Investigating Noble Gas Solubility in Molten Salt

Kyoung Lee, Wesley Williams, Joanna McFarlane,
David Kropaczek, and Dane de Wet

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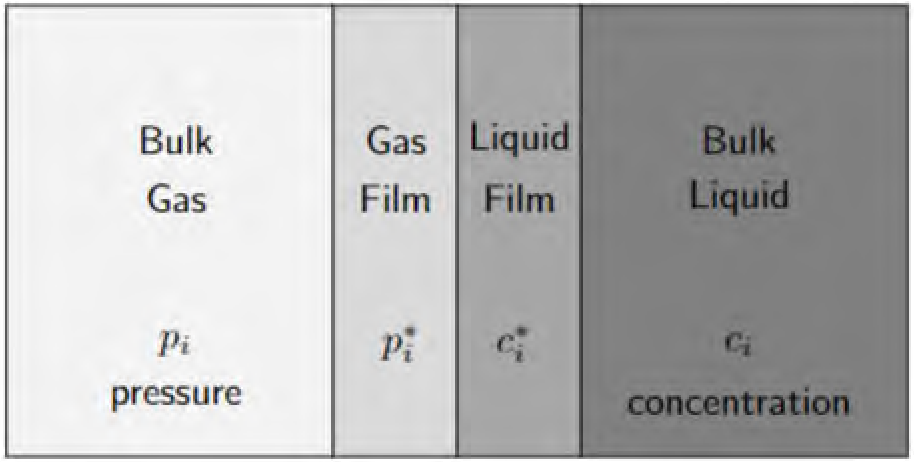
Henry's law constant

SCIENTIFIC REPORTS

Henry's law constant describes dissolved gas proportionality in liquid-gas equilibrium.

- Noble gas partitioning affects MSR performance.
- Liquid-gas mass transport in determining reactor parameters.
- Gibbs free energy essential for understanding phase transitions.



$$c_i^* = p_i H$$

$$p_i^* = c_i / H$$

The understanding of the gas–liquid interface is clarified by the two-film theory, which elucidates this phenomenon by utilizing partial pressures and concentrations, where H represents Henry's law constant.

Gibbs free energy $\Delta G = \Delta G_\gamma + \Delta G_v$.

$$\Delta G(r,T;\gamma(T),\alpha,\beta) = RT\ln(K_H) = 4\pi r^2\alpha\gamma(T) + \frac{4}{3}\pi r^3\beta RT,$$

surface tension

$$\gamma(T) = \frac{\partial\gamma(T)}{\partial T}(T - 273.15) + \gamma_0.$$

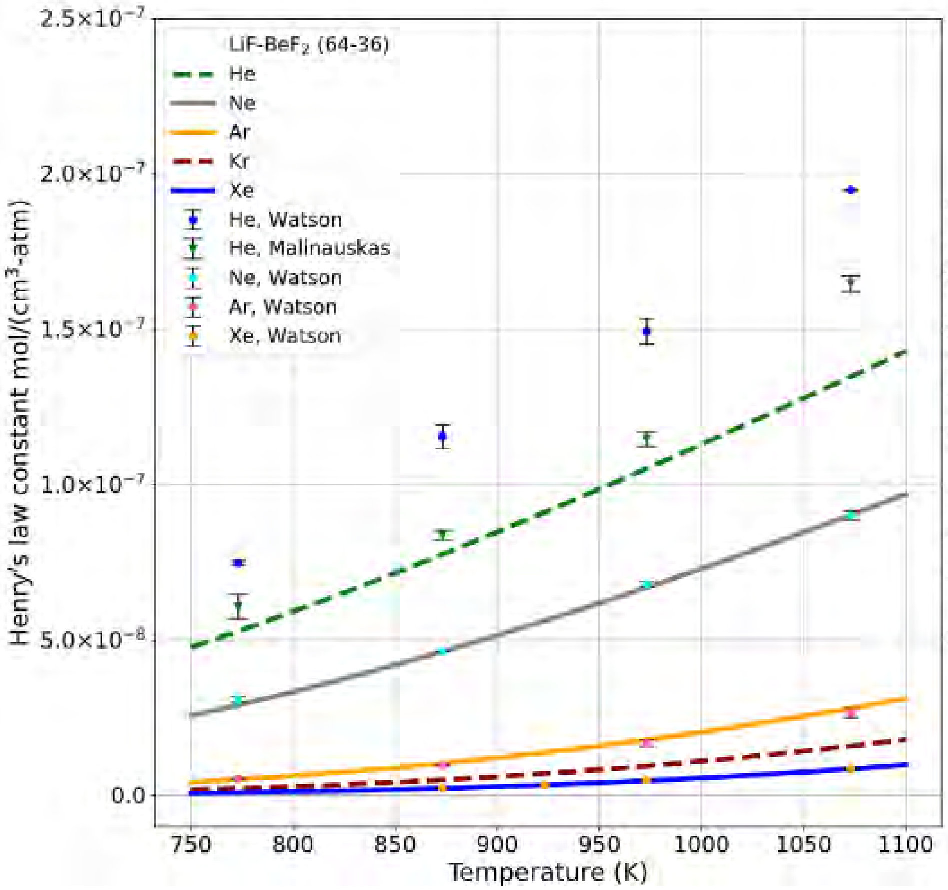
enthalpy change

$$\Delta H = RT^2\frac{d\ln(K_H)}{dT} = -4\pi\alpha r^2\gamma_0$$

entropy change

$$\Delta S = -8\pi\alpha r^2\frac{\gamma(T)}{T} + 4\pi\alpha r^2\frac{\partial\gamma(T)}{\partial T} - \frac{4}{3}\pi r^3\beta R.$$

Lee, Kyoung, Wesley Williams, Joanna Mcfarlane, Dave Kropaczek, and Dane de Wet. "Semi-Empirical Model for Henry's Law Constant of Noble Gases in Molten Salts." (2023) Scientific Reports, https://doi.org/10.21203/rs.3.rs-3352622/v1.



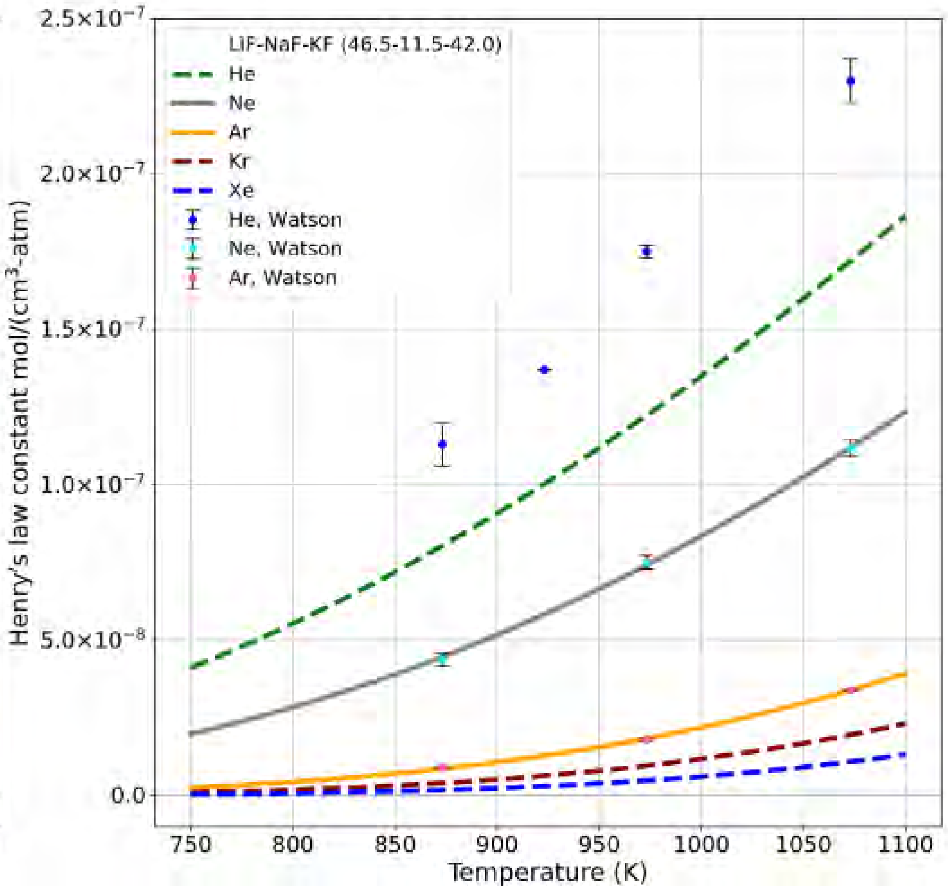
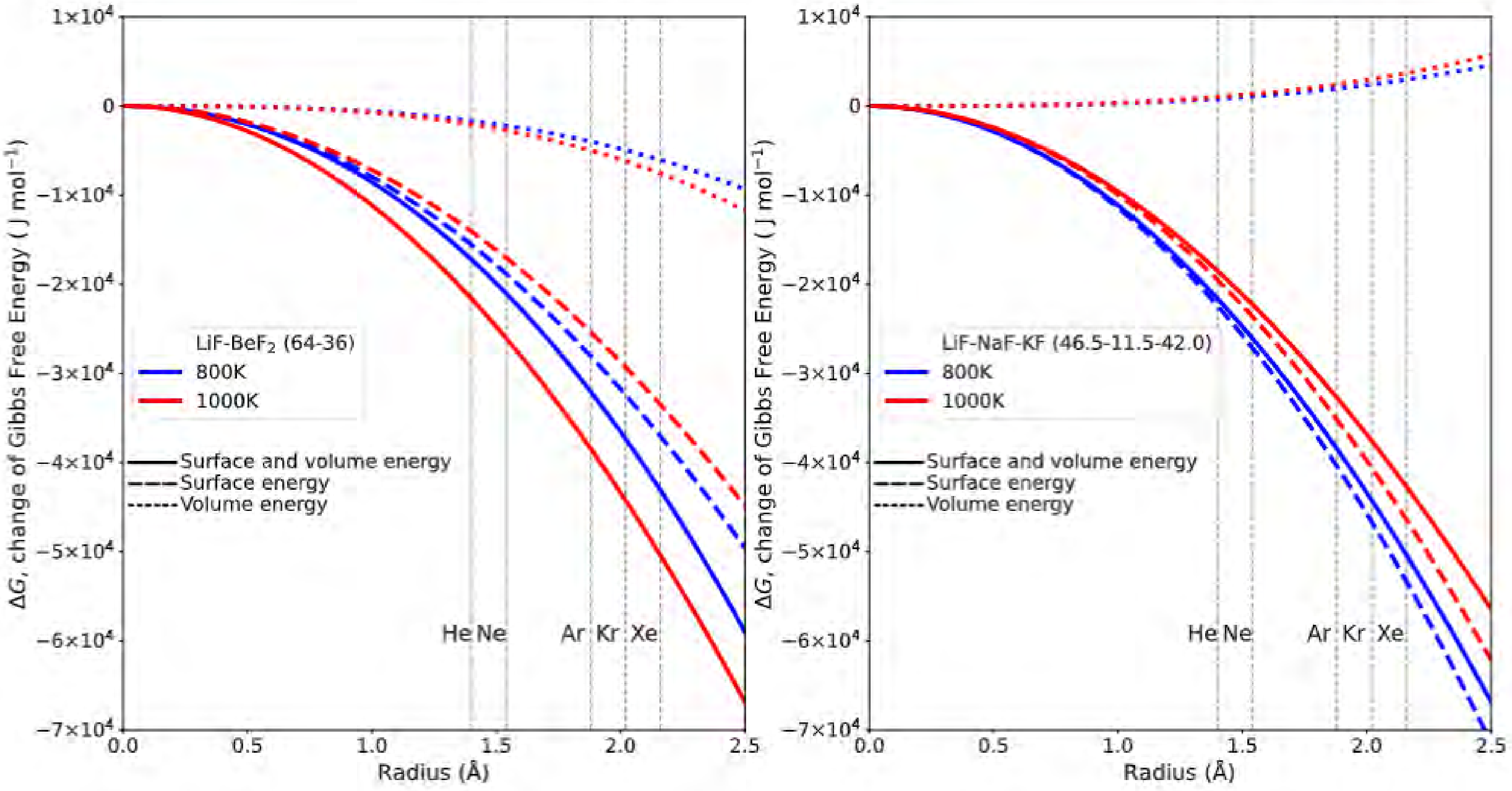


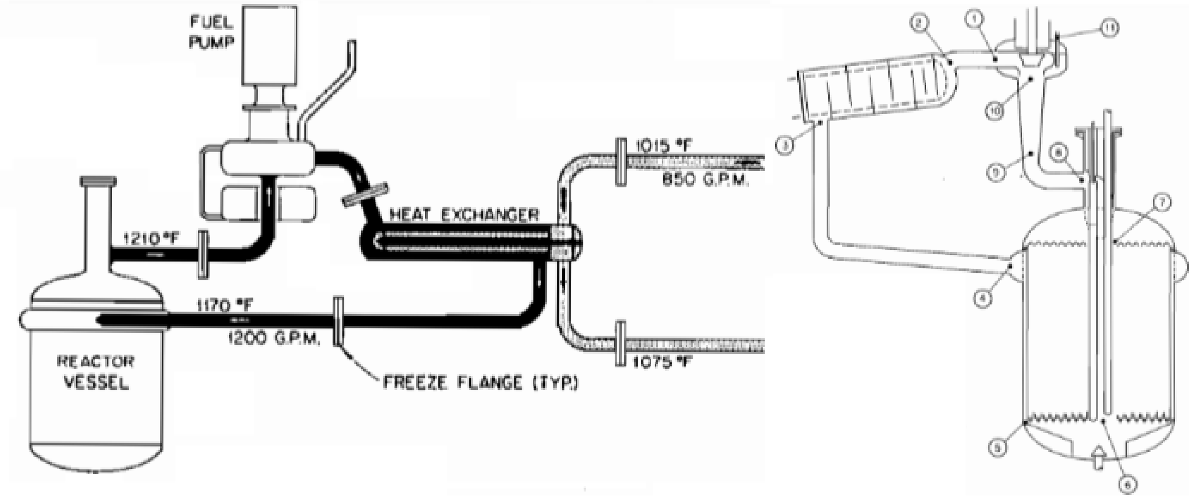
Table 1. The regression model's parameters, including R-squared and reduced chi-square and surface tension [erg/cm^2] (ref.[8]) are presented. The reduced chi-squared value is obtained by dividing the chi-squared value by the degrees of freedom (ν).

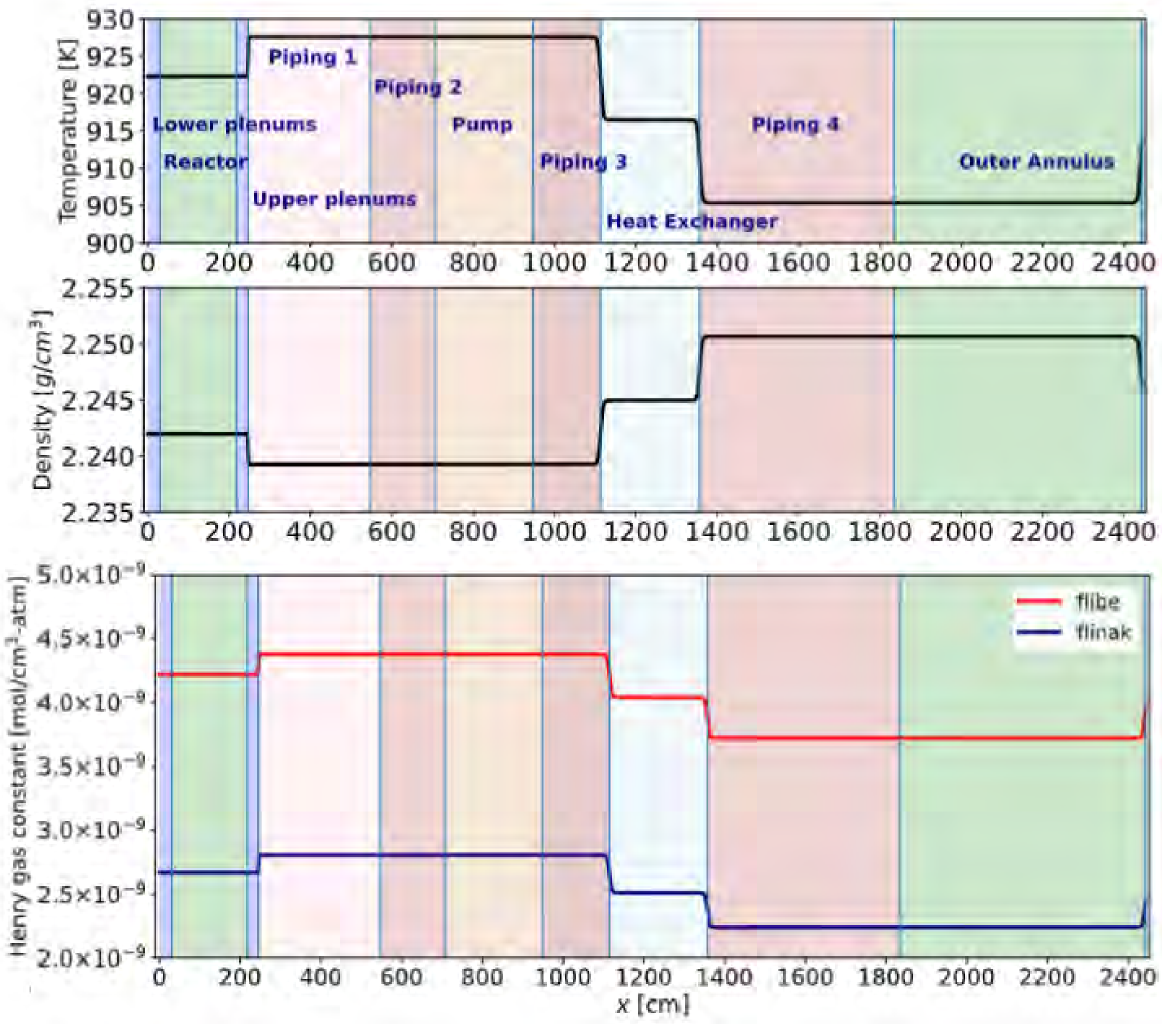
Parameter	$2LiF\text{-}BeF_2$	LiF-NaF-KF
R^2	0.9988	0.9841
χ^2_ν	144.2	162.4
α	-3.3584 ± 0.0645	-4.6541 ± 0.0938
β	-0.0215 ± 0.0016	0.0105 ± 0.0023
K_H^0	$7.8622\times10^{-7} \pm 0.2190\times10^{-7}$	$1.4246\times10^{-6} \pm 0.0644\times10^{-6}$
Equation (3)	$2LiF\text{-}BeF_2$	LiF-NaF-KF
$\partial\gamma(T)/\partial T$	-0.09	-0.0788
γ_0	235.5	237.0

		$2LiF\text{-}BeF_2$				LiF-NaF-KF			
	van der Waals	Model	$\ln(K_H^e)$			Model	$\ln(K_H^e)$		
Noble gas	radius (Å) (ref.[10])	ΔH	ΔH	ΔS	RPD	ΔH	ΔH	ΔS	RPD
He	1.40	21513.2	21657.2[8]	108.3	0.7	29635.0	28153.6[8]	100.7	5.1
			22568.9[9]	109.3	4.8	—	—	—	—
Ne	1.54	26031.0	24802.4[8]	111.8	4.8	35858.4	36746.6[8]	98.8	2.4
Ar	1.88	38794.0	36707.8[8]	111.0	5.5	53439.8	51669.7[8]	95.0	3.4
Kr	2.02	44787.0	—	—	—	61695.3	—	—	—
Xe	2.16	51210.2	51630.4[8]	106.1	0.8	70543.4	—	—	—



The change in Gibbs free energy within the 2LiF-BeF_2 and LiF-NaF-KF system is closely tied to the van der Waals radius. The radius for each noble gas in the system involves an evaluation of the two key components of Gibbs free energy analysis: volume energy and surface energy. Volume energy gives the potential for a phase transition---either evaporation or condensation--- to occur. Whereas surface energy quantifies the energy necessary for interface formation. The surface and volume energies are clearly shown along with the cumulative sum.





- The Mole code predicts the formation of fouling, erosion, and corrosion in molten salt reactor (MSR) fuel cycle loops and flow loops with thermophysical or thermochemical properties and phase equilibrium or transitions
- The Mole code performs macroscale/mesoscale diffusion and coupling with reactor codes to solve eigenvalue problems and perform transient analysis with improved fidelity for MSR safety analysis
- Decay and the transmutation of nuclides can be used to calculate the transition of the parent nucleus to a daughter nucleus of a static or dynamic radioisotope
    1. Bateman equations with/without advection with fission fragments and neutron sources
- Salt Dynamics for noble metals and noble gases
    1. Solid-liquid solution for convective mass transfer
    2. Salt interface in liquid–gas (bubble) transition for convective mass transfer
    3. Liquid species depositions on wall for convective mass transfer

Summary

- Gibbs free energy models tailored for noble gas behavior are examined, with a focus on temperature-dependent processes.
- Regression analysis is conducted to ascertain model parameters, consistently applied in calculating noble gas solubility within Flibe and Flinak.
- The impact of van der Waals radius on these parameters is noted.
- Physicochemical parameters are correlated with Gibbs energy, demonstrating significant alignment with experimental data.
- Forecasts for noble gas solubility are subsequently developed.

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Molten Salt Reactor PROGRAM

Modeling of ORNL salt experimental facilities

Robert Salko and Daniel Orea

Oak Ridge National Laboratory

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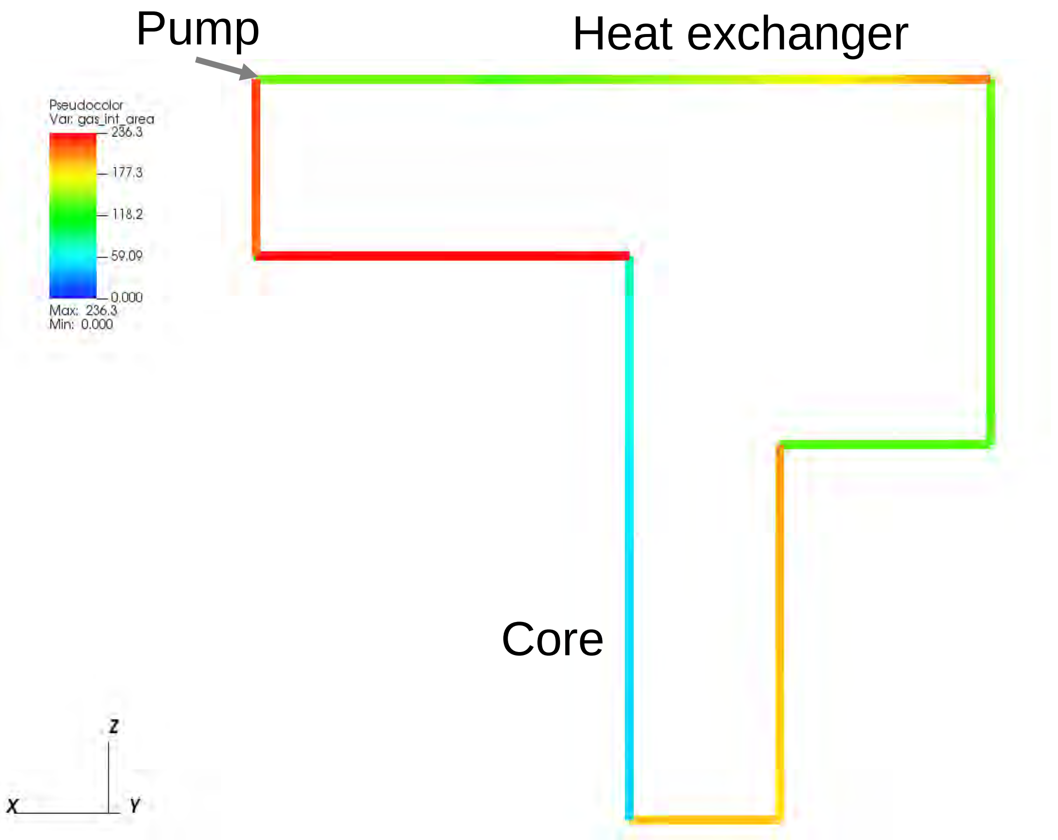
SAM System Code

- SAM is a system-scale thermal-hydraulic modeling tool written using the MOOSE framework and developed by ANL
- Solution of mass, momentum, and energy equations on 1D mesh
- Modeling capabilities were expanded by implementing a 4-equation drift flux model
- Incorporation of MSTDB-TP fluid properties through the Saline API

$$u_g = C_0 j + u_{gj}$$

Gas velocity calculated using drift-flux model, where gas distribution is dependent on salt viscosity and drift velocity is dependent on surface tension

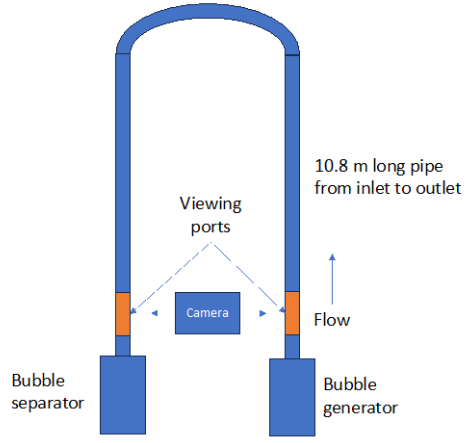


SAM prediction of interfacial area distribution in MSRE

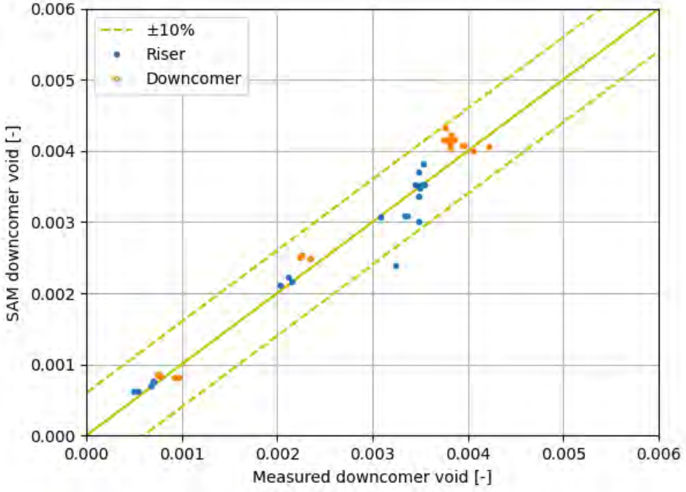
SAM gas model assessment

Model terms	Mass transient (III.A)	Momentum transient (III.B)	Energy transient (III.C)	Momentum advection (III.D)	Energy advection (III.E)	Drift flux tube (III.F)
Transient mixture mass	x					
Transient gas mass	x					
Transient mixture momentum		x				
Transient mixture energy			x			
Mixture mass advection	x	x		x		
Gas mass advection	x	x		x		
Mixture momentum advection		x		x		
Mixture energy advection				x	x	
Gas drift flux						x

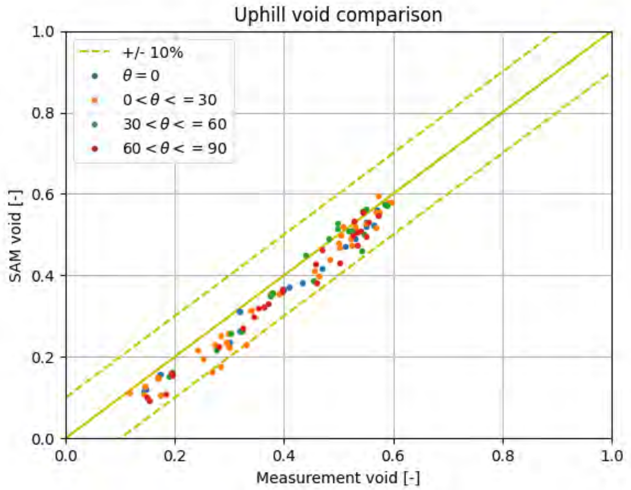
Code verification performed for a series of two-phase problems[1]



Kress[2] facility



SAM prediction of void in Kress



SAM prediction of void in air/water tests performed in tubes with various angles of inclination[3]

1. Salko, R, et al., “Implementation of a drift flux model into SAM with development of a verification and validation testing suite for modeling of noncondensable gas mixtures”, submitted to Nuclear Technology, 2024.
2. T. Kress, “Mass Transfer Between Small Bubbles and Liquids in Cocurrent Turbulent Pipeline Flow,” ORNL-TM-3718, 1972.
3. H. Beggs, “An experimental Study of Two-Phase Flow in Inclined Pipes,” PhD Thesis, The University of Tulsa, 1972.

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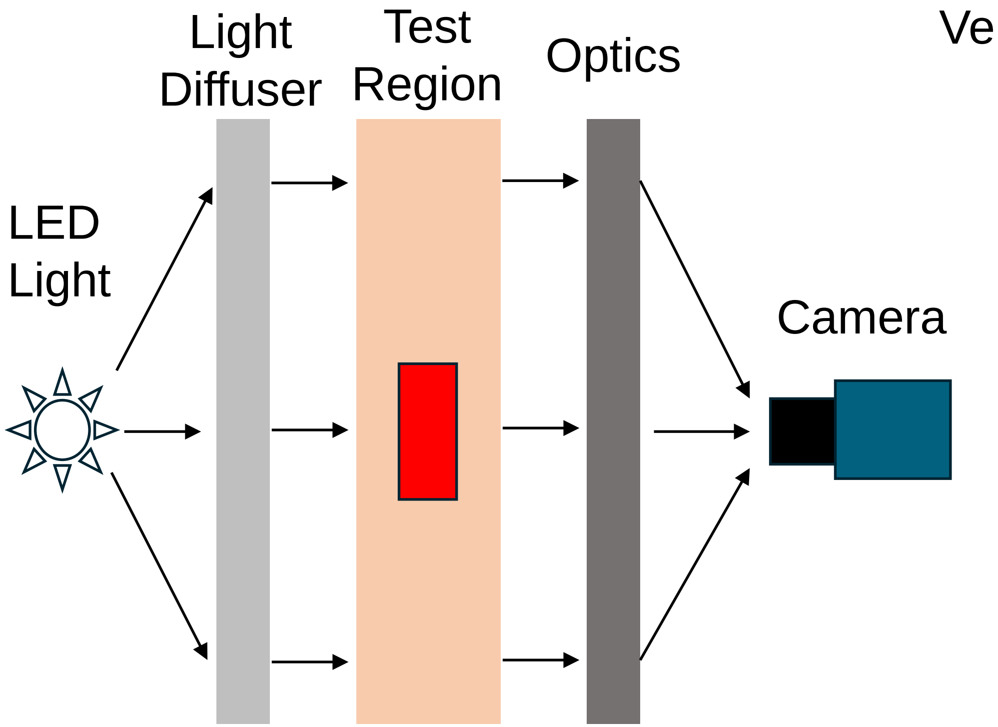
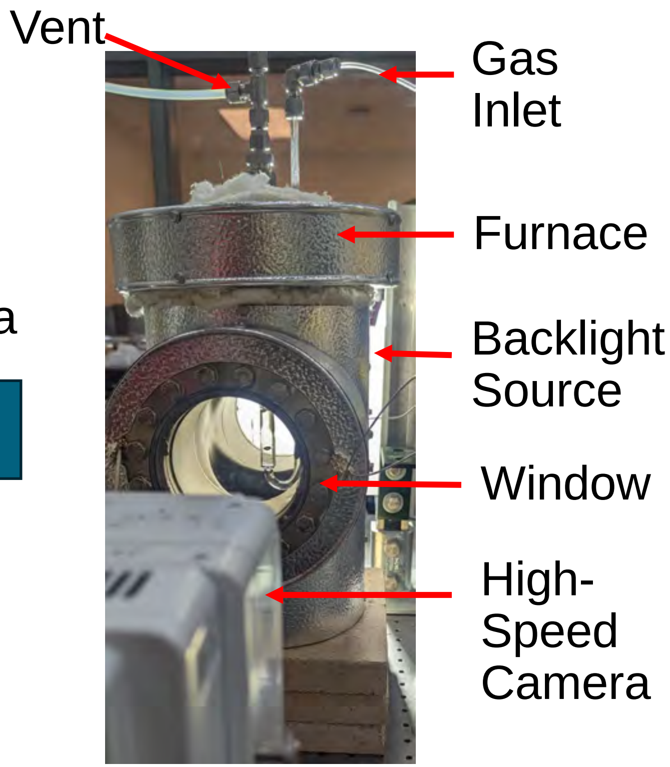
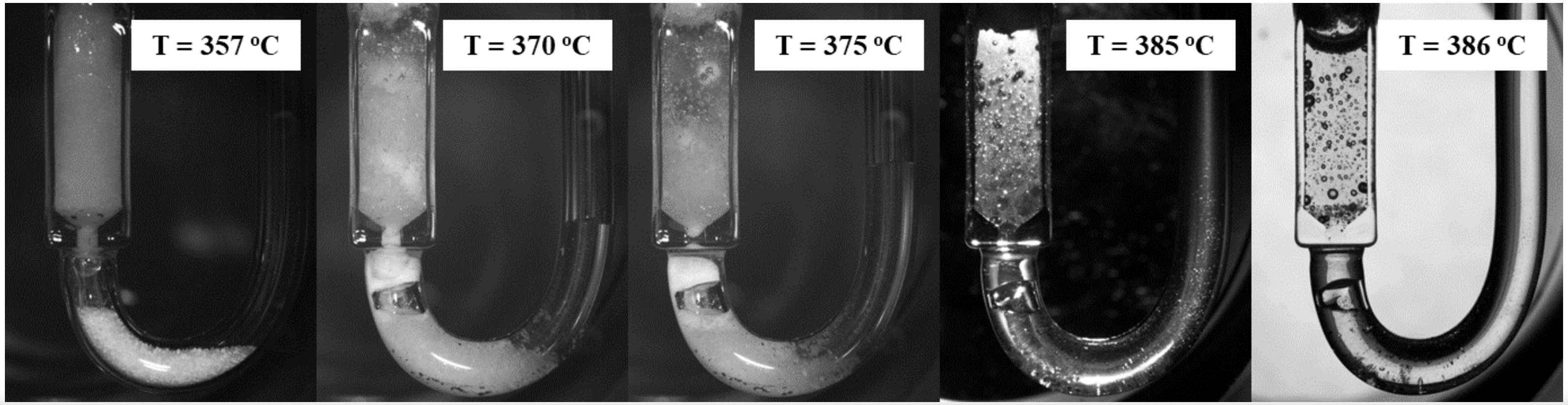
Importance of Noble Gas Transport

- Gas transport is important for the safe operation of MSRs with regards to fission transport and removal.
- The goal of the test series is to collect data on gas transport through molten salt, particularly, bubble size, rise velocity, and coalescence.
- Data will be used for model development / validation of radionuclide transport, and to provide information for licensing requirements regarding MSRs.
- Non-intrusive optical measurements deployed to visualize the salt.





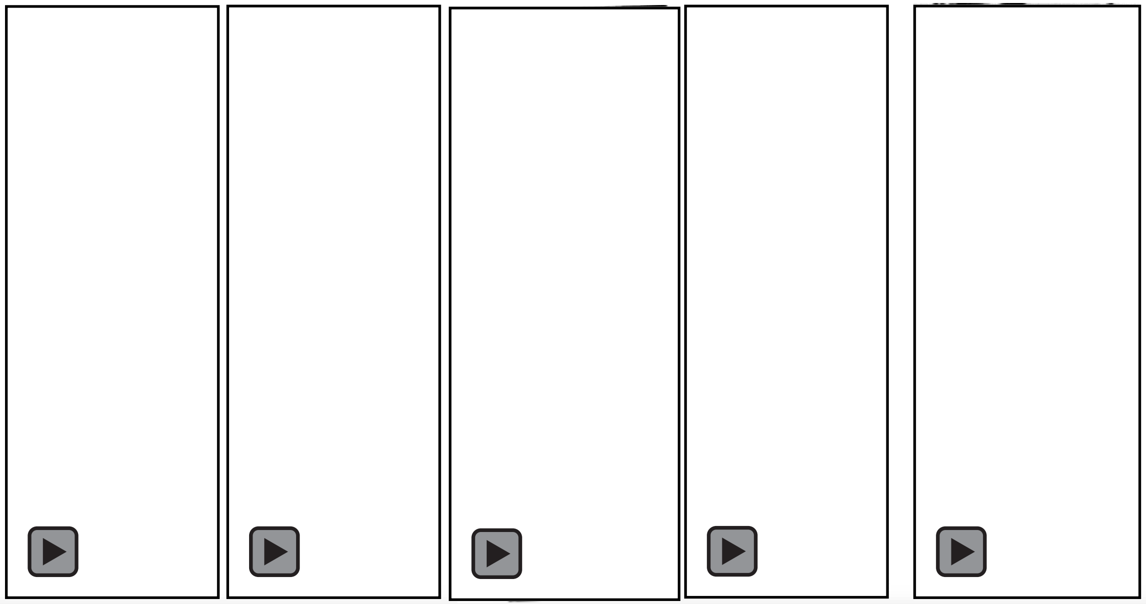
0.6 LiCl / 0.4 KCl [mol%]



Results from 10 mL Test Cell

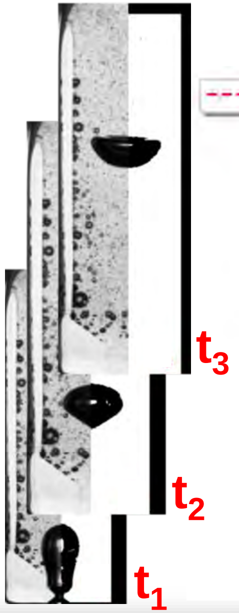
- Melting of the LiCl-KCl was recorded
- Helium injected at multiple flow rates
- Shadowgraph technique proved to be successful for the tracking of bubbles
- Comparison between experiment and models highlighted discrepancies
- Wall effects were non-negligible due to bubble size

Melt **2.5 ccm** **5.0 ccm** **10.0 ccm** **Coalescence 25.0 ccm**

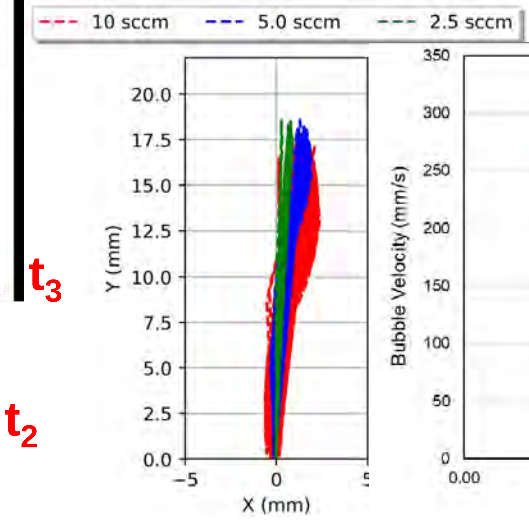


Experiment Helium Bubble Characteristics

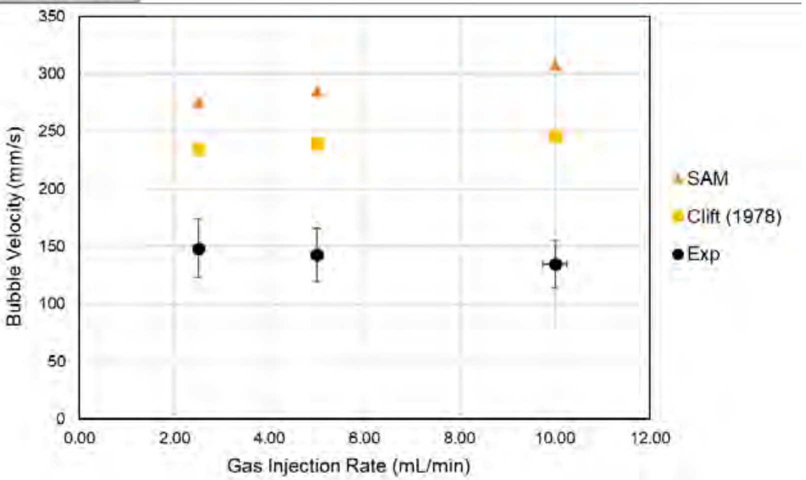
Flow Rate (ccm)	Diameter (mm)	Bubble Velocity (mm/s)	Eo (-)	Mo (-)	Ar (-)	We (-)	Re (-)
2.50	2.88	148.38	79.98	9.99E-06	4.00E-05	0.81	419.37
5.00	3.01	142.63	87.38	9.99E-06	4.58E-05	0.80	422.39
10.00	3.35	134.44	108.48	9.99E-06	6.33E-05	0.78	442.45



Bubble Tracks



Comparison between models and experiment



McFarlane, J., et al. "Design of Instrumentation for Noble Gas Transport in LSTL Needed for Model Development" Report. ORNL TM-2023-3138 (2023).

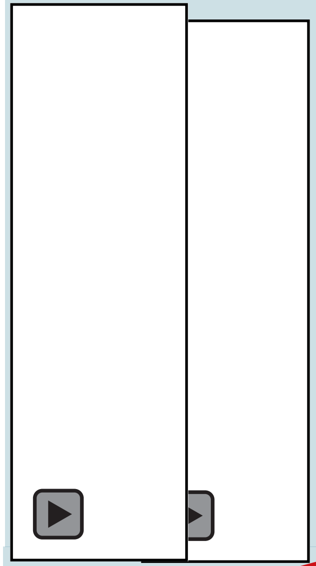
Clift, Roland. "Bubbles." Drops and Particles (1978).

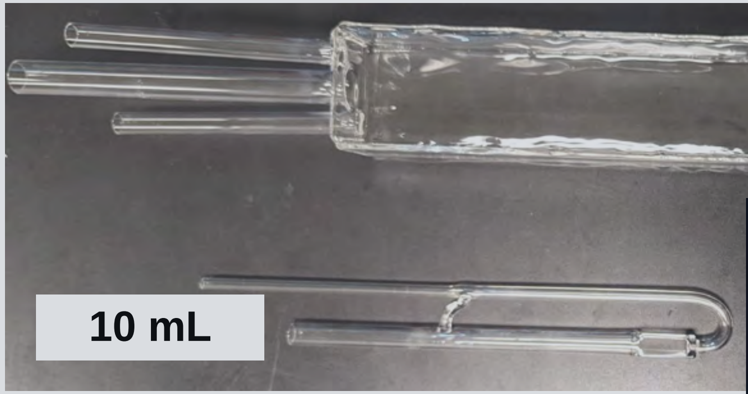
FY24: Current Effort to Improve Experiment

- Lessons learned from FY23 test series are being considered to further improve test apparatus.
  - Smaller bubbles needed to represent MSRE and MSRs in general.
  - Greater salt volume required to minimize wall effect and allow terminal velocity to be reached
- Custom capillary gas injector constructed
- Quartz test cell fabricated in-house by glassblowers
- Salt loading / storage pot added to transfer salt during and after experiments

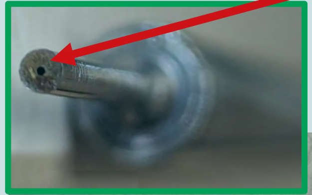
Capillary Bubbler Hydro Test

Single **Burst**

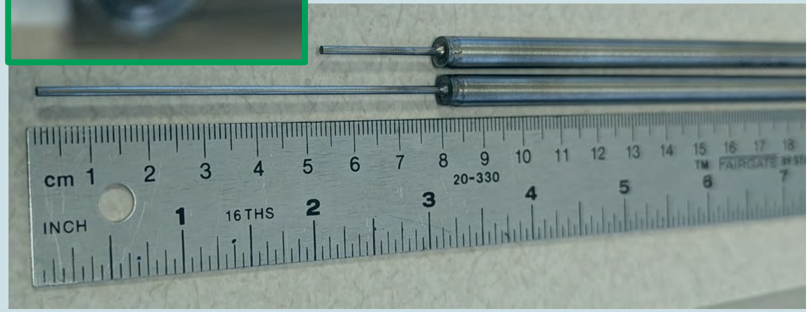


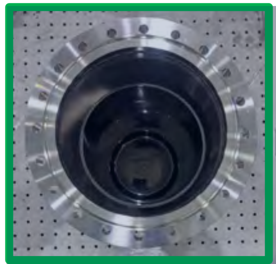


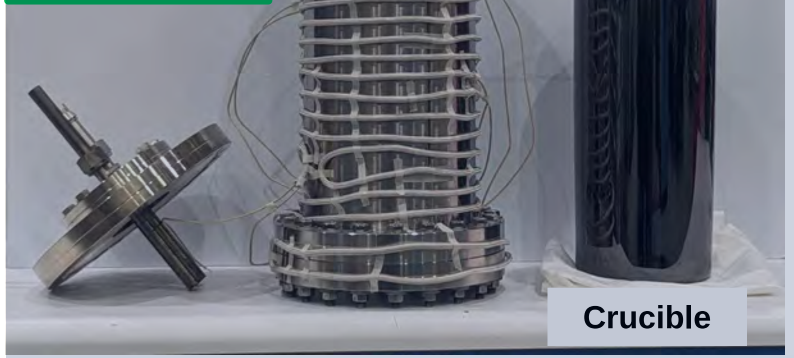
- New test cell sized to fit in existing custom viewing furnace



- **Two bubblers of different lengths**
- **Bubble range: 0.5 – 1.0 mm**
- **ID: 0.3 mm**

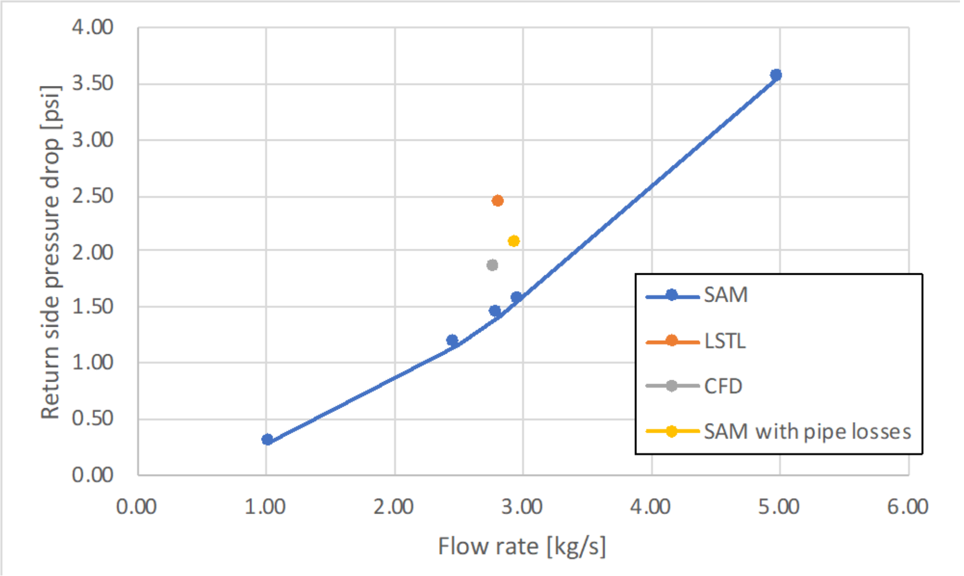




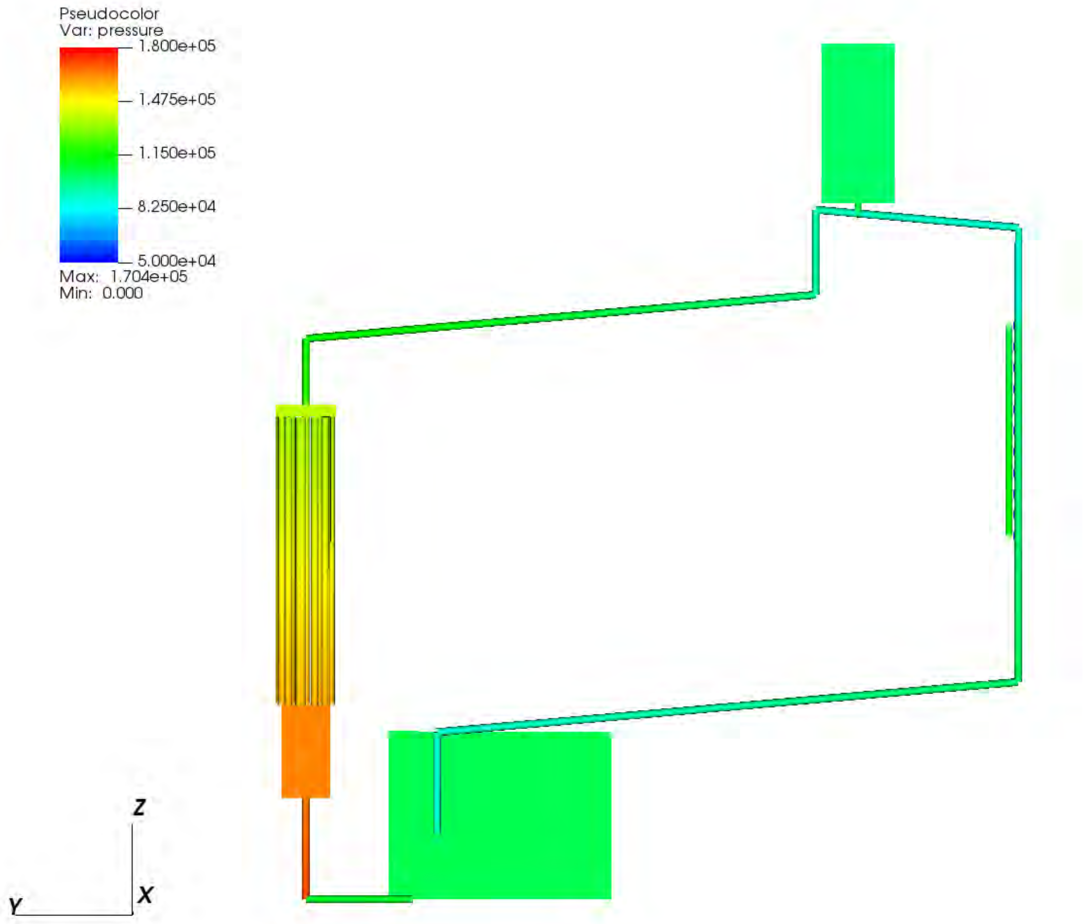


LSTL Model

- SAM model of LSTL facility created
- Existing TRACE model used for determination of geometry



Comparison of SAM prediction (no form losses) to CFD and experimental results



Pressure distribution predicted by SAM in LSTL

Future Work

SAM Gas Transport Model

- SAM model is being improved with addition of interfacial area transport equation
- Model new bubble injection tests
- Model FASTR loop
- New test cases will be needed from LSTL for tuning of model losses
- Bubble transport validation can be improved with additional data:
  - Flowing salt
  - Additional types of salts and gases
  - Impact of contaminants on bubble behavior
  - Measurement of gas void

Advancing Experimental Capabilities

- Custom furnace upgrades to allow additional measurements techniques
  - Particle Tracking Velocimetry (PTV)
  - Ultrasonic Sensors – Void fraction measurements
- Construction of optical clear test cells to accommodate variety of salts
- Transition from stagnant to flowing salt
  - Incorporate custom viewing apparatus design in a closed loop
  - Requires salt compatible materials
  - Design considerations needed to allow optical access

Thank you

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mcfarlanej@ornl.gov

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