

High Efficiency Thermal Energy Storage System for CSP

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SunShot CSP Program Review

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Project Start Date: October 1, 2012

Project Rationale

- Potential reduction in levelized cost to produce electricity (LCOE) can be realized by incorporation of thermal energy storage (TES) system
- By some estimates*, LCOE could be reduced by 25% for power tower systems for up to 13 hours storage operating at an annual capacity factor of 0.6-0.7
- Current two-tank molten salts based TES operate at low temperatures and require large quantities of storage media
- Push is for higher temperature, inexpensive phase-change materials with large latent heat to reduce the storage media volumes and associated system/capital costs
- However, due to low thermal properties of PCMs, the performance of salts in charging/discharging is limited

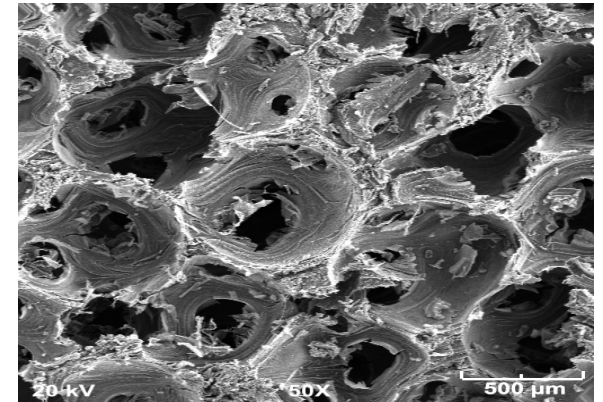
Improvements in thermal performance of high temperature PCMs is needed

* Concentrating solar power: its potential contribution to a sustainable energy future," EASAC policy report 16, November 2011.



Project Objectives

- The goal of this proof-of-concept project is to develop an efficient high temperature lab-scale thermal energy storage (TES) prototype by utilizing phase change materials (PCMs) in combination with new, high thermal conductivity graphite foams



- Targets/features of the proposed TES system:
 - high-temp ($>700^{\circ}\text{C}$) TES system
 - rapid charge/discharge times (< 8 h)
 - full utilization of PCM; even energy distribution, no dead zones
 - round trip efficiency $>95\%$
 - low density of foam does not impact the salt volumetric proportion
 - smaller TES systems
 - less number of heat transfer pipes
 - lower plant capital costs
 - LCOE will be reduced due to higher temperature TES and efficient and rapid charge/discharge cycles





Technological Barriers & Innovations

- Proposed concept has not been used for high-temperature TES system
- Process technologies to infiltrate graphite foam with appropriate PCM
- Oxidation of graphite -- coatings with appropriate interface will provide oxidation resistance without compromising thermal performance
- Joining of alloy components to foam
- Interaction of PCM with alloy components and graphite
- Development of a sealed system to prevent any oxygen ingress



Approach

- Budget Period 1 (12 months)
 - Task 1.1: Thermal energy storage (TES) device modeling and design
 - Task 1.2: Coating of graphite foam for improving strength, oxidation resistance, and surface heat transfer characteristics
 - Task 1.3: Salt based phase change materials (PCM)
 - Go/No-Go Decision Point 1

- Budget Period 2 (12 months)
 - Task 2.1: Joining technologies
 - Task 2.2: Corrosion interactions between alloys/PCM/graphite
 - Task 2.3: Process development for foam infiltration with PCM
 - Assemble TES device prototypes and conduct shake-out tests
 - Go/No-Go Decision Point 2

- Budget Period 3 (12 months)
 - Task 3.1: Performance data for TES device prototypes
transport properties, cycling performance, model refinements, scale-up strategy

- Project Deliverable
 - Lab-scale TES prototypes, associated technologies, and performance data
 - >700 °C operation, <8 hour charge time (extrapolate to full-scale system using model), 95% round trip efficiency



Accomplishments – since October 2012

- Modeling/Analysis
 - demonstrate the advantages of graphite foam/PCM as TES system
 - preliminary design for lab-scale prototype

- Graphite foam
 - baseline property characterizations
 - develop foam coating procedures
 - characterize post coating
 - preliminary oxidation tests

- Phase change material selection
 - Identify appropriate PCMs
 - characterize PCMs



Accomplishments: TES System Modeling and Design

- Charging/discharging heat transfer rates
 - 50 MWe CSP with 12 h storage
 - single tank storage utilizing high temperature salt PCM
 - vertical pipes in tank with pumped heat transfer fluid for charging/discharging
- Constraint: 8 hr charge/discharge time
- PCM – chloride salt, heat transfer fluid – FLiNaK ($T_{m,p} = 454^{\circ}\text{C}$)
- Goals
 - Determine amount of PCM utilized during charge/discharge
 - PCM only in LHTES tank
 - PCM & graphite foam in LHTES tank
 - Determine pipe requirements with/without foam



Accomplishments: TES Modeling and Design

- Analysis – governing equations and boundary conditions

$$\frac{\partial T_p}{\partial t} = \alpha_p \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_p}{\partial r} \right) \quad (1)$$

$$k_p r_o \frac{\partial T_p}{\partial r} = - \frac{T_b - T_o}{\frac{1}{hr_i} + \frac{1}{k_t} \ln \left(\frac{r_o}{r_i} \right)} \quad \text{where } r = r_o \quad (2)$$

$$T_p = T_m \quad \text{where } r = s \quad (3)$$

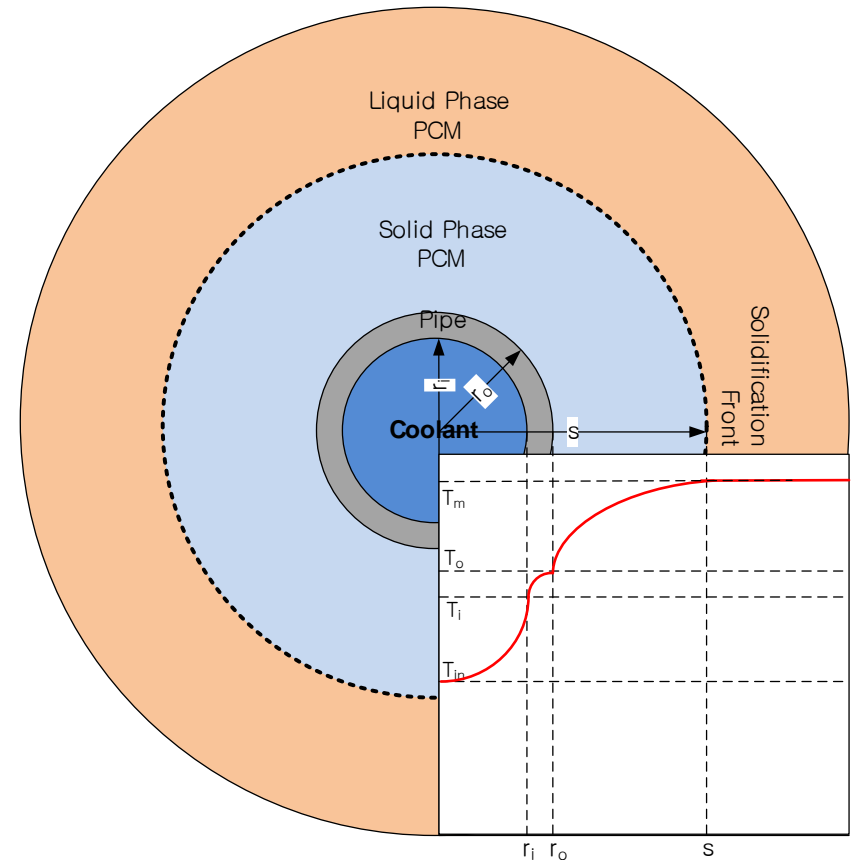
$$-k_p \frac{\partial T_p}{\partial r} = \rho H \frac{ds}{dt} \quad \text{where } r = s \quad (4)$$

- Analytic solution (Zhang & Faghri, 1996)

- variation of parameters
- 2nd order logarithmic form
- Resulting differential equation for solid/liquid front position, S, versus time :

$$\frac{dS}{dF_o} = \frac{\sqrt{1 + 2\theta_o Ste} - 1}{S \ln \left(\frac{S}{R_o} \right)} \quad (5)$$

- Numerical method used to solve equation (5)

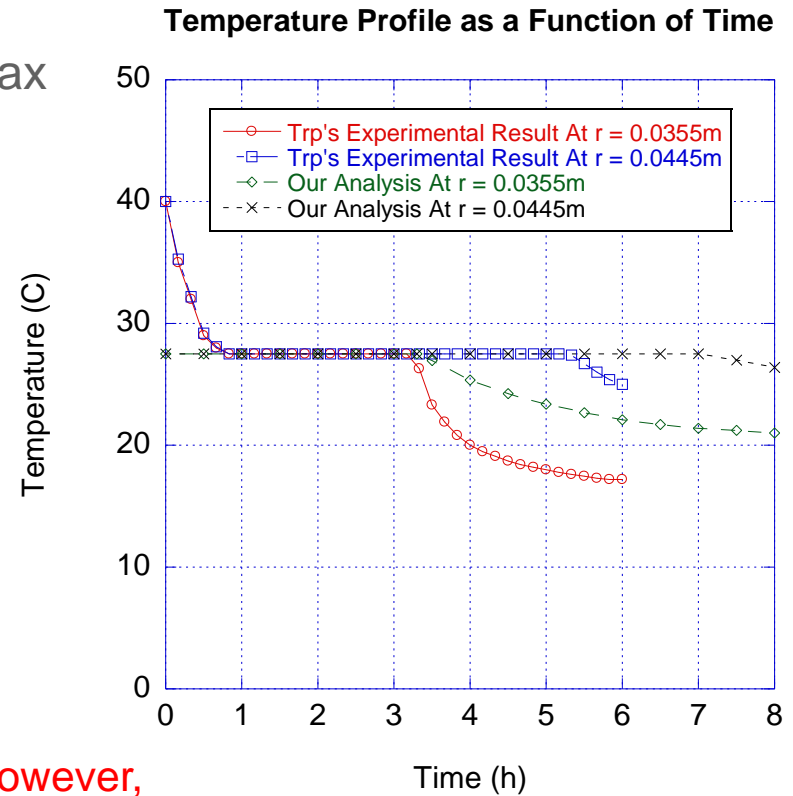


Schematic of solidification of PCM around a pipe

Accomplishments: TES System Modeling and Design

- Validation of analysis
 - Trp's* experiment using paraffin wax

	Our analysis	Trp's experiment
Solidification front passing time at $r = 0.0355$ m	3.2 h	3.1 h
Solidification front passing time at $r = 0.0445$ m	7.0 h	5.6 h



The reference experiment was 3-dimensional, however,
our analysis is 1-dimensional

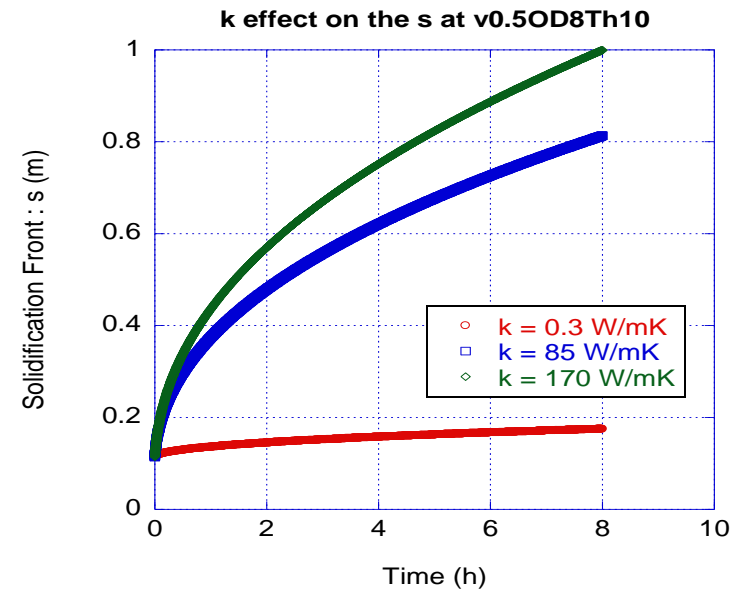
*Trp, A., Sol. Energy 79, 648-660, 2005.



Accomplishments: TES System Modeling and Design

■ Results

- At the end of the 8 hours discharge transient, the solidification front radii are seen to be **0.175 m**, **0.813 m** and **0.999 m** for effective PCM thermal conductivities of 0.3 W/m-K, 85 W/m-K and 170 W/m-K, respectively
- The solidification thickness increased by over a factor of **10** as the effective PCM thermal conductivity increased from 0.3 W/m-K to 85 W/m-K by the addition of the graphite foam
- Significant reduction in the number of pipes needed for the LHTES; **reduced TES capital costs**



Solidification front movement as a function of thermal conductivity at $v=0.5\text{m/s}$, Pipe OD = 8", Th= sch10

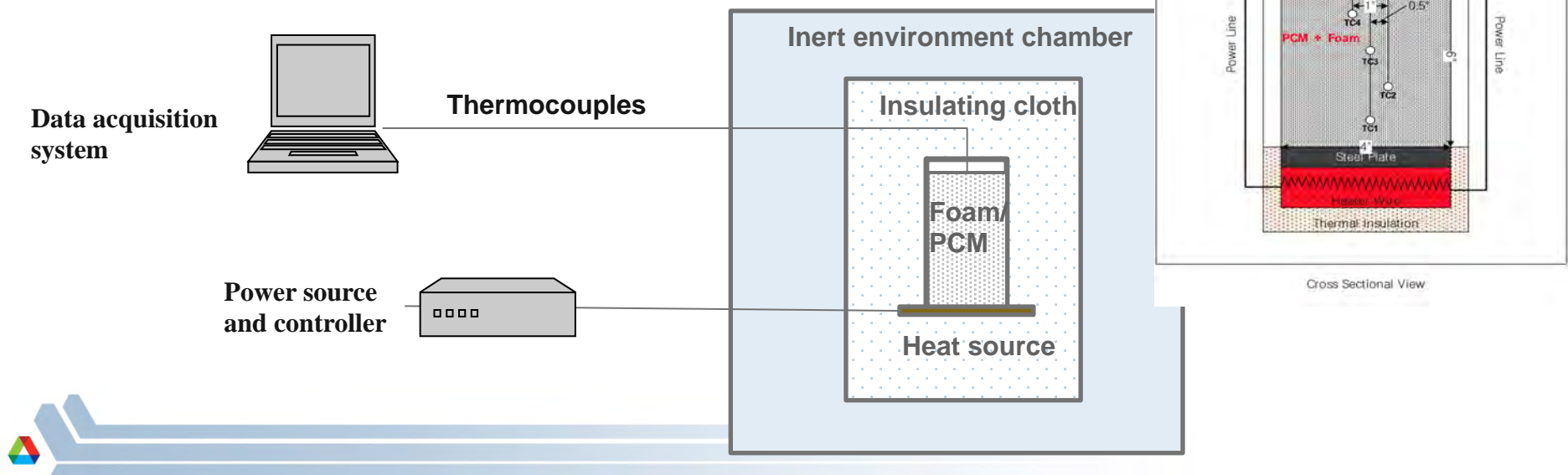
Heat transfer between PCM and heat transfer fluid can be enhanced dramatically by use of graphite foam



Accomplishments: Design of Lab-scale Test Set-up

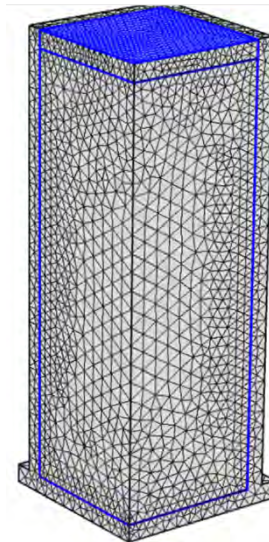
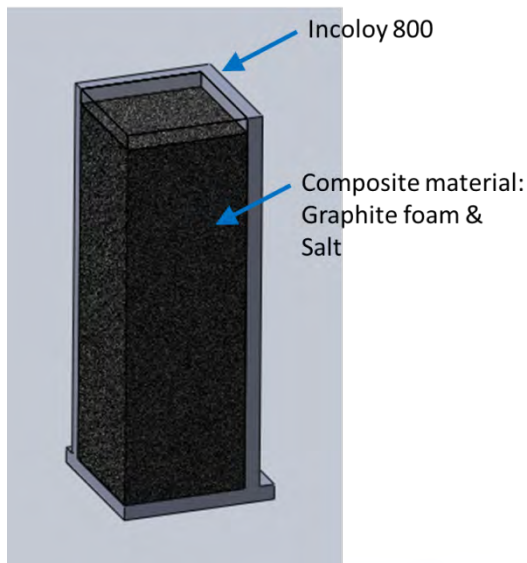
- Design and build a system with 0.22 g/cm^3 foam impregnated with MgCl_2 PCM
 - Metal box with foam bonded/brazed to bottom plate
 - Constant temperature hot plate heating in inert environment
- Compare experiments to model predictions
 - Utilize optimization software in MATLAB to solve for multiple unknown parameters (e.g., braze conductivity, foam/PCM composite properties, etc.)
- Based on the experimental parameters and model, predict the full-scale TES system performance

Proposed set-up for simple test to tune TES model



Accomplishments: Modeling/Design of Lab-scale Prototype TES System

- Utilizing COMSOL multiphysics software to design laboratory scale prototype
 - emulated boundary conditions of actual full-scale TES unit (e.g., constant temperature input using a hot plate set at 850 °C (1123K) contacting bottom surface of model)
 - design for reasonable size and melt times
 - 5 cm x 5 cm base x 7.6 cm height (2 x 2 x 3 inch)
 - Reasonable time for total melt or unit equilibrium
- Used rule of mixtures to calculate temperature dependent properties of foam/PCM composite (0.22 g/cc foam and MgCl₂ PCM - $T_{\text{melt}} = 714 \text{ °C}$ (987K))
- Temperature dependent specific heat with pulse behavior at melt used to capture energy absorption during melt (assume a melt temperature range of 30°C)



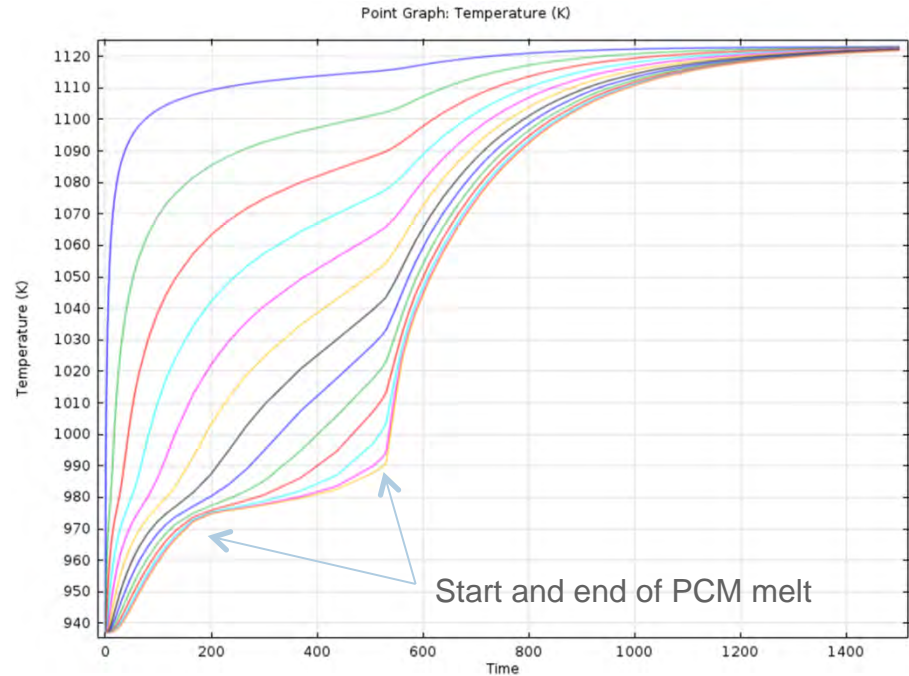
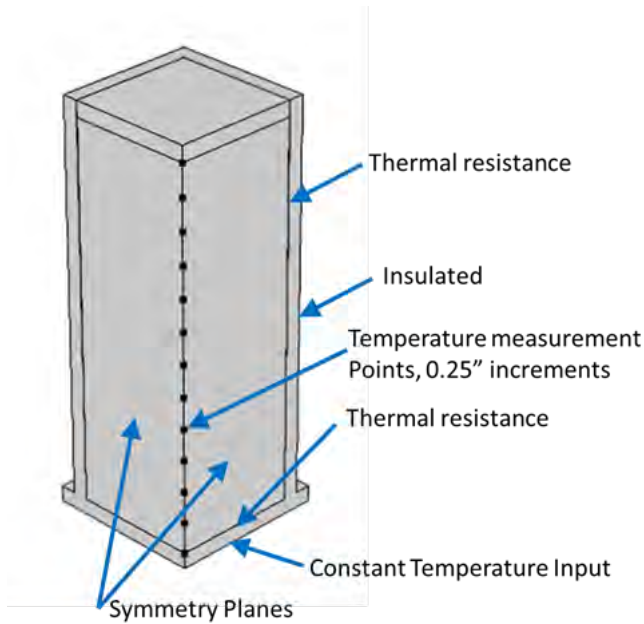
Interactive solid model

Meshed using tetrahedral elements



Accomplishments: Modeling/Design of Lab-scale Prototype TES System

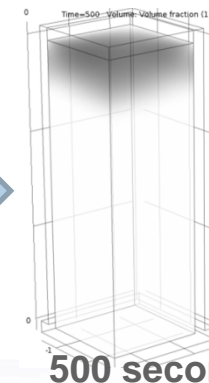
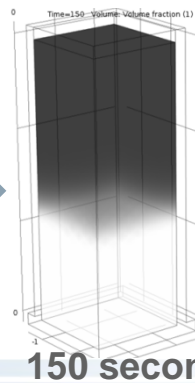
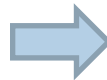
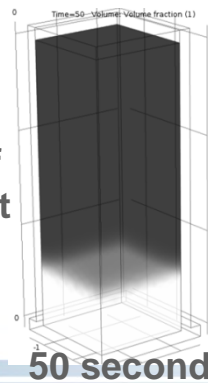
Preliminary Results of Graphite Foam/MgCl₂ Unit



Boundary conditions and input -1/4 model
(bottom surface = 850°C (1123K))

Temperature vs. time at multiple locations

Time based images of
progressing melt front

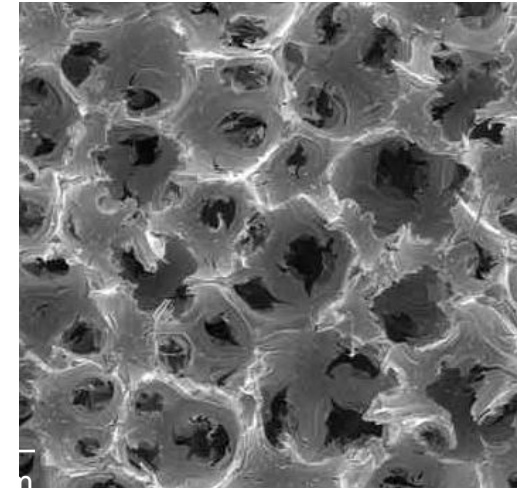


Accomplishments: Graphite Foams

- Graphite foams are available commercially in increased billet size
- Improved density uniformity through process modifications
- Down selected three density formulations



Nominal Properties of Foams



0.2 g/cc density foam

Foam Type	Foam Density (g/cc)	Solid Volume Fraction (%VF)	Pores/ inch (PPI)	Windows/ inch (WPI)	Bulk Thermal Conductivity, x-y plane (W/mK)	Bulk Thermal Conductivity, z direction (W/mK)
low	0.10-0.15	~6	24-41	~26-37	~25	~50
medium	0.20-0.25	~11	30-40	~23-31	~40	~80
high	0.45-0.55	~22	19-33	~8-20	~60	~120



Accomplishments: Development of Coatings for Graphite Foams

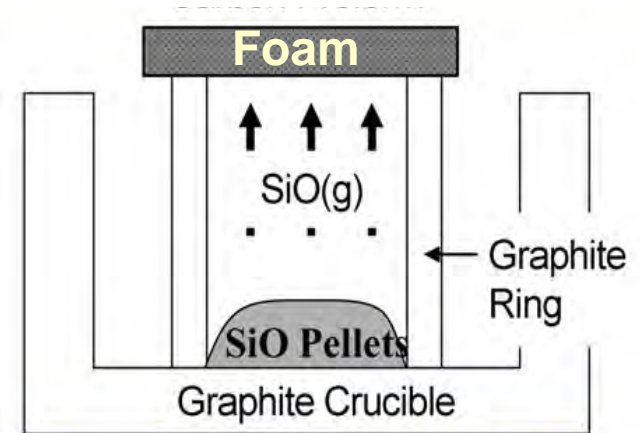
- Coating on graphite foam
 - prevent degradation (oxidation) of the foam at operating temperatures
 - enhance wetting of the graphite
 - minimize PCM and graphite interactions
 - provide structural reliability
- Three coating techniques being investigated
 - chemical vapor reaction (SiC)
 - commercial dip coating process (SiC/TiB₂)
 - polymer derived SiC coating
- Graphite foams of three densities were used for coating (~0.12, 0.24, and 0.44 gm/cm³)
- Samples of each density (1"x0.5"x0.5" and 1"x1"x1") coated for microstructural, mechanical property, and oxidation studies



Accomplishments: Development of SiC Coatings for Graphite Foams

Chemical Vapor Reaction (CVR) Coating

- Processing condition: $\sim 1400^{\circ}\text{C}$
- Samples of each density (1"x0.5"x0.5" and 1"x1"x1") coated for microstructural, mechanical property, and oxidation studies



Schematic of CVR Coating Set-up



Coated Foam Samples

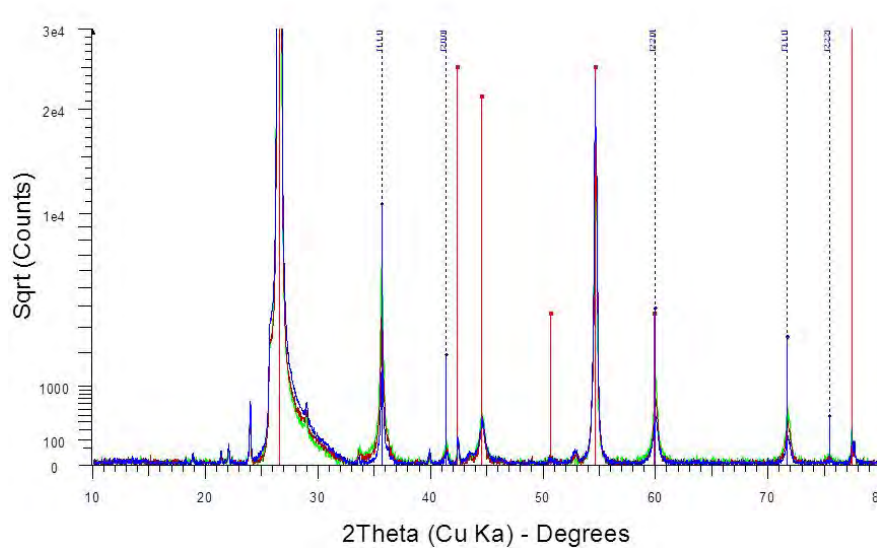
Medium Density Foam; 1"x1"x1"



Accomplishments: X-Ray Diffraction Analysis of SiC Coated Foams

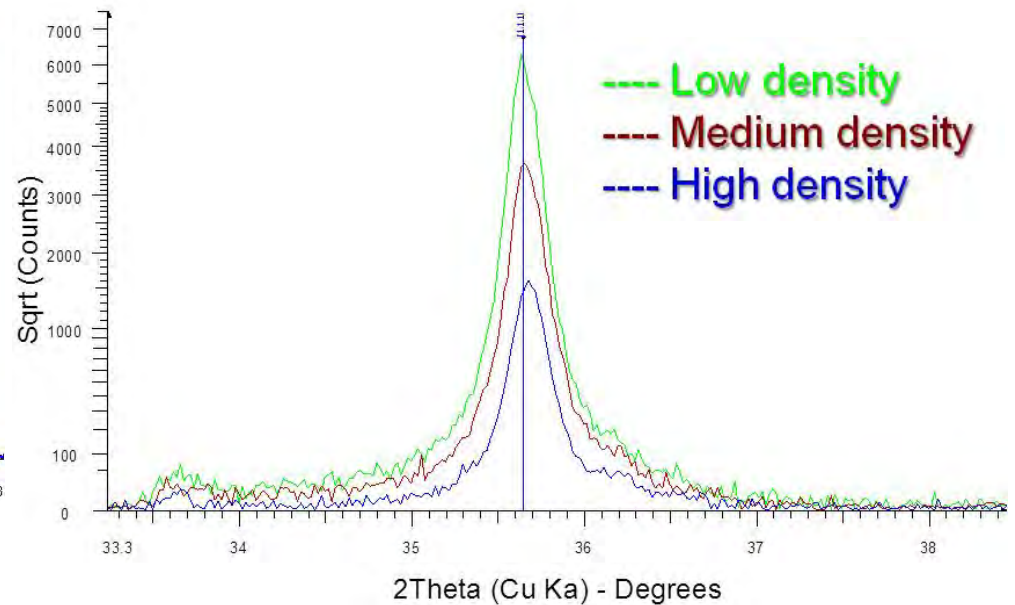
XRD Scans of SiC Coated Foam Samples

Graphite (002) peak truncated



---- Low density
---- Medium density
---- High density

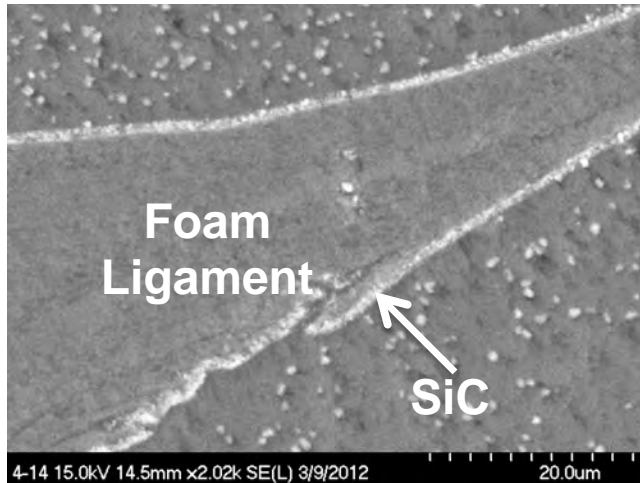
SiC-3C (111) peak in Coated Samples



For all SiC peaks, the order of peak intensity is low density > med density > high density. Because this order is consistent across all peaks, preferred orientation is ruled out and the differences can be attributed to the amount of graphite converted to SiC, relative to the other samples.

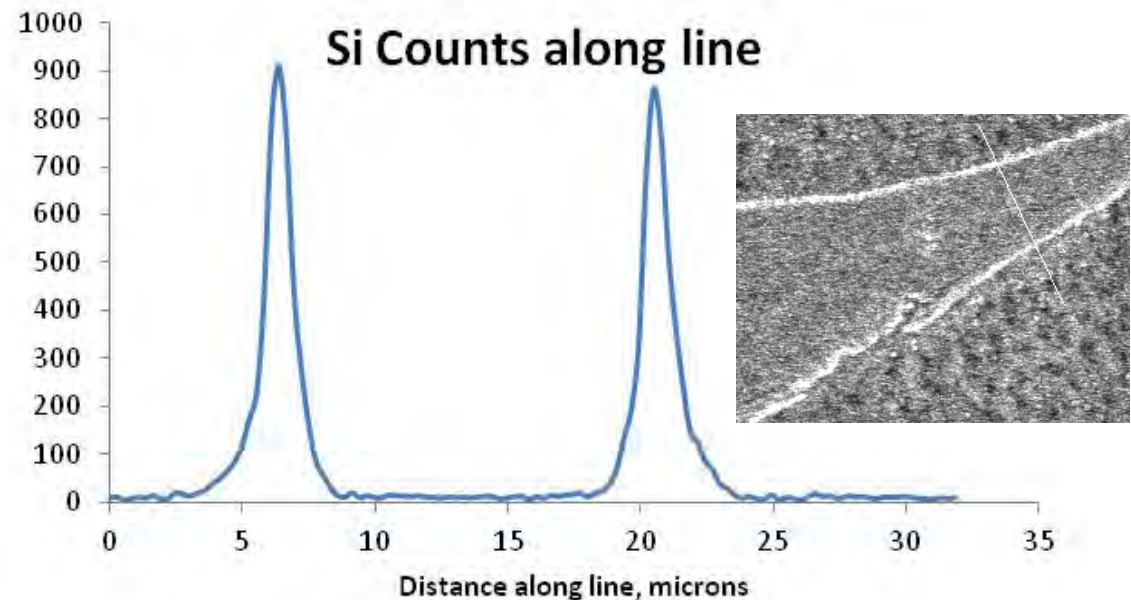
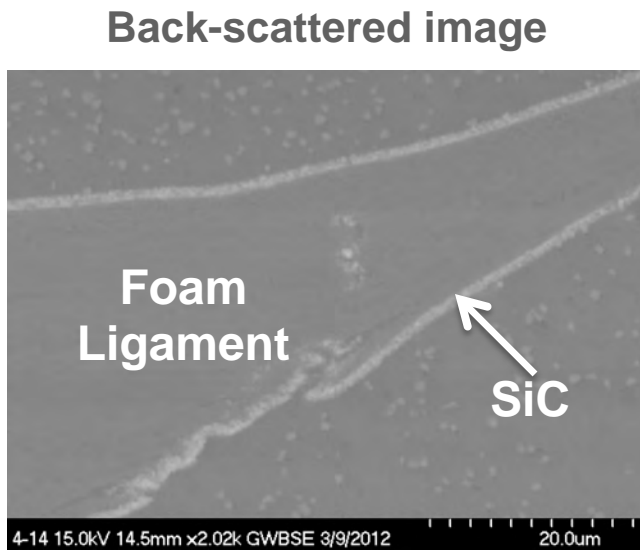


Accomplishments: Microstructure of Medium Density SiC Coated Foam (~0.2 gm/cm³)



- To evaluate coating uniformity and coverage in bulk, one inch coated foam samples were mounted, polished, and examined near the center
- SEM and EDS confirm the presence of Si at the ligament surface
- The coating appears to have uniform thickness of approximately 1 μ m

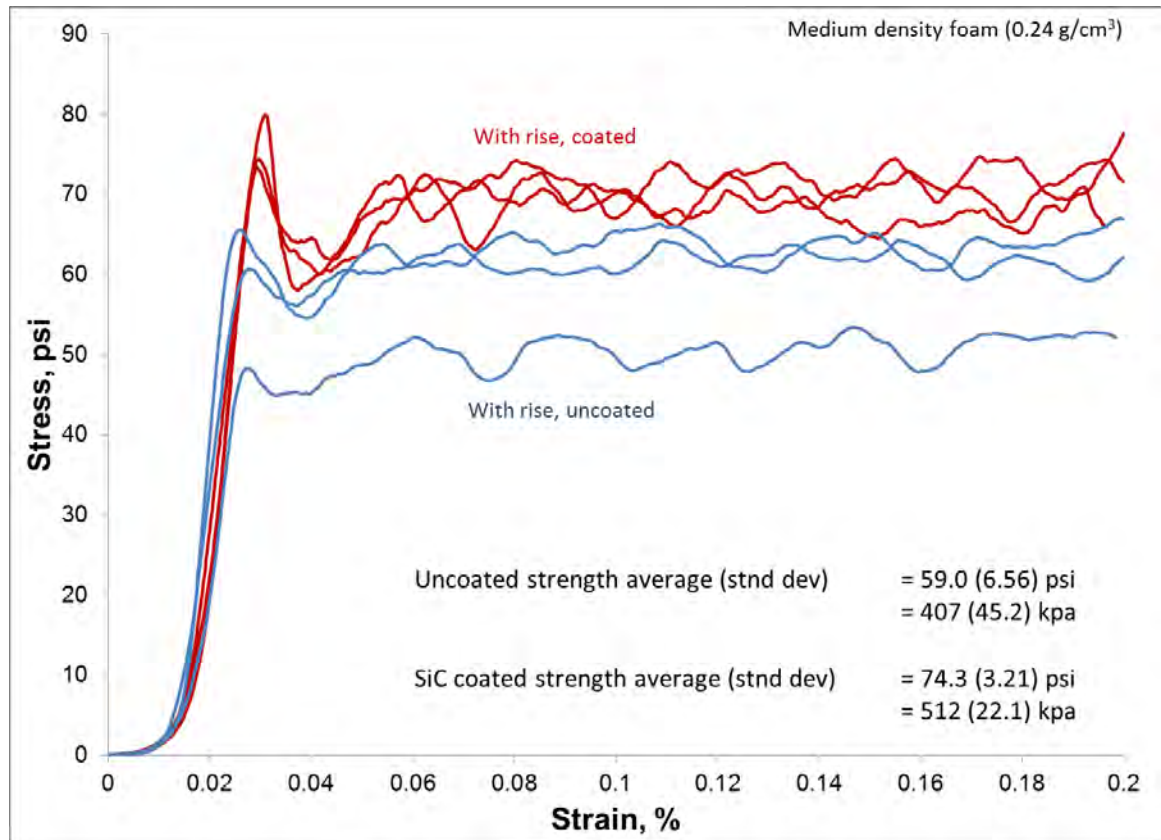
EDS Line Scan



Accomplishments: Compressive Strengths of Uncoated and SiC Coated Graphite Foams



1 inch cube specimens (25.4 mm)
New test procedures developed due to unique nature of graphite foams (e.g., specimen geometry, strain measurement techniques)



- Improvements in compressive strength due to SiC coatings (Foaming or “with rise direction”)
 - 26% increase for medium density graphite foam (~0.24 g/cm³)
- Flat, post failure strain response indicates consistent, constant density material
 - Large density variations would cause excessive peaks and values due to progressive failure of low density regions (not seen here)



Accomplishments: Oxidation Experiments

- Weight change as a function of exposure time at the test temperature
- Oxidation experiments were conducted in flowing inert gas atmosphere

Preliminary Oxidation Tests

Sample	Coating	Density	Temp.
Graphite Foam	Uncoated	0.22 g/cm ³	700°C
			800°C
			900°C
	SiC Coated (CVR)	0.22 g/cm ³	700°C
			800°C
			900°C
	TiB ₂ *	0.22 g/cm ³	700°C
			800°C
			900°C

* commercial product



SDT-Q600 calorimeter, continuous weight change monitored
weight ± 0.0001 mg

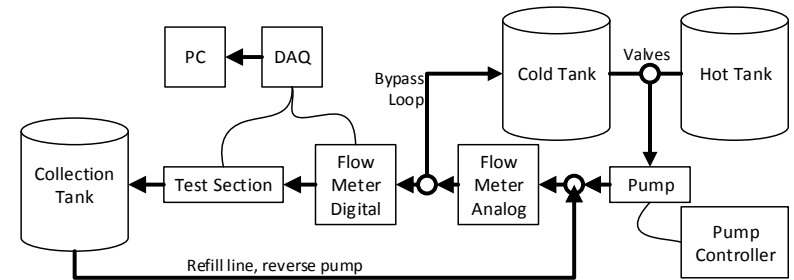
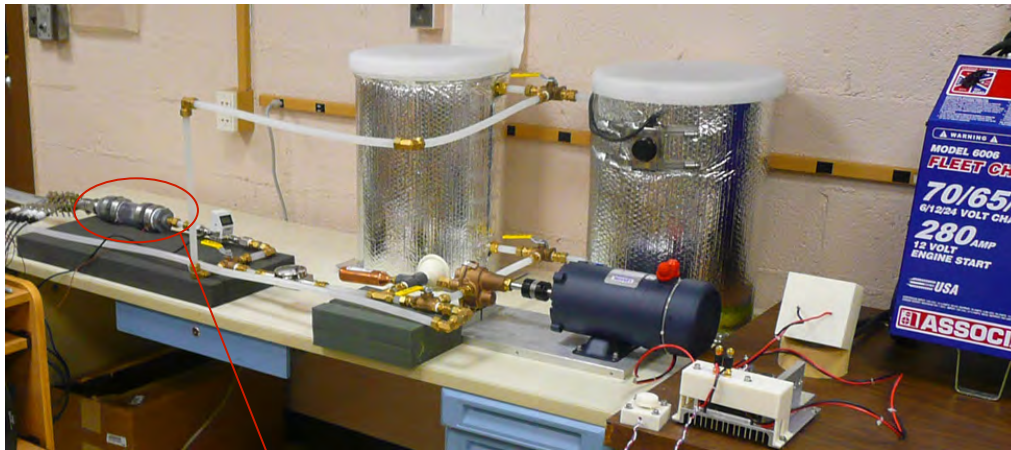


Atmosphere controlled furnace
weight ± 0.005 mg

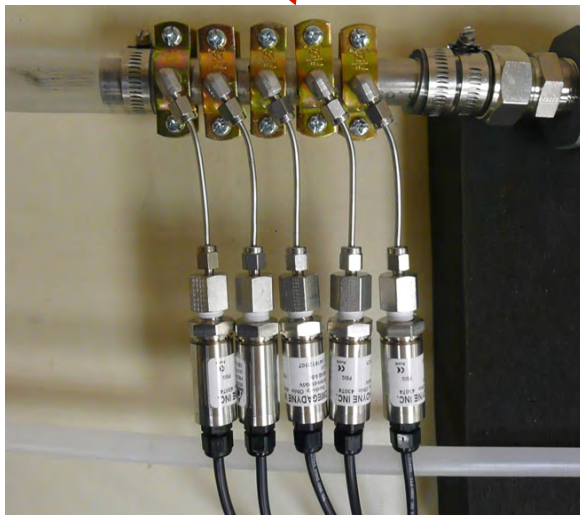
Tests for various times, temperatures, and coatings are currently being performed



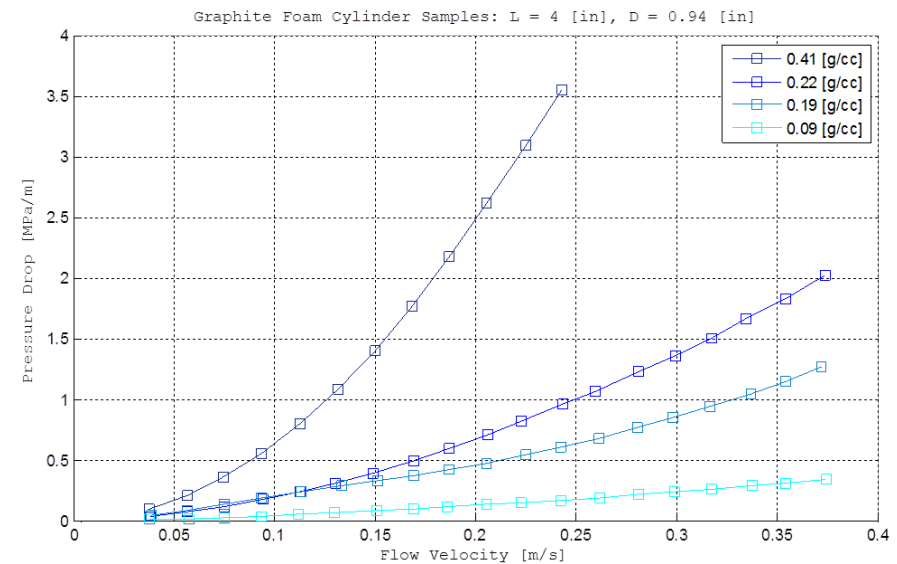
Accomplishments: Facility Development and Pressure Drop Experiments to Determine Porosity Changes as a Result of Coating



Samples size
2.5 cm dia. X 10 cm length (1in. X 4in.)



Test Section
Foam within metal tube with 5 pressure transducers along length of specimen



Results for multiple densities of uncoated graphite foams

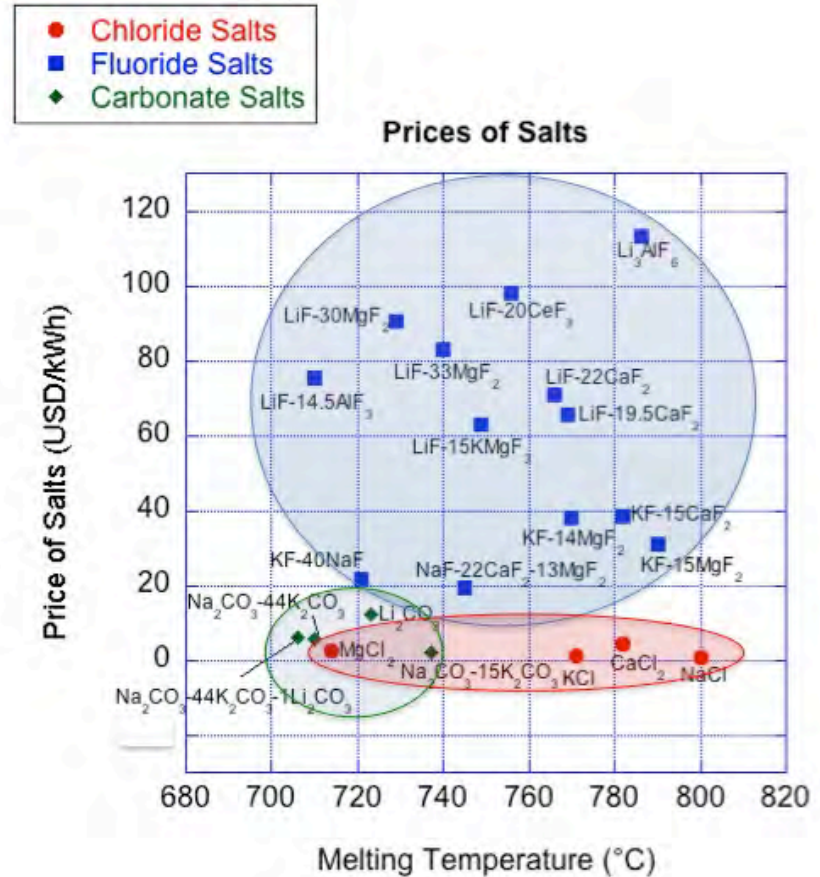
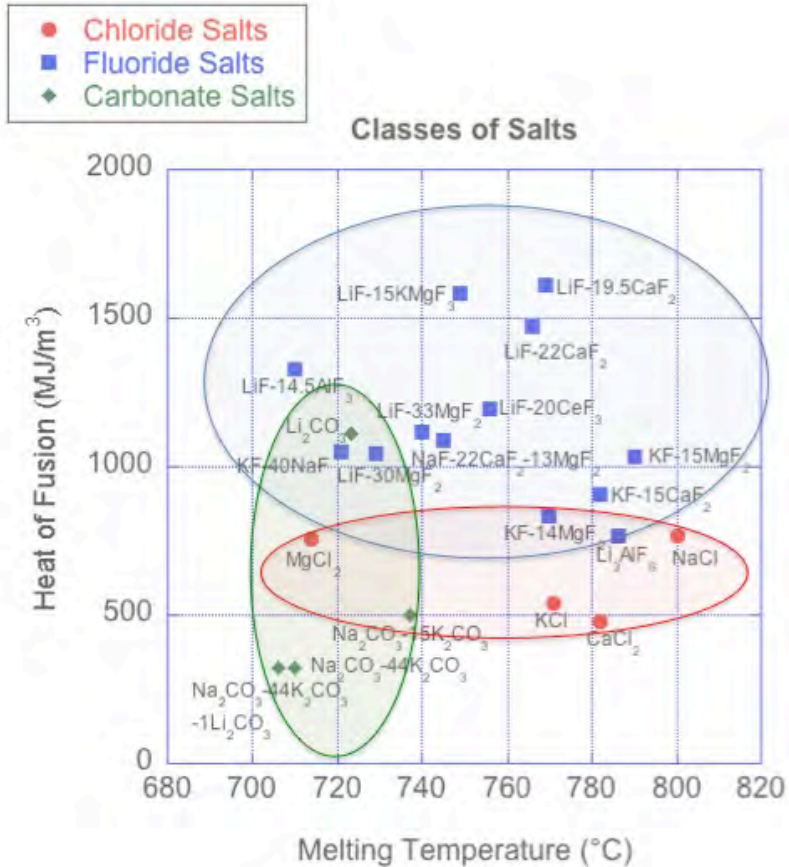


Accomplishments: Phase Change Materials

- Literature review conducted
- Parameters investigated
 - Physical
 - suitable phase change temperature ($T_{m.p.}=700^{\circ}\text{C}-800^{\circ}\text{C}$)
 - large volumetric heat of fusion
 - temperature cycling stability
 - little or no under-cooling
 - good thermal conductivity
 - Desired properties
 - low vapor pressure
 - small volume change
 - wetting properties of the PCM with graphite/coated graphite
 - chemical stability/corrosion of the PCM with other structural materials
 - safety constraints (non-toxic, non-flammable materials)
 - Economic/environmental
 - low price
 - PCM should be recycled: for environmental and economic reasons



Accomplishments: Phase Change Materials



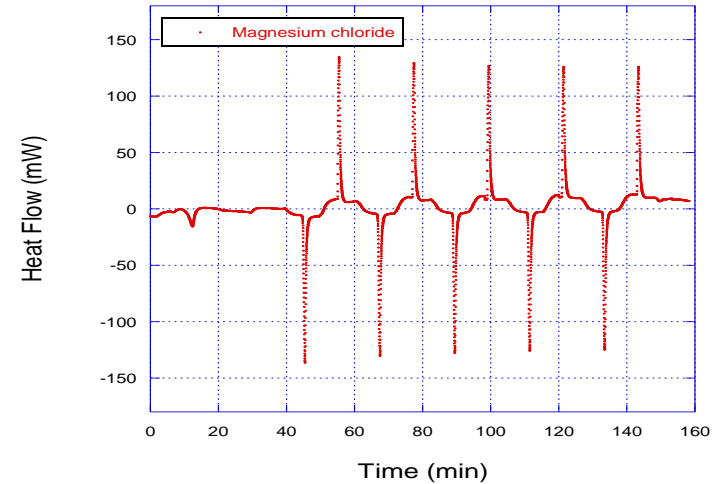
Chlorides and carbonates appear to be most promising in terms of storage density and cost



Accomplishments: Characterization of PCMs

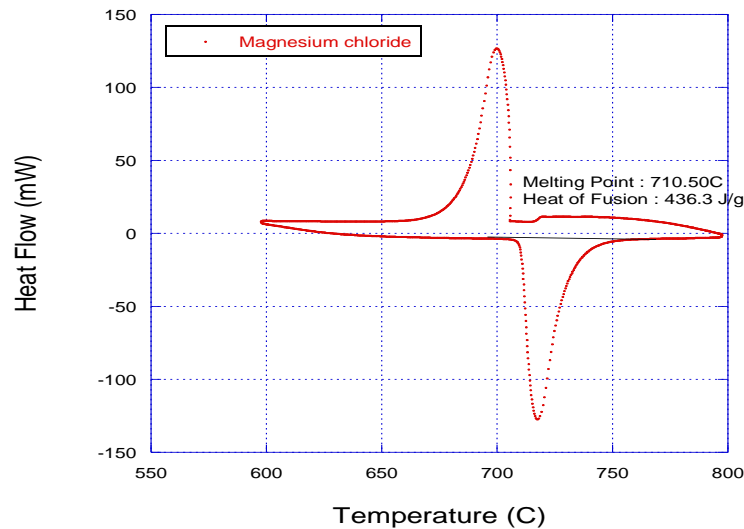
- Characterization of PCMs
 - Using a differential scanning calorimeter selected salts were characterized for their melting and freezing temperatures, under-cooling, heat of fusion, weight loss, and thermal cycling behaviors.

Heat flow of magnesium chloride



Heat flow vs. time for magnesium chloride

Heat flow of 3rd cycle



Heat flow vs. temperature for 3rd cycle of magnesium chloride

Similar experiments conducted for other PCM salts



Accomplishments: Characterization of PCMs

Salt	Measured Melting Point: T_m (°C)	Literature Melting Point: T_m (°C)	Measured Heat of Fusion (MJ/m ³)	Literature Heat of Fusion (MJ/m ³)	Measured Heat of Fusion (kJ/kg)	Literature Heat of Fusion (kJ/kg)	Measured Under Cooling (°C)
$MgCl_2$	710.5 (±0.1)	714	733.7 (±10.2)	758	437.3 (±6.1)	452	10.6 (±0.4)
$NaCl$	798.0 (±0.2)	800	675.1 (±3.4)	766	433.7 (±2.2)	492	13.3 (±0.3)
KCl	767.1 (±0.1)	771	516.5 (±4.6)	539	338.1 (±3.0)	353	9.9 (±0.2)
$CaCl_2$	753.7 (±3.4)	782	533.8 (±4.0)	478	256.6 (±1.9)	230	87.6 (±3.4)
Li_2CO_3	716.6 (±7.2)	723	674.4 (±193.9)	1109	368.3 (±105.9)	606	22.0 (±4.7)
Na_2CO_3 - K_2CO_3 (56:44 mol%)	699.1 (±2.4)	710	294.6 (±14.9)	322	149.8 (±7.6)	164	7.4 (±2.0)
Na_2CO_3 - K_2CO_3 (85:15 mol%)	789-731	790-737	340.8 (±57.4)	501	172.8 (±29.1)	254	11.9 (±1.9)

$MgCl_2$ is selected for infiltration studies



Summary

- Thermal analysis demonstrates the advantages of using PCM infiltrated graphite foam as a TES storage system
 - rapid (< 8 h) charge/discharge
 - significant reduction in number of heat pipes
- Preliminary analysis for lab-scale prototype complete
- Foam coating processes being optimized
- Coating of the foam provides increased compressive strength; oxidation tests are ongoing
- Characterizations of PCMs completed and MgCl_2 is selected for infiltration



Future Work (remainder of FY13)

- Complete lab-scale prototype analysis and design
- Complete oxidation studies and select the optimized coating procedure
- Establish any changes in transport (thermal, pressure drop, microstructural) properties resulting from foam coating
- Complete mechanical property characterizations (room and elevated temperatures & post oxidation tests)
- Perform optimization analysis of the overall TES system and determine the $\$/kW_{th}$ for various scenarios





Acknowledgements

Support from DOE' s SunShot Initiative

- DOE – SunShot Initiative
 - Dr. Ranga Pitchumani
 - Joe Stekli
 - Levi Irwin

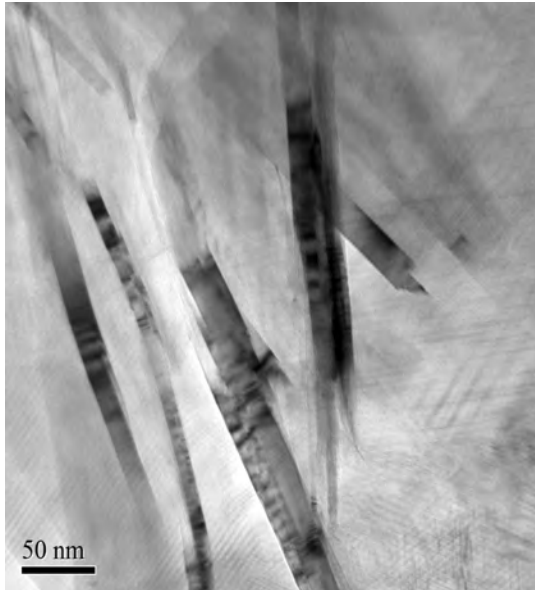




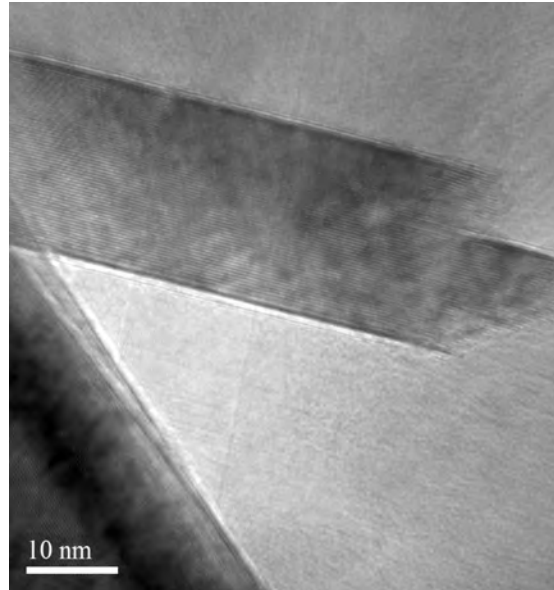
Backup Slides



Development of SiC Coatings for Graphite Foams

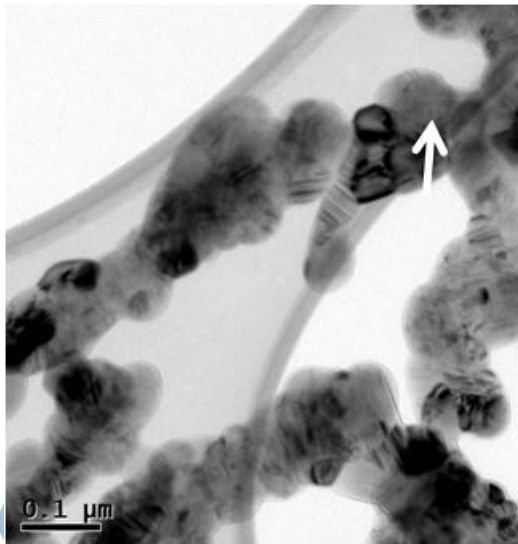


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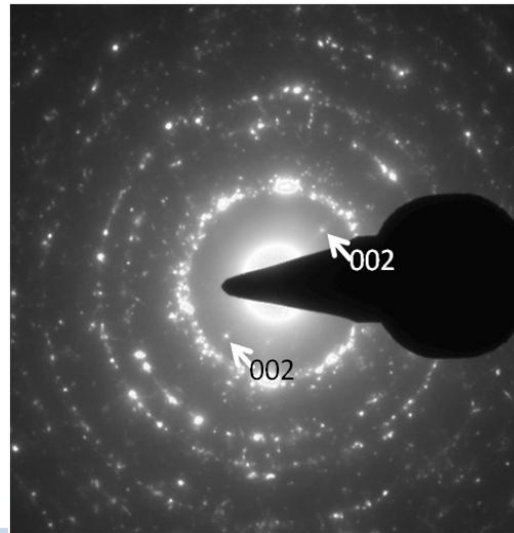


b

(a) TEM image showing highly oriented graphite grains and (b) HRTEM image showing two intersecting graphite grains.



c



d

TEM image showing grain morphology from a SiC coated graphite foam sample (c) and (d) is selected area electron diffraction indicating random orientation of polycrystalline grains.

