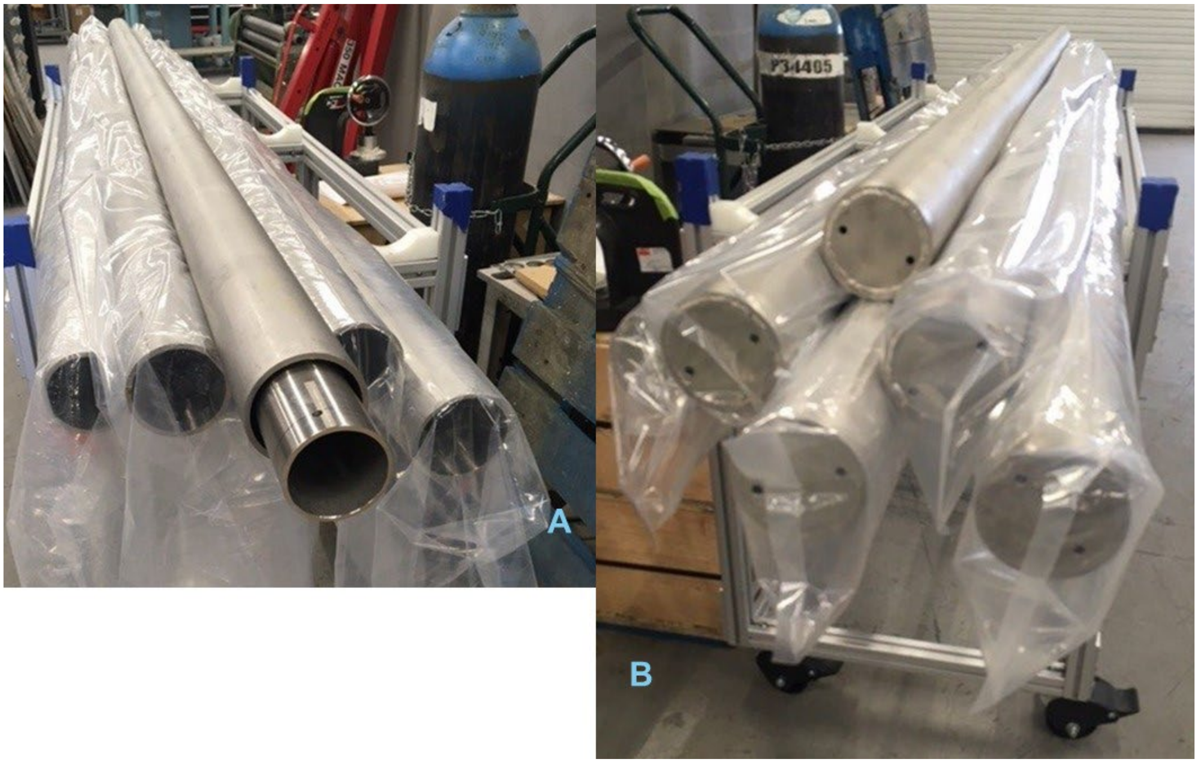

Figure 7: The six, 9.8-foot separations columns are comprised of a tube in a tube. A) The honed interior of the outer tube and the ground exterior of the inner are dimpled to house Inconel balls. The balls maintain the gap dimension over the length of the tubes. B) The bottom plates are welded onto the tubes.

6.0 Shakedown Testing of the TDIS System

Shakedown testing data for the new columns used isotopes of Ar, specifically lower natural abundance ^{38}Ar (0.068%) and ^{36}Ar (0.334%). Data acquired from the two-column system is shown in Figure 8. An in-line RGA was used to monitor the Ar isotopes in real time. Figure 8 indicates that the enrichment of ^{36}Ar is asymptotic in time. The 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 demonstrated that the tubes were working for the $^{36,38}Ar$ separations using hot wall temperatures between 200-400°C.

The same shakedown protocol will be executed in the six-column system. The thermalization of the extended TDIS system will require some time, but after the system has reached thermal equilibrium, the feed gas will be introduced to the columns and data collected over the predicted time until the enrichment process is completed for a given temperature. Increasing enrichment with time is shown in Figure 8 for $^{36,38}Ar$ and predicted for HCl is referred to as the startup dynamics behavior of a TDIS system. The length of startup time increases with increasing total length of the TDIS columns. Once the asymptote is reached, the system is in equilibrium. After the startup dynamics of the TDIS system are determined, all subsequent sampling of gas for enrichment measurements will happen well after the equilibrium enrichment is reached.

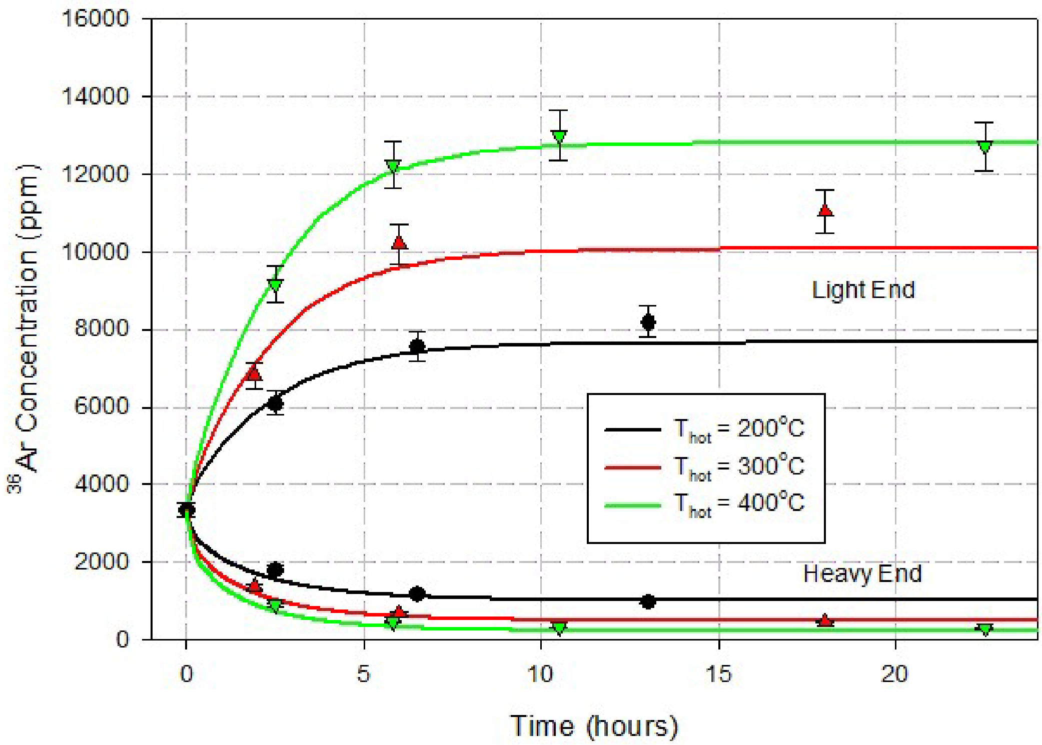

Figure 8: The measured isotopic enrichment of ^{36}Ar vs time based on an assumed uniform hot-side temperature profile. The points are measured data from an RGA with error bars. The solid lines are predicted based on the COMSOL MPP model using the known thermal diffusion constant for Ar.

7.0 Enrichment Predictions of the Extended TDIS System at PNNL

Based on the thermal diffusion coefficient data and the pressure dependence of the as-built system, the validated COMSOL MPP model provides design predictions for larger scale TDIS systems. Figure 9 provides temperature dependent curves for needed column lengths to reach desired enrichment targets. These curves are based on the measured data and extrapolations to higher temperatures based on the best fit line, shown in Figure 3. The plot provides the design data needed for reaching higher enrichments than the small-scale test TDIS columns used in FY23-24. As can be seen, 20 meters of total tube length with a hot side temperature of 500°C will yield 98% ^{37}Cl under no flow (infinite reflux) conditions. It is important to note that this is under infinite reflux conditions (static arrangement). While under bleed (pulling the product from the 6th column) and feed (while refilling the 1st column) conditions, more length will likely be needed. For comparison, under the same length and no flow conditions, 400°C will produce 92% enrichment, 300°C produces 74%, and finally 200°C produces 47% enrichment. While 200-300°C produce significant drop off in enrichment per length of tubing, one can envision that 400°C may be a good compromise of material durability and tube length. It is likely that temperatures above 400°C (the max design temperature of this work) will produce significant corrosion. This temperature is likely approaching the limit of Inconel 600's use range with $HCl_{(g)}$, as was described in openly published literature data.

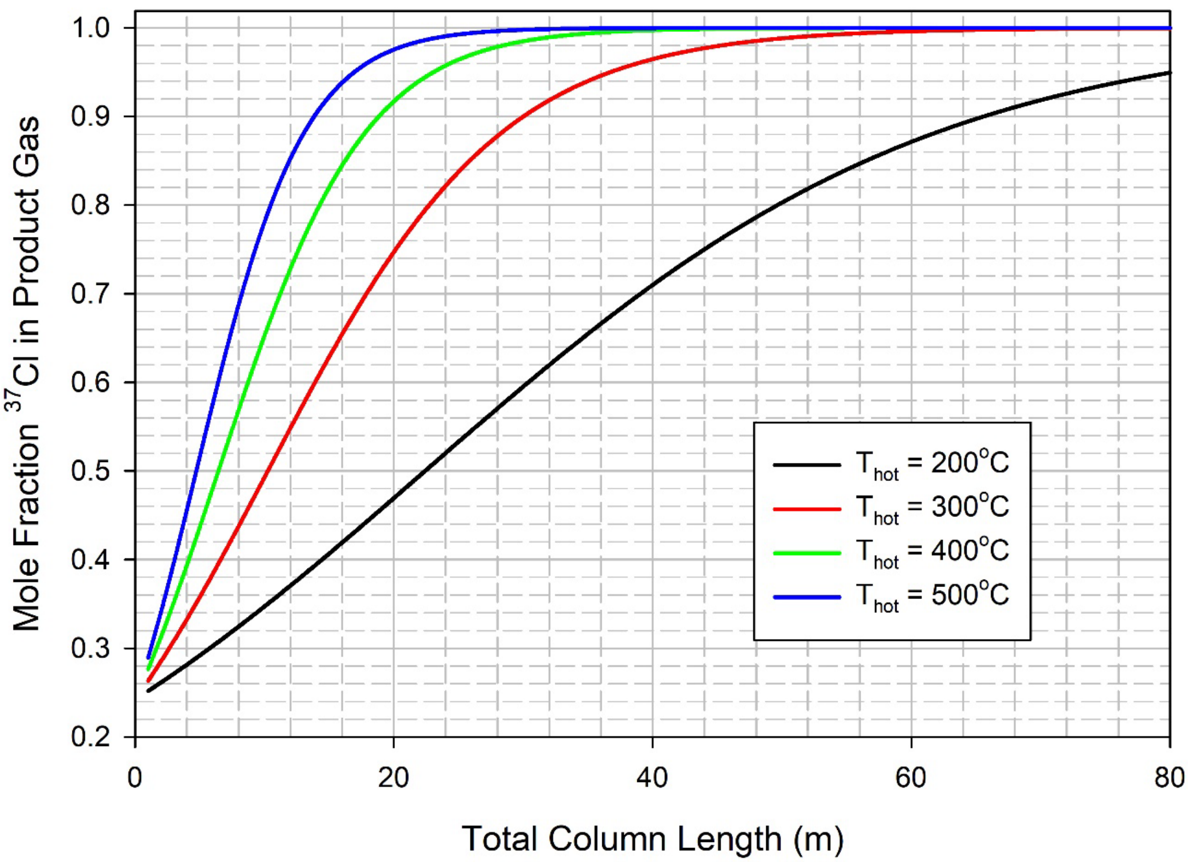

Figure 9: Predicted enrichment levels versus the total TDIS column lengths at varying temperatures.

The TDIS laboratory at PNNL, used specifically for chlorine isotopes separations, is limited in both its space and power to operate this extended system. We demonstrated above the separation that could be achieved in a single pass. Improvements in enrichment would require a second pass through the columns.

To understand the facility expansion required to achieve 99+% enrichments at a single pass, the data-validated model was used to predict the number of columns and their lengths that would be required. The prediction is plotted in Figure 10. Enrichments in ^{37}Cl for 30 and 45-m columns was considered using α and L (the column length) as chosen and the H and K values as calculated (see model M2AT-23PN110146 - Huber 2024) from data acquired on the test system described above. Operations at 350-400°C require tall columns, but this has been done before for other isotope separations. However, given a larger facility space, these enrichments would be done using cascaded columns. Re-enrichment scenarios for the addition of new feed versus slightly enriched and increasingly enriched material would be strategically determined by the data-validated model.

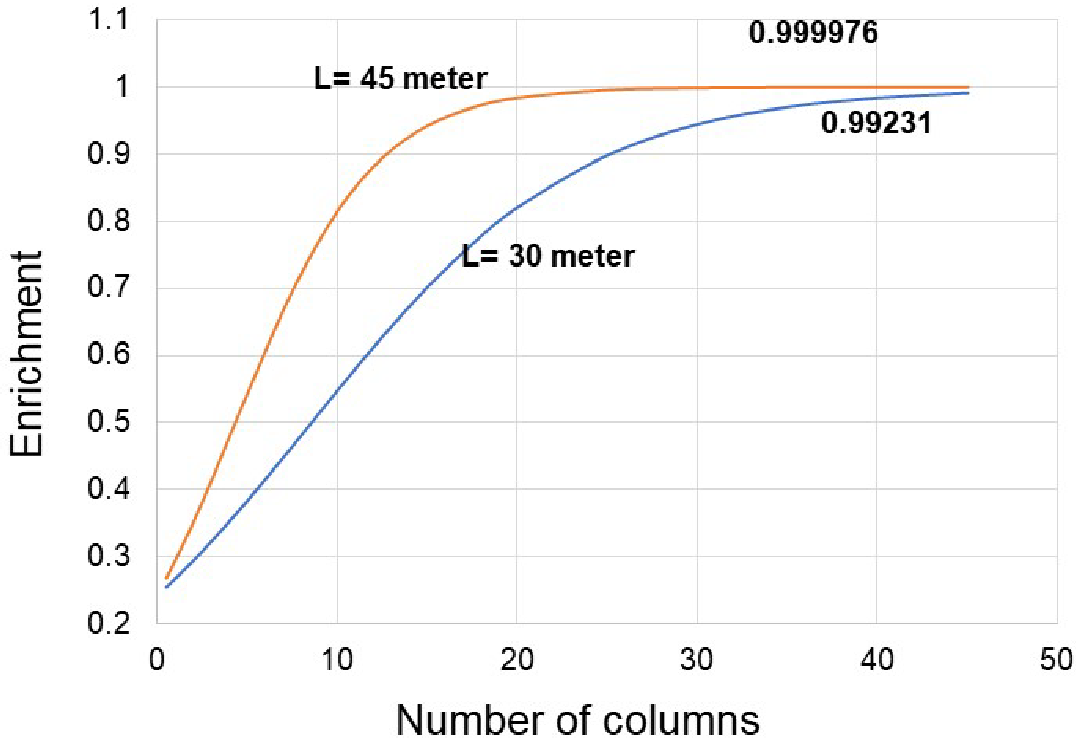

Figure 10: Enrichment in ^{37}Cl for 30-m and 45-m columns using α and L (the column length) as chosen and the H and K values as calculated from data acquired on the test system described above.

8.0 TDIS Facility Power Requirement Predictions

The COMSOL MPP model was also used to predict the cost of $H^{37}Cl$ product produced using bleed and feed operations for varying channel gaps (between T_{cold} and T_{hot} walls), pressure, and column cost. This early work used the literature values of the thermal diffusion constant (Figure 3) and compared a long and short lifetime scenario, where the tube cost differentiated the two scenarios. The short lifetime option considered relatively expensive columns ($6000 per meter) operated over a facility life of two years. The long lifetime option considered relatively inexpensive columns ($2000 per meter) operated over a twenty-year facility life. The power cost was kept constant at $0.15/kW-hr.

In the case of the long lifetime scenario, the power requirements of heating and cooling the columns are the major driver of cost. For all the channel gaps analyzed over varying operating pressures, the optimized product costs about $13 per gram of $H^{37}Cl$. Additionally, it was calculated that smaller gaps allow for a larger operating window of optimum system pressures. In contrast, the cost driver for the short lifetime scenario is a combination of the system heating and cooling costs and the column manufacturing costs. In this scenario, the smaller channel gaps offer reduced costs because the total column length required is shorter for the smaller gaps.

9.0 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. Examples of the number of serial columns required to reach successively higher enrichments in the heavy ^{37}Cl fraction are plotted in Figures 9 and 10. Additional factors beyond total column length and temperature also must be considered. Operational criteria will drive the entry location of the feed gas, production rate, storage of gas in cylinders, and the needed enrichment. The validated TDIS model in COMSOL MPP from the extend design at PNNL will greatly increase the ability to predict and design the serially aligned tubing cascades envisioned for meeting product demand.

10.0 Conclusions

Beginning in 2023, a separations apparatus for enrichment of ^{37}Cl in natural isotopic composition of HCl was initiated by the Chlorine Isotopes Team at PNNL. Data from the literature was used for an initial set of estimates that culminated in the design and construction of the first separations device. The device was relatively short (two 6-foot columns) and made of metal. Both deficiencies were anticipated from work done historically. The geometric construction of the device was guided by numerical simulation. Early data acquisition proved that the simulations worked well in several aspects of construction and in its operation. The model that was established is predictive of the separations column efficacy, thus is now a useful tool for design of larger separation systems. The prognostic capability of the model allows us now to numerically increase separations efficiency and to understand how rates of the ^{37}Cl will be optimized. Valuable data points for the coefficient of thermal diffusion were found with high precision, helping to fill in gaps from the existing historical data set.

There is no doubt that better materials of construction will more promptly allow enrichment and production. We know this also from the model. Under this funding, the Project examined the use of advanced coatings from a vendor with extensive industrial experience in high-temperature applications using silica-based coatings with HCl gas. The coating failed at temperatures near 435°C, as was experienced by the uncoated Inconel (600). For now, the result disqualified the immediate use of the coating until an understanding of the failure can be assessed.

Our decision to move forward in 2024 with the installation of a larger set of separation tubes and associated equipment was an aggressive one, but this was based on the successful development of the predictive model and demonstration of small-scale Cl enrichments that were completed in FY2024. The work was completed ahead of schedule and under budget. The stand-up of the 18-m serial separations system is near its completion for shakedown testing with the argon isotope system slated for the end of January. Demonstrative separations of high enriched $H^{35,37}Cl$ are expected to be completed by end of FY26.

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Appendix A – Key Team Members and Co-Investigators

Bruce McNamara (PM):
Bruce McNamara is a Chemist in the Actinide Chemistry Team at PNNL. He is the Principal Investigator for this project and works on system design and operations. He holds a PhD in physical chemistry from Purdue University. Bruce brings decades of experience in analytical gaseous chemistry and is an established expert in fluorination of actinides. Bruce currently works on national security missions for fluorination of uranium and conversion/deconversion using gaseous chemistry as well as many nuclear energy projects relating to fluorination.

Mike Powell
Mike Powell is a chemical engineer and leader of the Process Intensification Team at PNNL. He leads the work on system design, operation, and multi-physics modeling. His research interests include compact chemical reactors, heat exchangers, and advanced separation technologies. He received a MS in chemical engineering from Washington State University and joined PNNL in 1990.

Tyler Schlieder:
Tyler Schlieder is a chemistry Post-Doctoral Research Associate in the Ultra-Low Background Materials Team at PNNL. For this project he works on measuring Cl isotopic ratios via triple quadrupole (QQQ)-ICP-MS to validate ^{37}Cl enrichment efforts. He received his B.S. from Oregon State University, M.S. from Northern Arizona University, and Ph.D. from UC Davis, all in Geology/Geochemistry. Tyler currently works primarily supporting rare-event physics experiments. He also is involved in characterizing different mass spectrometry methods for use in making ultra-sensitive nuclear measurements

Appendix B – Conferences and Publications

- T. D. Schlieder N. D. Rocco, M. di Vacri, I. J. Arnquist, D.R. Bottenus, Z. F. Huber, B. K. McNamara. 01/20/2024. Rapid determination of chlorine isotopic ratios using qqq-icp-ms/ms with o_2 gas: application to molten salt reactor (msr) research. Presented by T. D. Schlieder at Winter Conference on Plasma Spectrochemistry, Tucson, Arizona. PNNL-SA-193910.

- T.D. Schlieder, N.D. Rocco, M. di Vacri, I.J. Arnquist, D.R. Bottenus, B.K. McNamara, Z.F. Huber. "Rapid and accurate determination of Cl isotope ratios in diverse sample matrices with QQQ-ICP-MS/MS using an O_2 reaction gas." J. Anal. At. Spectrom., 2024, 39, 2502

- B. K. McNamara, Z. F. Huber, M. R. Powell, T. G. Levitskaia, T. D. Schlieder, Chemistry of fuel cycles for molten salt reactor technologies. Presented by B. K. McNamara at the International Atomic Energy Agency, IAEA, Vienna, 2-6 October 2023.

- B. K. McNamara, Z. F. Huber, M. R. Powell, T. G. Levitskaia, T. D. Schlieder, Chlorine isotopes separation for fast spectrum msr, Presented by B. K. McNamara at the Annual MSR Campaign Review Meeting 2-4 May 2023.

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