Molten Chloride Salts for Thermal Energy Storage

Heat Storage for Gen IV Reactors for Variable Electrify from Base-Load Reactors
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Crescent Dunes Solar Energy Facility, USA

CSP Gen3 Molten Salts

- Higher thermal stability
- Lower cost

SolarReserve Crescent Dunes Molten-salt HTF plant (USA)

CSP Recent Salt History

- Halotechnics (2009): Combinatorial screening of chloride salts
- 2012 MURI "High Operating Temperature Fluids" (5 years, $5M)
  - UCLA (metals): Selected Lead-Bismuth eutectic
  - University of Arizona (salts): Selected NaCl-KCl-$ZnCl_2$ eutectic
- Gen3 Roadmap (NREL/TP-5500-67464, 2017) Conclusions:

Salt	Composition by wt.	Melting Point (°C)	Heat Capacity (J/g-K)	Density (kg/L)	FOB Cost ($/kg)	Cost* ($/kWh$_t$)
$NaNO_3/KNO_3$ (SolarSalt)	0.60/0.40	220	1.5	1.7	0.8	10
$ZnCl_2/NaCl/KCl$	0.686/0.075/0.239	204	0.81	2.4	0.8	18
$MgCl_2/KCl$	0.375/0.625	426	1.15	1.66	0.4	5
$Na_2CO_3/K_2CO_3/Li_2CO_3$	0.334/0.345/0.321	398	1.61	2.0	2.5	28

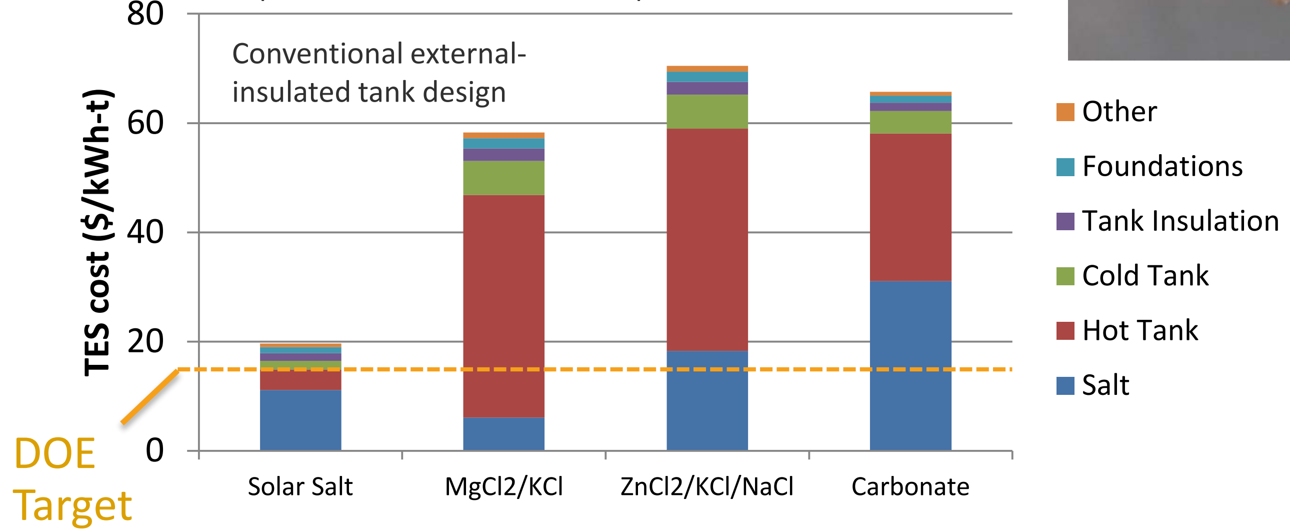
* DOE cost goal is < $15/kWh$_t$

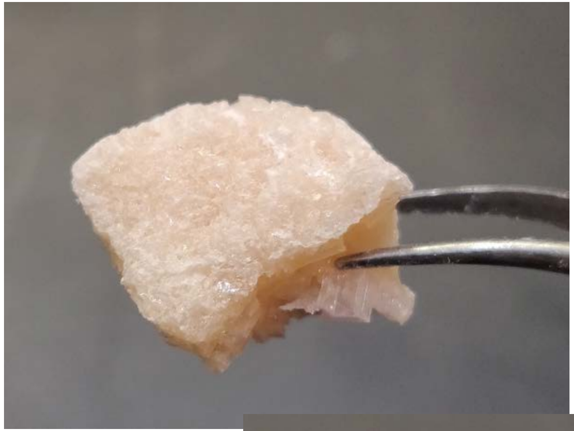
Gen3 CSP with Molten Chloride Salts

Primary Challenges

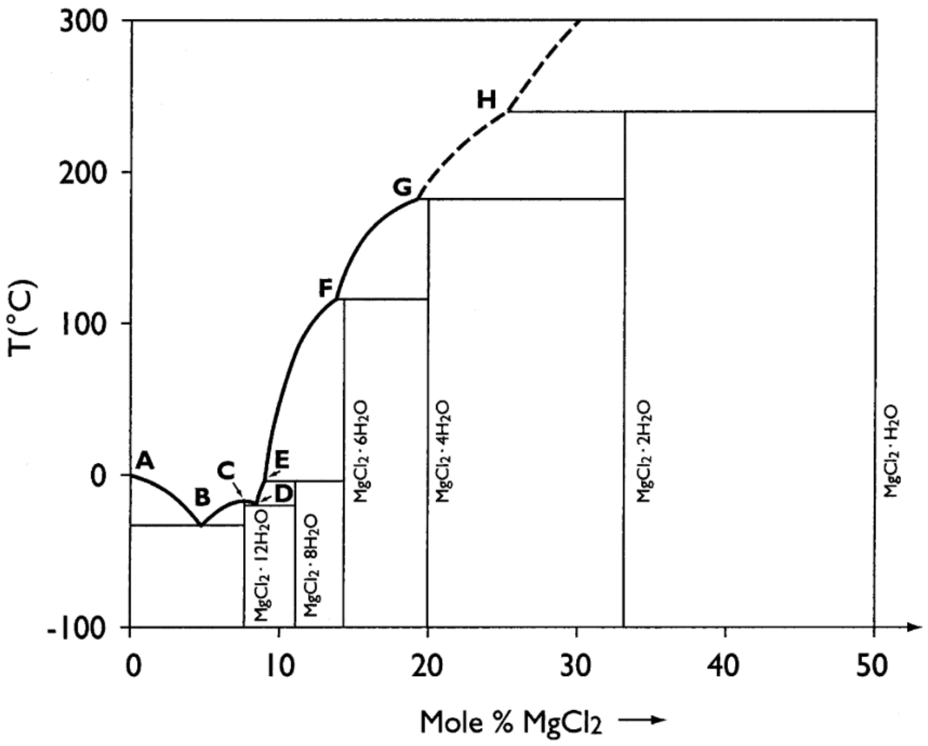
1) Corrosion control
2) Containment cost

Adapted from CSP Gen3 Roadmap: NREL/TP-5500-67464, 2017





Purification Protocol for $MgCl_2$ Salt Hydrates



G. Kipouros and D. Sadoway (2001)

Thermal purification

- Step-wise dehydration at 117°C, 180°C, 240°C, and 400°C
- Hydrolysis of $MgCl_2$ releases H_2O to form MgOHCl and HCl(g)

Chemical purification

- Reduction of MgOHCl and impurity cations by elemental Mg

Reactions during Purification

- Dehydration and hydrolysis at 117°–400°C

$$MgCl_2 \cdot xH_2O \rightarrow MgOHCl + HCl(g)$$

- Thermal decomposition of MgOHCl above ~550°C

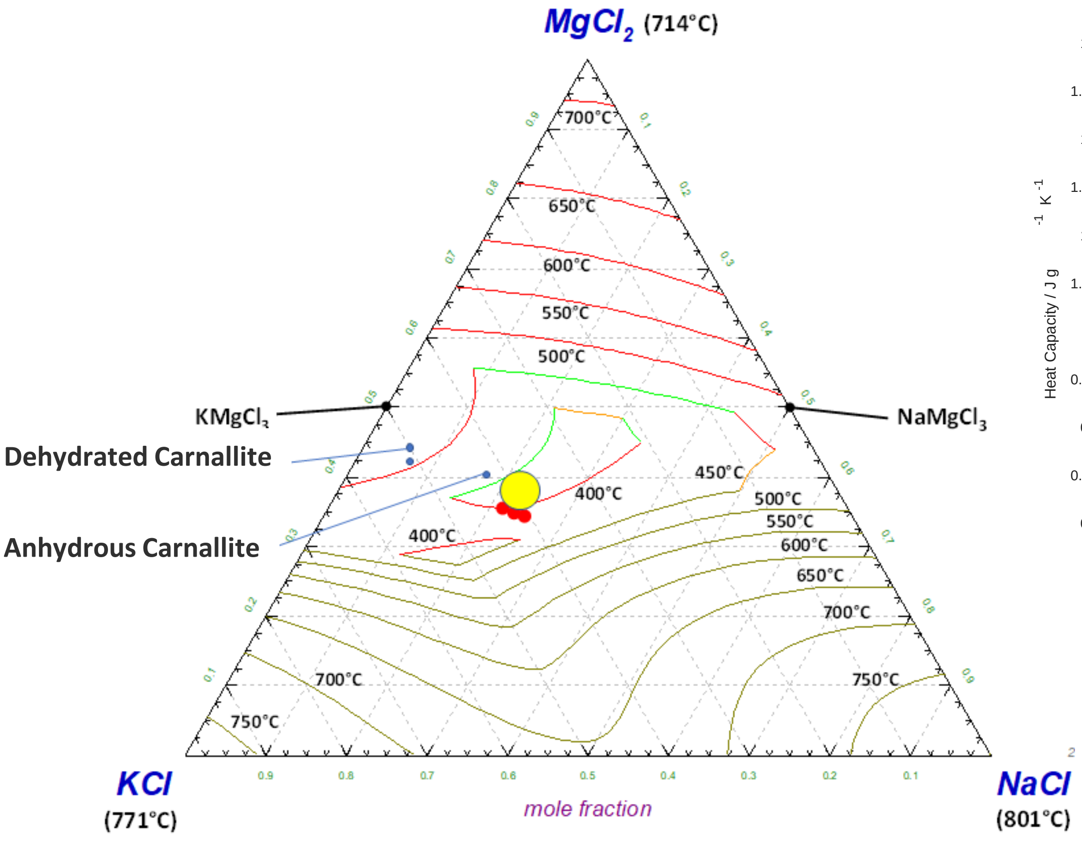
$$MgOHCl = MgO + HCl(g)$$

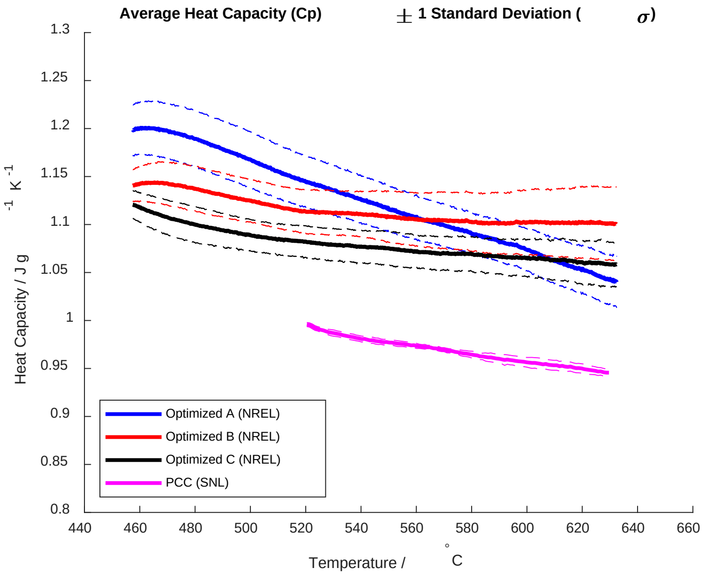
- Recovery of $MgCl_2$ during chemical purification at ~650°–800°C

$$MgOHCl + \frac{1}{2}Mg = MgO + \frac{1}{2}MgCl_2 + \frac{1}{2}H_2\text{(g)}$$

- MgOHCl is the major undesired species
  - Its formation by hydrolysis produces HCl(g): corrosion problem
  - Its thermal decomposition produces HCl(g): corrosion problem
  - Its thermal decomposition produces MgO (largely insoluble/non-recoverable): erosion problem

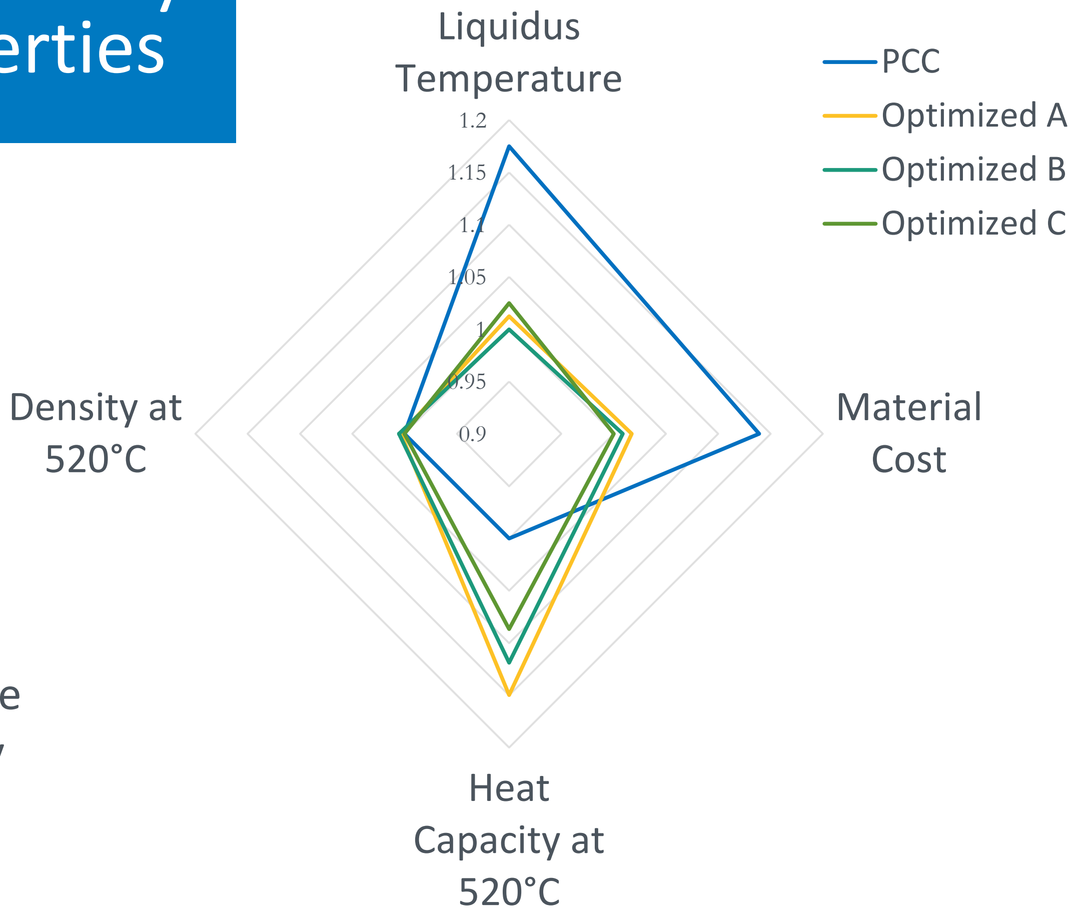
Optimizing Chloride-Salt Formulation





Phase diagram of Na/K/Mg–Chloride modeled with FactSage [Mohan et al., Energy Conversion and Management 167 (2018).

Performance Sensitivity to Different Properties



All values are normalized to the ***lowest*** value of each category

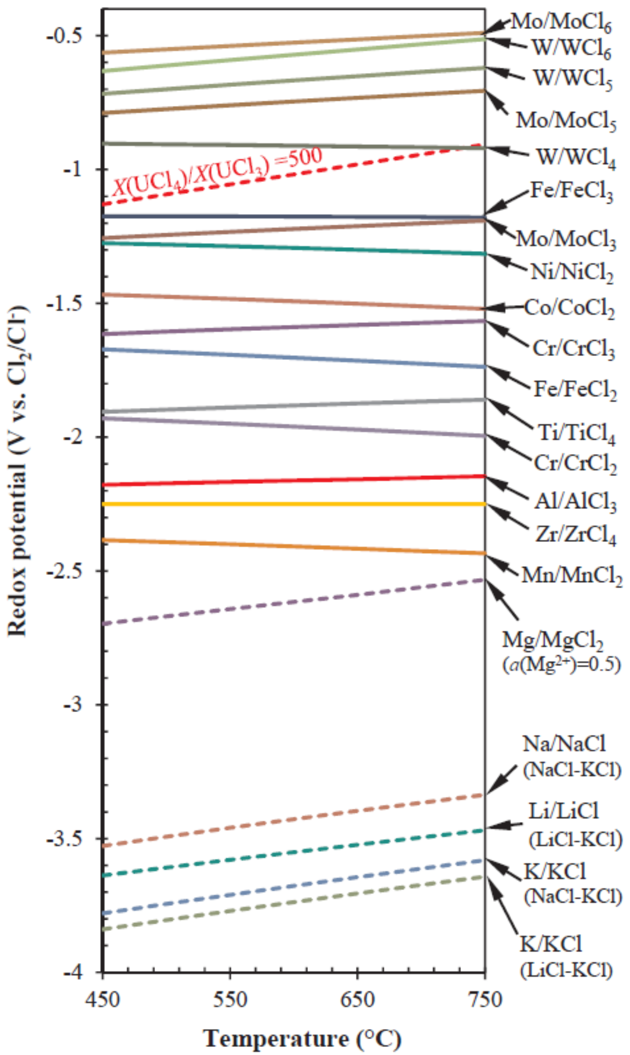
Industrial Experience: Salt Handling

ICL/DSM Handling Molten Chlorides for Magnesium Production:

- 260,000 tons per year of carnallite ($MgCl_2$/KCl) is dehydrated, melted, and mixed with NaCl as feedstock for Mg production
- This molten salt, and the melting/ purification technology, is being applied for the Gen3 project
- The salt melter and electrolytic vats are lined with refractories, to protect the carbon steel vessels; carbon steel tank shells have been in use for over 20 years

Corrosion Protection

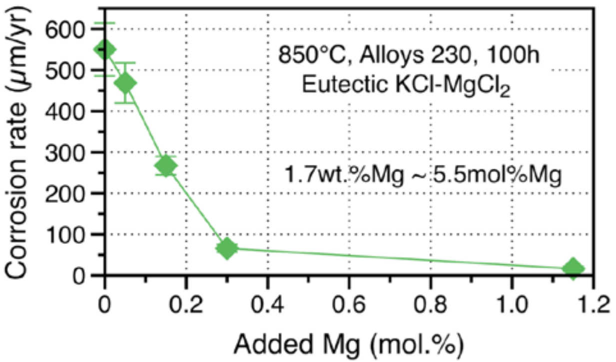
Mg^0 is used to protect other metals (e.g., Fe, Cr, Ni) within containment alloys against oxidation and extraction as mobile chlorides.



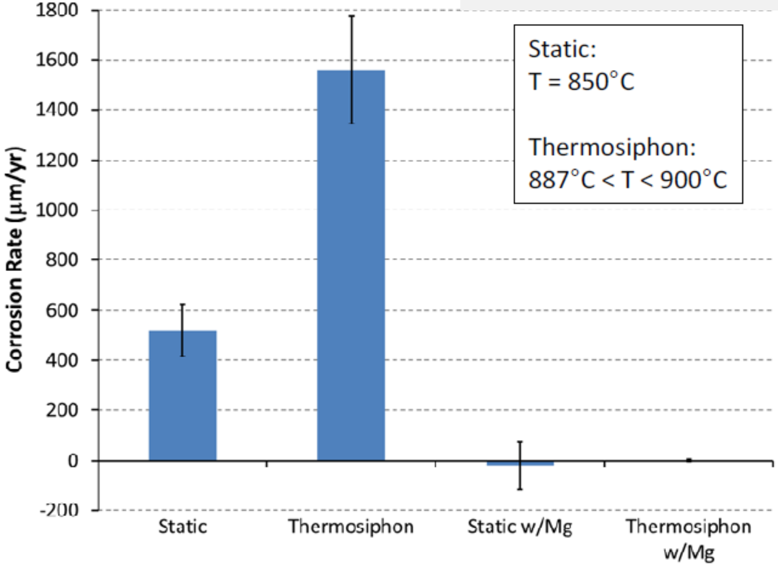
Redox potentials of various redox couples as a function of temperature in chloride salts.
Solid line: metal dissolution at aMn+ of 10−6
Dotted line: reduction of oxidants.
Guo et al., Progress in Materials Science, **97** (2018).

Corrosion Protection

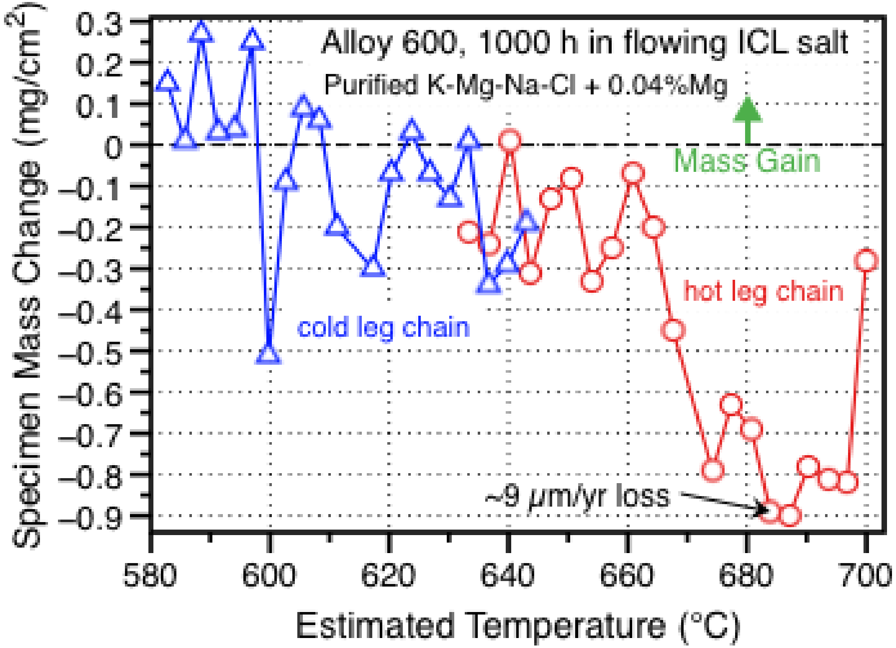
- Above 650 °C Mg metal in the melt acts as an oxygen getter and redox control to protect against corrosion
- Testing at Savannah River and Oak Ridge National Labs



Corrosion of Haynes 230 in chloride melt SRNL-STI-2019-00017



1000 h flowing salt experiment showed low attack (2018)



- 2.4 cm/s flow rate
  - Calculated from hot spot test
- Low mass changes observed
  - 1000 h operation
  - 20 specimens in hot and cold legs
- Near classic behavior apparent
  - Mass loss in hot leg = dissolution
    - Higher solubility
  - Mass gain in cold leg = precipitation
    - Lower solubility

Highest mass loss < 9 μm/year metal loss (goal is < 15 μm/year)

Pint et al. “Reestablishing the paradigm for evaluating halide salt compatibility to study commercial chloride salts at 600°-800°C,” Materials and Corrosion, (2019).

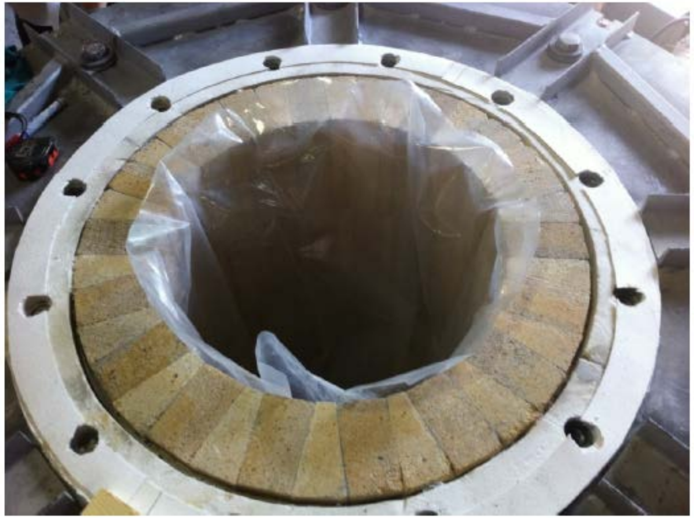
Chemical Sensors

Argonne National Lab’s Multifunction Voltammetry Sensor

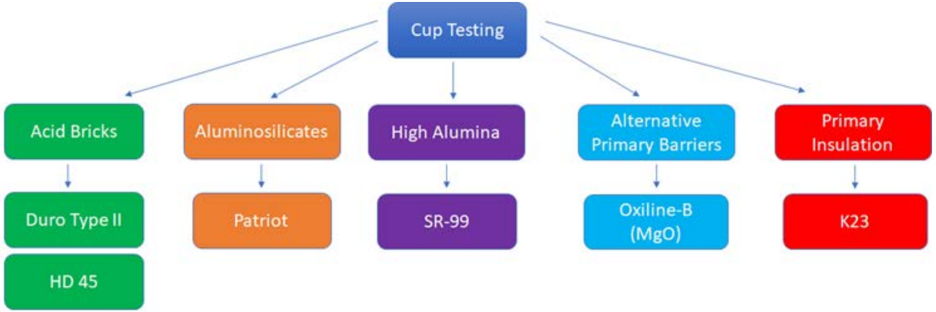
Measure concentration of:

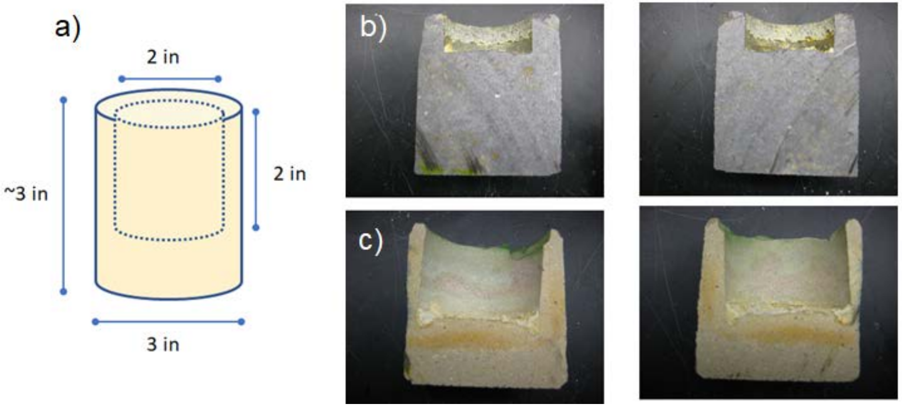
- impurity species, e.g., MgOHCl,
- corrosion products, e.g., Cr^{2+}, Fe^{2+}, etc.,
- soluble Mg,
- as well as Salt Redox Potential
  - Measurements of salt potential indicate salt health and the propensity for corrosion of structural metals to occur

Tank Design Requires Internal Insulation



Refractory-lined, stainless-steel tank tested for use with chloride salts (Jonemann 2013).





Salt Tank Modeling

Equipment Geometry: Floor

Hydrogen Content: 0%

Equipment Hot Face Temperature = 1328 °F

Layer Number	Material	Index Number	Material Maximum Temp (°F)	Layer Thickness (in)	Thermal Conductivity (BTU-in/hr-ft^2-F)	Hot Face Temperature (°F)	Mean Layer Temperature (°F)
1	Durrath HD 45	1818	2948	9	13.28	1328	1291.99
2	K-23	425	2400	6	1.37	1255.98	1015.45
3	WDS Flexipor	1802	2012	1	0.17	774.92	471.18

Equipment Cold Face Temperature = 167.43 °F

Equipment cold face emissivity: **0.85**

Cold face wind velocity: **0 mph**

Cold Face Convection Condition: **Natural**

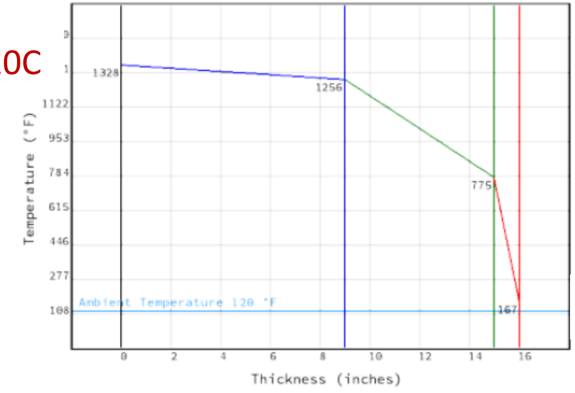
Total Thickness: **16 inches**

Heat Flux (q): **102.52 BTU/hr-ft²**

Ambient Temperature: **120 °F**

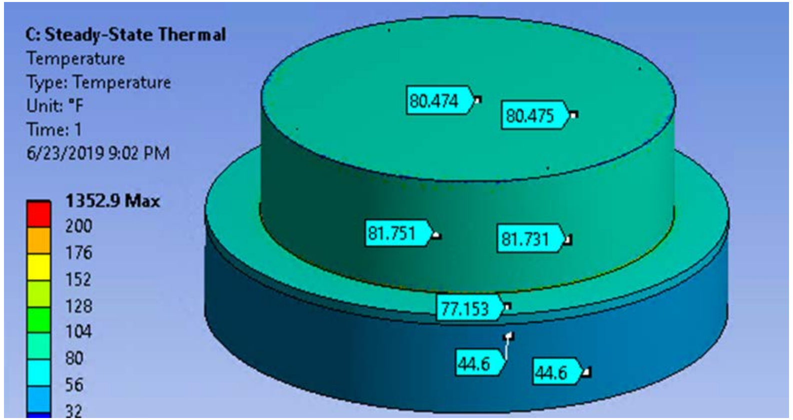
Temperature Profile

Hot salt at 720C

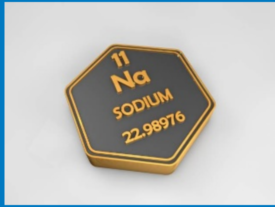


Steel tank wall at ~60C

16" thick, 3-layer refractory barrier required to insulate tank shell



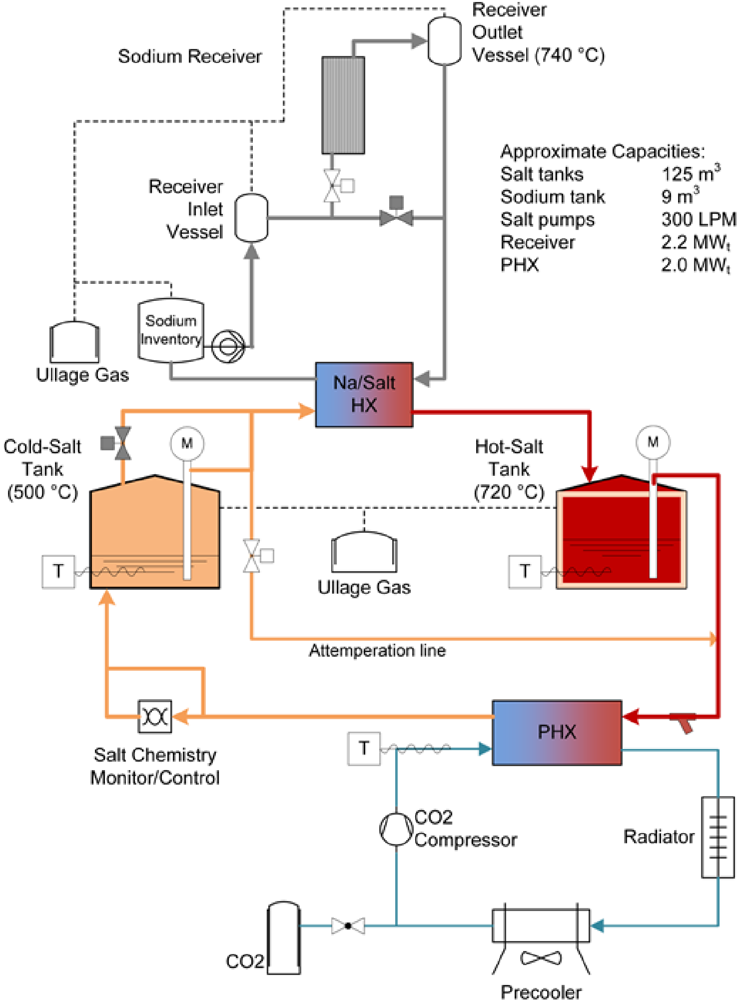
Tank wall and foundation modeling



The Case for Sodium

CSP considering the use of liquid sodium for the solar receiver:

- ✔ >100x higher thermal conductivity
- ✔ T_{mp} = 98 °C vs. 420 °C for salt
- ✔ Lower corrosivity



Integrated 2-MW_t System Test if Phase 3 funded

Phase 3 testing planned for Sandia's National Solar Thermal Test Facility

Key Risks to be Addressed:

1. Demonstrate effective salt chemistry and corrosion control
2. Fabricate cost-effective thermal storage tanks
3. Operate liquid-HTF receiver at 720°C
   - Confirm temperature and heat transfer rates
   - Demo startup, shutdown, and power ramping
   - Define guidelines for receiver operations
4. Validate pumps, valves, and piping
5. Validate primary HX performance
6. Perform component and system modeling and simulate full-scale performance

Thank you

www.nrel.gov

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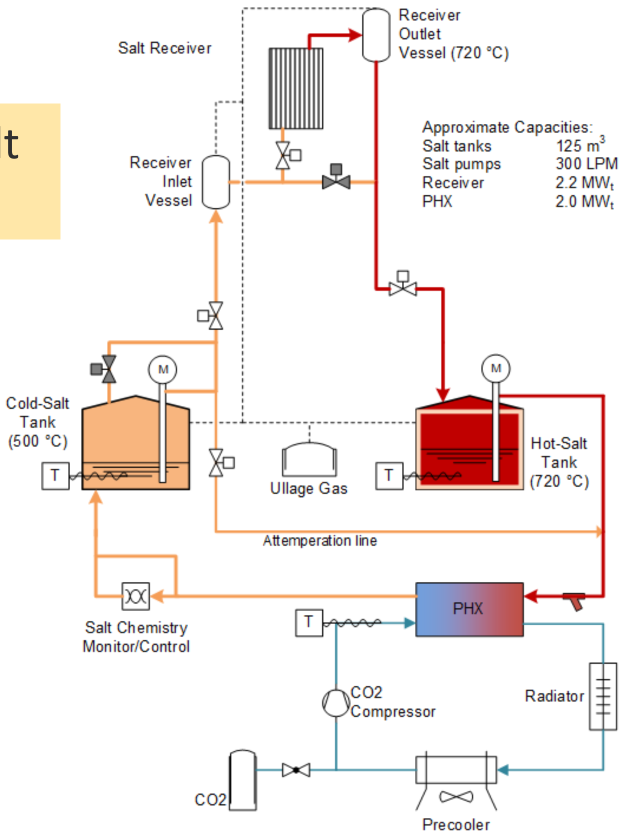
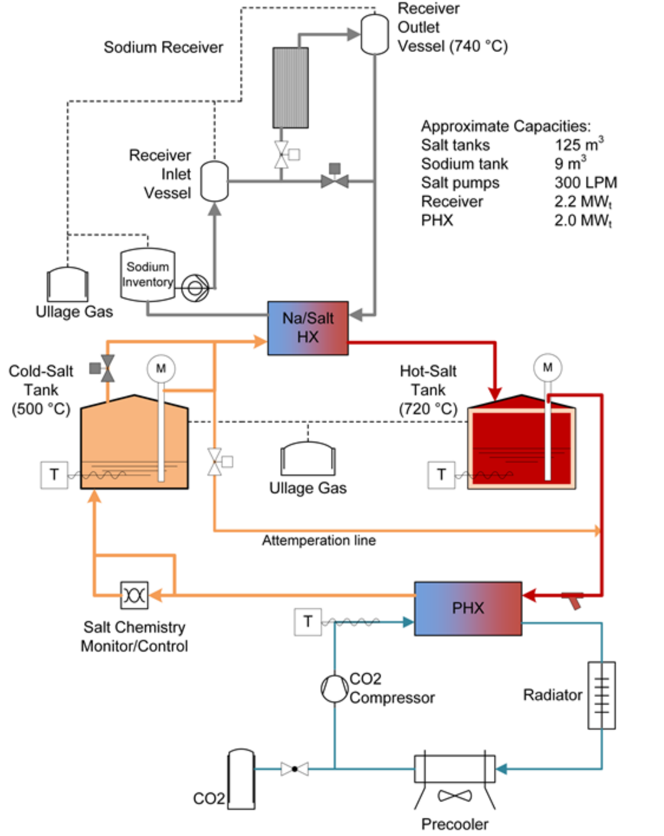
Liquid-HTF Pilot System Alternatives

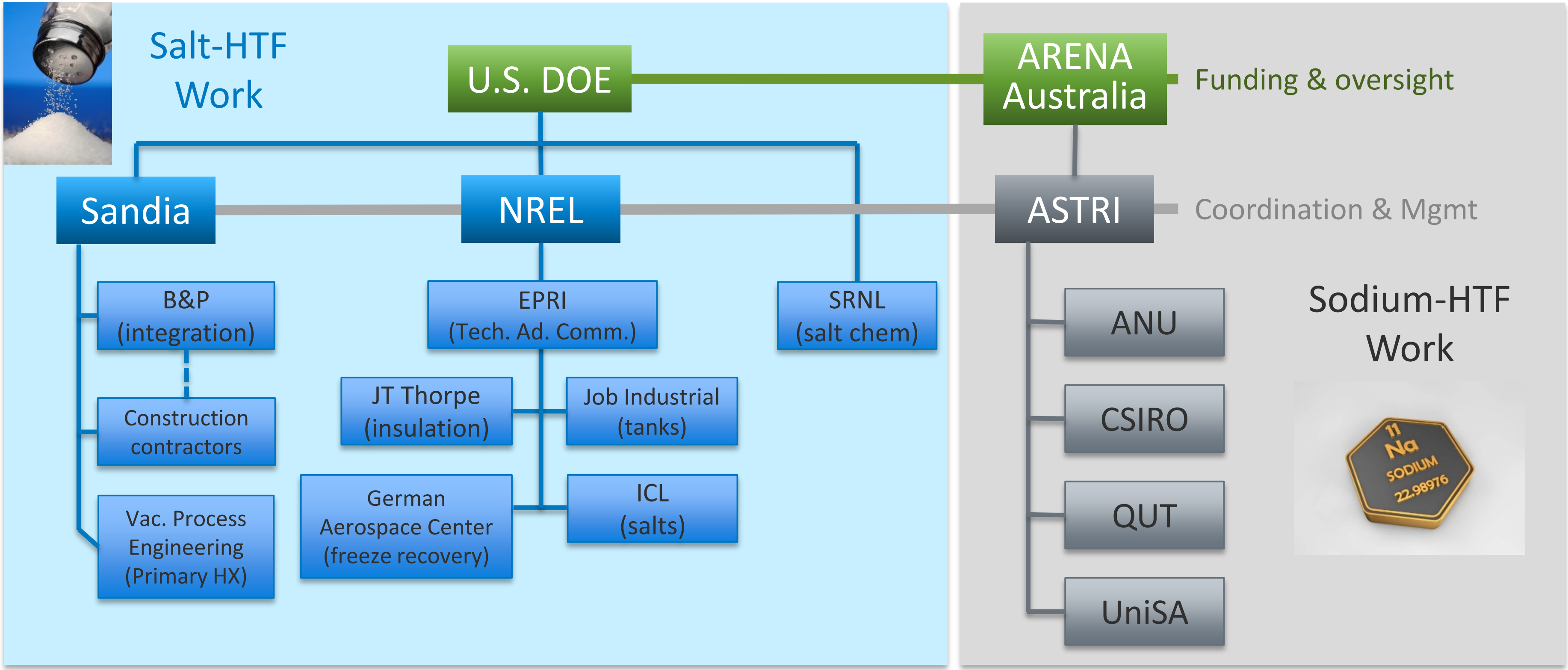
Cl-Salt HTF



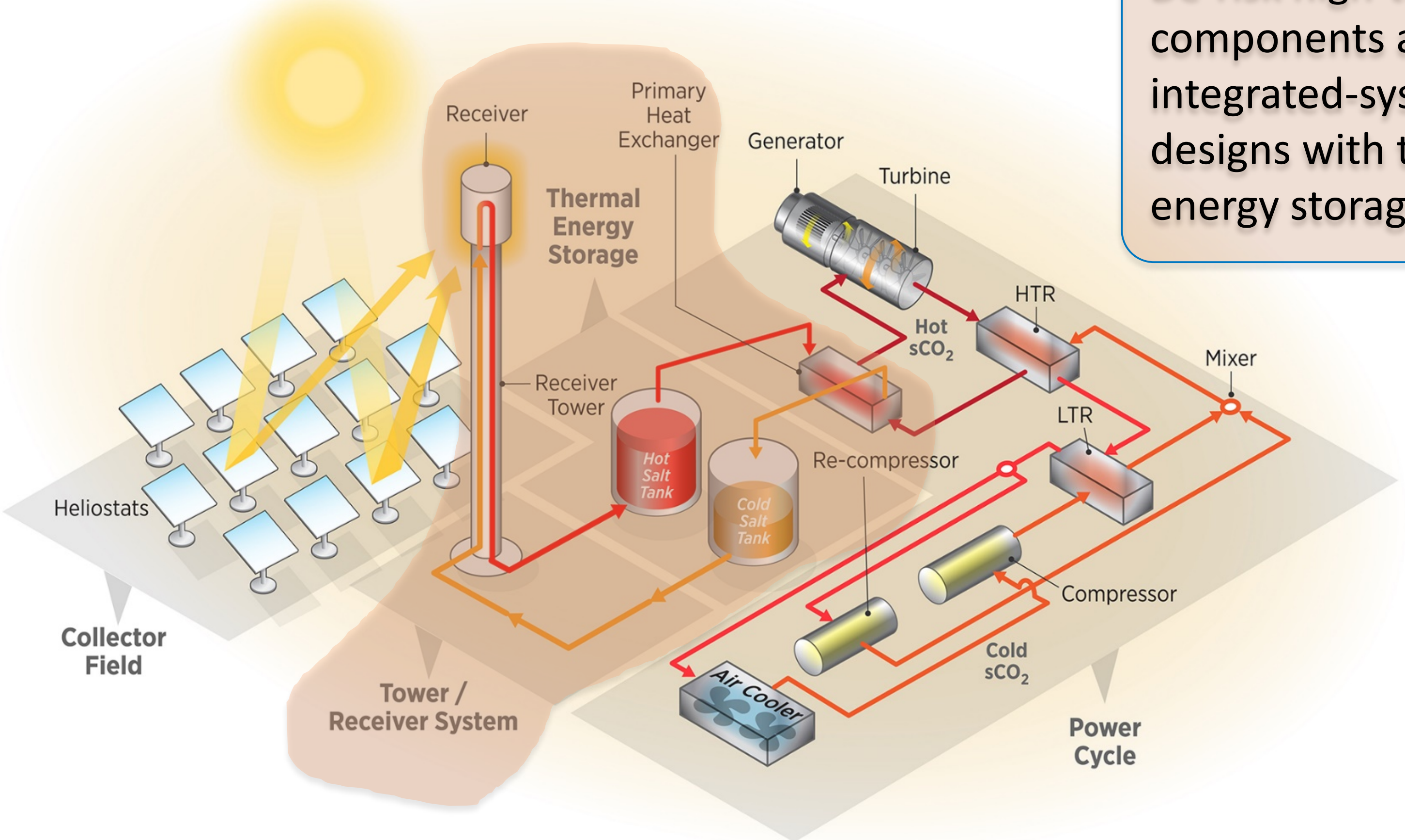
Sodium HTF



Liquid-Pathway Team



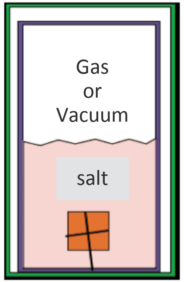
Gen3 Liquid Pathway Thermal Transfer System

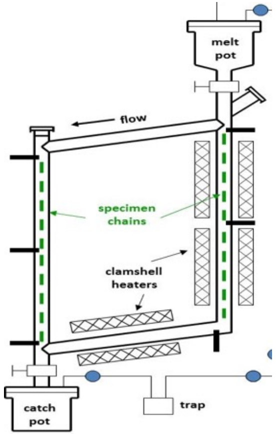


Goal:
De-risk high-temperature components and develop integrated-system designs with thermal energy storage at >700 °C

Assessing Compatibility -- ORNL

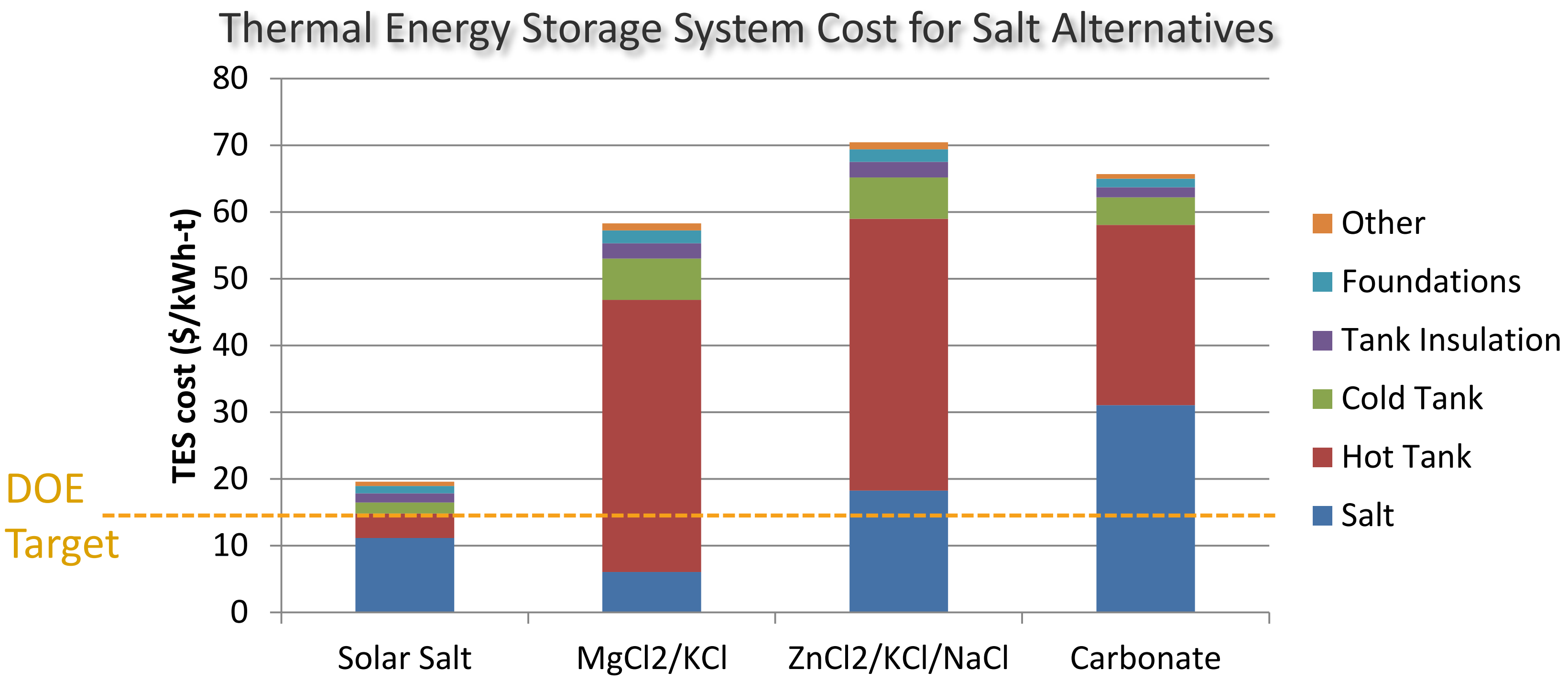
- Thermodynamics
  - First screening tool but data are not always available
- Capsule
  - Isothermal test, first experimental step
  - Prefer inert material and welded capsule to prevent impurity ingress
  - Dissolution rate changes with time: key ratio of liquid/metal surface
- Thermal convection loop (TCL)
  - Flowing liquid metal by heating one side of "harp" with specimen chain in "legs"
  - Relatively slow flow and ~100°C temperature variation (design dependent)
  - Captures solubility change in liquid: dissolution (hot) and precipitation (cold)
    - Dissimilar material interactions between specimens and loop material
- Pumped loop
  - Most realistic conditions for flow
  - Historically, similar qualitative results as TCL at 10x cost





Source: Pawel JNM 2017

Containment is the Primary Cost Issue



Adapted from CSP Gen3 Roadmap: NREL/TP-5500-67464, 2017