INL/CON-21-62048-Revision-0

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Changing the World's Energy Future

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Deliquescence of Eutectic LiCl-KCl Diluted with NaCl for Interim Waste Salt Storage

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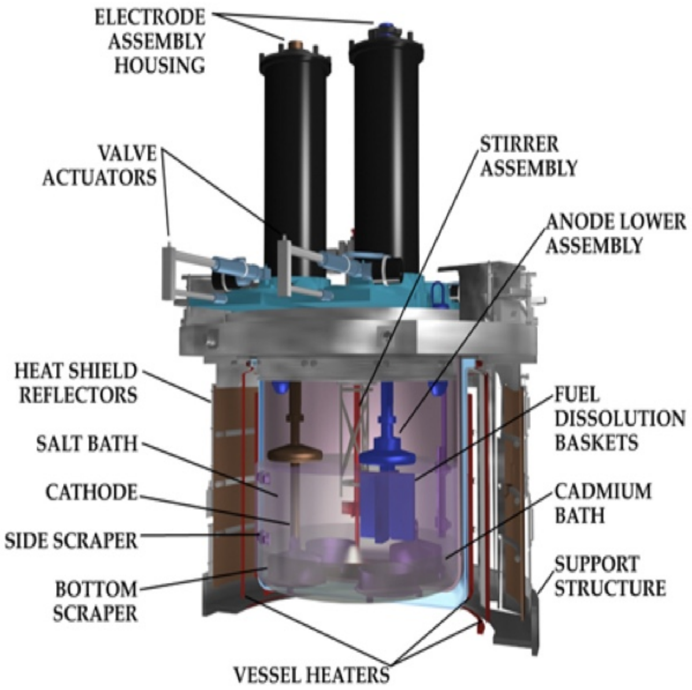
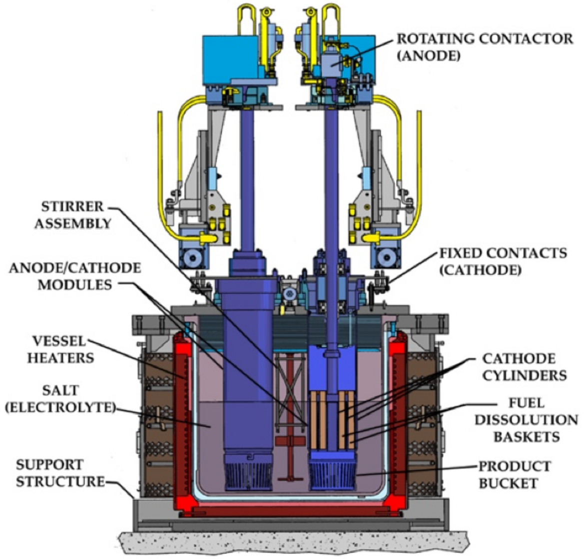
Introduction

- INL uses electrorefining in molten salts to separate uranium from transition metals, lanthanides, alkali elements, and transuranic elements in EBR-II spent fuel.
- Radioactive salt waste produced in the process in the Fuel Conditioning Facility must be immobilized and stored long term.
- The salt is primarily comprised eutectic LiCl-KCl, which is hygroscopic and deliquesces in ambient air.
- For assessment of interim storage outside of argon atmosphere hot cell, deliquescence needs to be studied and mitigated.
- One pathway for doing this is by dilution of LiCl-KCl with NaCl.

INL Mark-IV ER



INL Mark-V ER

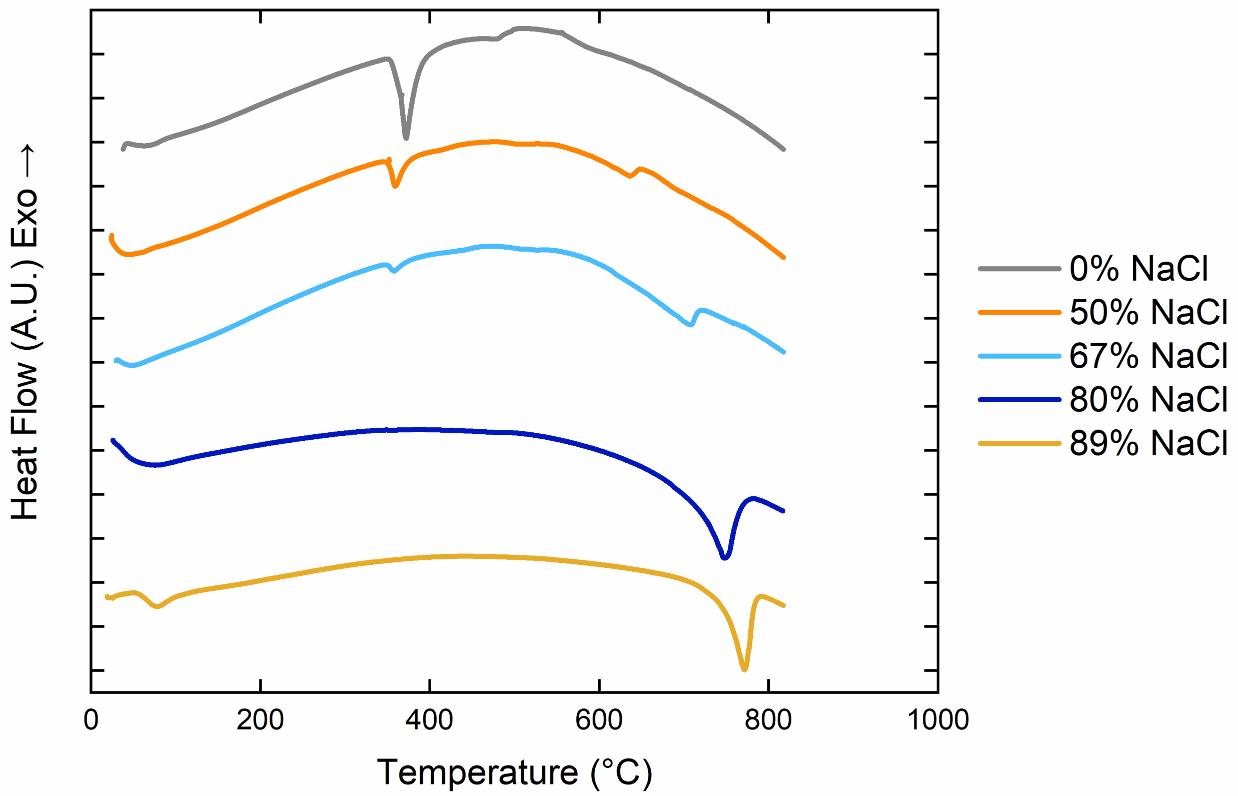


Experimental Study

1. Synthesize ingots of eutectic LiCl-KCl with variable amount of added NaCl. The objective is to determine if blending NaCl can mitigate deliquescence of ER salt.
2. Perform hydration testing in controlled temperature and humidity. The objective is to measure amount of water uptake as a function of NaCl concentration.
3. Assess corrosion of stainless steel in contact with salt samples subjected to controlled temperature/humidity. The objective is to determine potential benefit of adding NaCl to prevent corrosion of storage containers that may allow some ingress of air.

LiCl-KCl-NaCl Ingot Preparation and DSC

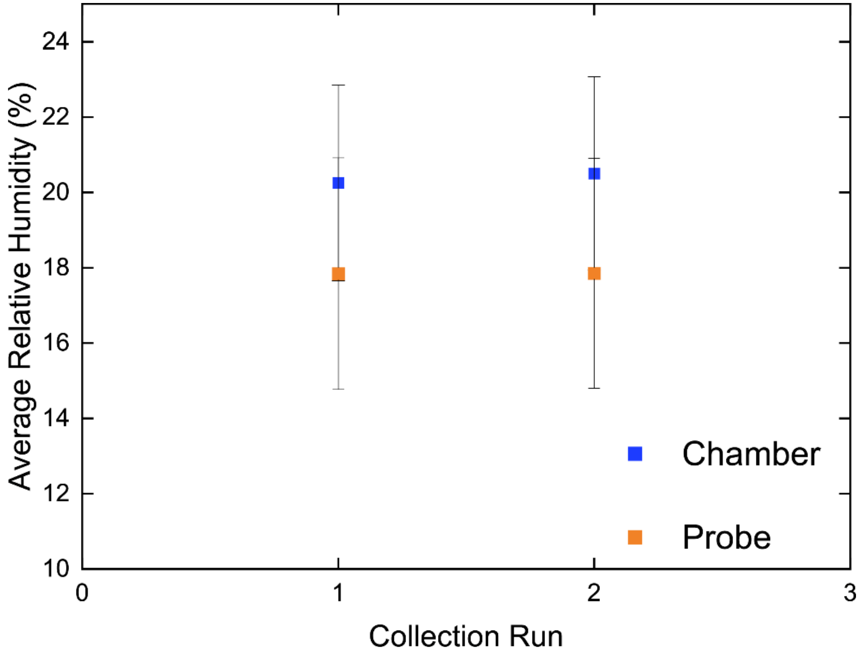
- Salts were mixed and melted in an inert atmosphere glove box
- Ingots made with powdered eutectic LiCl-KCl, diluted with 0, 50, 67, 80, and 89 mass % NaCl
- Batches containing more NaCl heated at 10°C/min, held at 800 °C for 60 minutes and cooled
- Batches containing less NaCl held at 400°C
- Hold temperatures based on thermographs (right)



Differential Scanning Calorimetry Shows Effect of NaCl Content on Liquidus Temperature

Hydration Testing in Humidity Chamber

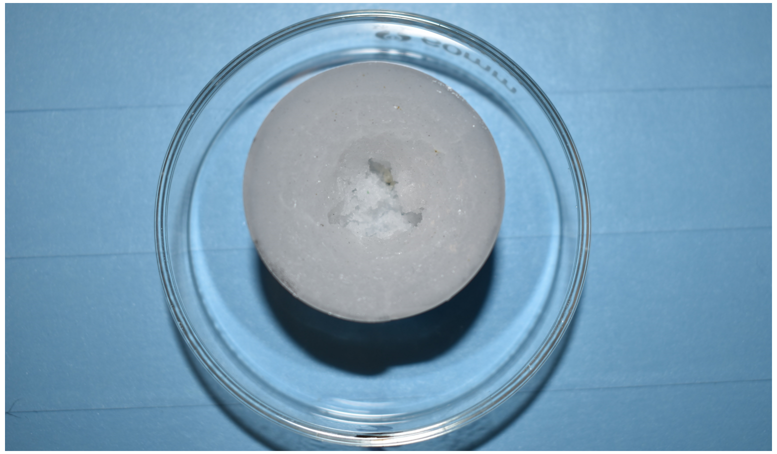
Test Equity TE-101 H-F model humidity chamber
This humidity chamber was operated at 40°C and 20% relative humidity to test the hydration of salt ingots

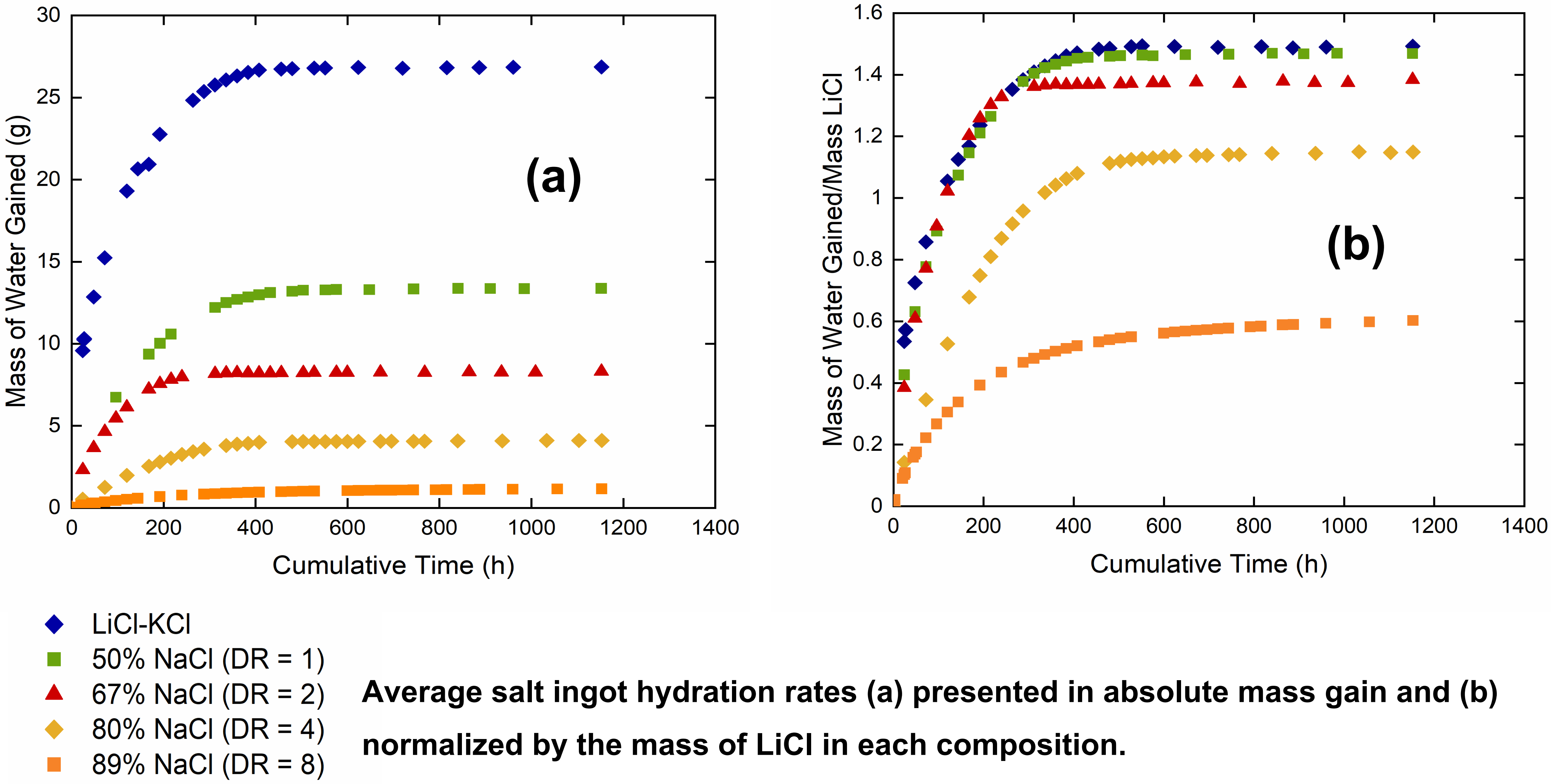


Steady state humidity measurements inside of the chamber were compared to values collected using an external humidity probe. Each set of measured values is within the uncertainty bands of the other set.

Hydration Testing Conditions

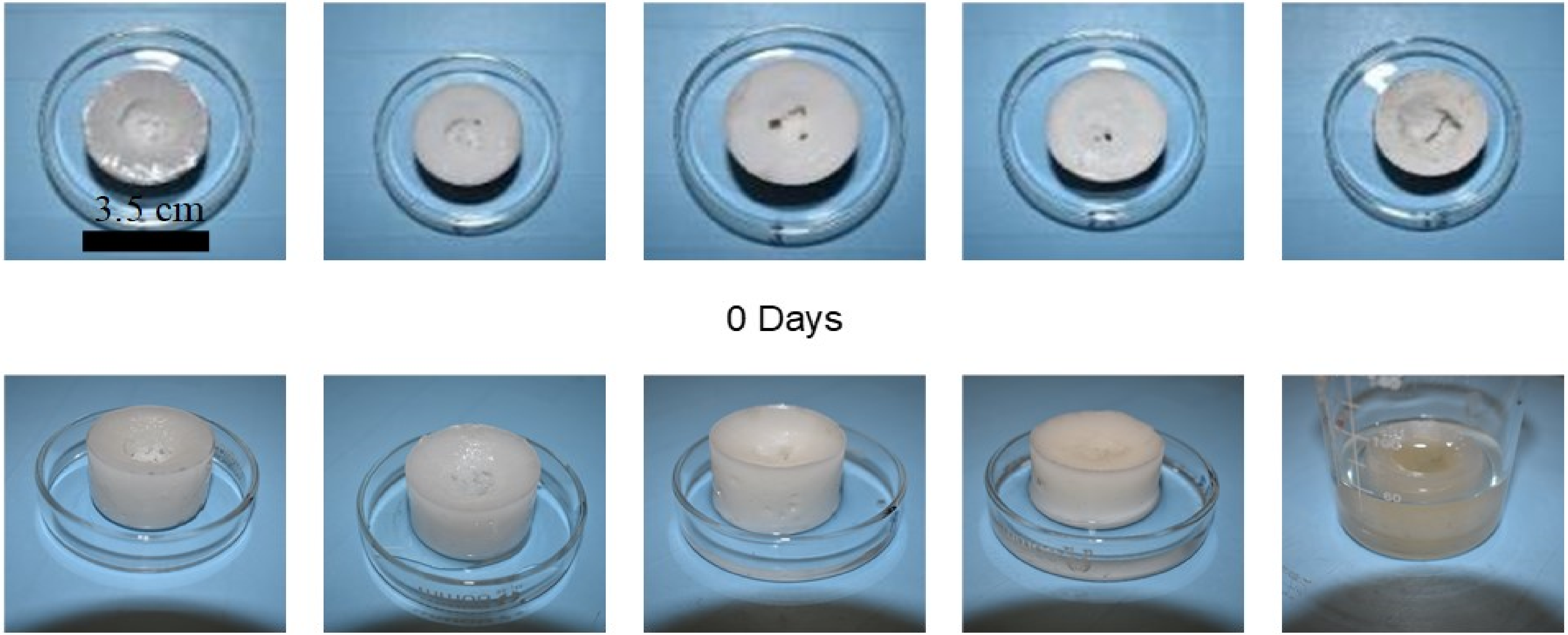
- The salt ingots were loaded into glass petri dishes (60 ml) and placed in the humidity chamber at 40°C and 20% relative humidity to assess rehydration capacity.
- Mass increase due to deliquescence was recorded over a 48-day period.
- Samples made with 80 and 89 mass% NaCl exhibited lower steady state water uptake than those with lower mass% NaCl.





Average salt ingot hydration rates (a) presented in absolute mass gain and (b) normalized by the mass of LiCl in each composition.

89% NaCl | 80% NaCl | 67% NaCl | 50% NaCl | LiCl-KCl



0 Days

48 Days

Ingot appearances after formation and after 48 days in the hydration chamber. Standing water was observed in all samples except those with 89% NaCl.

Deliquescent Relative Humidity (DRH)

Salt Species	DRH at 40°C
LiCl	11.6%
KCl	82%
NaCl	75.4%

Ref. Wexler and Hasegawa 1954

- DHR - The relative humidity (RH) at which an initially-dry solid first takes on liquid water when increasing RH
- Tests were performed at 20% RH
- Under this condition, LiCl expected to deliquesce
- Deliquescence driven by LiCl present in sample

Elapsed Time When Standing Water Was First Observed and Mass of Water Gained

Mass% NaCl	First Evidence of Standing Water (h)	Mass Gained Prior to Evidence of Standing Water (g)	Mass Gained After Evidence of Standing Water (g)	Total water gained (g)
0	≤24	9.91	17.31	27.22
50	24	3.65	9.72	13.37
67	48	3.39	4.94	8.34
80	192	2.79	1.32	4.11
89	NA	1.16	NA	1.16

Ingots were measured throughout the 48-day hydration period.

Dehydration of Hydrated Salt

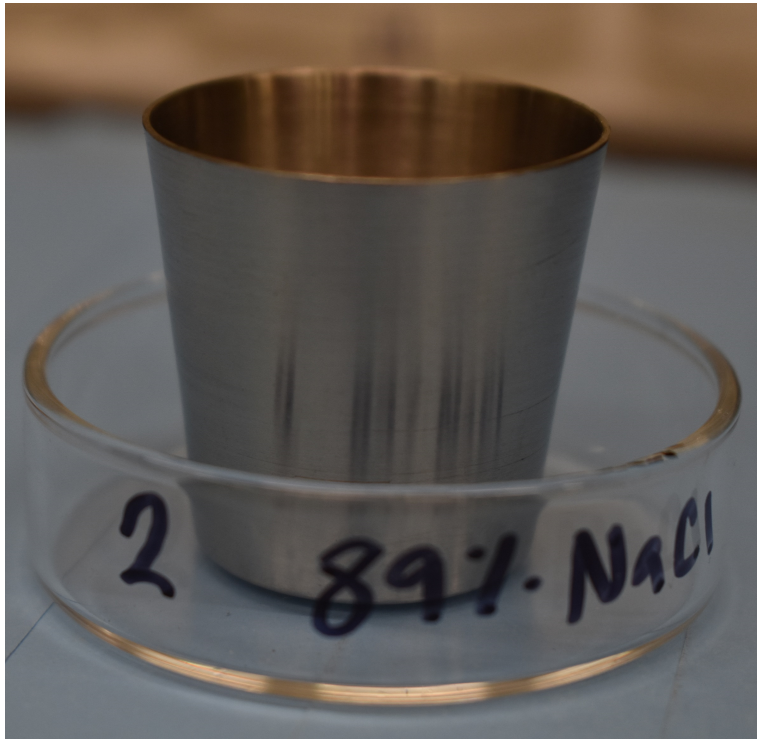
Dehydrating salt ingots can lead to the production of HCl gas

$H_2O + LiCl = LiOH + HCl$

$H_2O + 2LiCl = Li_2O + 2HCl$

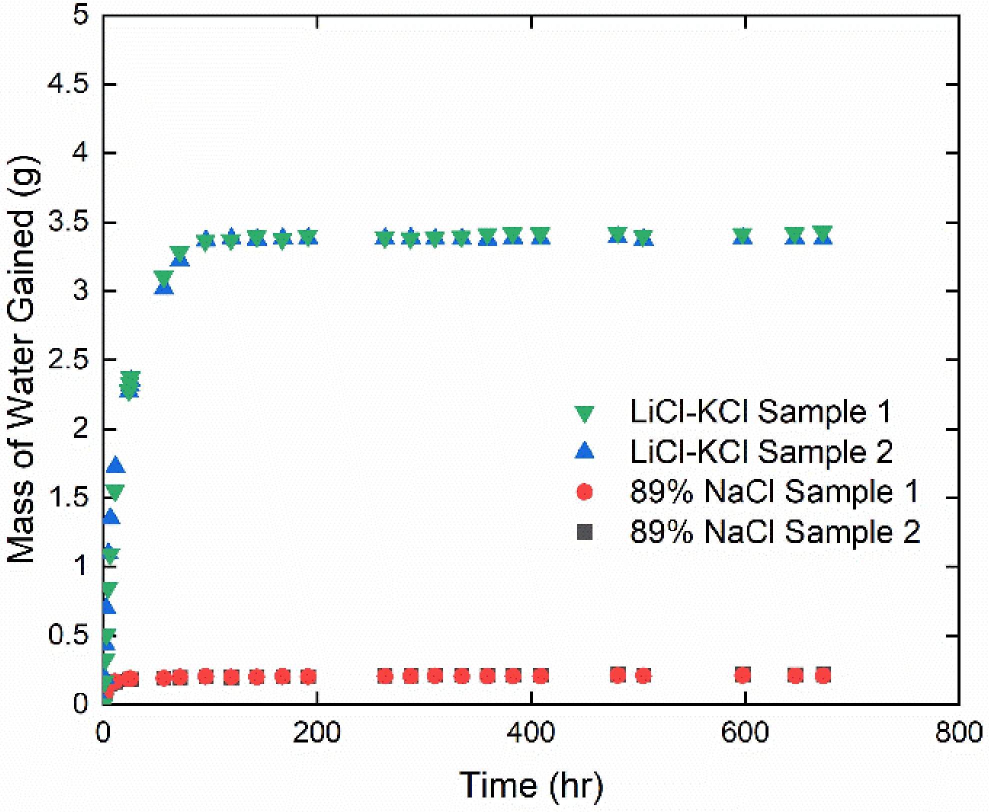
(include pictures of steel wool)

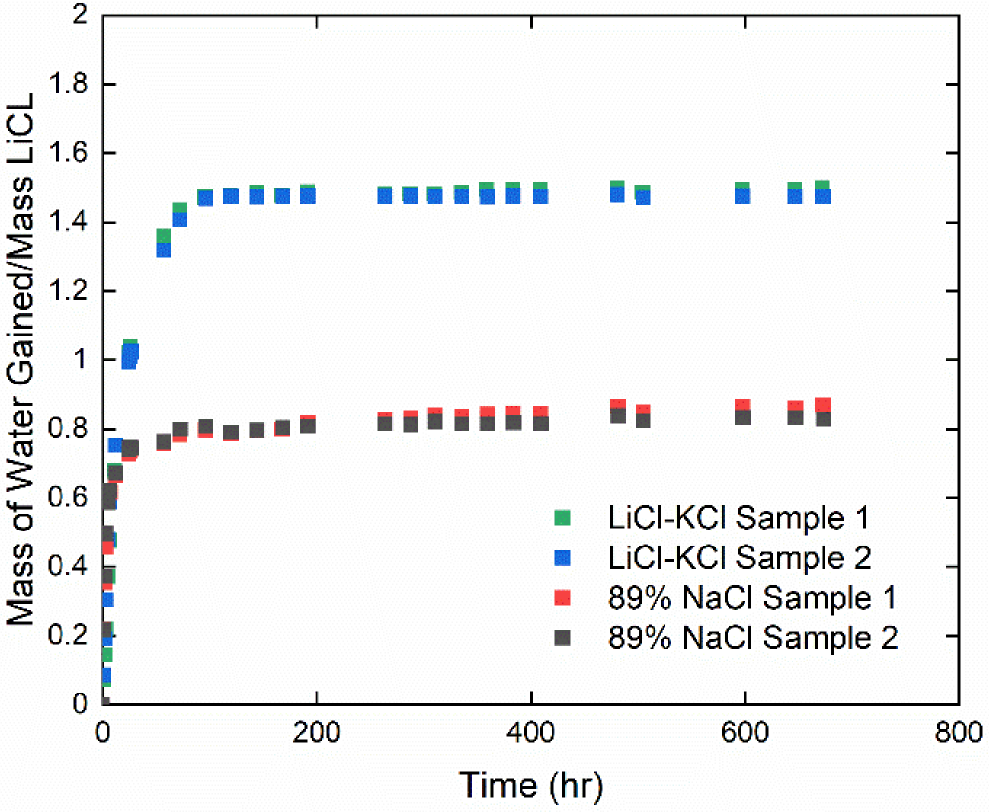
Corrosion Testing Conditions



- Pure LiCl-KCl and 89 mass % NaCl samples were loaded in 10-mL 304 ss crucibles.
- Salt particle size range of 45 to 250 µm.
- Humidity chamber at 40°C and 20% relative humidity.

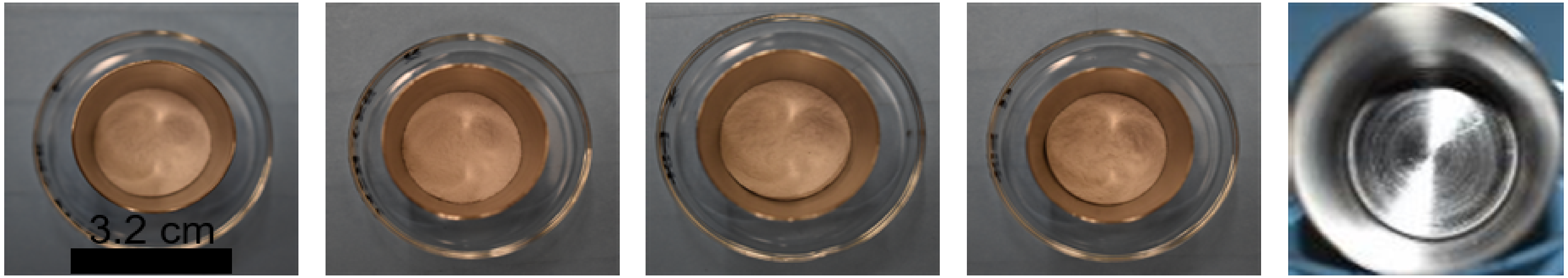
Hydration Behavior of Salt Powders (LiCl-KCl and 89% NaCl samples) In Stainless Steel Crucibles





Note fast uptake of water by salt powders compared to ingots.

89 mass% NaCl 1/2	89 mass% NaCl 2/2	LiCl-KCl 1/2	LiCl-KCl 2/2	Stainless Steel Reference



0 Days

21 Days

Images of salt-stainless steel interfaces with evidence of standing water and corrosion and crucibles containing pure LiCl-KCl. Evidence of corrosion is minimal in crucibles with 89% NaCl.

Conclusions

- LiCl-KCl-NaCl ingots require about 400 hr to achieve equilibrium water uptake in conditions of 40 ^{o}C and 20% RH.
- LiCl-KCl-NaCl powders equilibrate with water in less than 100 hr at these conditions.
- At under 80 mass% NaCl, amount of water uptake in LiCl-KCl-NaCl ingots correlates with the amount of LiCl in the salt. At 80% NaCl and higher, water uptake is reduced relative to LiCl content.
- Deliquescence reduced with increasing NaCl and was eliminated at an NaCl concentration of 89 mass%.
- When deliquescence was inhibited, corrosion of stainless steel was minimal.
- This approach to mitigating corrosion of storage containers comes at the cost of large volume increases (~10×) resulting from dilution.

Questions

Acknowledgements and References

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