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OAK RIDGE National Laboratory

Molten Salt Reactor PROGRAM

Overview of Technology Development and Demonstration

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Oak Ridge National Laboratory

Annual MSR Campaign Review Meeting 2-4 May 2023

R&D Goals and Overview of FY23 Plans

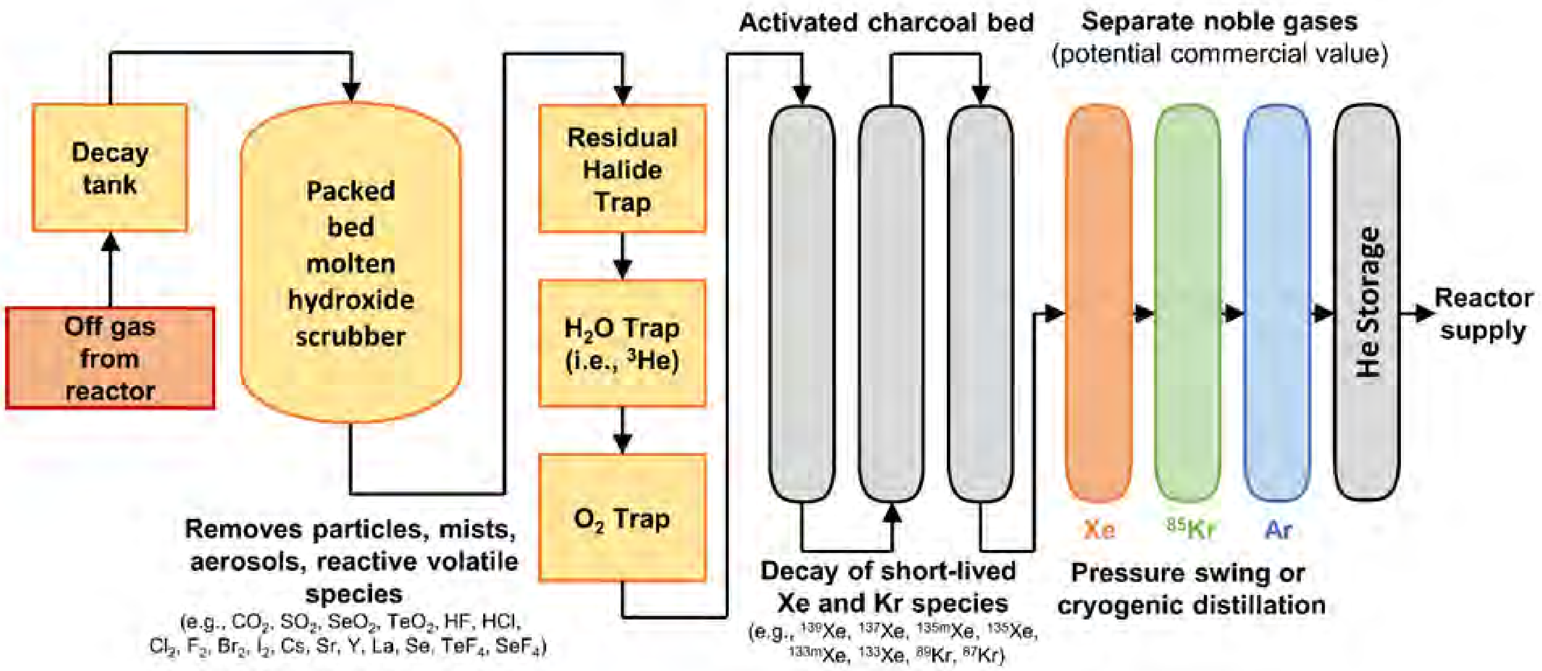
Obtain data on radionuclide gas and aerosol transport

- Large-scale test loop (ORNL – K. Robb)
- Sensor development and materials testing
  - Redox sensors (ANL – N. Hoyt)
  - MSR off-gas and tritium measurement (PNNL – A. Lines)
  - Tritium transport in pumped loop (INL – T. Fuerst)
  - Molten hydroxide scrubber (ORNL – S. Chapel, J. McFarlane)
- LIBS measurements applied to gas/liquid phases
  - Spectroscopy development for off-gas measurements (ORNL – H. Andrews)
  - MOF for noble gas separations (PNNL – P. Thallapally)
- Interfacial measurements (ORNL – J. McFarlane, K. Robb, J. Moon, H. Andrews)
  - Bubble and droplet behavior
  - Contact angle and surface tension

Modeling, Validation, Accident Analysis

- Modeling of liquid $\rightarrow$ vapor transport
  - Gas solubilities and transport (NEAMS – K. Lee, Thermal hydraulic model of LSTL – B. Salko)
- Accident analysis – Salt spill scenario (ANL – S. Thomas)

Focus for radionuclide transport is the MSR off-gas system



- Off-gas provides the pressure boundary for MSRs
- Volatilities dependent on FP speciation & salt conditions (chemical and physical)
- Requires online monitoring, testing of sensors in loops headspaces
- Demonstration of operation & components
- Compare data with models
- Off-gas has synergies with salt accident research (salt spill)

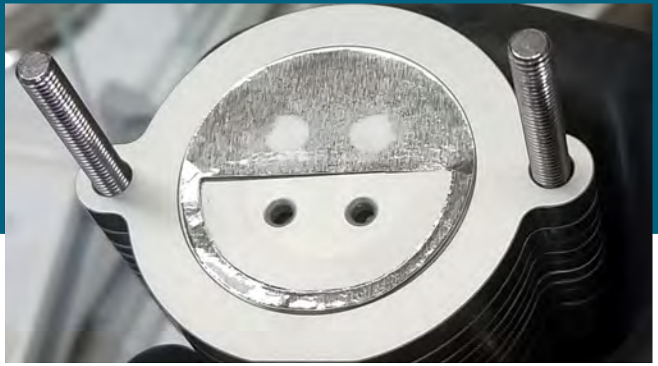
Large Scale Test Loop (LSTL) Testing of Sensors in Pumped Loop

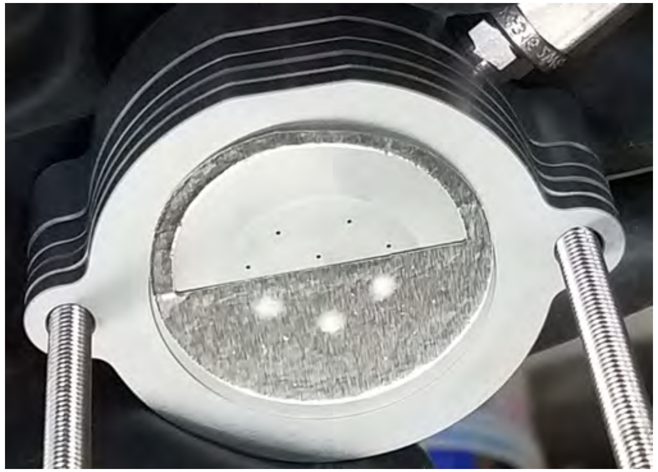
Kevin Robb (ORNL)

- FLiNaK heated > 600°C and pumped through LSTL
- Demonstration of operation & components
- Sensors placed in loop headspaces
  - Optics for Raman probe
  - Cascade impactor for aerosol loading
- Redox sensor in salt

Aerosols Transported in Head Space – Hunter Andrews (ORNL)

- Impactor stages retrieved and stored under inert conditions
- Cascade impactor stages to be analyzed by LIBS and ICP-MS



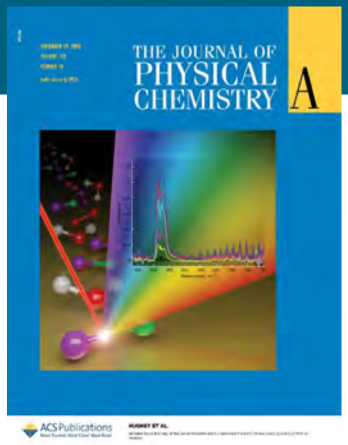


Optical Sensors' Materials Testing
Amanda Lines & Sam Bryan (PNNL)

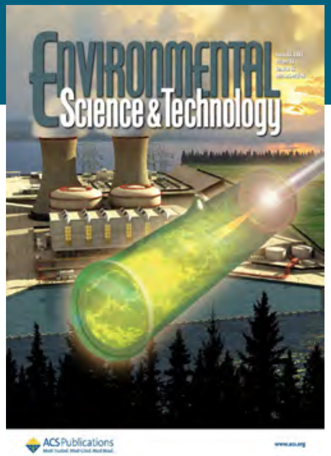
- Advancing gas phase probes to improve limits of detection and enable more flexible application and integration

- Collaborating with ORNL to test probe components within the LSTL

Leveraging advancements in iodine monitoring to



Hughey, K. D.; Bradley, A. M.; Tonkyn, R. G.; Felmy, H. M.; Blake, T. A.; Bryan, S. A.; Johnson, T. J.; Lines, A. M., ***J Phys Chem A*** *2020, 124* (46), 9578-9588.

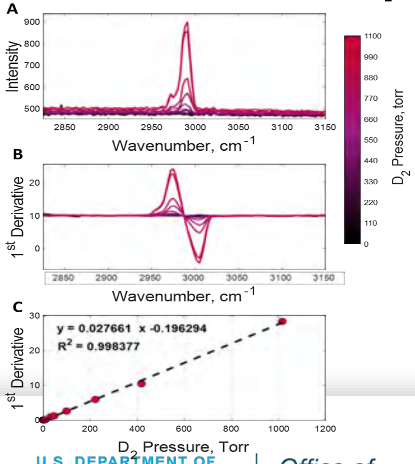


Felmy, H. M.; Clifford, A. J.; Medina, A. S.; Cox, R. M.; Wilson, J. M.; Lines, A. M.; Bryan, S. A. ***Environ Sci Technol*** *2021, 55, 6, 3898–3908.*

Dual phase gas treatment

Adan Schafer Medina, Heather M. Felmy, Molly E. Vitale-Sullivan, Hope E. Lackey, Shirmir D. Branch, Samuel A. Bryan, and Amanda M. Lines ***ACS Omega*** 2022 7 (44), 40456-40465

H isotope monitoring



405 nm 532 nm 671 nm

Molten Hydroxide Scrubber for Acidic Gas/Aerosol Capture
Shay Chapel (ORNL)

- Advantages
  - Hydroxides are radiation resistant
  - Iodine captured as iodate. Analysis by ICP-MS, UV-Vis
  - Online replacement of scrubbing agent
- Disadvantages
  - Introduces another salt chemistry
  - Residual H_2O and CO_2
- To be tested summer 2023

Iodine Chemistry and Analysis

$KIO_3 + 5NaI + 6H_2SO_4 \rightarrow 3I_2 + 3H_2O$

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

Excess iodide stabilizes the I_2 in solution – yellow color.

$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$

Titrate to determine I_2 concentration (starch indicator).

Tritration data agree with ICP-MS analysis

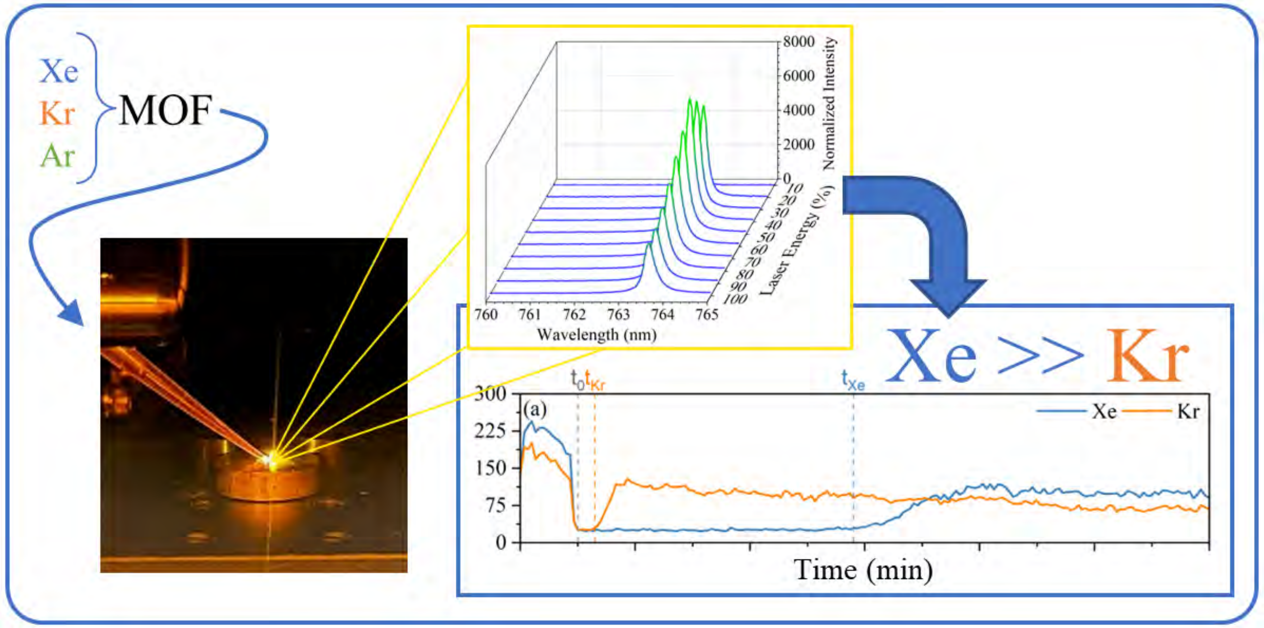
ICP-MS corroborates UV-Visible analysis

NE-43 fuel cycle project, Katie Johnson (ORNL)

Role of radiolysis on formation of I_2 not yet investigated.

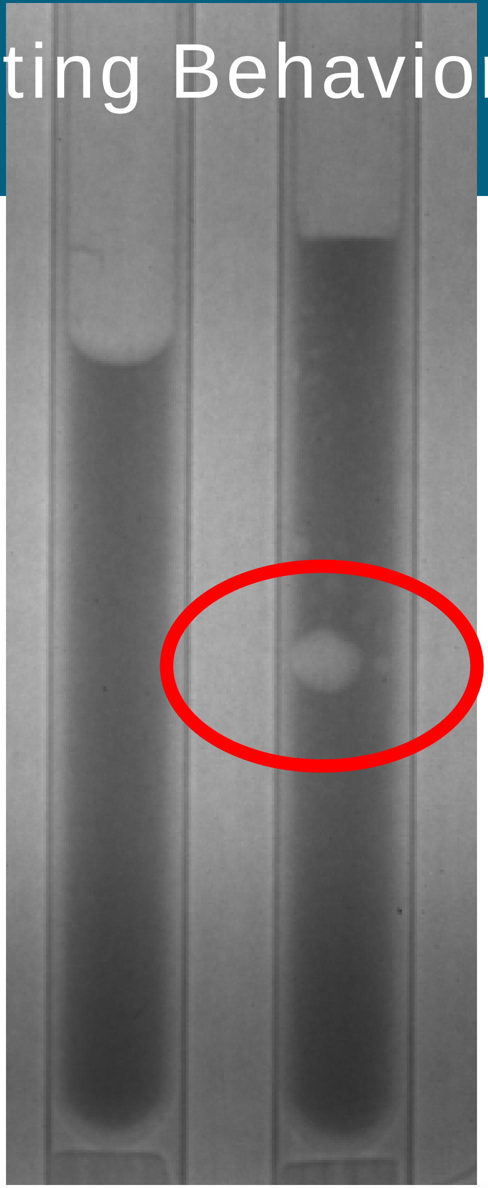
Xenon Monitoring – FY22 Activities
FY23 funding started March 2023

- A PNNL designed and manufactured metal organic framework (MOF) was sent to ORNL where Xe and Kr breakthrough tests were monitored via laser-induced breakdown spectroscopy.
- Cut out plot shows the LIBS signal breakthrough profiles used to calculate MOF Xe selectivity.
  - Kr always breaks through the MOF far faster than Xe despite changes in gas composition.
  - This illustrates the MOFs superior Xe selectivity.
- This was the first demonstration of LIBS being used to monitor and evaluate radionuclide capture systems for a molten salt reactor off-gas.



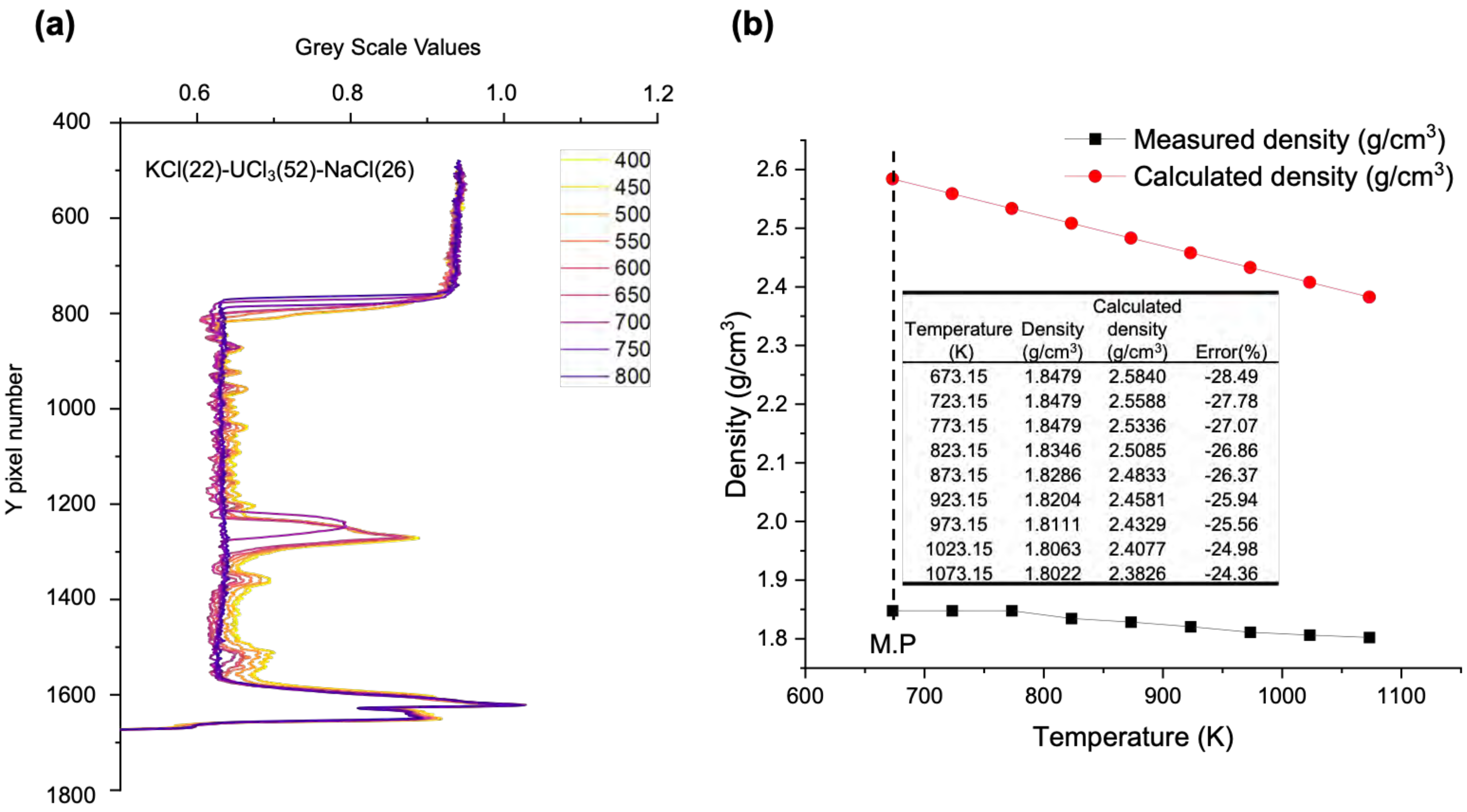
Molten Salts Have High Surface Tension and Wetting Behavior

- Affects measurements
  - Thermophysical properties
  - Solubility
- Affects reactor performance
  - Void behavior
  - Fission product transport
- Optical measurements planned for bubble transport in molten chloride salt



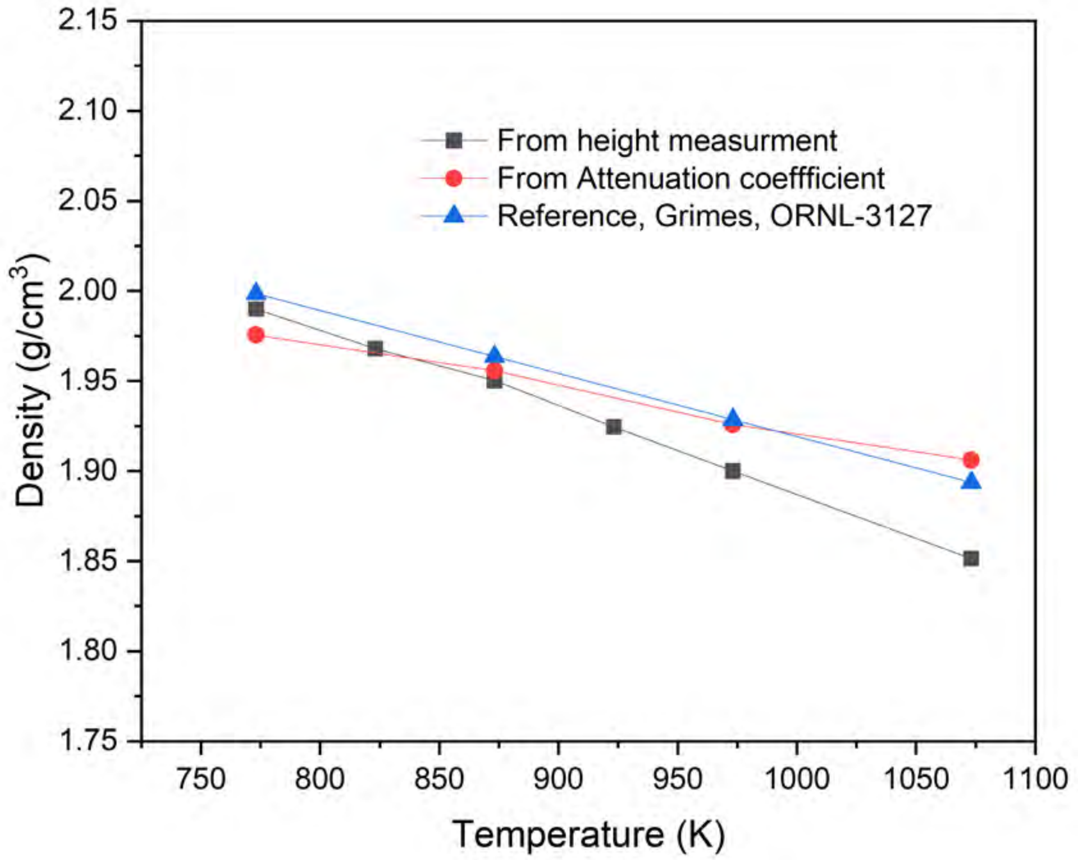
Densities – Voids & bubbles add uncertainty to results

- Density from volume expansion
- Compared with Redlich-Kister model
- Some systems shows large uncertainty



Temperature (K)	Density (g/cm^3)	Calculated density (g/cm^3)	Error(%)
673.15	1.8479	2.5840	-28.49
723.15	1.8479	2.5588	-27.78
773.15	1.8479	2.5336	-27.07
823.15	1.8346	2.5085	-26.86
873.15	1.8286	2.4833	-26.37
923.15	1.8204	2.4581	-25.94
973.15	1.8111	2.4329	-25.56
1023.15	1.8063	2.4077	-24.98
1073.15	1.8022	2.3826	-24.36

Use neutron attenuation to determine density

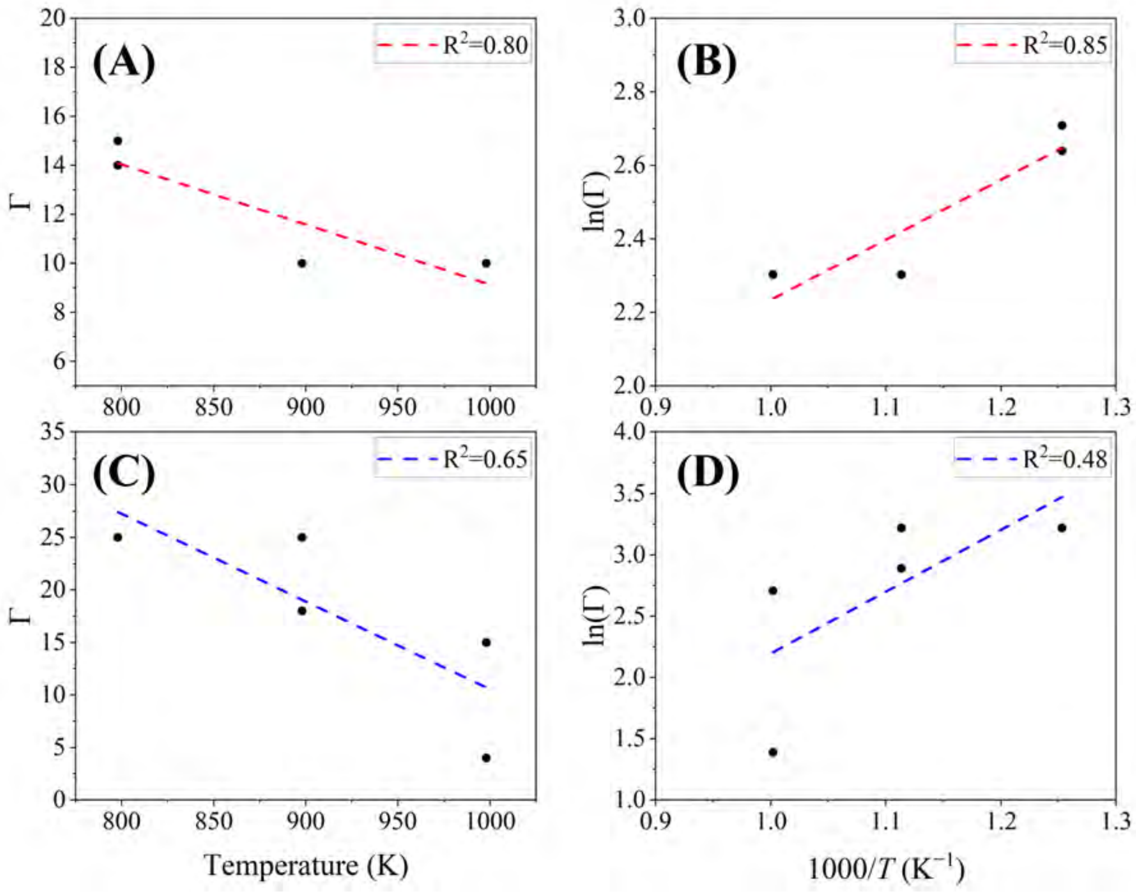


- Good agreement with Grimes with much smaller sample.
- Phase behavior, salt component segregation also available.

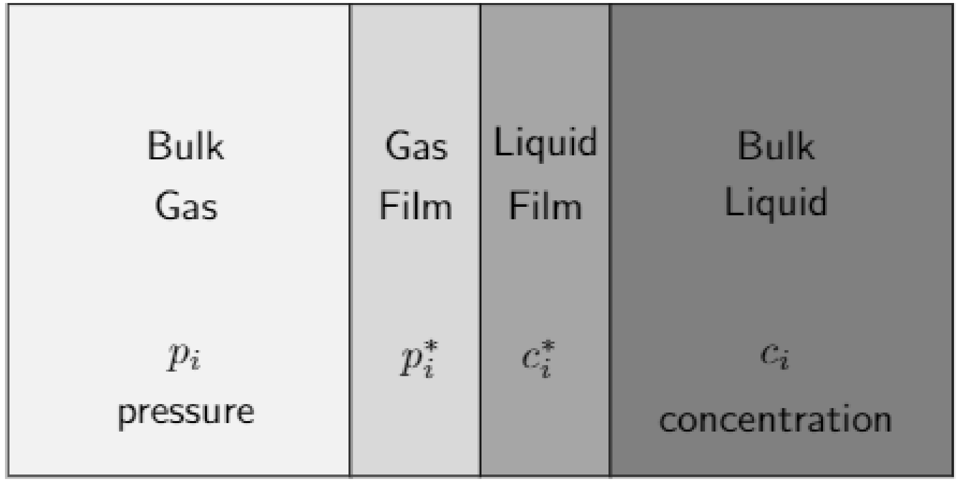
Gas solubilities measurements affected by wetting of containers (ARPA-E Meitner award) (ORNL & Moltex Energy)

- Solubility from pressure drop in isothermal, isochoric system
- Change in pressure related to Henry's Law constant
- Kinetic model of uptake (Librovich et al.) modified by Weber & Talyor (2022)

$$S_i(t) = \Gamma_i A \left(\frac{RT}{2\pi M_i}\right)^{\frac{1}{2}} \left(C_{g_i}^* - C_{g_i}(t)\right)$$



Mass Transfer across a Gas-Liquid Interface



$$c_i^* = p_i H$$

$$p_i^* = c_i / H$$

Figure 1:The gas-liquid interface of thefilm theory expressed in partial pressuresand concentrations

We have considered the mechanism of mass transfer between phases without convection. The overall mass-transfer coefficients were defined by $c_l = p_g H = c_g HRT$ and $K_G = K_L H$ where $p_g = c_g RT$ and $R = 82.05746[\mathrm{cm}^3 \cdot \mathrm{atm}/(\mathrm{K} \cdot \mathrm{mole})]$

$$\text{Liquid transport:}$$

$$\frac{\partial c_l}{\partial t} = K_L a \left(c_g HRT - c_l\right)$$

$$\text{Gas transport:}$$

$$\frac{\partial c_g}{\partial t} = K_G a \left(c_g RT - c_l / H\right)$$

where c is the concentration of species in liquid, p is partial pressure of species in gas phase, and H is Henry's gas constant. a is gas-liquid interfacial area per unit volume.

The overall mass transfer coefficients, K_G - gas phase and K_L - liquid phase are defined as:

$$\frac{1}{K_G} = \frac{1}{k_l H} + \frac{1}{k_g} \qquad \frac{1}{K_L} = \frac{1}{k_l} + \frac{H}{k_g}$$

Henry's gas constant calculations versus measurements

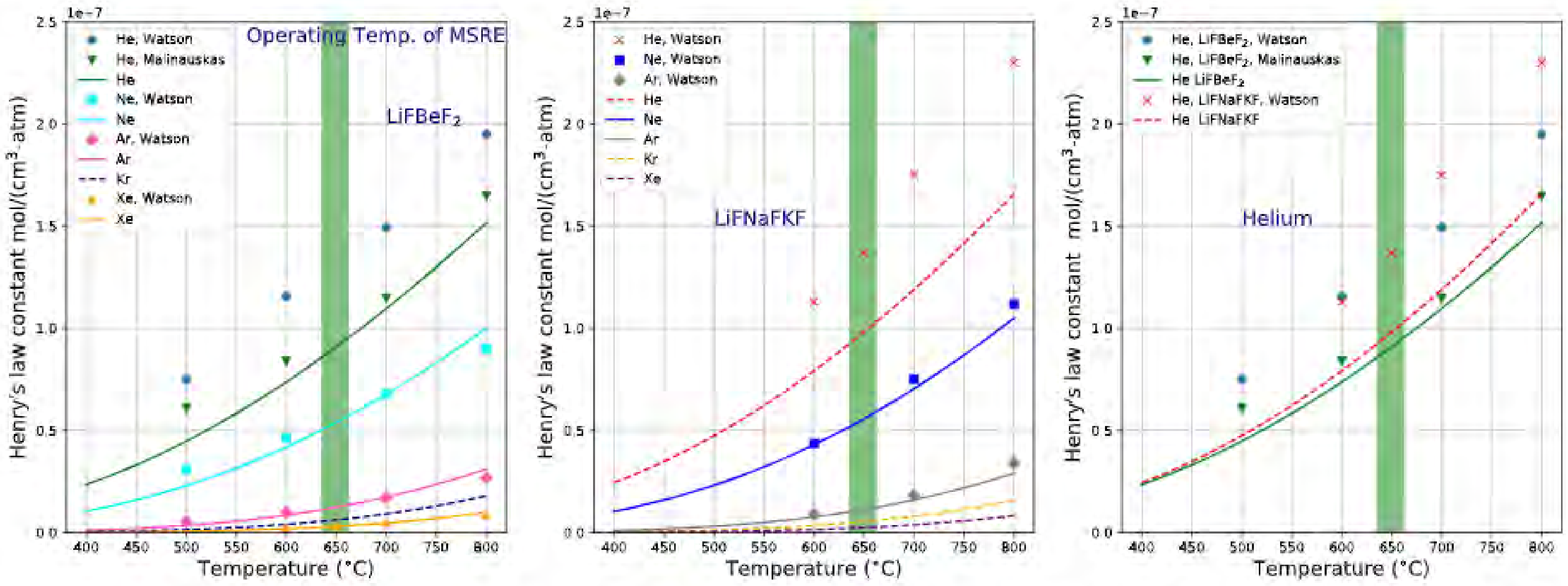


Figure 2: Henry's gas constant dependant on temperature (left $\mathrm{LiF\text{-}BeF_2}$, right, $\mathrm{LiF\text{-}NaF\text{-}KF}$)

The entropy change for an equilibrium process can be explained by the Gibbs free energy.

$$\Delta G = \Delta\mathcal{H} - T\Delta S$$

where $\Delta\mathcal{H}$ is Enthalpy change, and ΔS is Entropy change, and T is temperature in K. When the temperature of a system changes, the Henry's constant changes and is related to the Van 't Hoff equation. The least squares regression can find the arbitrary number, α and β.

$$\Delta G = RT\ln H = \alpha 4\pi r^2\gamma + \beta$$

where R is the ideal gas constant, r is Van der Waals radius, and γ is the surface tension.

- Gas diffusivity makes it difficult to determine which gas solute is the mixture from salt, air or vacuum involving flow through the pipes.
- Gas velocity is complex to define the system because Reynolds number is required to gas velocity.
- The overall gas mass transfer coefficient can be derived from Herny's gas constant. Thus Herny's gas constant can be considered as a key parameter for gas-liquid interface.
- When $(H/k_g)^{-1} \ll k_l^{-1}$, the overall mass transfer coefficients can be generalized to

$$K_L \approx k_l$$

$$K_G = K_L H$$

Variables governing bubble formation and transport

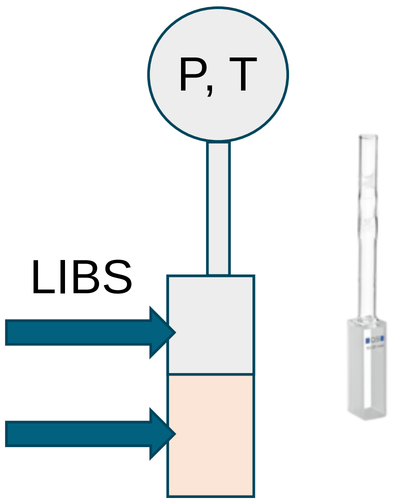
- Formation/size distribution
  - Concentration of solute in liquid phase
  - Concentration of solute in gas phase
  - Henry's law coefficients
  - Surface tension
- Transport
  - Bubble velocity
  - Pipe diameter & orientation
  - Densities of fluid and disperse phase
  - Viscosity of fluid
  - Liquid phase controlled axially-averaged mass transfer coefficients, k(l)
    - Schmidt number
    - Reynold's number
    - Sherwood number

Limiting conditions

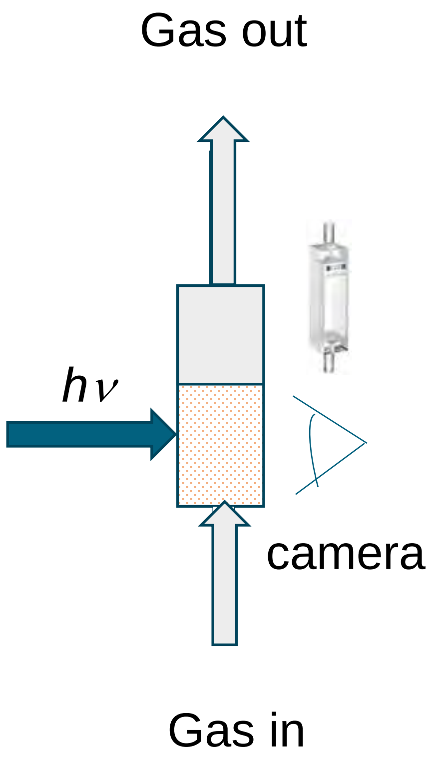
1. Very low Reynold's numbers
   E.g., Bubbles rising in a column, slow mechanical stirring
2. $Re_b>2$
   Bubbles transported by turbulent flow in loop

Small scale gas solubility/bubble formation tests

- Gas solubility
  - Salt premelted in tube
  - Seal salt in contact with known gas fraction
  - Heat salt
  - Allow to equilibrate
  - Measure partitioning between liquid and gas phases optically



- Bubble formation
  - Salt premelted in tube
  - Heat under vacuum and introduce gas flow
  - Track gas & bubble flow through salt with excitation and high speed camera
  - Bubble velocity & size distribution



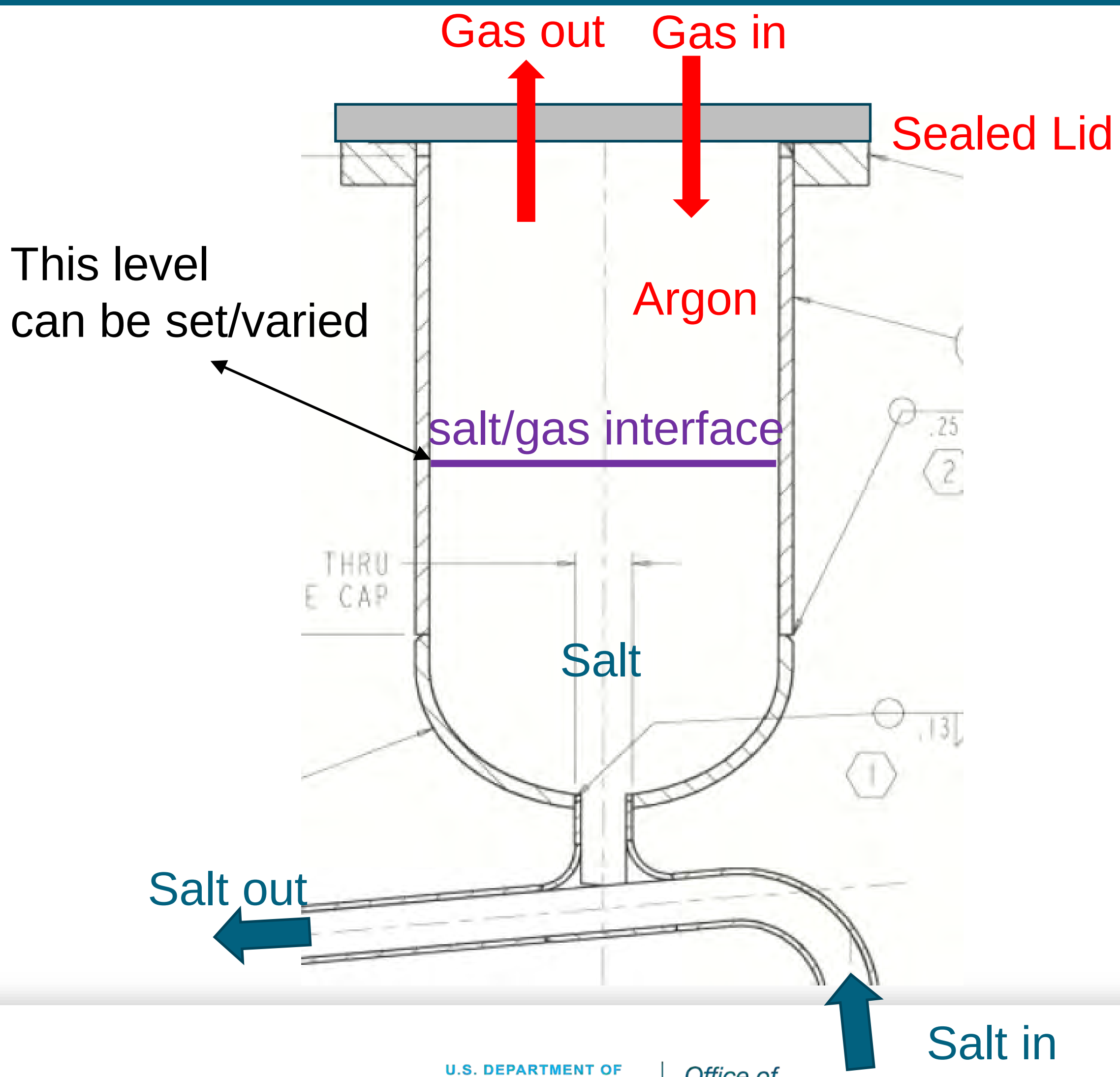
Validation data for bubble formation and transport

Assume:

- Argon gas flow of 100 sccm
- Salt is at 600 C and saturated with Xe, He, etc.
- Tank inner diameter = 7.98 inch
- Assume salt/gas interface is 10 inch below lid and assume bottom of tank is 15 inch below lid

Question:

- What is the expected concentration of Xe, He, etc. in the gas coming out?



Molten Salt Campaign – 2022/2023 Publications

- Andrews, H.B., et al. *Applied Spectroscopy* 76.8 (2022): 988-997.
- Andrews, H.B. et al. *Micromachines* 14.1 (2023): 82.
- Andrews, H.B. et al. *Frontiers in Energy Research* 10.1 (2023).
- Andrews, H.B. and Myhre, K.G. *Applied Spectroscopy* 76.8 (2022): 877-886.
- Felmy, H. M. et al.,. *Environ Sci Technol,* 55.6: (2021) 3898–3908.
- Myhre, K.G., et al, *Journal of Analytical Atomic Spectrometry* 37.8 (2022): 1629-1641.
- Hughey, K. D.; et al., *J Phys Chem A, 124.*46 (2020), 9578-9588.
- McFarlane, J., et al. *Frontiers in Energy Research*, DOI 10.3389/fenrg.2022.1102466 (2023).
- McFarlane, J. et al. Frontiers in Chemical Engineering, (2022) 10.3389/fceng.2022.811513 (2022)
- Medina, A.S., et al., *ACS Omega* 7.44 (2022), 40456-40465
- Moon, J. et al., *Ind. Eng. Chem. Res.*, (2022) DOI 10.1021/acs.iecr.2c02967
- Sprouster et al., ACS Applied Energy Materials 5, 8067-8074. (2022) DOI 10.1021/acsaem.2c00544

Molten Salt Campaign – 2022/2023 Presentations

- Andrews, H. et al. “Analysis of Aerosols and Gases Relevant to Molten Salt Reactor Off-Gas Monitoring Using Laser-Induced Breakdown Spectroscopy.” *Materials Research Society Conference*, 2022, Boston, MA.
- Andrews, H. “Recent Applications of Laser-Induced Breakdown Spectroscopy at Oak Ridge National Laboratory.” *SciX*, 2022, Cincinnati, OH.
- Andrews, H. et al. “Application of Laser-Induced Breakdown Spectroscopy for the Molten Salt Reactor Campaign” *ACS Fall Meeting*, 2022, Chicago, IL.
- Andrews, H. et al. “Development of a Laser-Induced Breakdown Spectroscopy Sensor for Molten Salt Reactor Off-Gas Stream.”
- Lee, K.O., “Mass Accountancy with the MOLE/GRIFFIN Code for the Molten Salt Reactor Experiment”, *MSR Workshop*, 2021, Oak Ridge, TN.
- McFarlane, J. and Riley, B. “Chemistry of Fission Products in Molten Salt Reactors and Uptake into Waste Forms”, *Materials Research Society Fall Meeting*, 2022, Boston MA.
- McFarlane, J. et al., “Noble Gas Solubility in Molten Salts”, *ACS Fall Meeting*, 2022, Chicago, IL.
- McFarlane, J., “Hazards Associated with Molten Salt Reactor Systems”, National Academy of Sciences, 2021.

2022/2023 Conference Involvement & Organization

ACS Fall Meeting 2023, Molten Salt Symposium Co-Chairs (H. Andrews and J. McFarlane)

- San Francisco, CA August 13-17
- Sessions on monitoring, redox chemistry and thermodynamics, radiation chemistry, material science, molten salt structure and dynamics, etc.

SciX 2023, LIBS Section Co-Chair (H. Andrews)

- Sparks, NV October 8-13
- Organizing an Early Career Session and a Nuclear LIBS Session

Materials Research Society Fall Meeting 2022, Session Chair (J. McFarlane)

- Boston, MA, Nov 27-Dec 2

MSR Workshop, ORNL (Fall 2022, Kevin Robb chair)

Thank you for your attention

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