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Molten Salt Reactor PROGRAM

Preliminary Density, Heat Capacity, and Volatility results for the KCl-$MgCl_2$ Binary System

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PNNL

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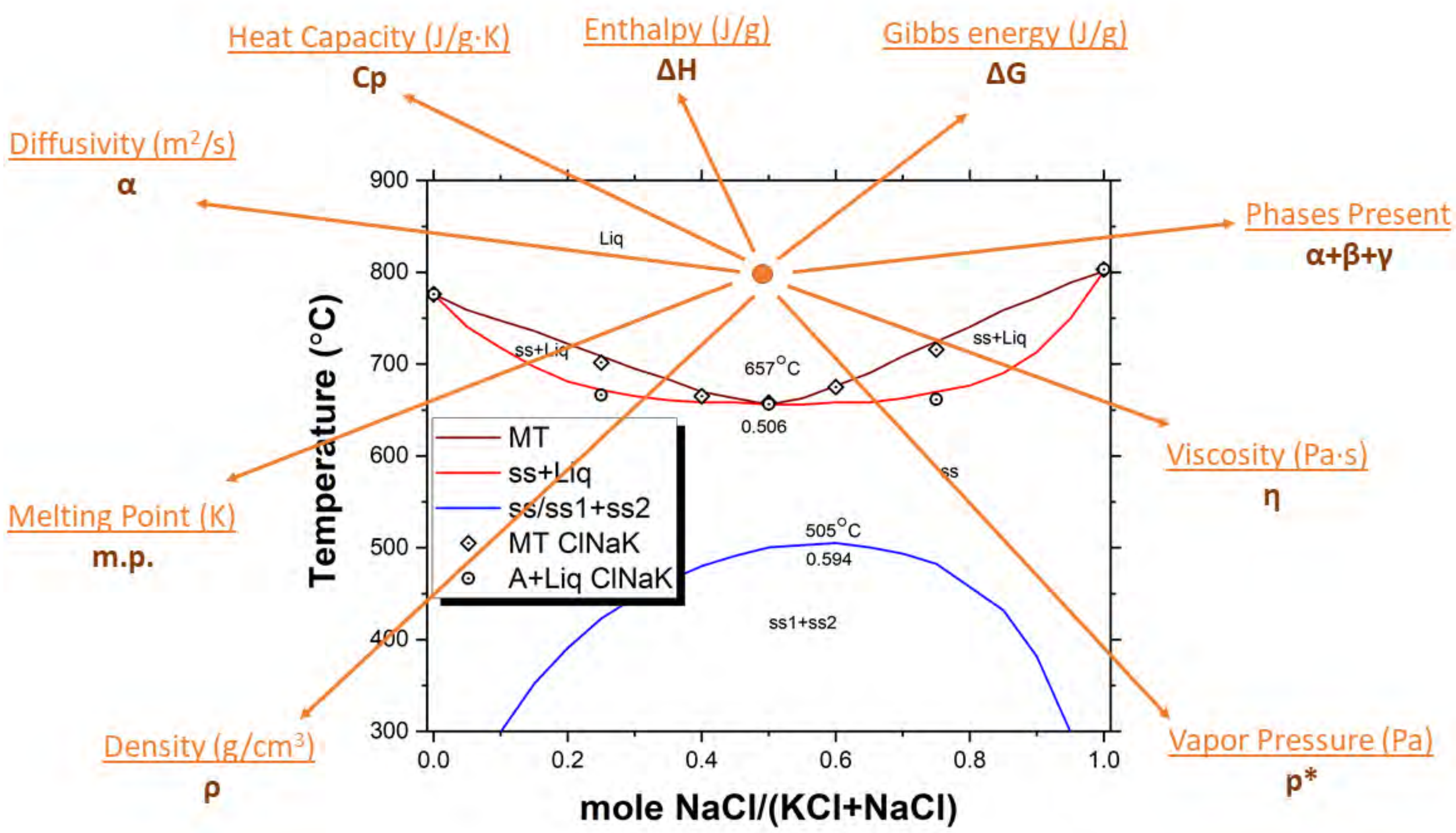
Goal: Provide Data to Support MSTDB

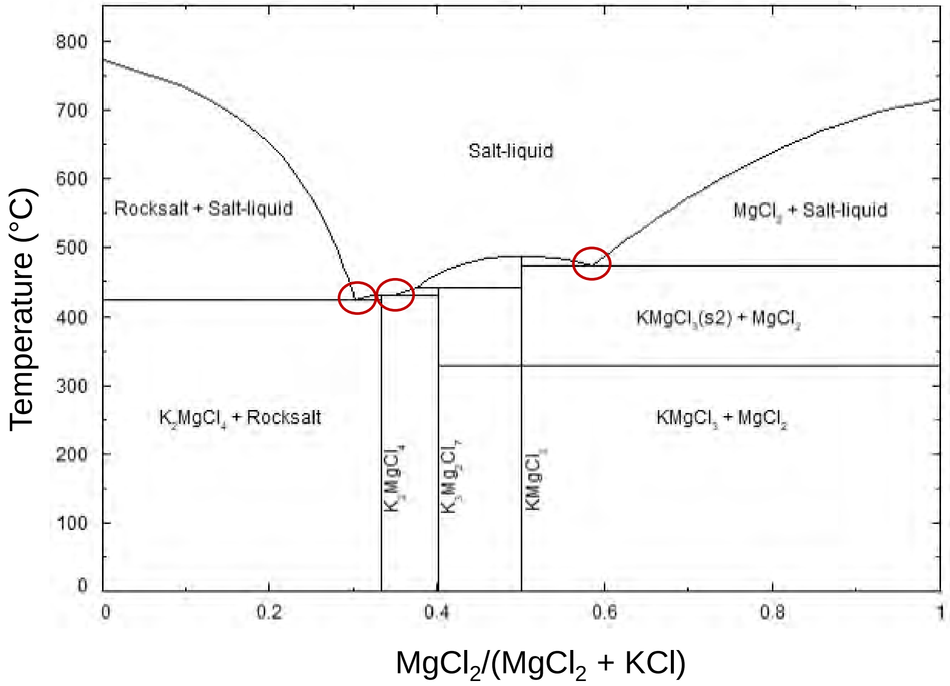
- Use PNNL and CSU expertise to perform thermophysical property measurements
  - ➢ Density via TMA
  - ➢ Heat Capacity via Drop Calorimetry
  - ➢ Volatility via XRD and EGA

- FY24 Achievements to date:
  1. Improved sample preparation methodology
  2. Density and volatility method development
  3. Thermophysical property data collection on the KCl-$MgCl_2$ binary system
  4. Error analysis for drop calorimetry using principles of the Guide to the Expression of Uncertainty in Measurement (GUM; JCGM 100:2008)



Goals for FY24

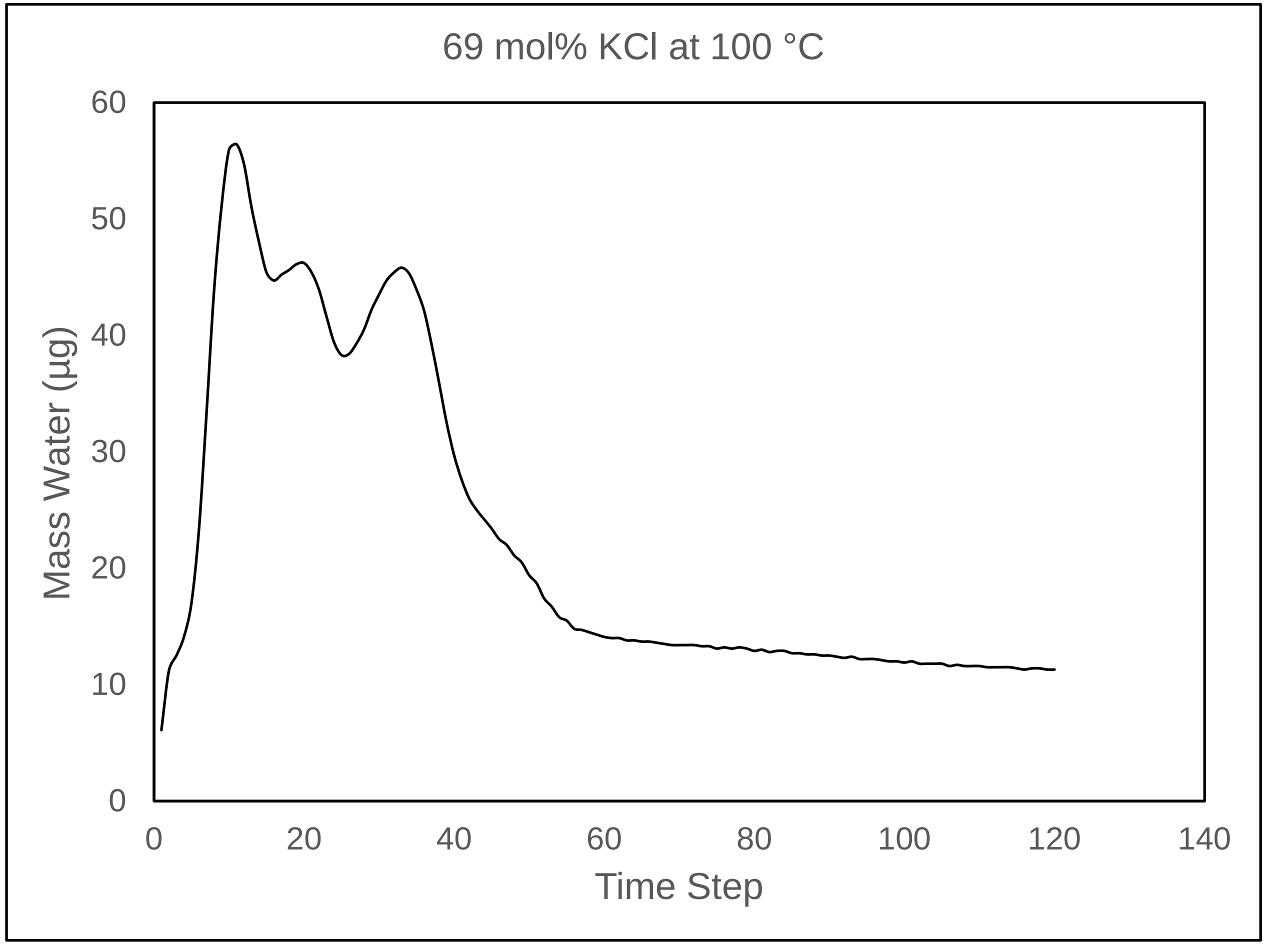
- 1.) Establish fundamental properties of 5 compositions in the KCl-$MgCl_2$ binary system
  - $MgCl_2$; KCl; 43-65-69 mol% KCl
- 2.) Determine the effect of water content and corrosion products on heat capacity, density, and volatility



https://www.crct.polymtl.ca/fact/phase_diagram.php?file=KCl-MgCl2.jpg&dir=FTsalt

Improvements in sample preparation

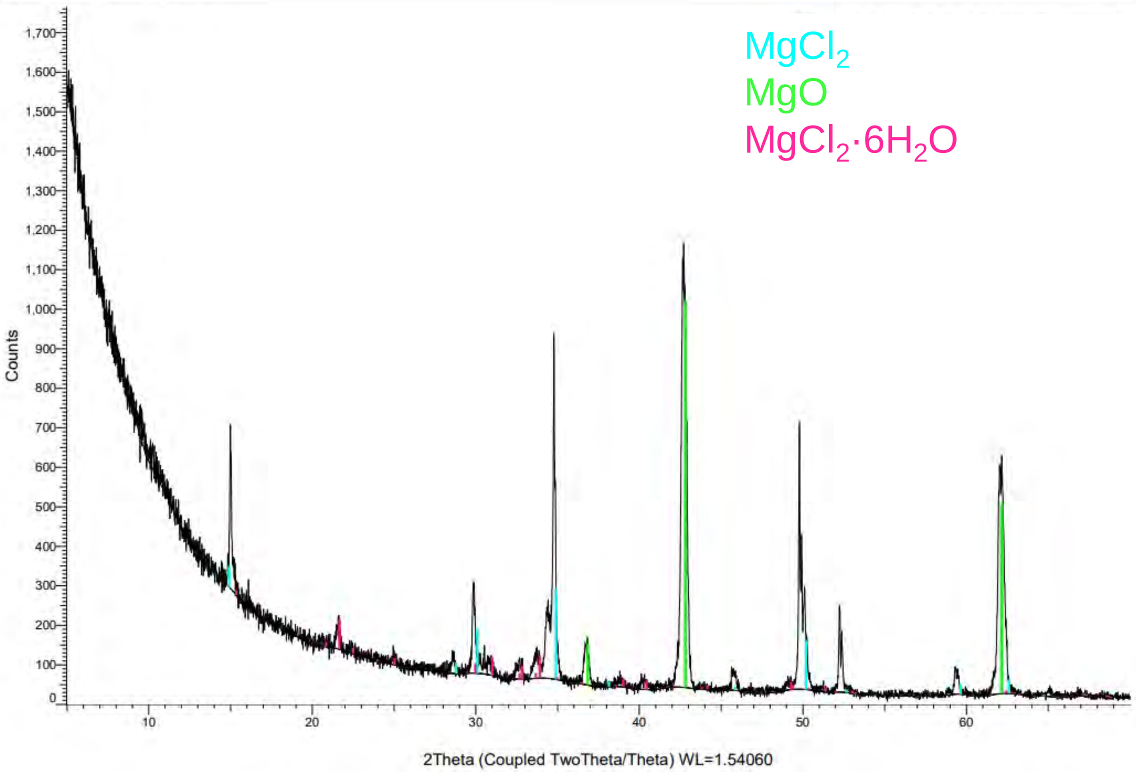
- Impurity content
  - Laser Induced Breakdown Spectroscopy (LIBS)
- Water Content
  - Coupled High-Temperature Furnace/Coulometric Karl Fischer Titration (KFT) Cell



Setback in initial measurements

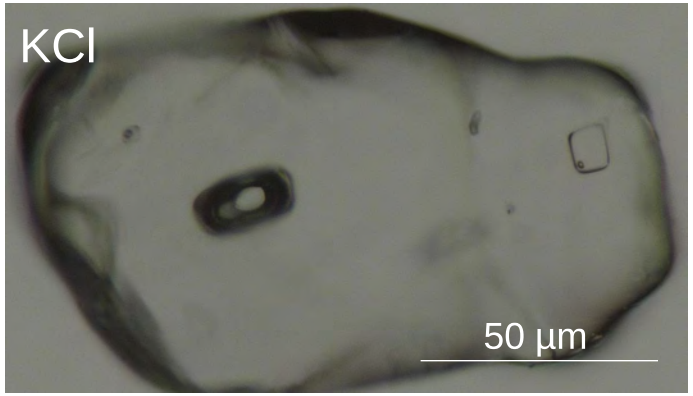
- First measurements in campaign were of $MgCl_2$ for evolved gas analysis
- However, the salt never melted
- Subsequent XRD analyses revealed presence of MgO
- Upon investigation, the following reaction occurs at low temperature:
  - $MgCl_2 + H_2O \rightarrow MgO + 2HCl$
  - But, from where does this water originate?

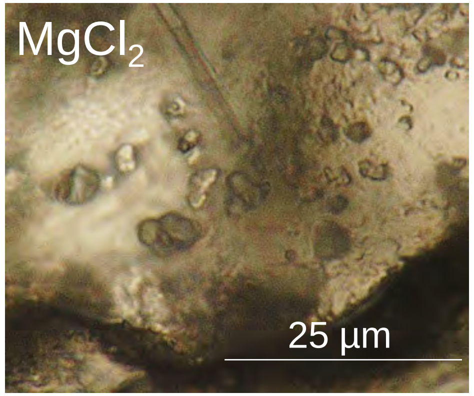
$MgCl_2$ Off-the-shelf After EGA

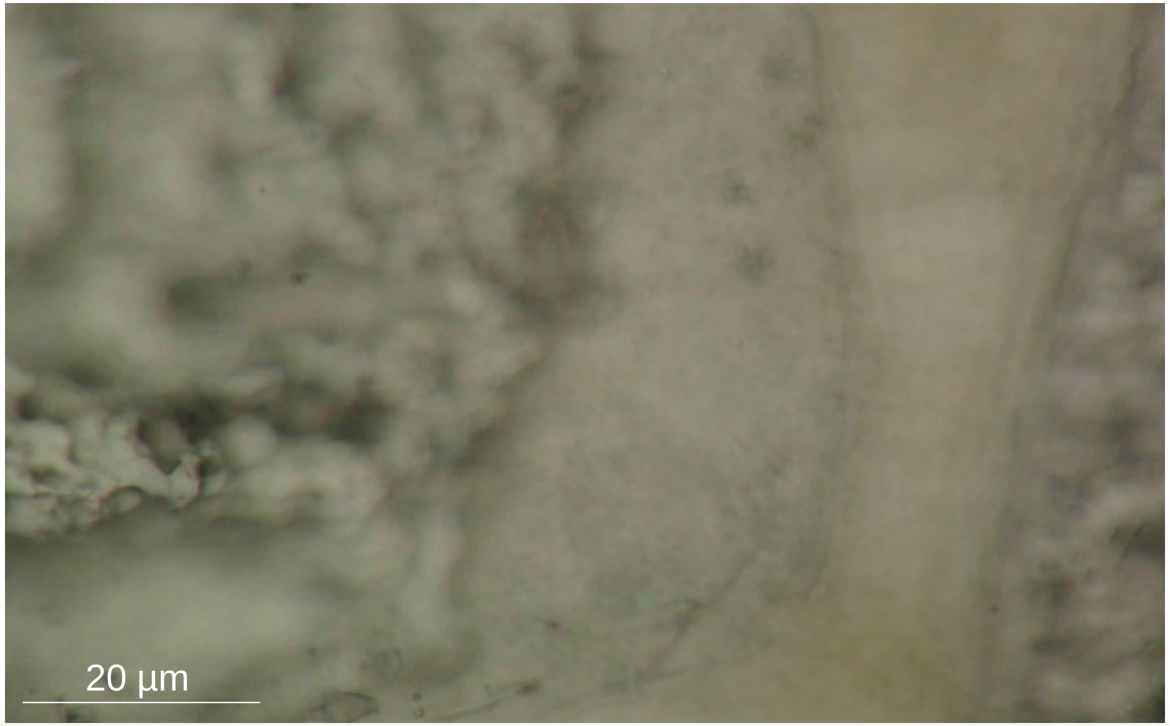


New Discovery in MSR-space?

- Optical microscopy reveals the presence of fluid inclusions
- Common phenomenon in geologic materials
- Can and does occur in most solids precipitated from a solution
- Will verify composition with micro-Raman







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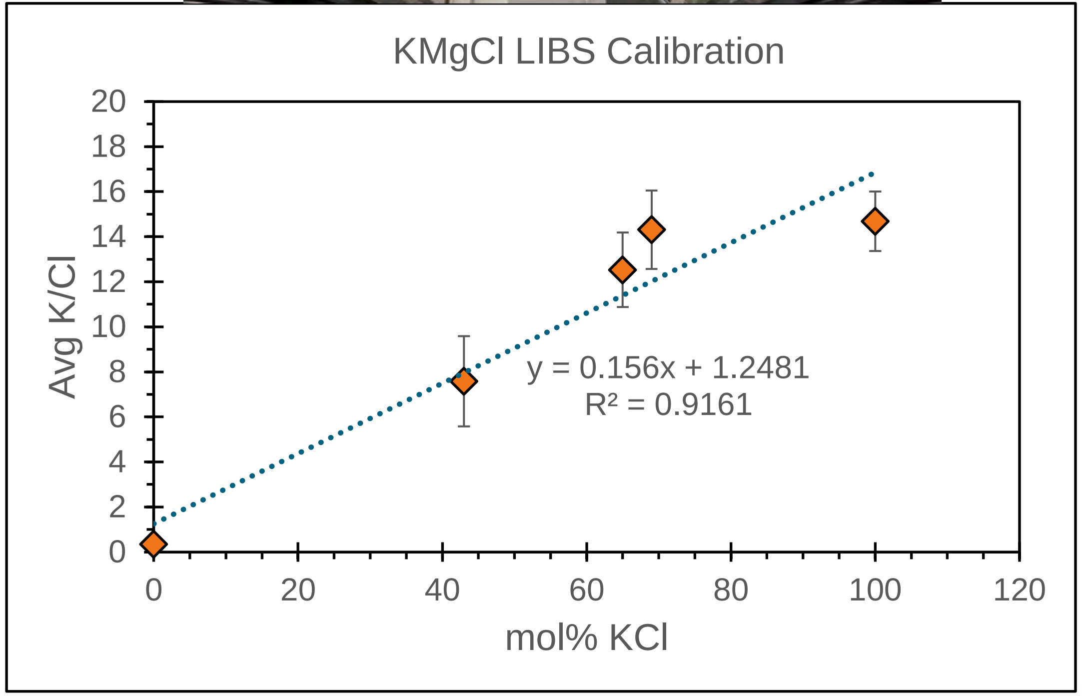
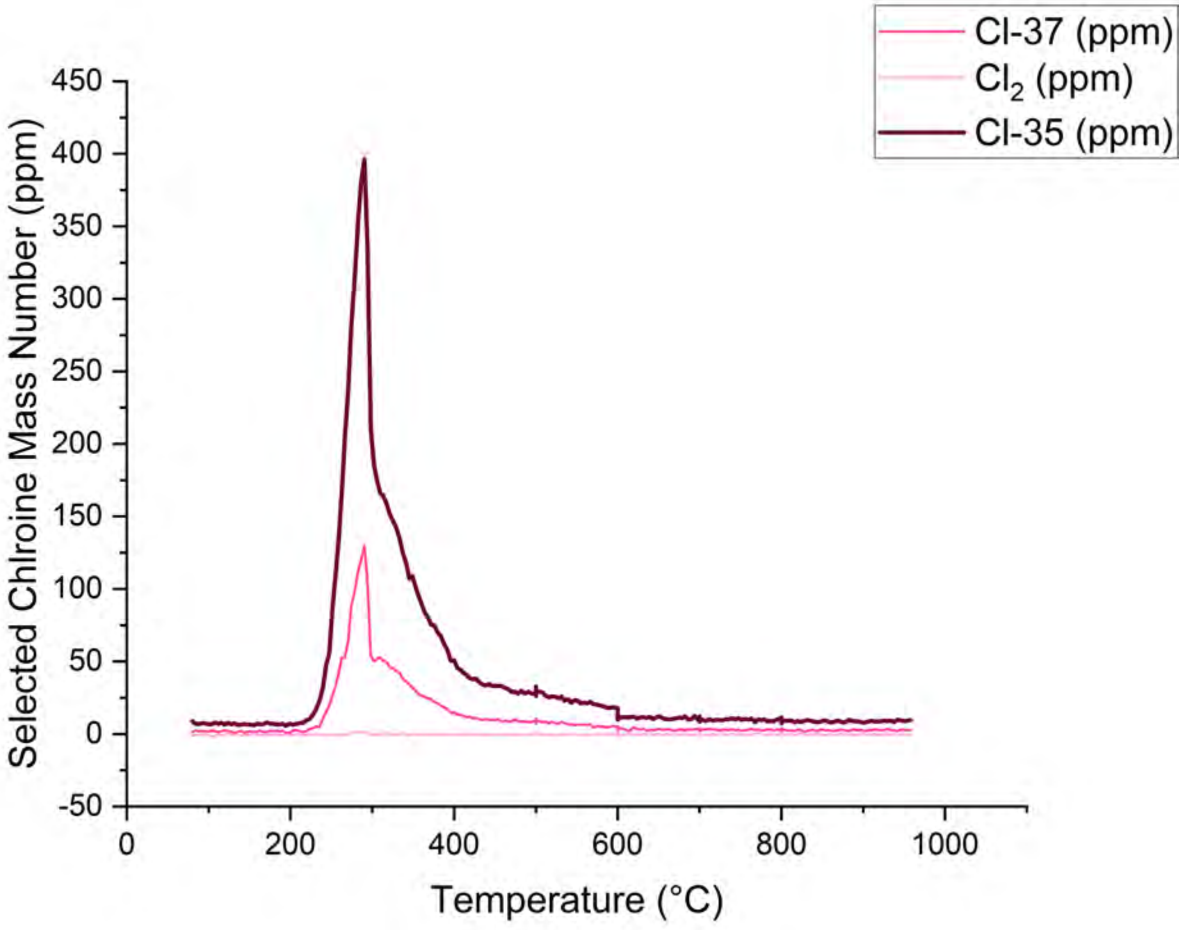
Improvements in sample preparation

- Procurement of ultra-dry salts
- Salt handling now occurs in an inert glovebox
  - Ball milling of batched compositions
  - Manual pellet press for KFT/LIBS
- Water content measured by KFT
- Eutectic compositions verified by LIBS



Volatility

- Evolved Gas Analysis (EGA) to detect species of off-gas
  - EGA is a shared instrument amongst other groups – not in an optimal configuration for MS research
  - XRD to confirm significant loss of salt using peak ratio
- Significant Chlorine gas in salts with elevated water content.



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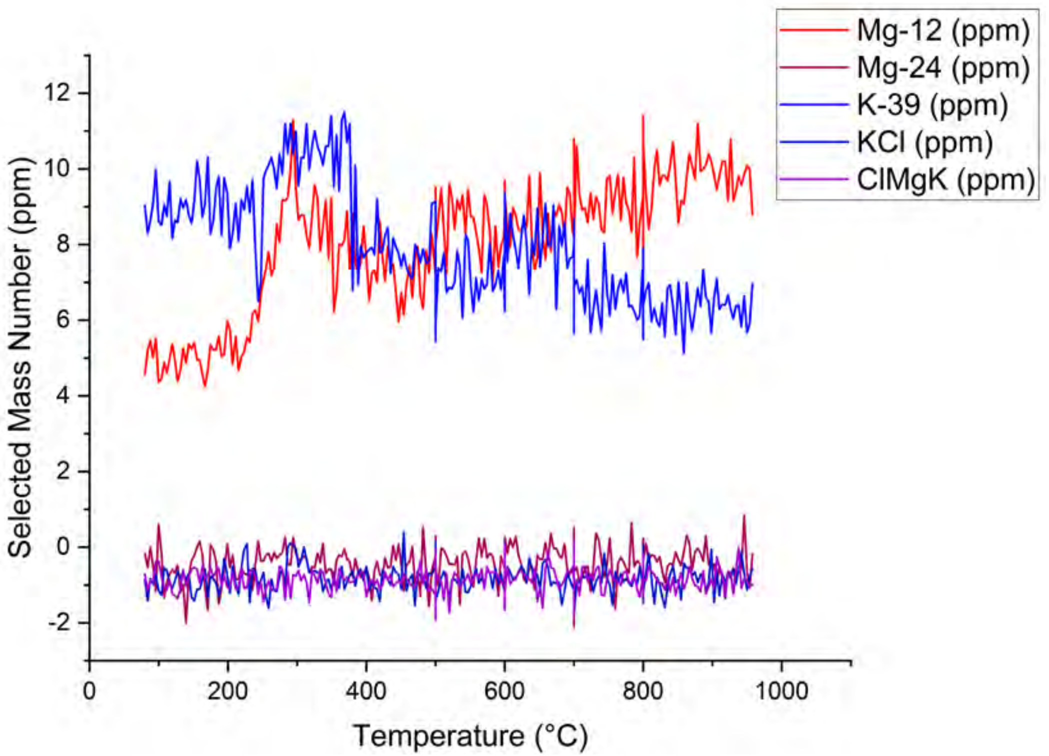
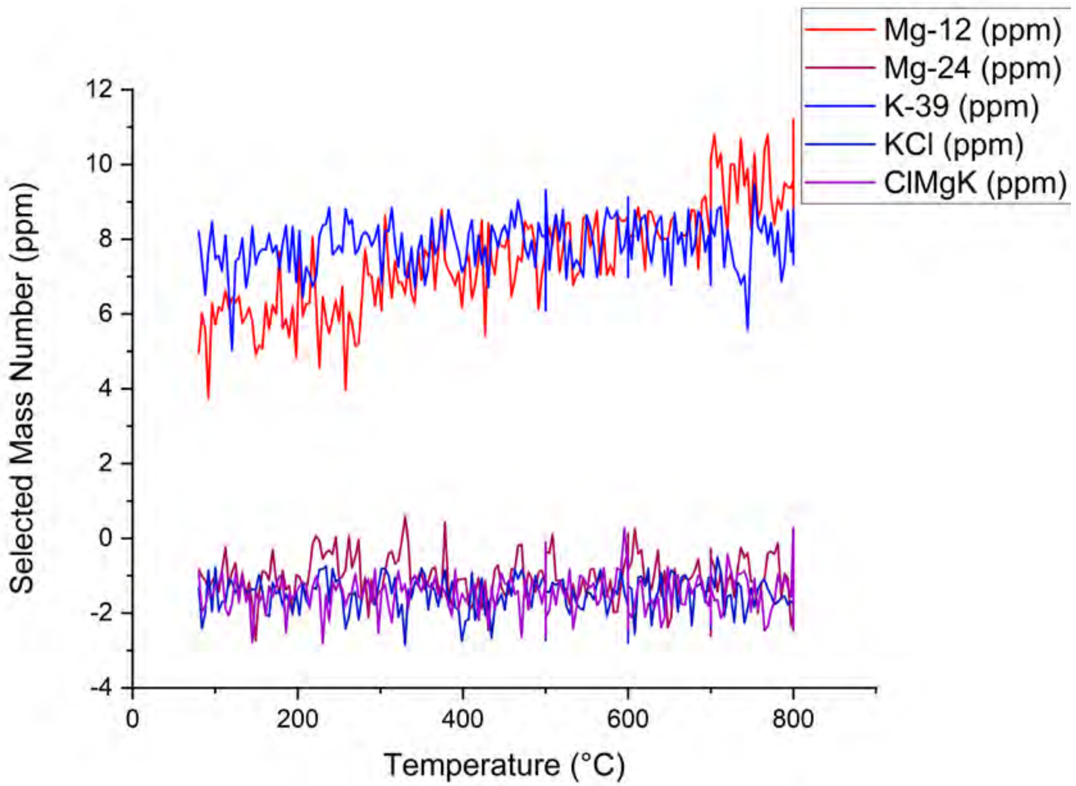
Volatility Continued

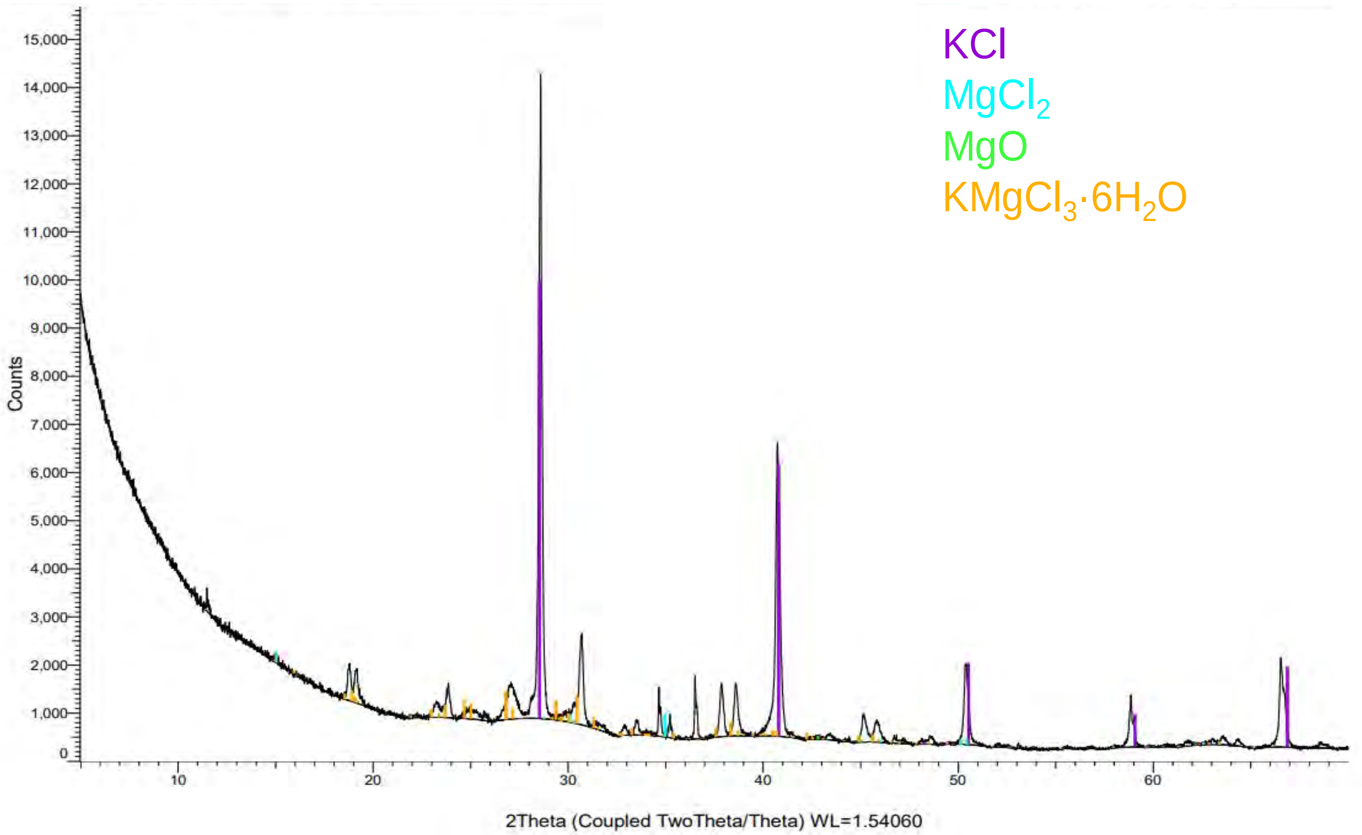




- Graphs show the results of two EGA trials of the 69% KCl, 31% $MgCl_2$ composition
- The data shows inconsistency in trends of KCl release with a gradual increase at mass 12
- Incongruent off-gas between KCl and $MgCl_2$, molar percent can be different than originally batched

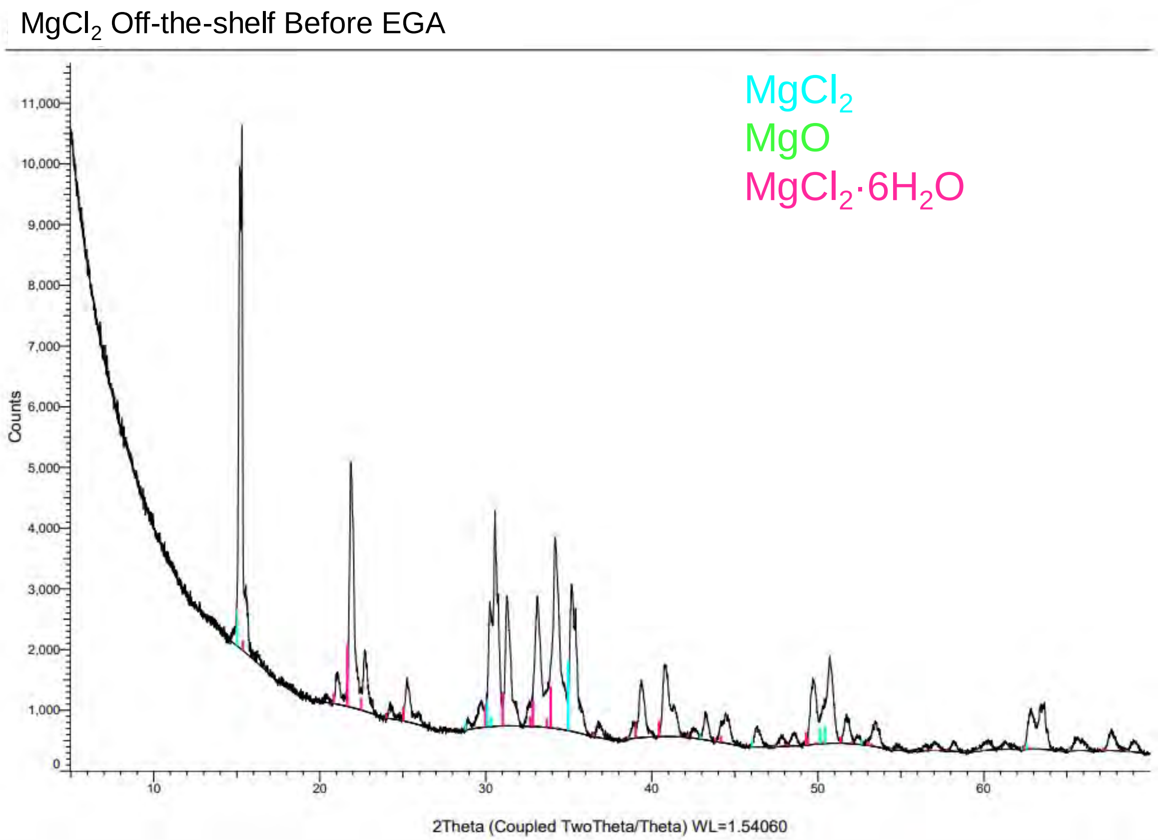
X-ray Diffraction of 69 mol% KCl after EGA

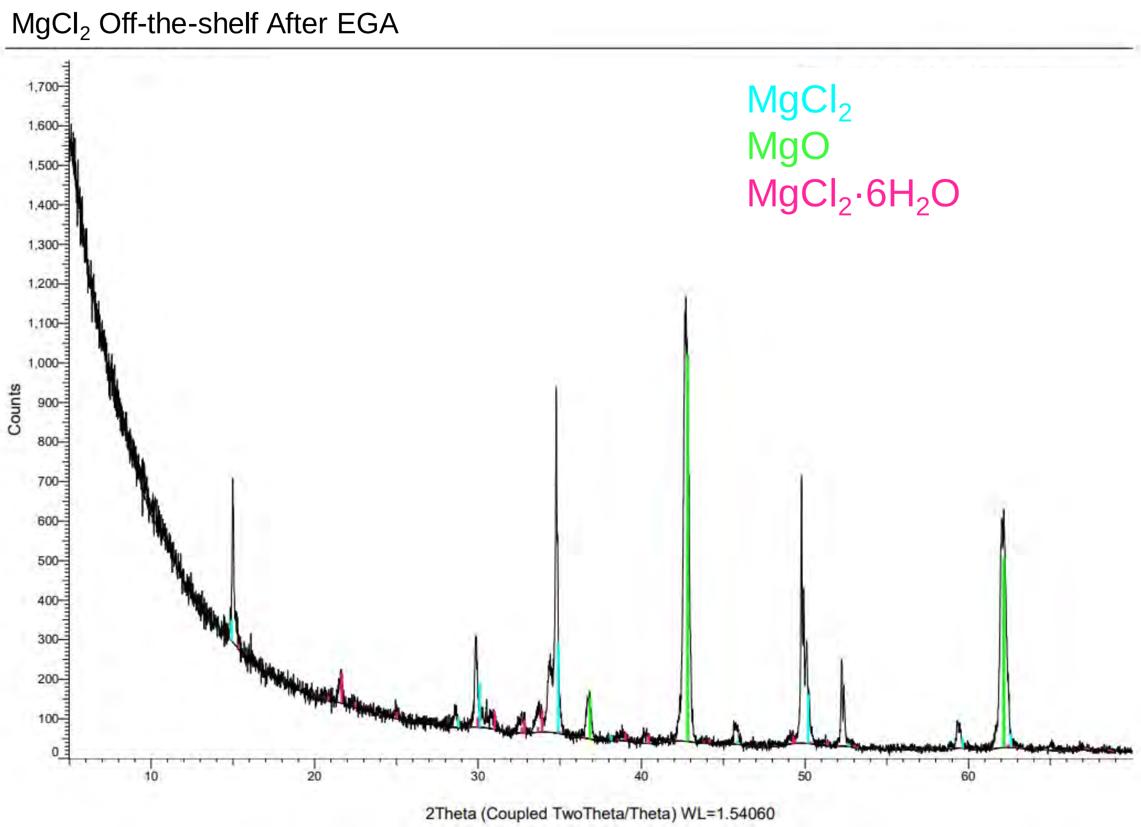
- Significant $MgCl_2$ loss during the heating profile of the EGA
- Conversion to MgO has occurred
- Mixed compositions are extremely hygroscopic



X-ray Diffraction Before and After EGA ($MgCl_2$)

- Preliminary results of XRD show the conversion of $MgCl_2$ to MgO during the EGA experiment.
- Further experiments will use alumina as a standard to monitor the change in Mg content pre- and post- EGA.

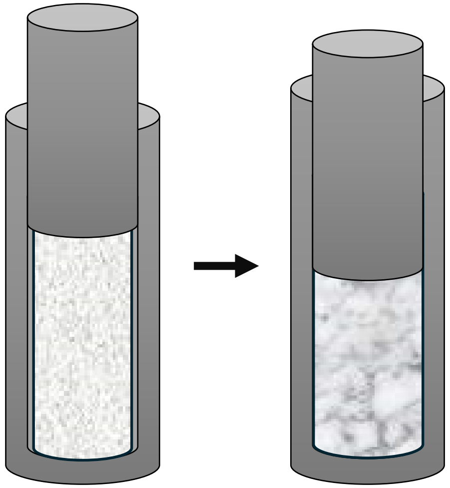




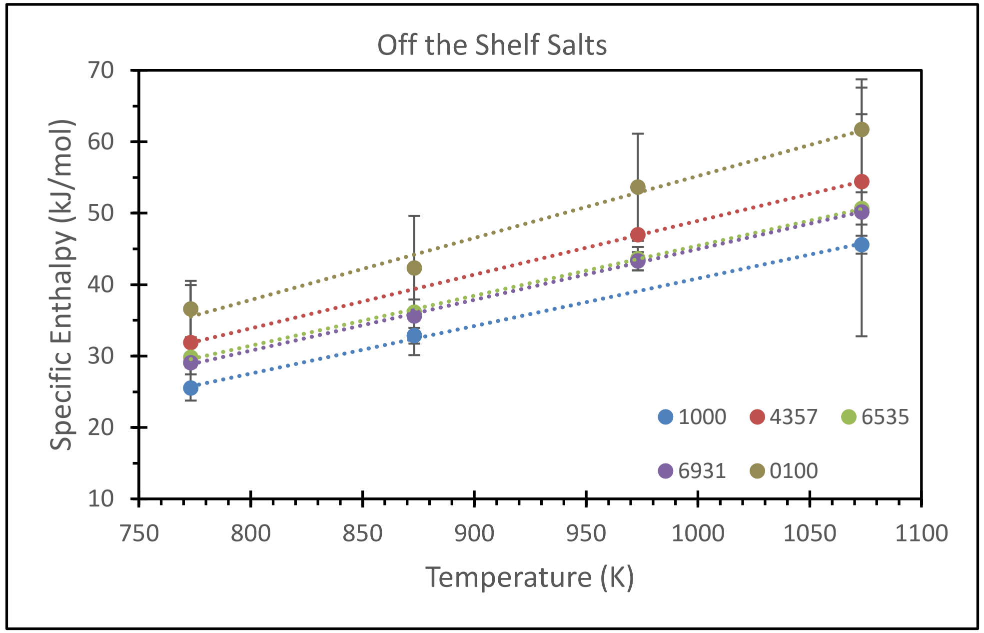
Density

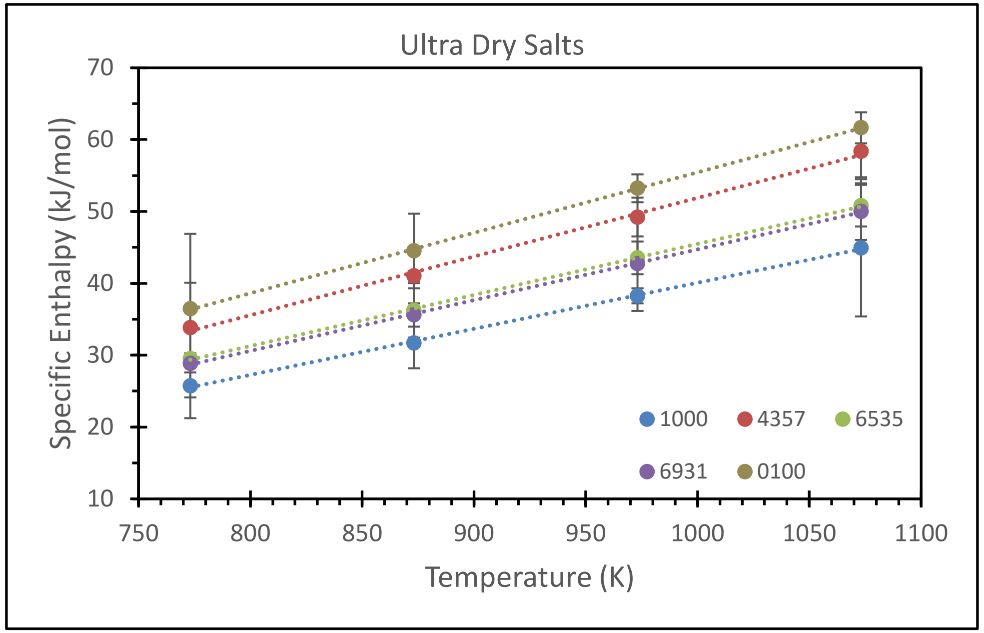
- Gravitational displacement
  - The change in height of the plunger results in the final volume of the salt.
    - $V_f = \pi r^2 \Delta h$, $\rho = m_f / V_f$
- Results show good alignment with literature values.

Ni Empty (g)	Ni + Pellet (g)	Height (cm)	Total Mass (g)	Final Mass of Salt (g)	Height Final (cm)	Density of 67 mol% KCl at 1050 K (g/cm^3)
15.8516	16.1521	1.0100	15.9116	0.0599	0.6210	1.57
15.8520	16.1514	1.0120	15.9117	0.0600	0.6190	1.64
15.8515	16.1520	1.0270	15.9116	0.0599	0.6160	1.56
15.8517	16.1518	1.0310	15.9117	0.0600	0.6120	1.59
15.8517	16.1515	1.0230	15.9117	0.0600	0.6090	±0.08
15.8517	16.1518	1.0206	15.9116	0.0600	0.6154	



Specific Enthalpy/Heat Capacity





- Drop calorimetry
  - Data processing includes the use of NIST JANAF values for KCl and $MgCl_2$
  - Slope defines heat capacity

deg K	774		874		974		1074		
mol% KCl	Avg Specific Enthalpy (kJ/mol)	sd	Avg Specific Enthalpy (kJ/mol)	sd	Avg Specific Enthalpy (kJ/mol)	sd	Avg Specific Enthalpy (kJ/mol)	sd	Molar Heat Capacity (J/mol*K)
100	25.5	1.1	32.8	1.3	N.D.	N.D.	45.6	3.1	64.0
43	31.9	0.4	N.D	N.D.	47.0	9.4	54.4	4.1	68.8
65	29.8	6.0	36.1	1.6	43.6	2.3	50.7	2.1	68.7
69	29.0	2.3	35.6	1.3	43.3	17.4	50.2	2.9	74.0
0	36.6	7.3	42.3	7.5	53.6	7.0	61.7	4.1	83.3
100	25.7	4.5	31.7	3.5	38.3	1.0	44.9	9.5	62.5
43	33.9	6.2	41.0	0.7	49.2	2.7	58.4	3.6	74.0
65	29.5	3.8	36.2	3.8	43.5	2.3	50.8	2.9	68.7
69	28.8	4.7	35.6	1.6	42.7	6.6	50.0	3.9	68.8
0	36.5	10.4	44.5	5.2	53.2	1.9	61.6	2.2	83.8

Off the shelf salts (first five rows)

Ultra dry salts (last five rows)

Error propagation in drop calorimetry

Using JCGM 100:2008 Guide to the Expression of Uncertainty in Measurement (GUM)

- Define Measurement Function
- Compute uncertainty for each input variable
- Compute uc(y)- the combined uncertainty
- Determine degrees of freedom for each variable
- Determine effective degrees of freedom for each variable
- Determine coverage factor, k
- Multiply k-factor by the combined uncertainty, result is the expanded uncertainty, U = k*uc(y)
- The measurand is then expressed as Y = y ± U

The Measurement Function:

ΔH=[(Ts - ((Pba/Pbm)*Psm))*Cf]/{Ms/1000} * Dhf * Db * Bsi

Sources of Error for Propagation	Units	Assigned Error Type	Term	Value	std dev	n obs	deg freedom
Batching ratios	unitless	type A	Db	1			
Heat flow stability of instrument	unitless	type A	Dhf	1			
Average baseline pan mass	mg	type A	Pbm	actual			
Average baseline pan signal	µV*s	type A	Pba	actual			
Sample pan mass	Mg	type A	Psm	actual			
Total signal (sample + crucible)	µV*s	type A	Ts	actual			
Sample mass	mg	type A	Ms	actual			
Avg temp of room	K/1000	type A	Tr	actual			
Avg temp of calorimeter	K/1000	type A	Tc	actual			
Average mass of calibrant	mg	type A	Mc	actual			
Total signal (standard + crucible)	µV*s	type A	Tst	actual			
Total pan mass of calibrant pan	mg	type A	Pst	actual			
Calibration factor	J/µV*s	type B	Cf	actual			
Formula Weight	g/mol	type B	Fw	actual			
Manual picking of baseline and integration	unitless	type B	Bsi	1			

Where:
Cf = ({[Schomate's eqn at Room Temp (Tr)] - [Schomate's eqn at Calorimeter Temp (Tc)] * 1000} * [(Mc/1000)/Fw])/[Tst-(Pba*Pst)]

And where uncertainty for:
Dhf = sd of n observations of background heat flow
Db = $\mathrm{sqrt}[(\text{sd mass}_1^2)+(\text{sd mass}_2^2)+(\text{sd mass}_n^2)]$

Allows for evaluation of which term introduces the greatest error on the measurand

Plans for Rest of FY24

- Finish testing the benchmark KCl-$MgCl_2$ system.
- Add iron, chromium, and nickel contaminants to KCl-$MgCl_2$ and test the thermal properties.
- Investigate the effects of water content on the KCl-$MgCl_2$ system.

Thank you

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