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Thermal property testing of nitrate thermal storage salts in the solid-phase

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Value of Thermal Storage

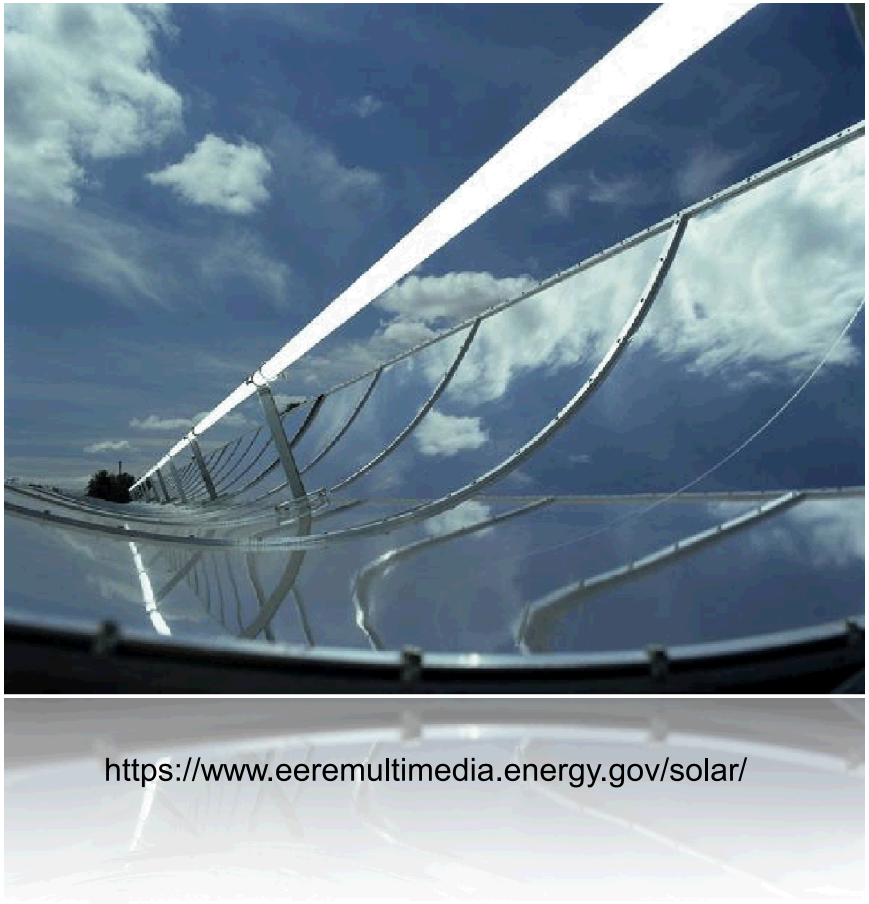
Sioshanshi and Denholm, 2010, NREL-TP-6A2-45833

- **Energy**
  - Allows generation to be shifted to higher priced hours
  - Can reduce some efficiency loss by shifting generation to hours with lower ambient temperatures
  - Increases the use of thermal energy from the solar field
- **Capacity**
  - Allows energy collected by the solar field to be used by placing excess energy that would overload the power block into thermal energy storage (TES) for future use
  - Can similarly increase solar multiple to further increase power block usage
- **Ancillary services**
  - Regulation, spinning, non-spinning reserves

Storage for Parabolic Trough

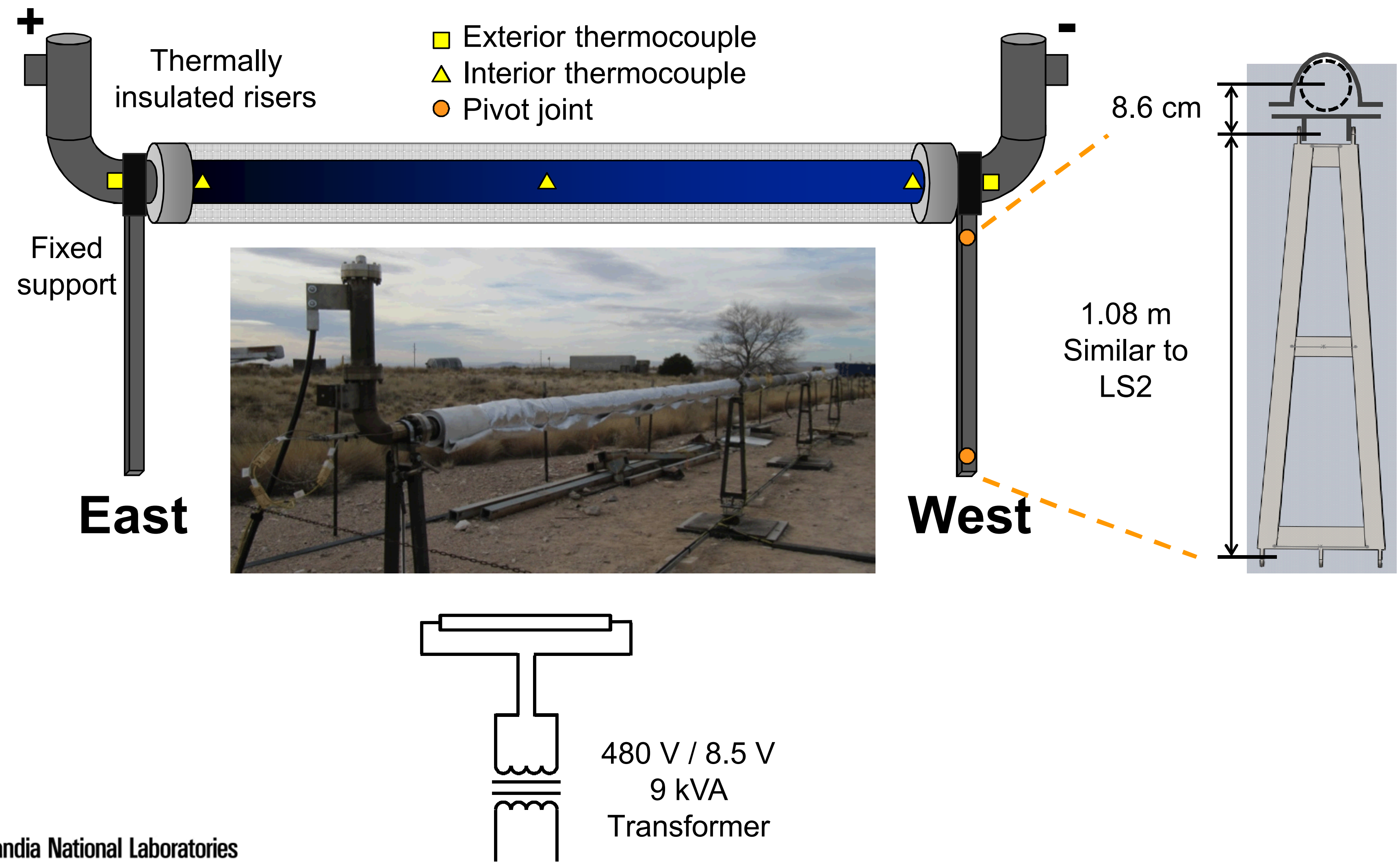
- Replacement of working fluid with salt
  - Increases operating temperature limit
  - Increases ΔT through field
- Leads to more power production at higher efficiency
- Direct storage reduces efficiency loss in heat exchanger (over indirect)
- Implementation concern
  - Freeze possibility
  - Recovery from freeze event

Kearney *et al.*, 2003, JSEE, 170-176
and
Kolb *et al.*, 2010, ASME Energy Sustainability

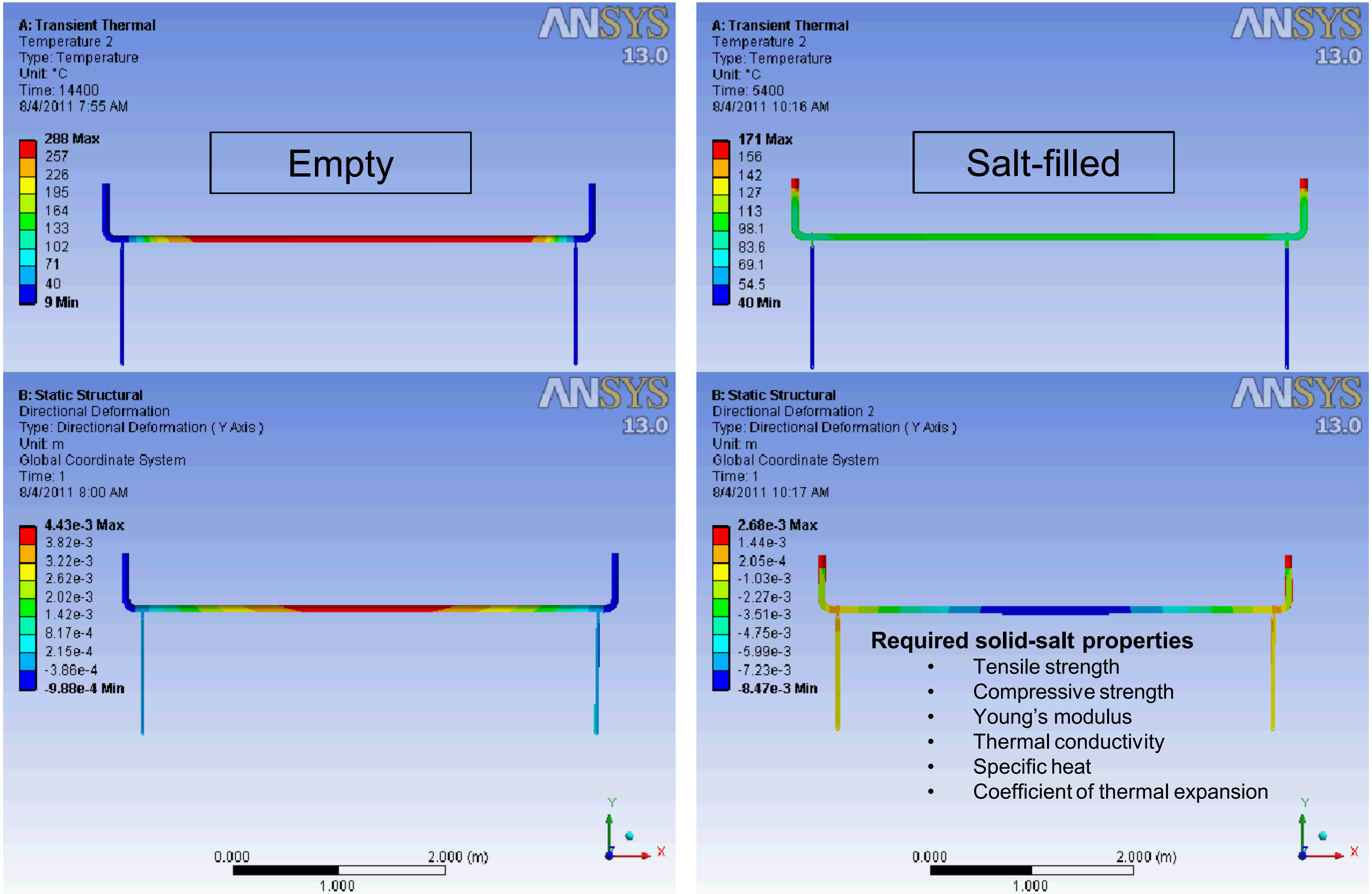


https://www.eeremultimedia.energy.gov/solar/

Freeze/Melt Test Facility



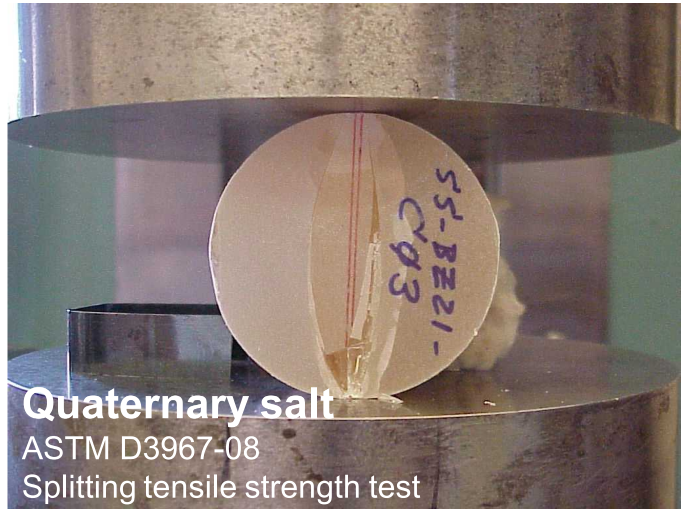
Material Property Needs



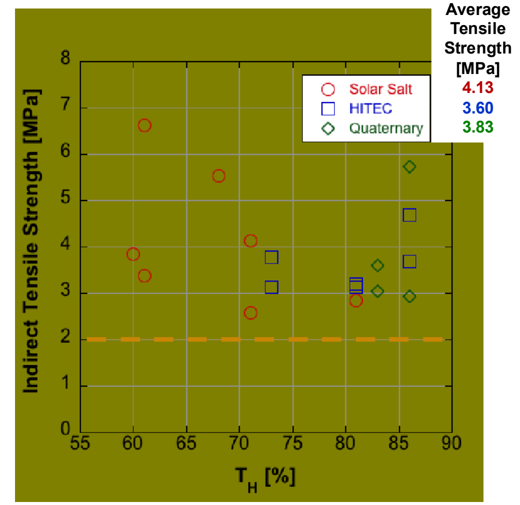
Required solid-salt properties

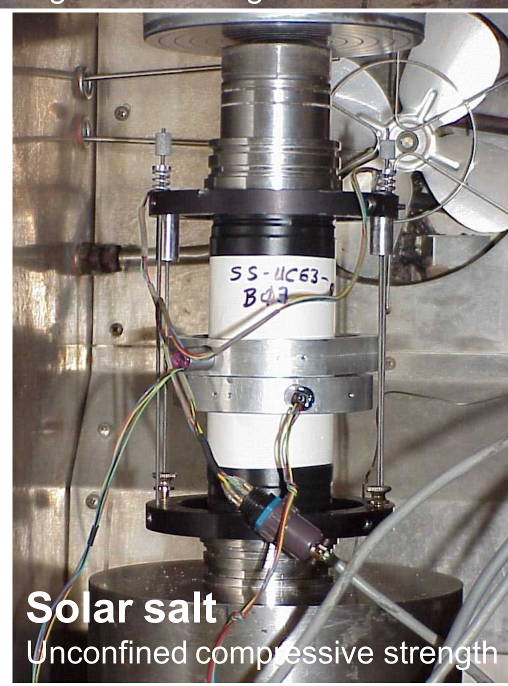
- Tensile strength
- Compressive strength
- Young's modulus
- Thermal conductivity
- Specific heat
- Coefficient of thermal expansion

Mechanical Properties

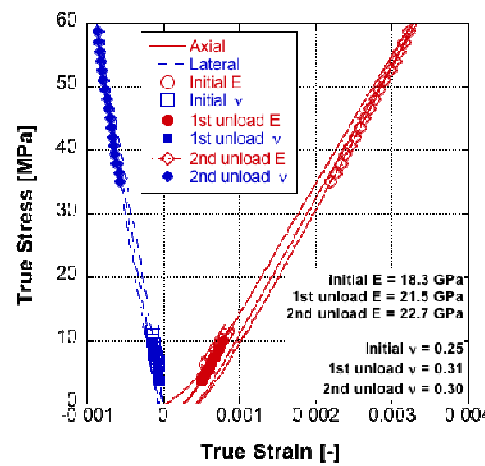


Quaternary salt
ASTM D3967-08
Splitting tensile strength test





Solar salt
Unconfined compressive strength



Iverson et al., 2010, SolarPACES

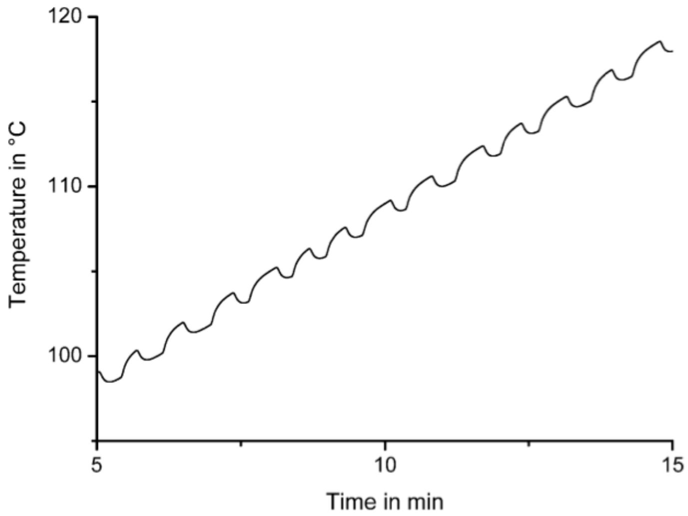
Thermal Property Test Matrix

Salt Type	Specific heat	CTE	Thermal conductivity
Solar salt [4, 5] $T_{m,A} = 221$ °C	0 to 325 °C	30 to 200 °C	30 to 35 °C
HITEC [6] $T_{m.B} = 142$ °C	0 to 250 °C	30 to 120 °C	30 to 35 °C
Quaternary [7] $T_{m.C} = 90$ °C	-50 to 250 °C	30 to 75 °C	n/a

Constituent	Solar salt	HITEC salt	Quaternary salt
$NaNO_3$	60%	7%	12.1%
KNO_3	40%	53%	42.3%
$NaNO_2$	-	40%	-
$Ca(NO_3)_2$	-	-	39.4%
$LiNO_3$	-	-	6.1%

Weight percent %

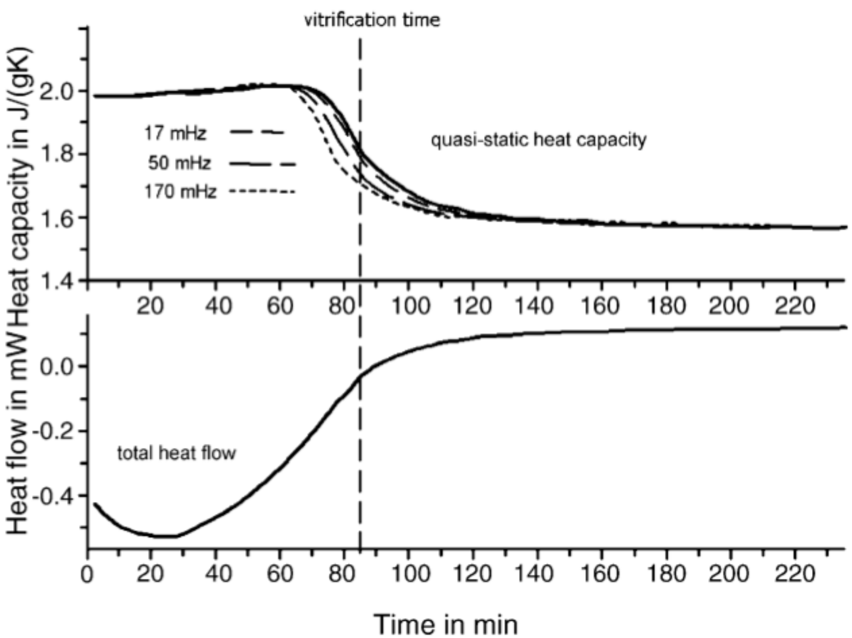
Specific Heat using Calorimetry



TOPEM: Temperature modulated differential scanning calorimetry (TMDSC)

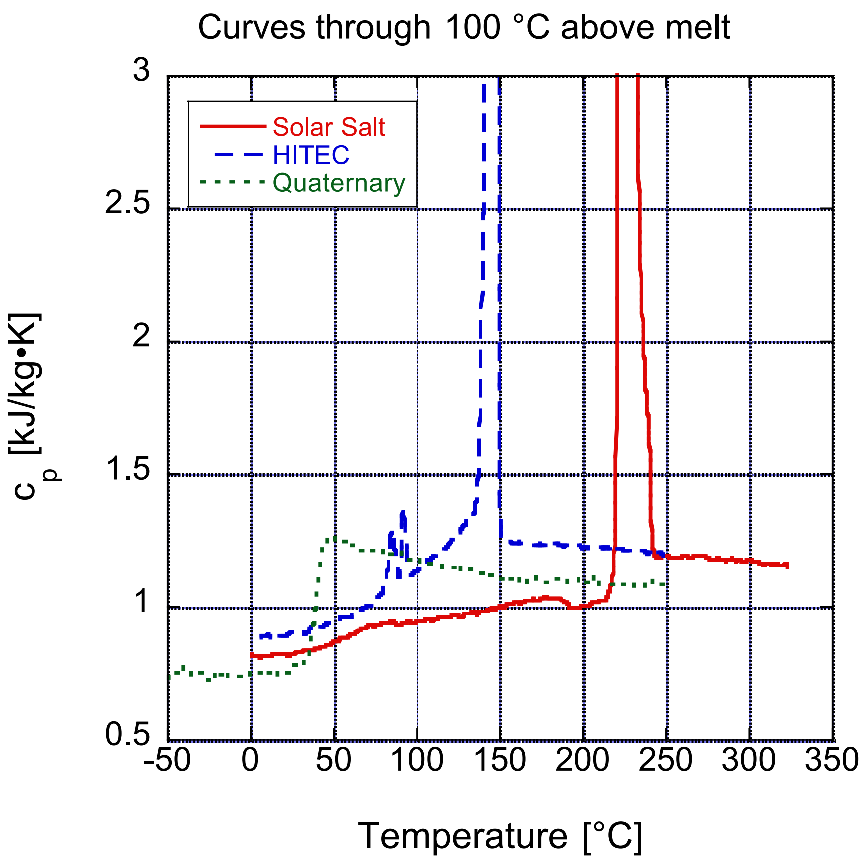
- The samples were subjected to a linear temperature-increase rate with a superimposed stochastic modulated temperature fluctuation.
- Based on the frequency response of the heat flow profile, the heat capacity can be obtained from the sample.

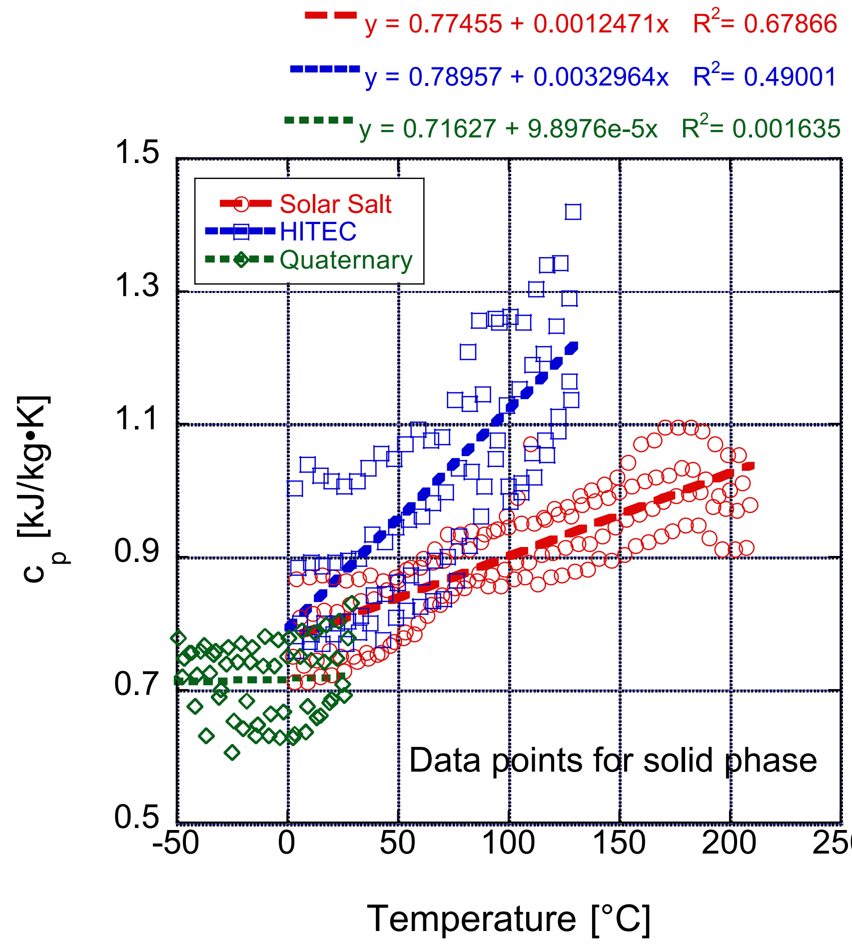
- Method yields both heat capacity and heat flow.
- Allows for direct measurement of the specific heat capacity instead of requiring an indirect comparison with a standard material.



Schawe *et al.*, 2005, UserCom 22, Mettler-Toledo
Schawe *et al.*, 2006, Thermochimica Acta

Specific Heat

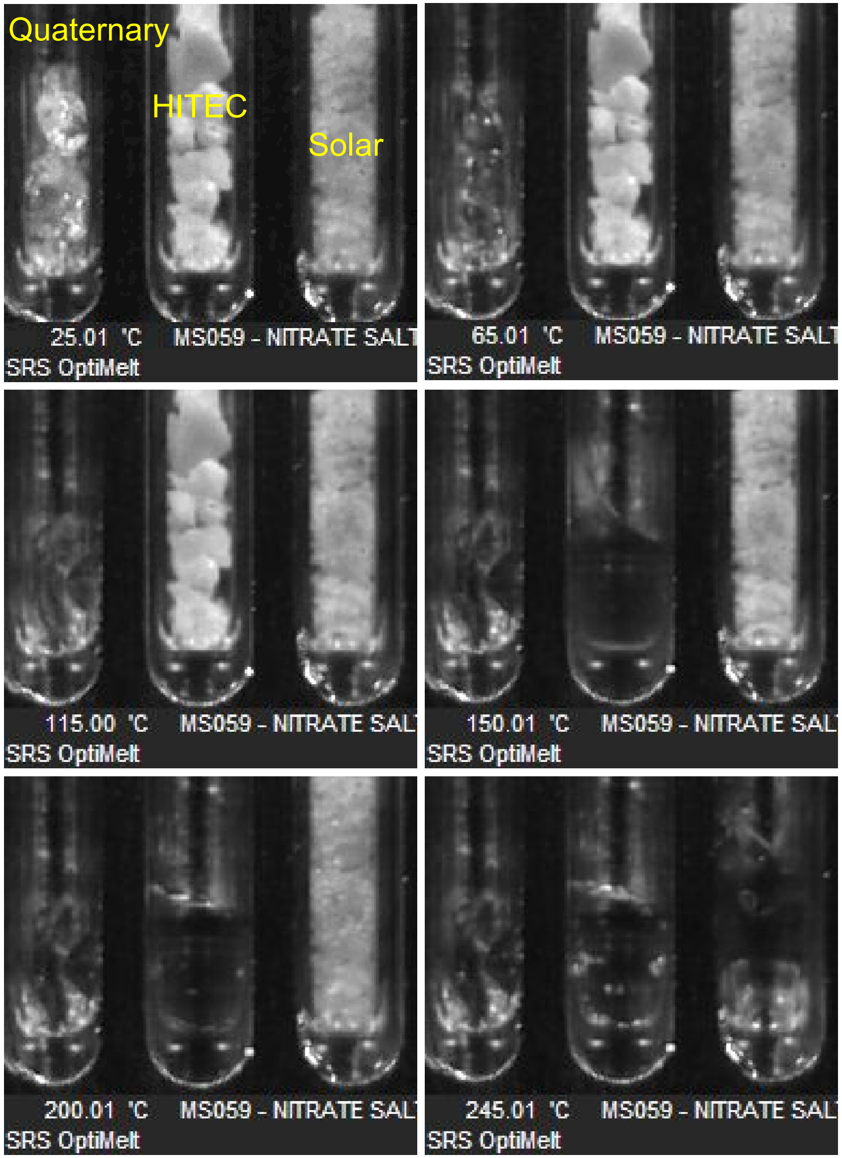




Quaternary salt not a eutectic → melt occurs over a range of temperatures

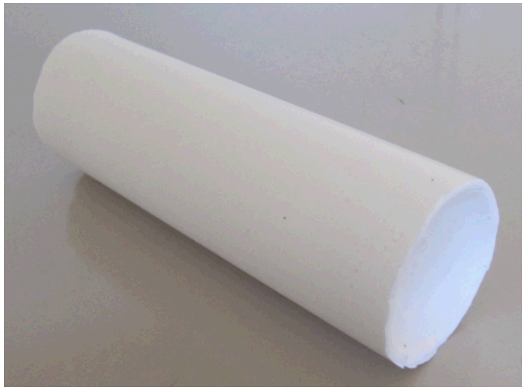
Melting Transition

- Light intensity indicates amount of solid-phase
  - Lighter colors indicate less light passage due to the presence of the solid-phase.
- Temperature ranges from 25-245 °C.
- Transition to melt visually observed for quaternary salt



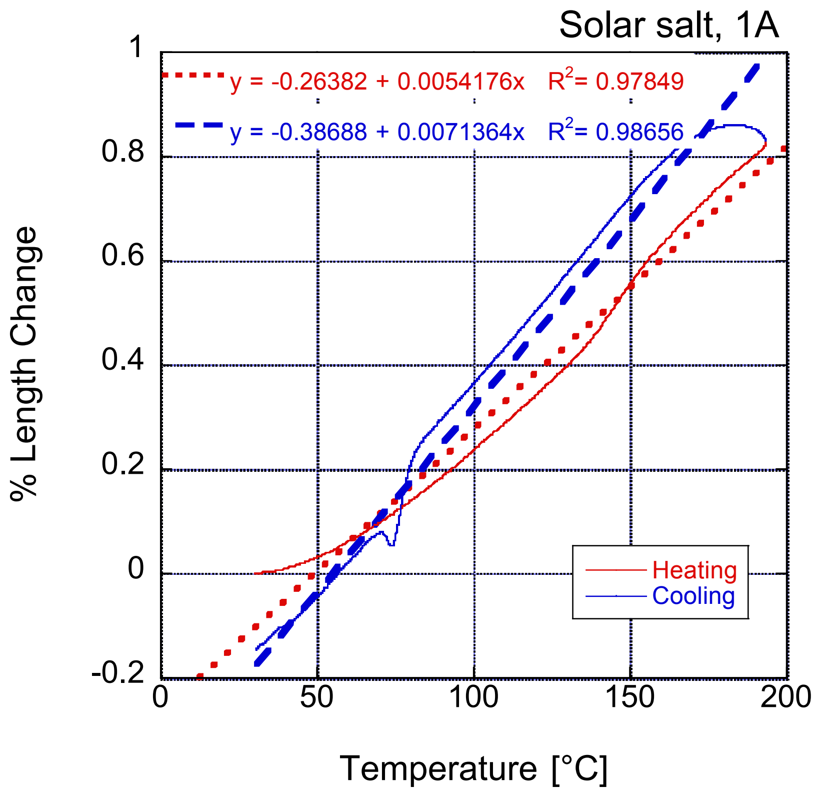
CTE

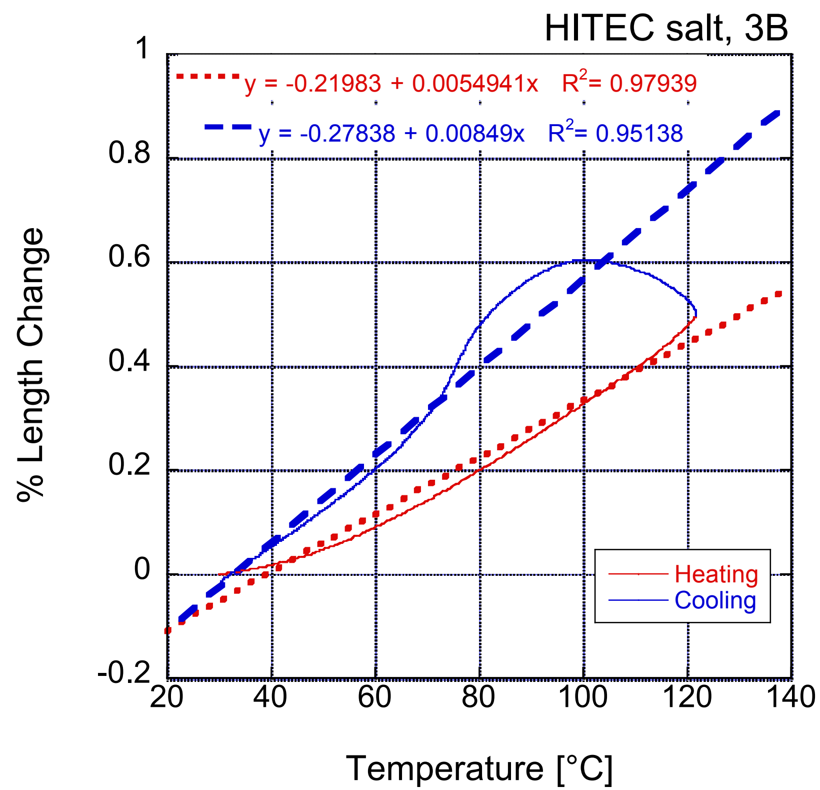
- Follows ASTM standard E228
- Parts cast at room temperature and cut to length
- Heated to 90% of the melt temperature and cooled
- Expansion recorded with linear displacement transducers
- Two tests per salt type on different samples




Courtesy Harrop Industries

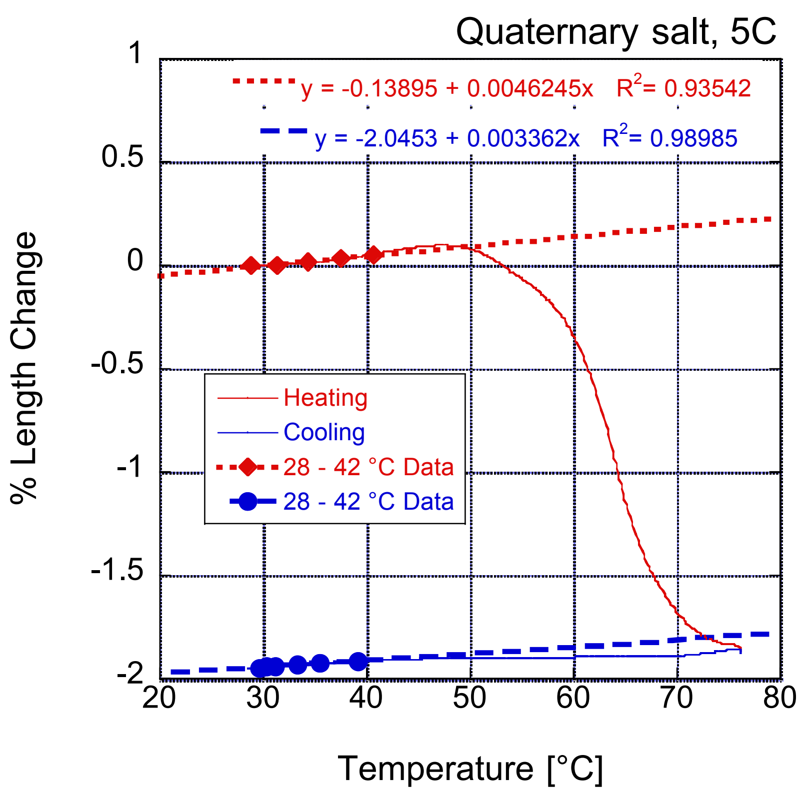
CTE





- Data points are taken at 0.1-0.2 °C increments with error values of <0.05% in length change and ±1 °C in temperature.
- Ramp rate of 3 °C/min
- Trend lines are generated using all data points from the heating or cooling regions.
- CTE 30+% higher than naturally occurring Halite (NaCl)

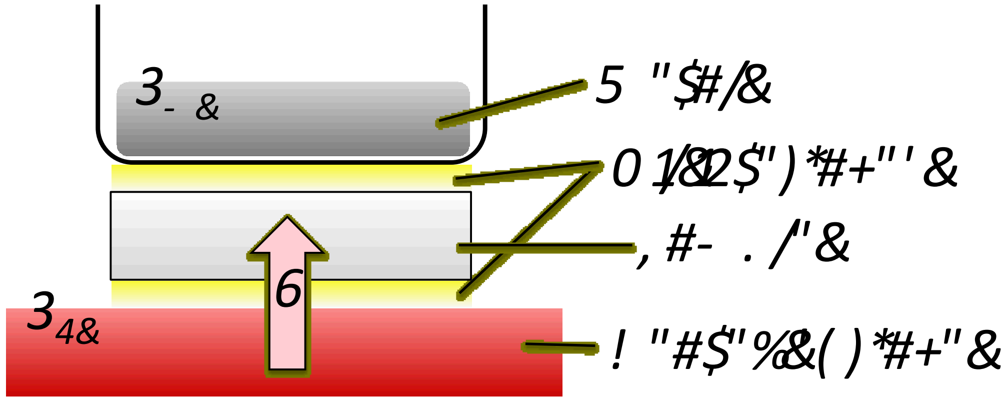
CTE



Salt type	Sample	Heat/cool range [°C]	α / 10^{-6} °C^{-1} Best fit	α / 10^{-6} °C^{-1} Avg
Solar salt	1A	Heat 30.1 – 193.3	54.2	Heat 54.7
		Cool 193.3 – 30.4	71.4	
	2A	Heat 30.0 – 199.2	55.2	Cool 70.6
		Cool 199.2 – 30.4	69.8	
HITEC	3B	Heat 30.0 – 121.6	54.9	Heat 55.8
		Cool 121.6 – 30.4	84.9	
	4B	Heat 30.0 – 120.2	56.7	Cool 84.3
		Cool 120.2 – 30.4	83.7	
Quaternary	5C	Heat 28.0 – 42.0	46.2	Heat 56.4
		Cool 42.0 – 28.5	33.6	
	6C	Heat 25.0 – 42.0	66.5	Cool 29.2
		Cool 42.0 – 35.7	24.8	
Halite (NaCl)	N/A	Heat (~75 °C)	~ 40 [8]	
		unknown	45.0 [9]	

- Ramp rate of 1 °C /min
- Trend lines are generated using all data from 28-42 °C, consistent with observed melt transition from DSC c_p

Thermal Conductivity



$$q = \frac{\Delta T}{\Sigma R} = \frac{T_h - T_m}{R_{int} + R_s + R_{int}}$$

k_{direct}

$$R_{t,\,int} = R_{int} + R_{int}$$

$k_{regression}$

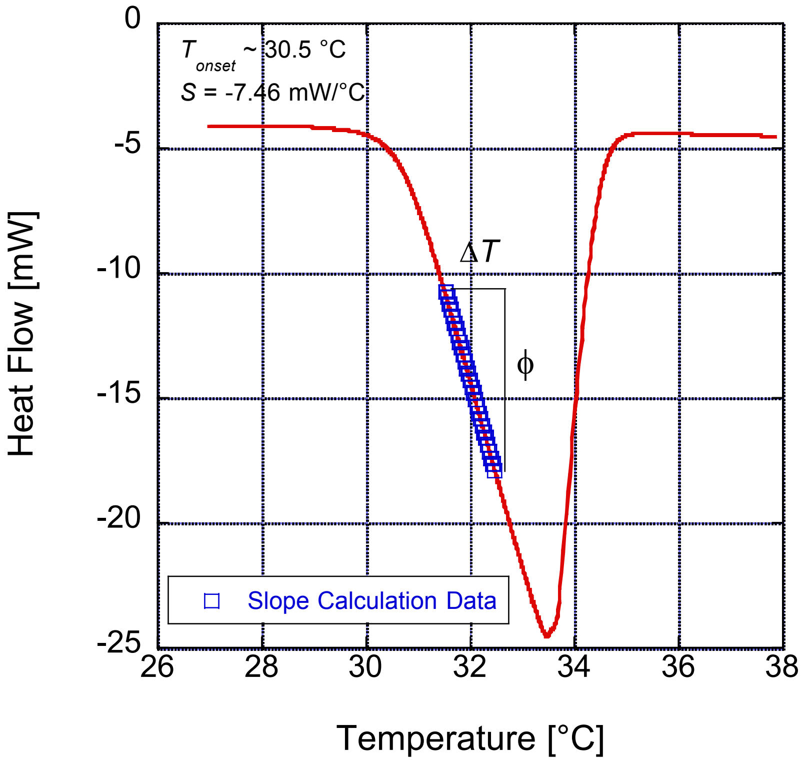
$$q = \frac{L}{kA}\left(T_h - T_m\right)$$

$$S = \frac{q(t) - q_{onset}}{T_h(t) - T_{onset}} = \frac{1}{R_{t,\,int} + L/kA}$$

Riesen, R., 2005, UserCom 22, 2/2005, Mettler-Toledo, pp. 19-23.

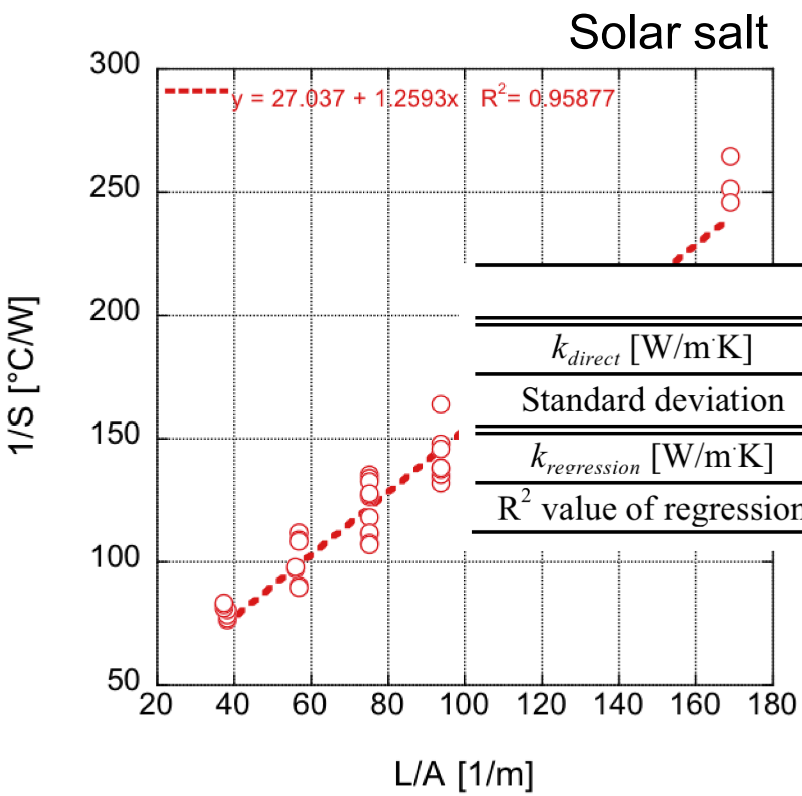
Thermal Conductivity

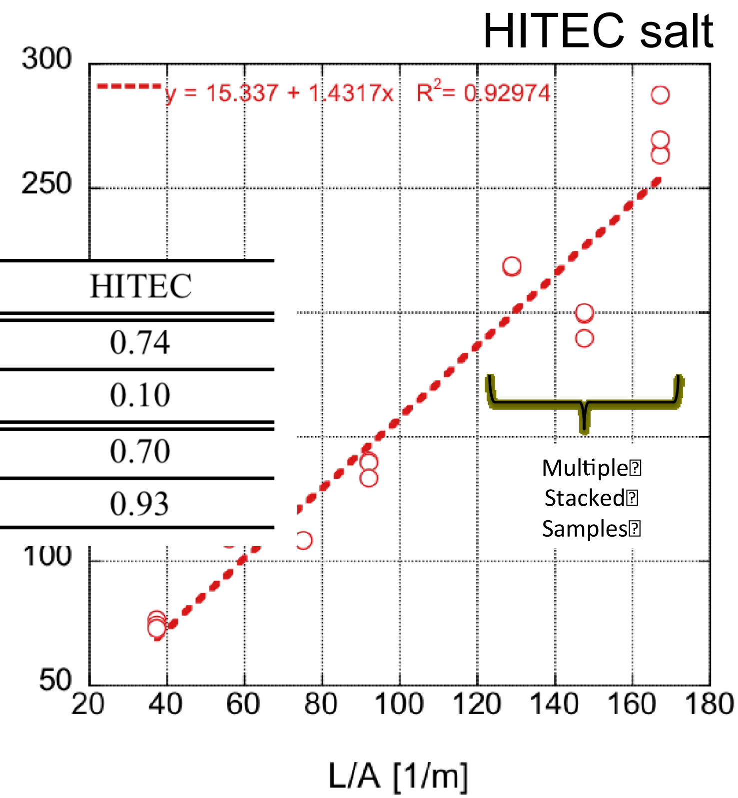
$$\frac{1}{S} = \frac{L}{kA} + R_{t,int}$$



Solar salt, 2.5 mm sample

Thermal Conductivity





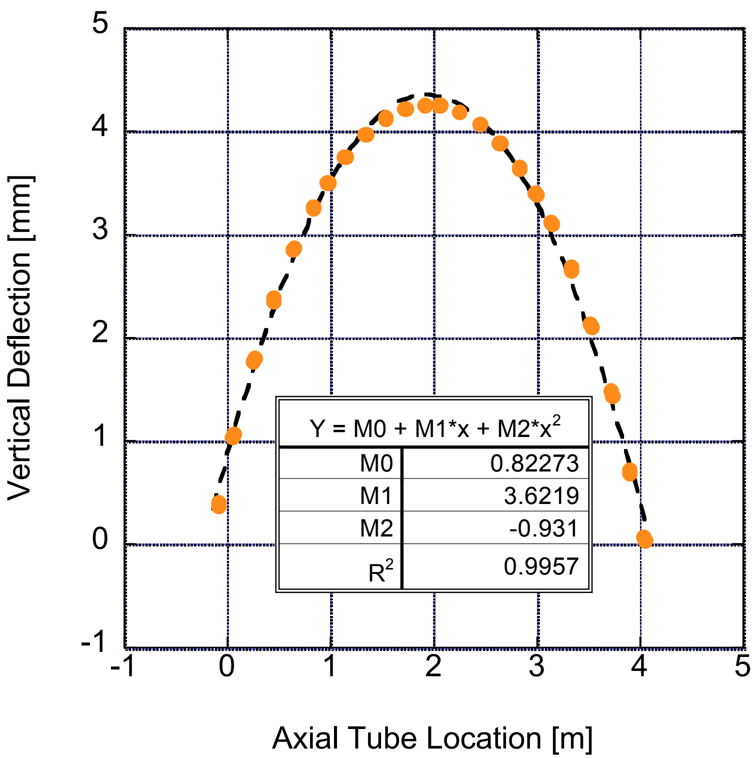
	Solar Salt	HITEC
k_{direct} [W/m·K]	0.76	0.74
Standard deviation	0.12	0.10
$k_{regression}$ [W/m·K]	0.79	0.70
R^2 value of regression	0.96	0.93

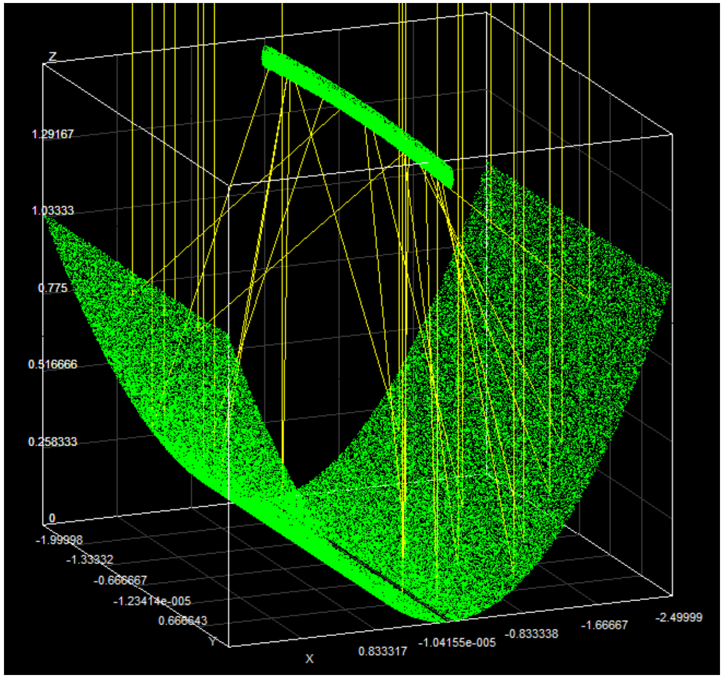
Conclusions

- Solid-phase thermal properties for three salt compositions were obtained
  - Specific heat
  - Coefficient of thermal expansion
  - Thermal conductivity
- Quaternary salt (with relatively high $Ca(NO_3)_2$ concentration) exhibits glass-like behavior and has a temperature range over which melting occurs; off-eutectic
- CTE for Solar and HITEC salt 30+% higher than naturally occurring Halite
- Combined with mechanical property data, recovery from solidification can be modeled.

Future Work

- Measurements and analysis of tube deflection for various tube and heating conditions
- Study impact on solar intercept





Iverson et al., 2011, SolarPACES

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