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

Molten Salt Reactor PROGRAM

Chlorine-37 and Its Utility to Enhance Reactor Longevity

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Joint IAEA-NEA-EC/JRC Workshop on the Taxonomy and Related Terminology of Fuel Cycles for Molten Salt Reactors

Chlorine-37 and Its Utility to Enhance Reactor Longevity

PNNL TEAM

Bruce McNamara	*Physical Chemist (PI)*
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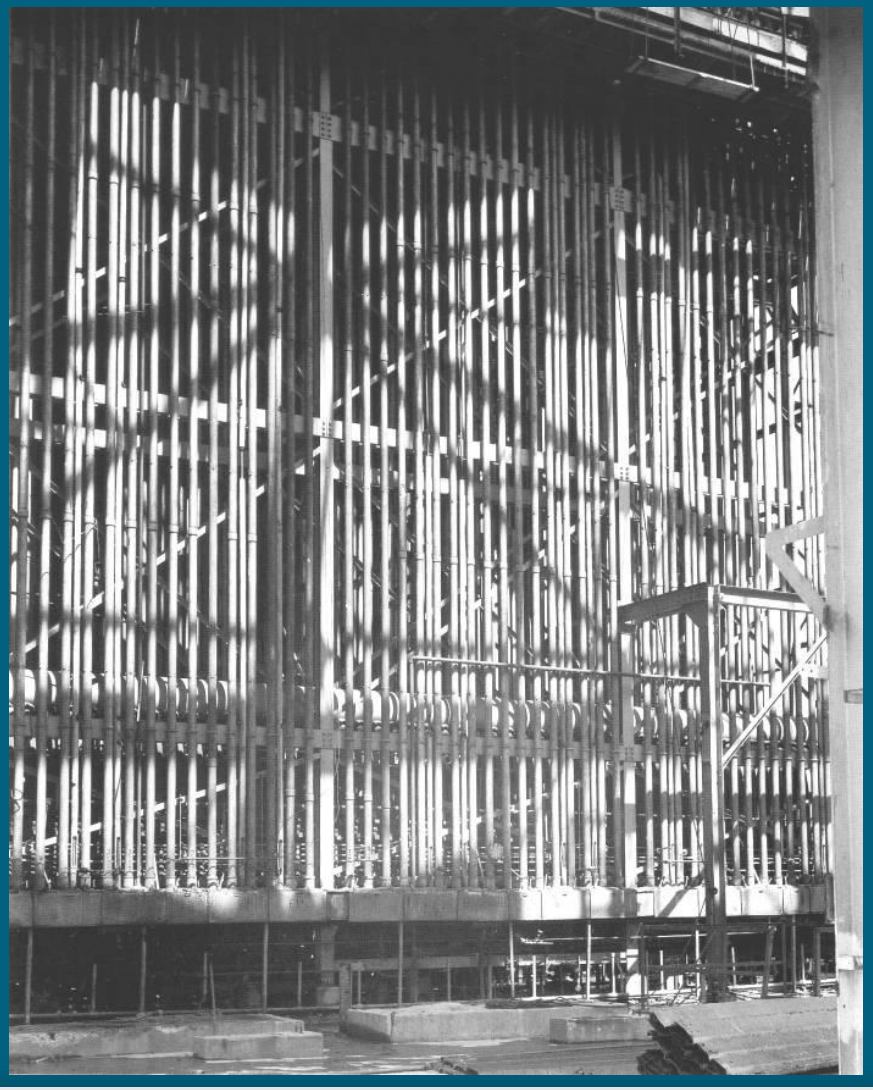
Update on the Chlorine Isotopes Project at PNNL

- **The Chlorine Isotopes Project was granted to PNNL by DOE-NE in FY2022.**
  Prototype built- FY22-23
  Extended system design/construction FY24-26
- **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.**

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
- Infinitely tall column = infinite purity
- 31,237 m, 102816 ft



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.

With Concern to Reactor Longevity

- The $^{35}Cl(n,p)^{35}S$ reaction, which decays back to ^{35}Cl. The analogous reaction $^{36}Cl(n,p)^{36}S$ produces stable ^{36}S. 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-}, S^0. A few thousand ppm S are corrosive to Ni, Mo and additionally react with fertiles. $H_2/HCl + S_x = H_2S$

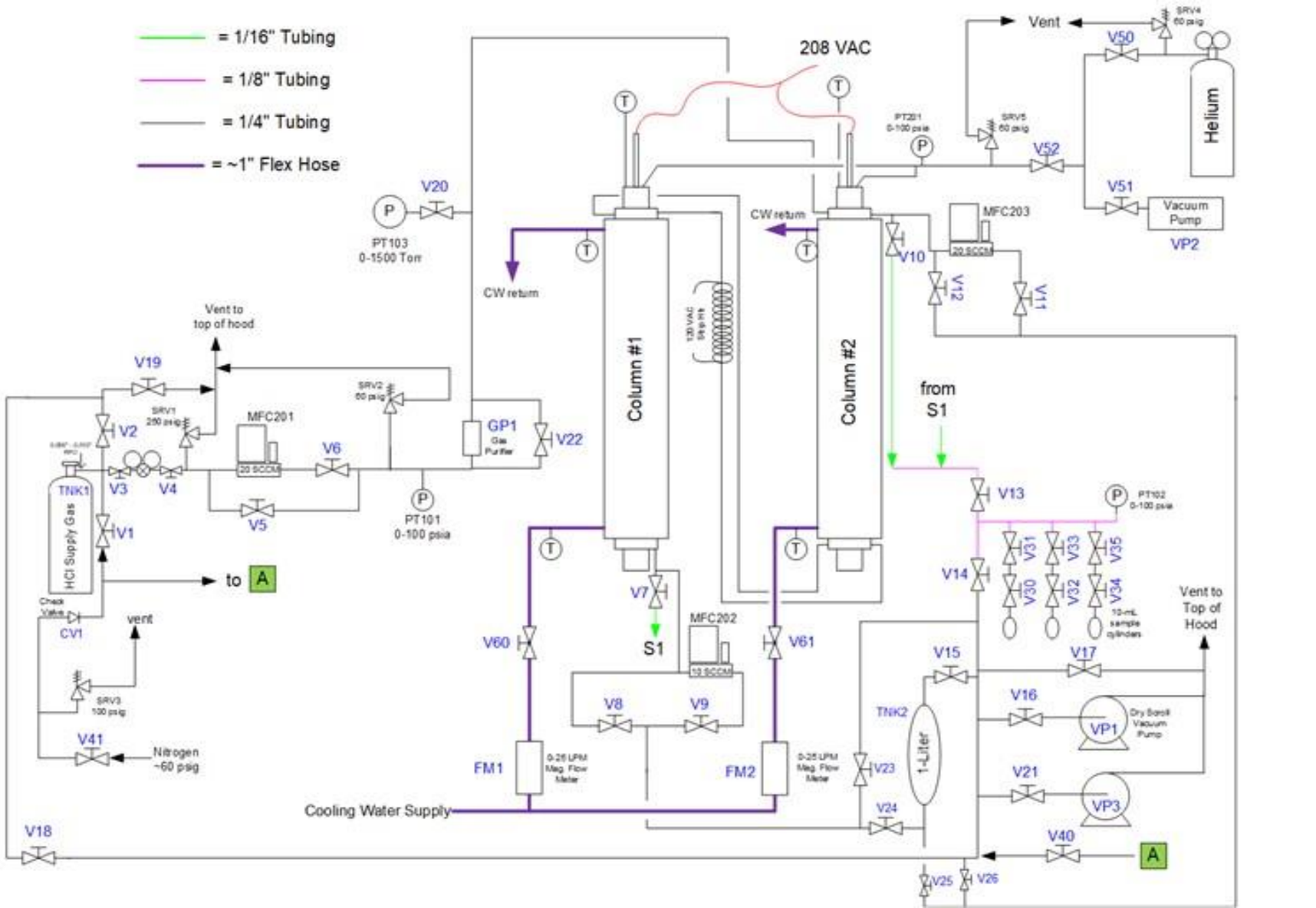
$UCl_3 + H_2S = U_xS_{y\ (ppt)}$

$PuCl_3 + H_2S = Pu_xS_{y\ (ppt)}$, Where Pu_xS_y = PuS, Pu_3S_4, Pu_5S_7, Pu_2S_3

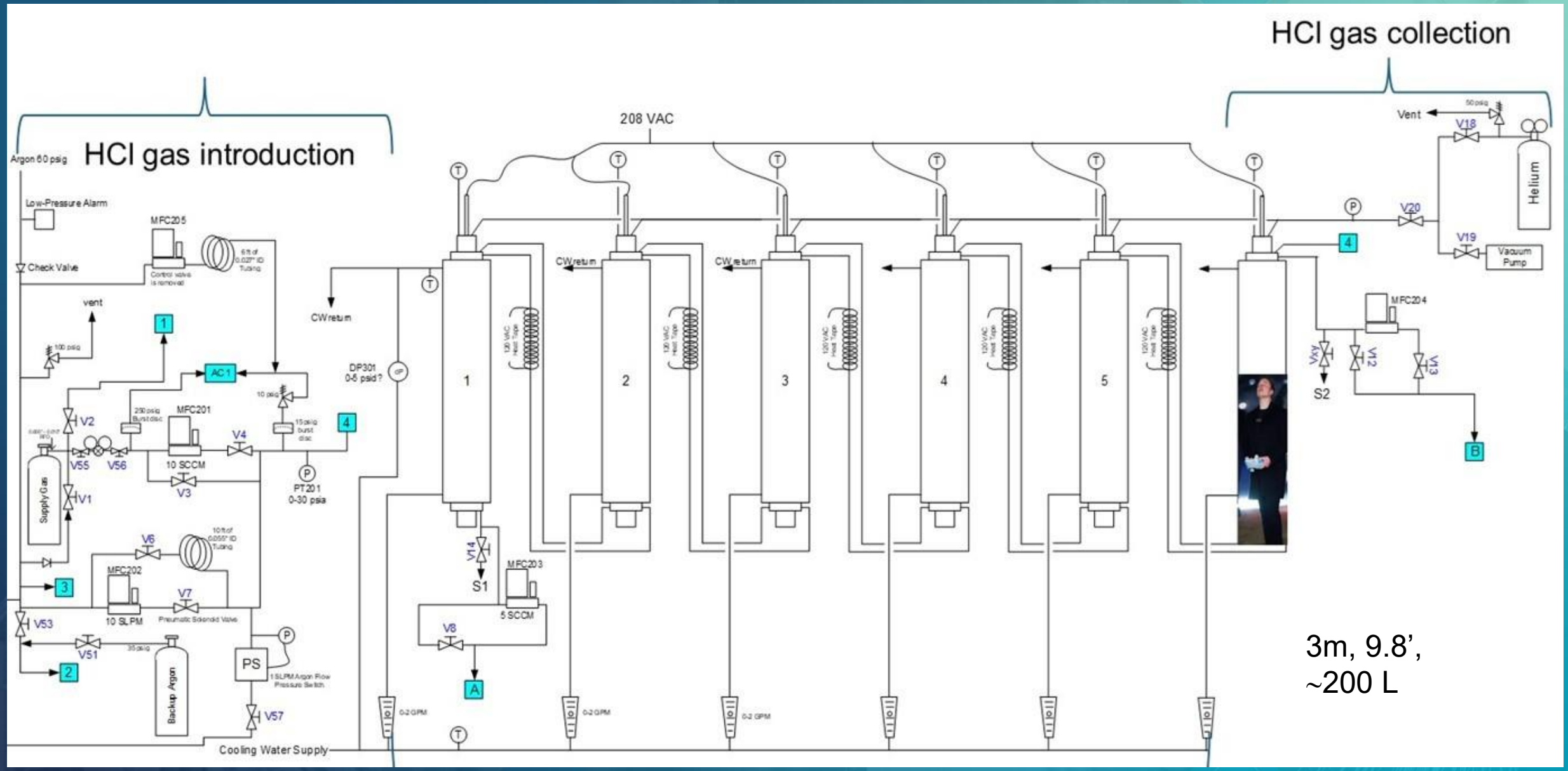
- The $^{35}Cl(n,\alpha)^{32}P$ produces radio-phosphorus ($t_{1/2}$= 14d) that also decays to more sulfur. P can interact with these MOCs as PCl_3 or more reduced forms of phosphorous

P&ID for the Two, 6-Foot Serial Columns and Associated Apparatus

- Apparatus built in the 1st quarter of 2023
- Completed shakedown testing in July of 2023
- Two serially connected columns, 3.6m
- Internal volume of ~7.4 L for HCl
- Validated model

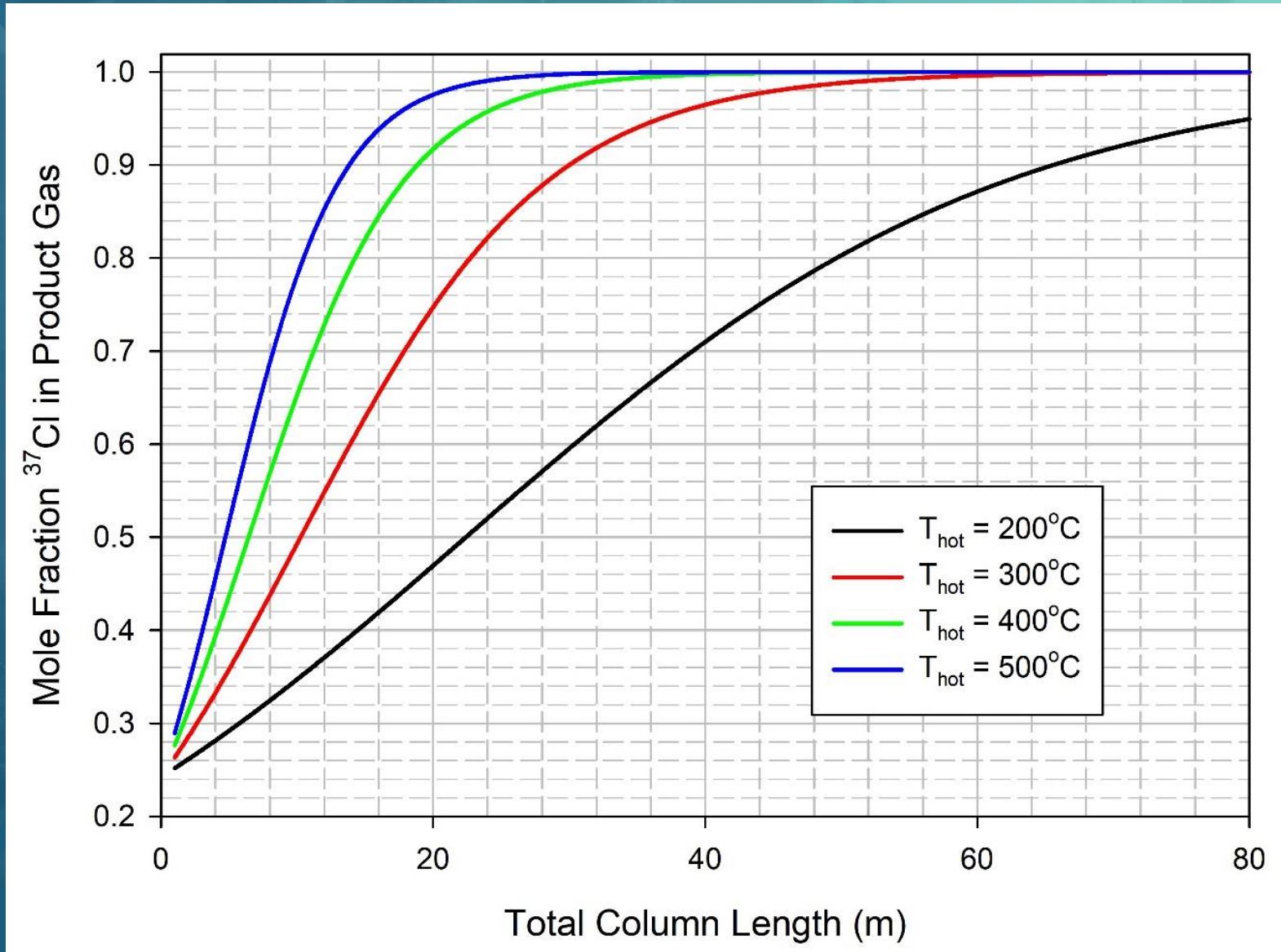


P&ID for the Extended TDIS System



Enrichment Predictions of the Extended TDIS System

- The validated COMSOL MPP model provides design predictions for larger scale TDIS systems
- 6 columns total serial length 18 m
- ~200 L



Fuel Salt, Flush salt, Salt Synthesis ^{37}Cl

The fuel salt in a chloride molten salt fast reactor (Cl-MSFR), might be comprised of a specific eutectic composition of alkali and/or alkaline earth chlorides that solubilize major and minor actinide chlorides as the fertile component(s).

Synthesis / purification using enriched ^{37}Cl

The reasons for alternative synthetic pathways provided by MSRE

Costs of Raw Materials Used in MSRE Fluoride Production

Material	Quantity	Unit Cost (dollars)	Total Cost (dollars)
^{7}LiF	12,919 lb	16.50[a]	213,164
BeF_2	11,472 lb	5.70	65,390
ZrF_4	2,265 lb	8.00	18,120
UF_4	90 kg (^{235}U basis)	12,000.00	1,080,000
		Total	1,376,674

[a]Includes $1.82 per pound for preparation as fluoride salt.

Salt Purification and Reactor Preparation by Flush

Impurity Concentrations

Fluoride Production for the MSRE –
Average of Chemical Analyses of Salt Batches

Salt Mixture	Chemical Composition (mole %)	Average Concentration of Impurities (ppm)				
		Cr	Ni	Fe	S	Oxide Removed
Coolant	^{7}LiF-BeF_2 (66-34)	19	26	166	<5	1460
Flush	^{7}LiF-BeF_2 (66-34)	16	39	123	<5	1650
Fuel solvent	^{7}LiF-BeF_2-ZrF_4 (64.7-30.1-5.2)	21	15	77	<5	728
Depleted fuel concentrate	^{7}LiF-$^{238}UF_4$ (73-27)	9	15	50	<5	386

Flush Salt with H_2/HF versus H_2/ $H^{37}Cl$

Impurity concentrations handled by removal with 10/1 H_2/HF 100L/min (volatile H_2S, PH_3) *Faster reduction with Be, Zr metal*

reduction products and mechanism determine appropriate process, e.g., use of $H^{37}Cl$ alters the corrosion mechanism and products (PH_4Cl solid), leading to time, temperature, flow rate sparging studies

$$P_4 + 6H^{37}Cl = 2P^{37}Cl_{3(g)} + 2PH_{3(g)}$$ *This is a campaign!*

Salt Purity by Synthetic Design

$(NH_4)_2CO_{3(s)} + 2H^{37}Cl_{(g)} \rightarrow 2NH_4{}^{37}Cl_{(s)} + CO_{2(g)} + H_2O_{(g)}$

$Na_2CO_{3(s)} + 2H^{37}Cl_{(g)} \rightarrow 2Na_2{}^{37}Cl_{(s)} + CO_{2(g)} + H_2O_{(g)}$

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

$COCl_2$?

$NH_4{}^{37}Cl_{(s)} + NaOH\ (aq) \rightarrow NH_3 + Na^{37}Cl + H_2O_{(g)}$

$NH_{3(g)} + H^{37}Cl_{(g)} \rightleftharpoons NH_4{}^{37}Cl_{(s)}$

$Na^0 + H^{37}Cl_{(g)} \rightarrow Na^{37}Cl + 1/2H_2$

$K^0 + H^{37}Cl_{(g)} \rightarrow k^{37}Cl + 1/2H_2$

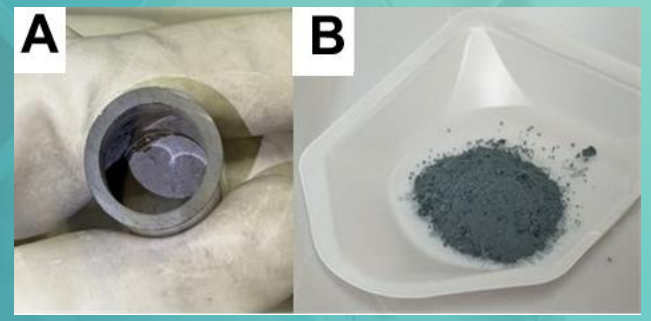
ρ_{Na} = 0.9 g*cm-1, bp= 883°C

ρ_K = 0.83 g*cm-1, bp= 760°C

ρ_{Mg} = 1.74 g*cm-1, bp= 1090°C

This is a campaign!

Recovery of Fertiles Content from UNF for Conversion to ^{37}Cl Forms



In FY2025, we co-opted a well-known method to scavenge fertiles populations in used nuclear fuel (UNF) for conversion to their chloride forms as required for their solubility in a Cl-MSFR. Because UNF fuel reprocessing is a mature art with several fuel types and evolving separative techniques, the molten salt community has a tool box of methods to target the major and minor actinides from cooled nuclear fuels and fresh fuel.

$$Pu_2(C_2O_4)_3.10H_2O + xsNH_4{}^{37}Cl_{(s)} \overset{\Delta}{\leftrightarrow} 2Pu^{(III)}{}^{37}Cl_3 + 6NH_3 + 6CO_2 + yHCl + xH_2O$$

The method follows for U, Np, Pu, Am, Cm, Ln‘s It’s another campaign!

Similarly, the carbonates and others can be ppted chlorinated and sublimed

Harvest of Fertiles from UNF for Conversion to ^{37}Cl

We modeled speciation of selected actinides, fission products, and corrosion products in proportions typical for an irradiated fuel dissolver solution used in the PUREX process.

- The feed solution contains 26 components in 2 M HNO3.
- 1.2 M oxalic acid in 2 M HNO_3 is added to the feed solution to achieve 1.2-to-1 molar ratio of oxalate to uranium. Third column of Table 1 shows concentrations for Ni, Nd, Sr, U, Pu, and Am in solution of 0.6 M oxalic acid in 2M HNO_3 calculated for this condition of two equal volumes mixed.

Harvest of Fertiles from UNF for Conversion to ^{37}Cl

Table1 shows initial and final concentrations of 6 representative metals. Table 2 shows the protonation constants of oxalate anion, ^{37}Cl binding constants for 1:1 and 1:2 complexes of Ca^{2+}, Ni^{2+}, Nd^{3+}, UO_2^{2+}, Pu^{4+}, and Am^{3+} with oxalate, as well as solubility products of oxalate salts for these metal cations with most of these values found in technical literature for 0.5 to 2M ionic strength.

Component	Original concentration, mol/L	Initial concentration for simplified 7-component feed after introduction of oxalic acid solution, mol/L
Ce	8.0×10^{-3}	
Cr	2.9×10^{-2}	
Cs	9.1×10^{-3}	
Eu	4.4×10^{-4}	
Fe	6.0×10^{-2}	
Gd	4.9×10^{-4}	
La	4.1×10^{-3}	
Mo	5.8×10^{-3}	
Nd	1.3×10^{-2}	6.5×10^{-3}
Ni	4.3×10^{-2}	2.15×10^{-2}
Pd	6.8×10^{-5}	
Pr	3.6×10^{-3}	
Rb	1.2×10^{-3}	
Ru	5.1×10^{-3}	
Sm	2.4×10^{-3}	
Sn	2.0×10^{-4}	
Sr	4.1×10^{-3}	2.05×10^{-3}
Te	8.6×10^{-4}	
Y	2.3×10^{-3}	
Zr	1.9×10^{-2}	
U	1.0×10^{0}	5×10^{-1}
Np	1.0×10^{-3}	
Pu	1.5×10^{-2}	7.5×10^{-3}
Am	1.94×10^{-3}	9.7×10^{-4}
Tc	1.8×10^{-3}	
HNO_3	2.0×10^{0}	2.0×10^{0}
Oxalic Acid	Not present	6×10^{-1}

Species	Log beta	Log K_{sp}	Calculated precipitation yield, %
OxH	3.66		
OxH_2	4.64		
OxCa	1.64		
Ox_2Ca	2.68		
OxNi	3.7		
Ox_2Ni	6.6		
OxU(VI)	6.42		
$Ox_2U(VI)$	10.64		
OxPu(IV)	8.74		
$Ox_2Pu(IV)$	16.92		
OxAm(III)	4.17		
$Ox_2Am(III)$	7.77		
H-1	-13.8		
CaOx(solid)		-6.53	No precipitation
$Nd_2Ox_3(solid)$		-30.89	99.66
NiOx(solid)		-9.43	91.35
U(VI)Ox(solid)		-9	98.69
$Pu(IV)Ox_2(solid)$		-21.4	99.55
$Am(III)_2Ox_3(solid)$		-30.65	99.61

Fuel Reprocessing: Chloride Volatility as an Option for Continuous Processing of an Irradiated Chloride Salt

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

Cl volatility is another campaign!

Actinide	Sublimation Point, C	Boiling Point, C
UCl_4	in vacuum at 600–650°	791
UCl_5	Decomposes at 100°	
UCl_6	75	
$NpCl_4$	500	
$NpCl_3$	>500	
$PuCl_3$	600-800	
$CmCl_3$	~350	

Lanthanide Chloride	Boiling Point, C	Ln(II) boiling, C
La	1812	-
Ce	1727	-
Pr	1710	-
Nd	1600	-
Pm	1670	-
Sm	Decomp	1310
Eu	Decomp	2190
Gd	1580	-
Tb	180–200	-
Dy	1530	Decomp
Ho	1500	-
Er	1500	-
Tm	1488	Decomp
Yb	1900	1900
Lu	1422	-

Fuel Reprocessing: Chloride Volatility as an Option for Continuous Processing of an Irradiated Chloride Salt

	Melting Point,°C	Boiling Point,°C	Sublimation point,°C
AgCl	455	1550	——
$TeCl_4$	224	380	200
$TeCl_2$	209	328	yes
$ZrCl_4$	——	437	331
$ZrCl_3$	627	——	——
$ZrCl_2$	727	1292	——
$NbCl_5$	204	254	yes
$NbCl_4$	decom>800	no	275
$NbCl_3$	dis>600	no	no

(^{95}Zr:$t_{1/2}$=64d)

↓ β

(^{95}Nb: $t_{1/2}$=35d.

4.5 TBq/mmol

Noble Metals and Others of Interest

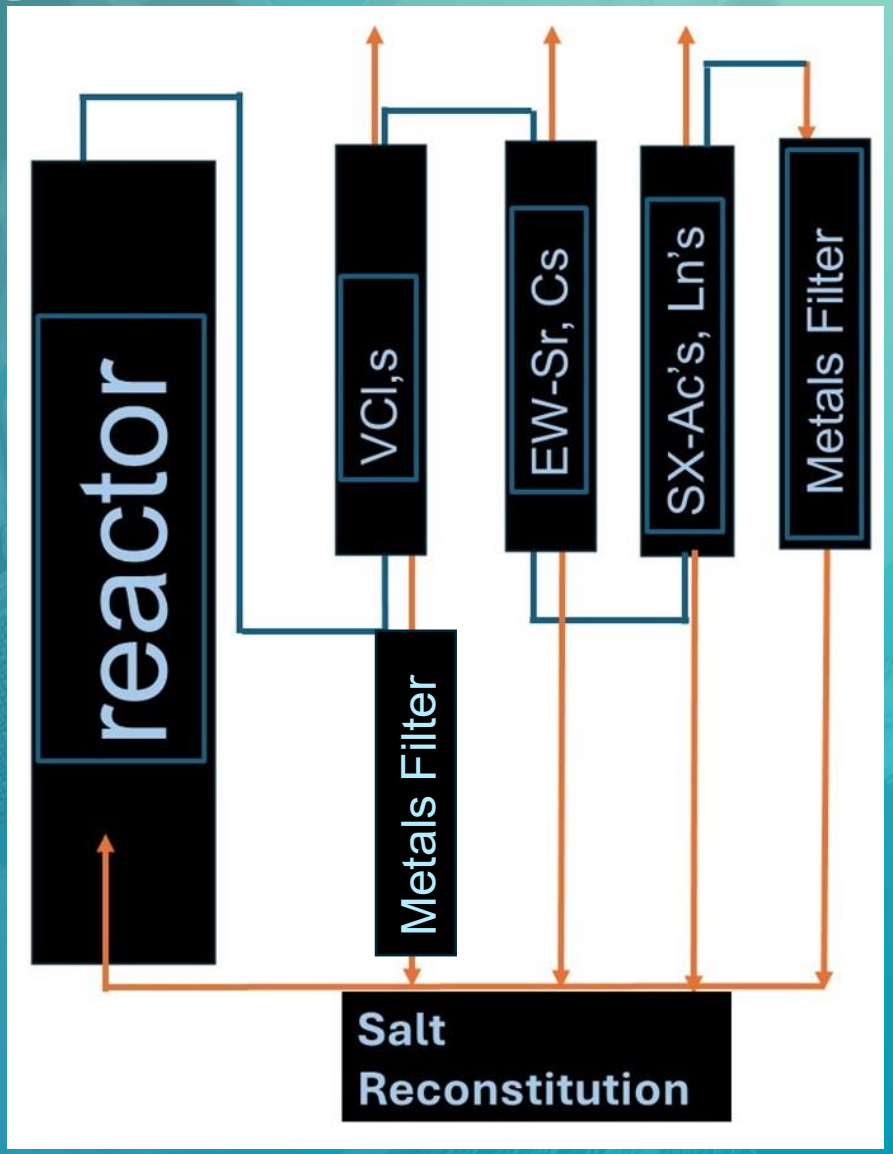
	Melting Point,°C	Boiling Point,°C	Sublimation point,°C
$MoCl_5$	194	268	-----
$MoCl_4$	552	-----	-----
$TcCl_4$	decomp	300	?
$TcCl_3$	-----	> 450 decomp	-----
$TcCl_2$	-----	> 450 decomp	-----
$RuCl_4$	> -32 decomp	-----	< -30 decomp to $RuCl_3$
$RuCl_3$	> 500 decomp	-----	-----
$RuCl_2$	-----	-----	-----
$RhCl_3$	> 450 decomp	-----	800
$PdCl_2$	> 680 decomp	-----	590

Optimized Salt Reprocessing of a CI-MSFR

With exception ^{37}Cl-volatility the processes listed may not require ^{37}Cl addition

Reconstitution of salt requires the metal filter

Continuous salt processing with eutectic reconstitution is another campaign!



Thank you

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