SALT HYDRATE EUTECTIC THERMAL ENERGY STORAGE FOR BUILDING THERMAL REGULATION

Final Technical Report | DOE EERE BTO BENEFIT Program

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ABSTRACT

Thermal energy storage is anticipated to play an important role in developing the power grid of the future - a power grid that meets increasing demands of users, is resistant to disruptions, but also allows for greater penetration of renewable resources. Specifically, thermal energy storage materials can be integrated into HVAC systems and building envelopes, where they can be used to shift power demands for building climate control from periods of peak demand to periods of low demand. Phase change materials (PCMs) are compelling as low-cost, high energy density thermal energy storage materials for building thermal management. However, there is a lack of high performance low-cost PCMs within the specific temperature ranges which would most effectively allow for power load shifting.

Inorganic salt hydrates represent a promising class of PCMs, but their inherent limitations cause them to be currently unavailable for reliable building applications. The overarching goals of this research effort are to: 1) Discover low-cost, high volumetric density salt hydrate eutectic PCMs to store low-quality heat (10 to 40 °C); 2) Introduce a high thermal conductivity matrix to reduce the time constant for energy storage to ~0.1 to 1 hr, incorporate nucleation catalysts to decrease undercooling, and utilize microencapsulation and shape stabilization approaches, minimizing moisture loss/gain, mitigating phase separation, and maintaining stable melting behavior over the lifetime of the compounds; 3) Evaluate the impact these systems have on peak load shifting, and the potential for overall energy savings under different climatic scenarios and building configurations.

These goals will be achieved by an integrated research program consisting of six cohesive research subtasks: 1) Materials discovery of eutectic salt hydrate PCMs by using computationally predicted thermodynamic equilibria, coupled with high-throughput experimental validation, 2) Rapid experimental screening of nucleation catalysts identified through robust computational databases, 3) Embedding salt hydrate PCM into a low cost and scalable high conductivity matrix, 4) Microencapsulation of salt hydrate microspheres using hybrid inorganic-polymer microencapsulation approach, 5) Shape stabilization by thermoreversible salt hydrate salogels, and 6) Analysis of end-use using thermal simulations, and characterization of mock-up energy storage finished components.

EXECUTIVE SUMMARY

Thermal energy storage (TES) can be incorporated into buildings to improve energy efficiency by creating a thermal reservoir, which is charged/discharged daily, allowing for i) peak-load shifting, ii) improved demand-side energy management, and iii) higher thermodynamic efficiencies for HVAC systems by rejecting heat at optimal ambient temperatures. For typical environmental temperatures, phase change materials (PCMs) are a compelling solution for low-cost passive energy storage for buildings. State of the art commercial PCMs used in building climatic control are dominated by paraffins, which present a number of deficiencies (high cost, flammability, low volumetric energy density, low thermal conductivity), which have limited further market penetration. While inorganic salt hydrates have both energy density and cost advantages, they require a comprehensive suite of associated technologies to reduce their inherent limitations (supercooling, potential for phase segregation, or materials degradation/ corrosion).

This project consisted of a set of high-level project goals (**PG1** to **PG3**), which were accomplished by a series of 6 specific research objectives (**R1** to **R6**), resulting in micro- or macro-encapsulated forms (Fig. 1).

PG1 Discover low-cost (<$2/kWh), high volumetric density (>100 kWh/m^3), salt hydrate eutectic PCMs to store low-quality heat (10 to 40 °C) through computationally predicted thermodynamic equilibria, coupled with high-throughput experimental validation. [**R1**] Under this task, we predicted and computationally evaluated a series of nitrate and chloride salt hydrate eutectics, identifying different families of eutectics which achieved cost and energy density metrics.

PG2 Develop the cooperative materials technologies required to achieve robust, stable thermal energy storage capability. Composite TES materials include nucleation catalysts (to maintain ΔT <5 °C for >10 yr) [**R2**], high thermal conductivity additives (to reduce the thermal 'charging' time to ~0.1 to 1 hr) [**R3**], microencapsulation approaches (minimizing moisture loss/gain, maintaining >90% ΔH_{fus} over a lifespan of >10 yr) [**R4**], and shape stabilization (to mitigate phase segregation and aid in processing, maintaining >90% ΔH_{fus}) [**R5**]. The composite TES material must satisfy these diverse requirements, while maintaining a low cost (<$15/kWh).

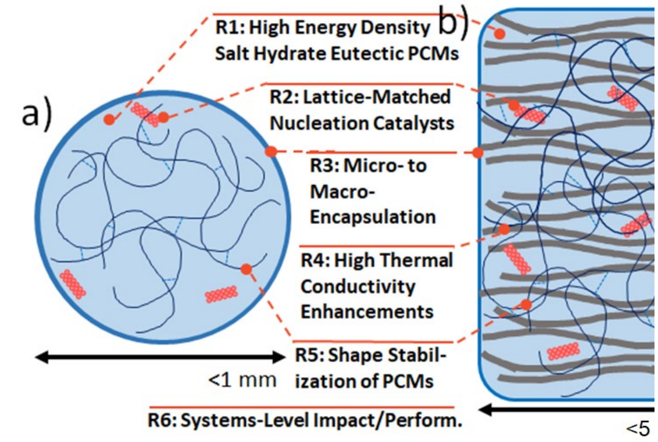


Fig. 1. Proposed research thrusts to achieve technologically mature a) micro-, or b) macro-encapsulate TES composites.

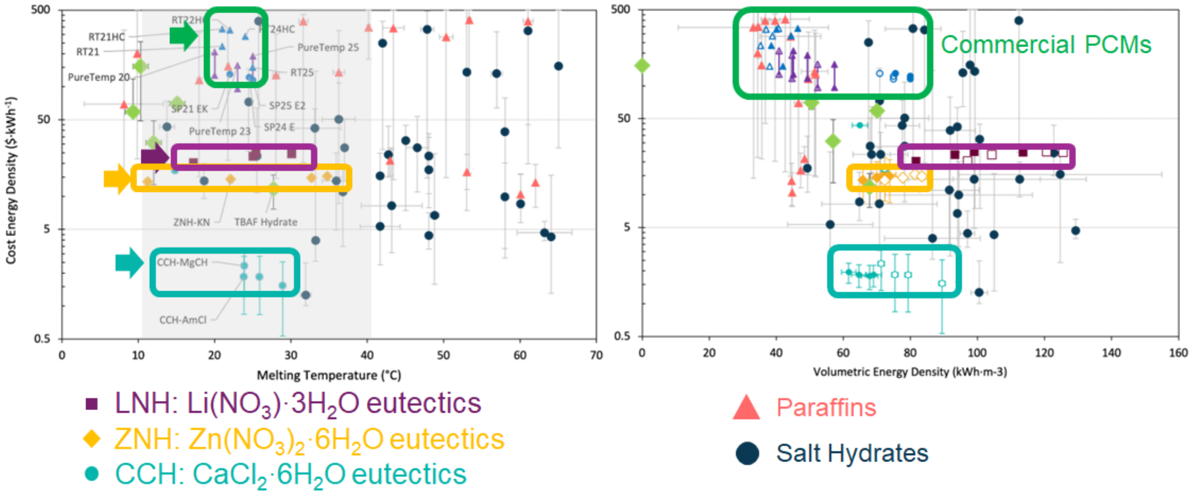
PG3 Evaluate the ability of centralized and distributed TES materials (Fig. 3) to 1) shift peak load, and 2) result in net energy savings under different climatic scenarios and building configurations. Test performance of TES materials incorporated into building components. Identify the materials metrics necessary to achieve competitive performance under different use cases, and evaluate tradeoffs (*e.g.*, higher material cost, but faster heat absorption rate) [**R6**].

SUMMARY OF PROGRAM TARGETS

The objective of this project is to develop a novel salt hydrate eutectic phase change material (PCM) for residential and commercial applications capable of the following:

Description	Minimum Target	Project Targets
Phase Change Temperature	10 ^{o}C – 40 ^{o}C, depending on operating temperature of residential or commercial application.	Target optimal temperatures T_c* and T_h* (+/- 2 C) identified during budget period 1, and refined during component-level transient modeling.
Cost	<$15/kWh projected at >10 L scale (i.e., component scale).	<$5/kWh PCM cost, <$15/kWh composite TES material cost (at >10 L scale).
Energy Density	>100 kWh/m^3	>100 kWh/m^3
Thermal Conductivity	>1 W/m·K	1-5 W/m·K, adjustable to target charge/discharge times of 0.1 – 1 hr (based on component design)
Thermal Reliability	>90% after >10,000 cycles	>95% after >10,000 cycles, >95% after 1 year aging at relevant humidity conditions
Safety	Non-toxic, non-flammable, non-explosive, and non-reactive	Non-toxic, non-flammable, non-explosive, and non-reactive
Corrosion	Non-corrosive	Non-corrosive within designed environment

SUMMARY OF SALT HYDRATE EUTECTIC FAMILIES DEVELOPED UNDER THIS PROJECT



As the primary deliverables, we focused on three families of salt hydrate eutectics under this effort, demonstrating highly repeatable cycling, invariant point (single defined temperature) melting point behavior, and meeting or exceeding various cost and energy density target metrics. A summary of these families of eutectics, including their cost energy density, melting point, and volumetric energy density are illustrated above. Specifically, we demonstrated very high volumetric energy densities in $Li(NO_3){\cdot}3H_2O$ eutectics (exceeding 100 kWh/m^3), very low cost energy densities in $CaCl_2{\cdot}6H_2O$ eutectics (< $2/kWh), and exceptional overall properties in $Zn(NO_3)_2{\cdot}6H_2O$ eutectics (tunable melting points from 10 to 35 ^oC).

SUMMARY OF TECHNICAL SCOPE AND ACTIVITIES

Budget Period 1:

During period 1, we developed a predictive thermodynamic model, and validated this model against known single-component eutectic compositions and melting temperatures. We applied the model to identify new high energy density nitrate eutectic and chloride eutectic phase change materials (PCMs), characterizing the fundamental thermophysical properties of these compounds. Nucleation catalysts were identified for promising nitrate eutectic and chloride eutectic salt hydrate systems. Furthermore, we synthesized thermally conductive layers for graphite/salt hydrate composites, demonstrated a robust methodology for micro-encapsulation, and demonstrated the formation of salogels with ternary nitrate eutectics.

Task 1.1 (R1) – [Discover ternary nitrate hydrate eutectics and nitrate chloride eutectics]:

Computationally predict thermodynamic equilibria in nitrate hydrate eutectic and chloride hydrate eutectic systems based on published salt solubility data. Synthesize predicted compounds and validate predicted melting temperature and enthalpy of fusion.

Task 1.2 (R2) – [Discover nucleation agents for prototypical ternary nitrate hydrate and chloride hydrate systems]:

Employ crystallographic databases to rapidly screen large potential phase space for potential heteroepitaxial phases. Down-select a small number of promising insoluble phases. Experimentally validate the activity of nucleation agents using high throughput optical techniques, and high resolution calorimetry. Prototype ternary hydrates for this task will be Ca/Mg nitrate hydrate and Ca/Mg chloride hydrate.

Task 1.3 (R3) – [Optimize conductive graphitic layers]:

Develop continuous R2R process for spray deposition of graphite particles. Demonstrate fabrication of continuous layers with variable thickness (~0.1 to 1 mm).

Task 1.4 (R4) – [Encapsulation of Salt Hydrates]:

Introduce Pickering emulsion template and mechanical agitation to create microencapsulated particles. Tune fluid ratios, particle concentrations, and rate of mechanical agitation to control particle size dispersion.

Task 1.5 (R5) – [Form PVA/PEO eutectic hydrate salogels]:

Synthesize nitrate salogels with 1) poly (vinyl alcohol) (PVA) with variable degrees of hydrolysis, and 2) poly (ethylene oxide) (PEO) of variable molecular weights. Characterize thermophysical properties of gels for viscosity and gelation temperature.

Task 1.6 (R6) – [Building-level lumped thermal model]:

Develop non-linear thermal model, assuming lumped thermal behavior of TES components. Initial down-select of energy storage embodiments, and relevant operating temperatures (T^* +/- 5 C)

Task 1.7 (R6) – [Component validation under real use environments]:

Develop experimental setup to measure thermal energy charge / discharge rates under realistic conditions (variable air/refrigerant flows, different RH of air) for components of different forms, incorporating composite TES materials developed.

Budget Period 2:

During period 2, we extended our predictive thermodynamic model to mixed nitrate-chloride eutectic systems, and experimentally characterized promising low-cost predicted eutectic PCMs in the desired temperature ranges (T_c^* and T_h^*), characterizing the thermophysical properties of these compounds. Building off initial results for nucleation catalysts in nitrate and chloride systems, nucleation catalysts will be identified for promising mixed nitrate and chloride eutectic salt hydrate systems. We researched the stability of different salt hydrate micro-capsules, and demonstrated control over T_{gel} through the use of chemical crosslinkers.

Task 2.1 (R1) – [Characterize ternary nitrate hydrate and chloride hydrate eutectics]:

Characterize thermophysical properties (density, thermal conductivity, heat capacity, thermal diffusivity) of initial promising ternary nitrate hydrate and chloride hydrate eutectic phases.

Task 2.2 (R1) – [Discover ternary mixed nitrate/chloride hydrate eutectics]:

Computationally predict thermodynamic equilibria in mixed nitrate/chloride hydrate eutectic systems based on published salt solubility data. Synthesize predicted compounds and validate predicted melting temperature and enthalpy of fusion.

Task 2.3 (R2) – [Discover nucleation agents for mixed nitrate/chloride hydrate eutectics systems]:

Employ crystallographic databases to rapidly screen large potential phase space for potential heteroepitaxial phases. Down-select a small number of promising insoluble phases. Experimentally validate the activity of nucleation agents using high throughput optical techniques, and high-resolution calorimetry.

Task 2.4 (R3) – [Optimize conductive graphitic composite sheets]:

Optimize R2R process for spray deposition of graphite particles. Optimize milling time and binder content for conductivity. Incorporate chemical surface treatment to allow for wetting of graphitic layer.

Task 2.5 (R3) – [Fabricate multi-layer TES composites]:

Demonstrate continuous R2R manufacturing process to produce individual graphitic layers with variable thickness. Control deposition processes and substrate surface to attain lift-off with high yield of recoverable graphitic films.

Task 2.6 (R4) – [Encapsulation of Salt Hydrate Materials]:

Modify solvents, encapsulant precursors, and processing conditions during encapsulation to control encapsulant thickness (targeting > 90 vol.% PCM phase).

Task 2.7 (R4) – [Stability/Cycling of Encapsulated PCMs]:
Characterize performance of encapsulated PCMs over large number of cycles. Particularly, characterize microencapsulate failure rates with cycling.

Task 2.8 (R4) – [Incorporation of Nucleation Catalysts in Encapsulated PCMs]:
Modify microencapsulation synthesis process to incorporate suspended (solid) nucleation catalyst particles in microencapsulated PCMs. Investigate the effect of nucleation catalyst particle size on yield (fraction of microencapsulated particles which contain nucleation catalysts).

Task 2.9 (R5) – [Form PVA/PEO eutectic hydrate salogels]:
Synthesize chloride salogels with 1) PVA with variable degrees of hydrolysis, and 2) PEO of variable molecular weights. Characterize thermophysical properties of gels for viscosity and gelation temperature.

Task 2.10 (R5) – [Add crosslinker to tune T_{gel} in salogels]:
Introduce chemical crosslinkers (di- and triamine hydrocarbons) to nitrate salogels to vary T_{gel}. Characterize gelation behavior and resulting ΔH_{fus}, ΔT_m of salogels.

Task 2.11 (R5) – [Validate long-term stability of salogels]:
Age salogels at different temperatures. Investigate the tendency for the viscoelastic properties of salogels to degrade over time, and for nucleation behavior (*i.e.*, undercooling) to change due to degradation reactions which may deteriorate salogels over time.

Task 2.12 (R6) – [Building-level lumped thermal model:
Apply non-linear lumped thermal model of TES components. Refine target operation temperatures. Incorporate the effects of undercooling on overall efficiency and optimal/allowable range of T^*. Analyze the effect of TES on displacing electrical energy, and on overall energy utilization. Evaluate simple payback and technological potential under different use scenarios.

Task 2.13 (R6) – [Component-level thermal model]:
Develop discrete numerical transient thermal model to evaluate thermal energy storage at the component level. Validate numerical transient thermal model against experimental data.

Task 2.14 (R6) – [Component validation under real use environments]:
Collect preliminary data from characterization of TES components.

Budget Period 3:

During period 3, we down-selected the 3-5 most promising eutectic salt hydrates identified over the previous 2 budget periods, and focused on more detailed characterization of their properties, as well as both cyclic and long-term aging stability. Similarly, the stability of nucleation catalysts in these phases with cycling and aging was determined, as well as cooling-rate dependent undercooling. We selected and developed best-performing PCM shape-stabilized salogels. Furthermore, we produced

TES composites in feasible forms to integrate with building materials, and to test their thermal properties.

Task 3.1 (R1) – [Characterize ternary mixed nitrate/chloride hydrate eutectics]:
Detailed characterization of the thermophysical properties (density, thermal conductivity, heat capacity, thermal diffusivity) of 3-5 of the most promising ternary eutectic systems identified in previous budget periods.

Task 3.2 (R1) – [Characterize cyclic and long-term stability of select eutectic systems]:
Experimentally characterize cyclic and long-term stability of 3-5 promising candidate eutectic systems based on results from previous budget periods.

Task 3.3 (R2) – [Long-term stability of nucleation catalysts]:
Test nucleation activity (undercooling) in salt hydrates that have been exposed to salt hydrate for periods of up to 1 yr under accelerated (high temperature) conditions.

Task 3.4 (R3) – [Fabricate multi-layer composites]:
Develop continuous R2R manufacturing process to compact graphitic layers together with salt hydrate salogel phase. Volume fraction of PCM controlled by roll compression. Characterize effective thermal properties of composite (conductivity, energy storage).

Task 3.5 (R3) – [Fabricate encapsulated composites]:
Develop slurry-based manufacturing process to deposit graphite/encapsulated PCM composites. Volume fraction of PCM controlled by graphite/PCM ratio. Characterize effective thermal properties of composite (conductivity, energy storage).

Task 3.6 (R4) – [Stability/Cycling of Encapsulated PCMs]:
Characterize performance of encapsulated PCMs for prolonged periods of time (both static, and undergoing cycles over long periods of time). Particularly, characterize susceptibility to changes in melting behavior due to moisture absorption/loss over time.

Task 3.7 (R4) – [Incorporation of Nucl. Catalysts in Encaps. PCMs]:
Modify microencapsulation synthesis process variables (mechanical vibration, rate of particle synthesis, use of different solvents) to improve yield (fraction of microencapsulated particles which contain nucleation catalysts).

Task 3.8 (R5) – [Form PVA/PEO eutectic hydrate salogels]:
Synthesize mixed nitrate/chloride salogels with 1)PVA with variable degrees of hydrolysis, and 2)PEO of variable molecular weights. Characterize thermophysical properties of gels for viscosity and gelation temperature.

Task 3.9 (R5) – [Add crosslinker to tune T_{gel} in salogels]:
Introduce chemical crosslinkers (di- and triamine hydrocarbons) to chloride and mixed nitrate/chloride salogels to vary T_{gel}. Characterize gelation behavior and resulting ΔH_{fus}, ΔT_m of salogels.

Task 3.10 (R5) – [Validate long-term stability of salogels]:

Characterize stability of salogels subject to >10^2 melting cycles. Monitor stability of physical properties (viscoelasticity), and thermal properties (T_{gel}, T_m, ΔH_{fus}).

Task 3.11 (R6) – [Component-level thermal model]:

Utilize transient thermal model to critically analyze material properties and different use cases. Evaluate rate of thermal charge/discharge at the component level, and dependence on different material properties (thermal diffusivity, enthalpy of fusion, etc.). Evaluate tradeoffs between cost and component-level performance metrics (e.g., charge/discharge time).

Task 3.12 (R6) – [Component validation under real use environments]:

Experimentally characterize charge/discharge rates of composite TES components. Optimize composite structure and component shape and form to maximize energy storage per unit volume under different charge/discharge conditions.

Task R1. Discovery and assessment of salt hydrate eutectics

Thrust Lead: P. Shamberger

Table R1.1: Highlights of technical milestones achieved during this effort.

Milestone Number	Milestone Description	Result Presented
1.1	Establish predictive model of thermodynamic equilibria in nitrate and chloride hydrate eutectics; apply to combinations of Na, K, Ca, Mg, Mn, Fe, and Al nitrate and chloride hydrates. Validate model by testing against known salt hydrate eutectic compositions (within +/- 5 wt% composition) and melting points (within +/- 10 C).	Multiple Nitrate eutectics. *P. Shamberger et al., in prep.*
1.2	Synthesize >10 nitrate hydrate and/or chloride hydrate eutectics (~g scale) with T_m ~10 to 40 °C (further down-selected during yr 1 based on based on predictive model; validate predicted T_m, ΔH_{fus}. Eutectics will be selected based on overall project metrics: relevant T_m, predicted energy storage density (J/m3, J/$).	Multiple Nitrate eutectics. *P. Shamberger et al., in prep.*
1.3	Preliminary data set of thermophysical properties (density, thermal conductivity, heat capacity, thermal diffusivity) of ~2 to 5 candidate nitrate or chloride PCMs. Eutectics will be selected based on overall project metrics: proximity of T_m to (T_c* and T_h*), predicted energy storage density (J/m3, J/$).	Multiple Nitrate eutectics. *P. Shamberger et al., in prep.* $Zn(NO_3)_2·6H_2O$ eutectics. *S. Ahmed et al., doi: 10.1021/acsaenm.3c00444.*
1.4	Experimentally measure nitrate hydrate or chloride hydrate eutectic PCMs with low cost ($2/kWh to $5/kWh), and high volumetric density (70 to 90 kWh/m^3).	$CaCl_2·6H_2O$ eutectics. *D. Ibbotson et al., in prep.*
1.5	Demonstrate long-term stability of 3-5 eutectics of interest (up to 200 cycles, < 95% degradation in enthalpy of fusion)	$Zn(NO_3)_2·6H_2O$ eutectics. *S. Ahmed et al., doi: 10.1021/acsaenm.3c00444.*
1.6	Experimentally measure salt hydrate composites which achieve overall project metrics, and high volumetric density (>100 kWh/m^3).	$Li(NO_3)·3H_2O$ eutectics. *P. Shamberger et al., in prep.*

Technical Highlights:

Prediction and Evaluation of Nitrate Eutectics

Salt hydrate phase change materials (PCMs) represent a promising class of materials for thermal energy storage in buildings and environmental climate control systems, but are currently limited by the lack of compounds with reversible invariant point melting-solidifying behavior within particular temperature ranges of practical use. Here, we computationally predict 55 different pseudo-binary, 40 different ternary, and 52 different pseudo-ternary eutectics in the ($Mg(NO_3)_2$, $Ca(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Li(NO_3)$, $Na(NO_3)$, $K(NO_3)$, $(NH_4)(NO_3)$ hydrated systems using the modified BET method. These result in a nearly continuous spectrum of eutectic melting points, T_{eu} between 0 and 80 °C. We experimentally evaluate 28 pseudo-binary eutectics, demonstrating stable invariant point melting behavior in

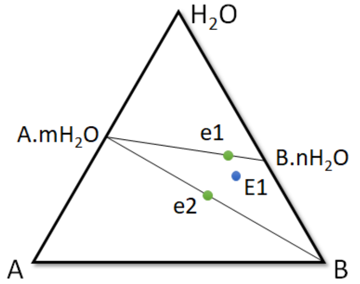


Fig. R1.1. Generic ternary phase diagram consisting of two nitrate salt components (A, B) and water, illustrating a Type I pseudo-binary eutectic (e1, $A.m(H_2O) + B.n(H_2O) \leftrightarrow L$), a Type II pseudo-binary eutectic (e2, $A.m(H_2O) + B \leftrightarrow L$), and a ternary eutectic (E1, $A.m(H_2O) + B.n(H_2O) + B \leftrightarrow L$).

23 of these compounds. In particular, we observe the anhydrous salt components Na(NO$_3$), K(NO$_3$), and (NH$_4$)(NO$_3$) to be particularly effective in forming eutectics, where the magnitude of the melting point depression depends primarily on the maximum solubility of this component in a particular nitrate salt hydrate. This generally follows the sequence $T_{\text{eu, Na}} < T_{\text{eu, K}} < T_{\text{eu, NH4}}$. This data set greatly increases the expanse of known salt hydrate eutectic systems.

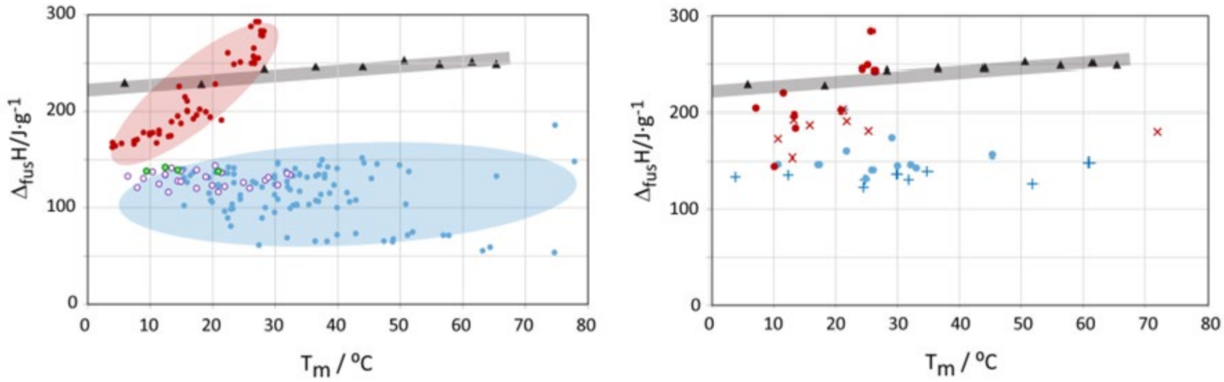


Fig. R1.2. a) Calculated nitrate salt hydrate eutectics, including pseudo-binary and ternary eutectics (blue points), type 1 pseudo-ternary eutectics (purple empty points), and type 2 pseudo-ternary eutectics (green points). Red points illustrate eutectics with a major lithium nitrate salt component, illustrating the dependence of energy density on the concentration of lithium nitrate in the eutectic. b) Experimentally measured pseudo-binary nitrate salt hydrate eutectics. Red points illustrate eutectics with a major lithium nitrate salt component; blue points illustrate all other nitrate eutectic systems. Red x and blue + represent previously published literature. Paraffins illustrated with black triangles for reference.

Related Manuscripts: **P.J. Shamberger**, *et al.* Eutectic nitrate salt hydrates, *in prep.*

Development of Zinc Nitrate Eutectic Family

Here, we investigated a family of pseudobinary eutectics based on zinc nitrate hexahydrate (ZNH), in combination with different anhydrous nitrate salts. ZNH and related eutectics have been identified as a favorable family of PCMs for use in building thermal energy storage applications, as they transform near room temperature (T_{eu} = 10 to 35 °C) with low cost energy densities ≤ \$15/kWh while having enthalpies >130 $J\cdot g^{-1}$ and >60 $J\cdot cm^{-3}$. This combination of attributes is ideal for low-cost thermal energy storage applications, where the particular temperature at which heat is stored may vary across the attainable range of eutectic temperatures.

This ZNH pseudobinary eutectics described in this study merit further investigation, in particular in combination with additives to stabilize the shape of the salt hydrates, which can alleviate concerns surrounding volume expansion and cycling in smaller temperature ranges. In particular, one potentially promising method to mitigate these issues is to combine the salt hydrates with small concentrations of gel-forming polymers and thereby exploit the stabilization provided by the resulting polymer network. Additionally, the long-term stability of salt hydrate pseudobinary eutectic PCMs should be evaluated at smaller temperature ranges near the working conditions of TES media for a particular application. In particular, conditions in which the system exhibits extended periods of phase coexistence could introduce additional vectors for instability and degradation of the system over time.

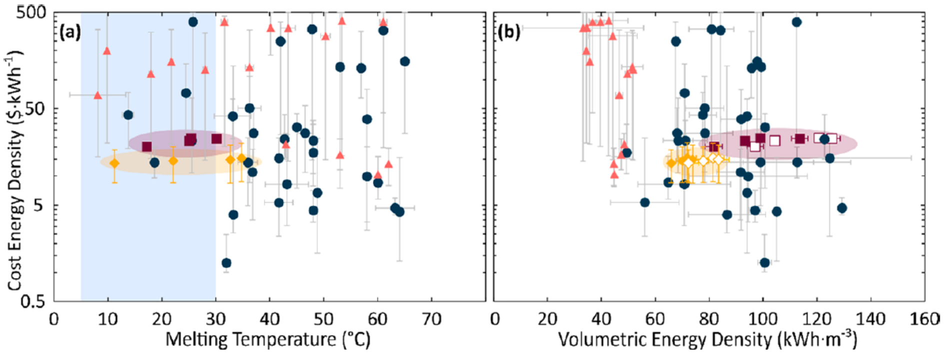


Fig. R1.3. Cost-energy density as a function of (a) melting temperature of the PCM and (b) volumetric energy density of the PCM. Solid shapes represent salt hydrates in the liquid phase, and outlines represent the solid phase. Yellow diamonds are $Zn(NO_3)_2 \cdot 6H_2O$ eutectics (reported here), maroon squares are $LiNO_3 \cdot 3(H_2O)$ eutectics, pink triangles are paraffin, and blue circles are other salt hydrates. The blue shaded section in (a) indicates the desired temperature range for TES media in buildings. Figure reproduced from doi: 10.1021/acsaenm.3c00444

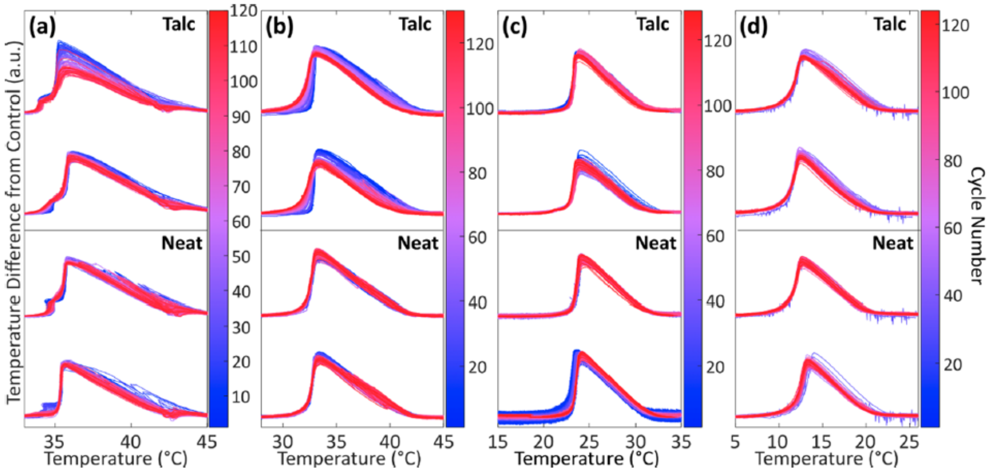


Fig. R1.4. Melting curves from stainless steel cells cycled repeatedly through melting and cooling cycles. Calculated difference between the cell thermocouple reading and the control thermocouple in an unhoused cell are plotted against temperature for (a) ZNH, (b) ZNH-$NaNO_3$, (c) ZNH-KNO_3, and (d) ZNH-NH_4NO_3. The top two curves of each plot are talc-inclusive samples, and the bottom two are neat samples. Figure reproduced from doi: 10.1021/acsaenm.3c00444

Related Manuscripts: S. Ahmed, D. Ibbotson, C. Somodi, **P.J. Shamberger**. Zinc Nitrate Hexahydrate Pseudobinary Eutectics for Near-Room Temperature Thermal Energy Storage, *ACS Appl. Engineer. Mater.*, 2(3), 530-541 (2023). doi: 10.1021/acsaenm.3c00444

Other Related Manuscripts Under this Task:

1. D. Ibbotson, **P.J. Shamberger**. Evaluation of calcium chloride hexahydrate pseudo-binary eutectics, *in prep*.

Task R2. High throughput screening of lattice-matched nucleation catalysts

Thrust Lead: Shamberger

Milestone Number	Milestone Description	Result Presented
2.1	Identify potential nucleation catalysts for principle Na, K, Ca, Mg, Mn, Fe, and Al nitrate hydrates from crystallographic databases (avg. lattice mismatch < 2%). Down-select to 2 closest lattice matched phases (which are also synthesizable, stable, low cost, non-toxic) per hydrate of interest.	Database reported to EERE.
2.2	Demonstrate decreased supercooling ΔT in at least 2 to 5 nitrate or chloride hydrate eutectic phases of interest to < 5 C by use of nucleation catalysts.	$Zn(NO_3)_2 \cdot 6H_2O$ eutectics. *S. Ahmed et al., doi: 10.1021/acsaenm.3c00444.*
2.3	Decrease ΔT in ~2 to 5 chloride hydrate eutectic phases of interest to < 5 C minimum (<2 C target) when measured at relevant volumes.	$CaCl_2 \cdot 6H_2O$ eutectics. *D. Ibbotson et al., in review.* $CaCl_2 \cdot 6H_2O$ eutectics. *D. Ibbotson et al., in prep.*
2.4	Validate long-term stability of nucleation catalysts under cyclic conditions over relevant temperature ranges (T_m +/- 10 C; ΔT remains ≤2 ^oC), over >1 yr.	$CaCl_2 \cdot 6H_2O$ eutectics. *D. Ibbotson et al., in review.* $CaCl_2 \cdot 6H_2O$ eutectics. *D. Ibbotson et al., in prep.* $Zn(NO_3)_2 \cdot 6H_2O$ eutectics. *S. Ahmed et al., doi: 10.1021/acsaenm.3c00444.*

Technical Highlights:

Nucleation in Zinc Nitrate Hexahydrate Pseudobinary Eutectics

Here, we investigated a family of pseudobinary eutectics based on zinc nitrate hexahydrate (ZNH), in combination with different anhydrous nitrate salts. During this work, talc was identified as an inert and stable nucleation particle (NP) that can dramatically increase the observed nucleation rate (thereby decreasing undercooling) in all investigated ZNH pseudo-binary eutectics. The implementation of eutectic salt hydrates into TES applications has been impeded because of concerns of metastability due to (1) their susceptibility to undercool at high degrees and (2) the potential for phase segregation to accompany metastable solidification in cases where different phases exhibit different degrees of undercooling. In the ZNH-based eutectic systems investigated in this study, while large degrees of undercooling are observed, solidification appears tooccur simultaneously for both solid phases. In the case in which an NP is added to promote nucleation in the primary phase (ZNH), solidification of both crystalline solids still appears to occur simultaneously, at small degrees of undercooling. Accordingly, there is no evidence for phase segregation or other forms of degradation to occur under the investigated conditions. Thus, the ZNH-based pseudobinary eutectics investigated in this paper are dissimilar from the previously investigated lithium-nitrate-trihydrate-based eutectics, which do demonstrate solidification at different times, and which may therefore be susceptible to degradation caused by phase segregation.

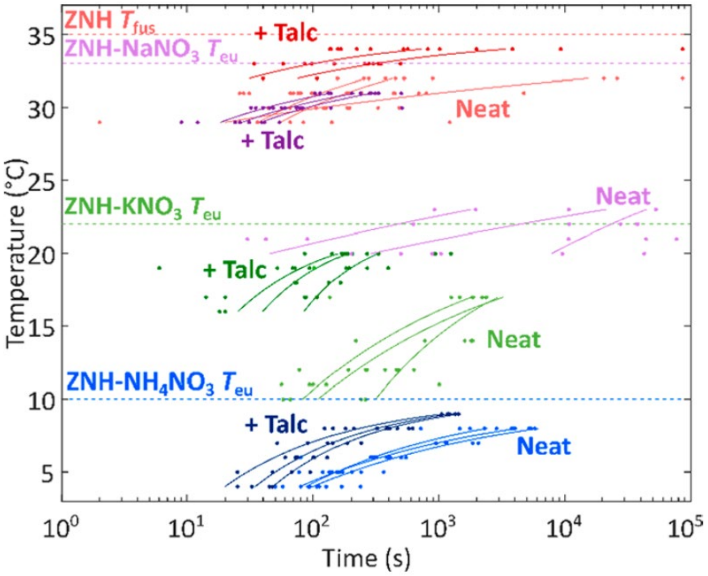


Fig. R2.1. Isothermal crystallization times at various temperatures for ZNH (red) and eutectics containing $NaNO_3$ (purple), KNO_3 (green), and NH_4NO_3 (blue) in the presence and absence of the talc nucleation particles. Darker shades of the two colors presented at a temperature represent samples that contain 2 wt % of talc. Curves represent isothermal nucleation times for 25, 50, and 75% probability of nucleation. Figure reproduced from doi: 10.1021/acsaenm.3c00444

Related Manuscripts: S. Ahmed, D. Ibbotson, C. Somodi, **P.J. Shamberger**. Zinc Nitrate Hexahydrate Pseudobinary Eutectics for Near-Room Temperature Thermal Energy Storage, *ACS Appl. Engineer. Mater*., 2(3), 530-541 (2023). doi: 10.1021/acsaenm.3c00444

Mutability of Nucleation Particles in $CaCl_2 \cdot 6H_2O$

Nucleation particles are solid phases that are added to a system to lower the energy required for the system to solidify or undergo a phase transition. Usually, an effective nucleation particle is chosen based on its structural or interfacial energy interaction with the host phase, but this method is premised upon the idea that the nucleation particle is nonreactive with the host phase. In this study, we demonstrate the occurrence of chemical reactions between precursor compounds and a reactive salt hydrate host phase change material, which generate solid products that dramatically reduce undercooling in the host phase change material. While this reactivity complicates the identification of a single phase which is primarily responsible for the nucleation activity, it also introduces a novel approach to harness in situ reactions to generate active nucleation sites within a phase change material.

In this study, it was found that the barium-based nucleation particles react with calcium chloride hexahydrate through a cation substitution reaction, resulting in both insoluble calcium and barium precipitates. However, no single chemically pure phase that was observed in diffraction data can be identified as being uniquely responsible for the reduction in undercooling of the CCH. Based on these findings, we hypothesize that the efficacy of barium-based nucleation particles in reducing undercooling in CCH is potentially due not to underlying lattice or structural relationships, but rather to the existence of atomic-scale defects on the surface of a solid solution phase. Thus, under this hypothesis, the reactivity between the PCM (CCH) and the original NP is essential to generate a heterogeneous solid template which is observed to be active as a nucleation surface. This strategy potentially introduces a more general approach to identifying NPs for reactive PCMs, including salt hydrates.

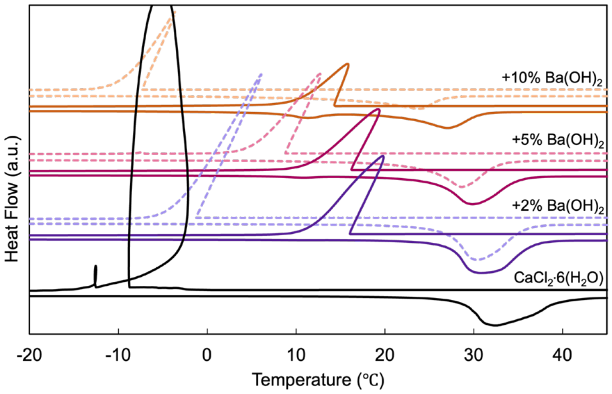


Fig. R2.2. DSC graphs of calcium chloride hexahydrate samples, both with (solid lines) and without (dashed lines) the insoluble particles from the nucleation particles $Ba(OH)_2$ in CCH.

Related Manuscripts: D. Ibbotson, S. Ahmed, **P.J. Shamberger**. Mutability of Nucleation Particles in Reactive Salt Hydrate Phase Change Materials, *in review.*

The Degradation and Rejuvenation of $SrCl_2{\cdot}6H_2O$ as a Nucleation Particle for $CaCl_2{\cdot}6H_2O$

In this study, we evaluated the efficacy of strontium chloride hexahydrate (SCH) as a nucleation particle for calcium chloride hexahydrate (CCH) and defined the limits of its utilization. It was observed that after prolonged periods of time (generally 1 to 2 d), small concentrations (<5 wt%) of SCH immersed in CCH above its melting point would lose their efficacy as a nucleation particle for CCH. However, if the CCH+SCH system was allowed to cool to a low temperature (<-20 °C) and held at a cold temperature for an extended period of time (~5 minutes or more), then strontium chloride hexahydrate was able to regain its efficacy as a nucleation particle for calcium chloride hexahydrate. Following previously published solubility data in the $SrCl_2$ - $CaCl_2$ – H_2O system, this is believed to indicate the dissolution, followed by reprecipitation of SCH. Thus, this study reveals that while isostructural compounds hold much potential for utility as nucleation particles, due to their structural similarities, they are, in many cases, also limited by their solubility within the liquid host phase.

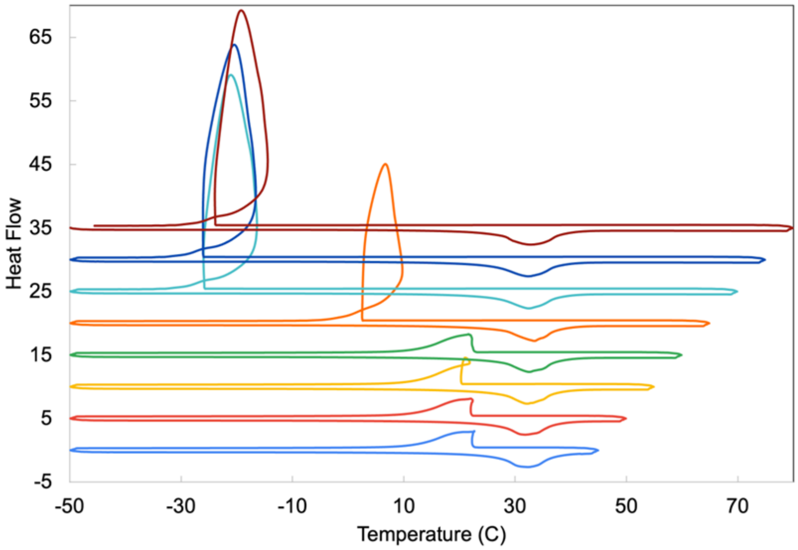


Fig. R2.3. Sequential DSC melting/solidifying cycles of calcium chloride hexahydrate (CCH) containing strontium chloride hexahydrate (SCH), increasing upwards. After heating above 60 °C, SCH dissolves, resulting in much larger observed undercooling.

Related Manuscripts: D. Ibbotson, **P.J. Shamberger**. The degradation and rejuvenation of strontium chloride hexahydrate as a nucleation particle for calcium chloride hexahydrate, *in prep.*

Other Related Manuscripts Under this Task:

1. A. Chakraborty, J. Noh, **P.J. Shamberger**, **C. Yu**. Unveiling Real-time Crystallization of Zinc Nitrate Hexahydrate Using Zinc Acetate Dihydrate Nucleator and Carboxymethyl Cellulose Thickener, *Energy Storage*, **e417**, (2022). doi: 10.1002/est2.417
2. A. Chakraborty, J. Noh, **P.J. Shamberger**, **C. Yu**. In-Operando Crystallization Study of Zinc Nitrate Hexahydrate Using Zinc Oxide Nucleators, *Energy Storage*, **e372**, (2022). doi: 10.1002/est2.372
3. S. Ahmed*, R. Mach*, H. Jones#, F. Alamo#, **P.J. Shamberger**, 'Solidification of Salt Hydrate Eutectics Using Multiple Nucleation Agents', in *REWAS 2022: Energy Technologies and CO2 Management (Volume II)*, ed. F. Tesfaye, L. Zhang, D. Post Guillen, Z. Sun, A. Abullahi Baba, N. R. Nellameggham, M. Zhang, D. E. Verhulst, S. Alam, (TMS, 2022), pp. 139-147. doi: /10.1007/978-3-030-92559-8

Task R3. Micro-scale thermal conductivity enhancement

Thrust Lead: Yu

Milestone Number	Milestone Description	Result Presented
3.1	Optimize graphite layer processing to achieve >10 W·m^{-1}·K^{-1} in individual layers and good wetting with salt hydrates (contact angle < 90^{0}).	*A. Chakraborty et al., doi: 10.1016/j.est.2022.104856.*
3.2	Demonstrate increase of thermal conductivity in graphite-based TES composites. Effective thermal conductivity of >1 W·m^{-1}·K^{-1} for >90 vol.% PCM, and survivability for >1000 melt/freeze cycles with minimal degradation of thermal properties (<5 % decrease in thermal conductivity, heat of fusion).	*A. Chakraborty et al., doi: 10.1016/j.est.2022.104856.*
3.3	Demonstrate R2R process of graphitic layer deposition and lift-off with >90% recoverable film yield.	Database reported to EERE.

Technical Highlights:

Stability of Expanded Graphite Matrix

For the practical application of phase change material (PCM) composites within TES systems, reliable thermal performance throughout its operational lifetime is essential. Nevertheless, the reliability of thermal conductivity in multi-phase composites over relevant numbers (>10^{3}) of melt/freeze cycles has barely been studied, particularly for composites containing fillers for thermal conductivity enhancement. Here, we introduce a preform-type expanded graphite (EG)/paraffin wax composite possessing highly robust heat transfer and storage properties even after 10,000 melt/freeze cycles.

This work reports the influence of fabrication process, expanded graphite (EG) particle size (750 and 1520 μm), vol% of EG (10, 14, 17 and 20 vol%), binder amount (3 and 7 vol%), and compaction on the thermal conductivity of paraffin wax composites containing EG fillers. The preform-type fabrication yielded superior thermal conductivity as a result of the connected EG particles which barely suffer from separation due to the intervening PCM between EG particles, unlike the slurry-type composites. Therefore, subsequent processing conditions employed the preform-type method. The smaller EG particles provided a higher conductivity, and the different concentrations of SBR binders did not significantly affect thermal conductivity. While more EG particles raised thermal conductivity, it is remarkable the largest improvement in thermal conductivity resulted from the compaction process, which could be attributed to the improved thermal contact between EG particles rather than the smaller porosity. A trade-off between thermal conductivity and latent heat is suggested, which greatly helps in selecting desired processing conditions for a specific application of interest. Our modeling analysis identified the highest thermal conductivity, 25.1 W·m^{-1}·K^{-1} from the composite containing 20 vol% EG comes from the thermally connected EG particles. Thermal reliability was well-retained up to 10,000 melt/freeze cycles particularly for the composite containing 10 vol% EG, albeit the drop of thermal conductivity was relatively more pronounced for the higher EG content composites. We believe that the outcomes are valuable in selecting a suitable recipe for the properties of desired TES systems.

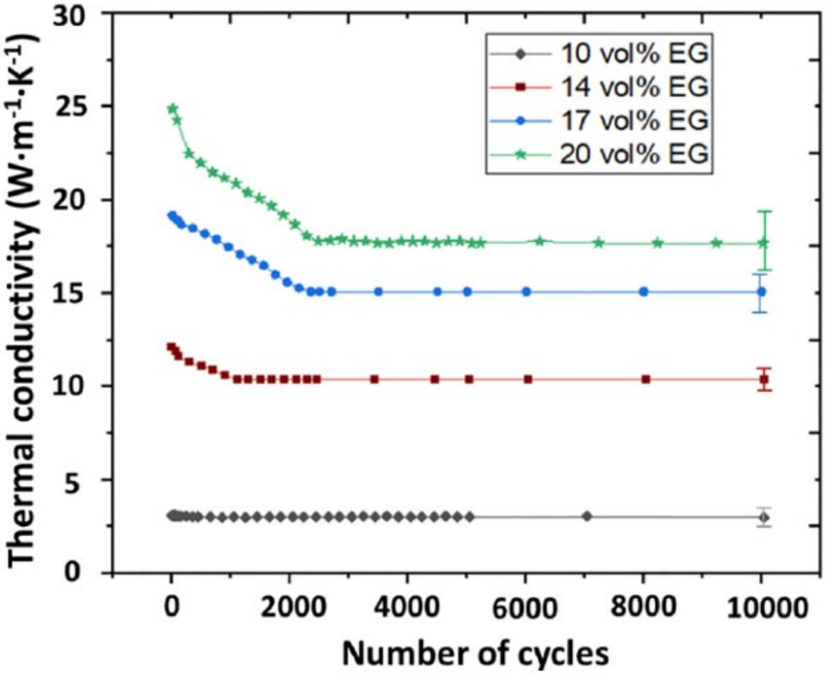


Fig. R3.1. Variation of thermal conductivity with a long-term thermal cycling for compacted, preform-type PCM composites containing EG-750. Error bars were obtained via the error propagation method and indicated on the last number of cycles for brevity. Figure reproduced from doi: 10.1016/j.est.2022.104856

Related Manuscripts: A. Chakraborty, J. Noh, R. Mach, **P.J. Shamberger**, **C. Yu**. Thermal Energy Storage Composites with Preformed Expanded Graphite Matrix and Paraffin Wax for Long-term Cycling Stability and Tailored Thermal Properties, *J Energy Storage, **52**, 104856* (2022). doi: 10.1016/j.est.2022.104856

Task R4. Encapsulation of Salt Hydrates

Thrust Lead: Pentzer

Milestone Number	Milestone Description	Result Presented
4.1	Validate encapsulation of salt hydrates using the Pickering emulsion approach. Measure yield (target > 90%), by DSC of encapsulated PCM particles. Test with both nitrate- and chloride- based systems.	*S. Lak et al., doi: 10.1016/j.jcis.2022.08.083* *N. Starvaggi et al., doi: 10.1039/d4cc00736k*
4.2	Demonstrate capsules of salt hydrates in the 10-1,000 um particle size range with < 10 vol% shell. Measure ability to control size distribution of particles through processing parameters.	*N. Starvaggi et al., doi: 10.1039/d4cc00736k*

Technical Highlights:

Encapsulation of Hygroscopic Liquids via Polymer Precipitation in Non-aqueous Emulsions

In this study, we report a novel single-step soft-template approach for encapsulation of water-miscible or hygroscopic materials that uniquely gives pristine core material and shells of readily accessible commodity polymers. By probing our hypothesis that commodity polymers can be precipitated onto nanosheet-stabilized droplets in non-aqueous emulsions, we demonstrated, for the first time, a single step method to fabricate capsules with a high loading of core material (>80 wt%), as with the ionic liquid [Emim][PF6] and the salt hydrate phase change material magnesium nitrate hexahydrate (MNH). This method is not limited by the viscosity of the core liquid, as with microfluidics, nor is it multi-step or require harsh reagents, as with most hard-template approaches. Further, this approach overcomes limitations of traditional soft-template approaches which require interfacial polymerization, and thus cannot be used with core material that chemically interact with monomers (e.g., a reactive ionic liquid) or where the composition of the core is highly sensitive to composition (e.g., cannot have excess water with salt hydrates). Not only do we demonstrate that this new approach is applicable to different core materials, but also that different commodity polymers can be used as shell, as demonstrated with poly(methyl methacrylate), polystyrene, and polyethylene. The capsules are robust to thermal cycling, in which the core material repeatedly melts and solidifies, indicating sustained shell integrity. Moreover, the alkylated nanosheets serve as nucleating agent for the salt hydrate PCM which overcomes undesired undercooling associated with small volumes. We envision that this new microencapsulation approach offers researchers across science and engineering the ability to readily tailor composition (both core and shell) of capsules with pristine core materials, critical to application-oriented properties and delineation of structure-processing-property-application relationships. Ongoing work in our lab focuses on expanding the types of polymers that can be used for shell formation as a route to controlling permeability to moisture and CO_2 for enhanced performance in thermal energy management and carbon capture.

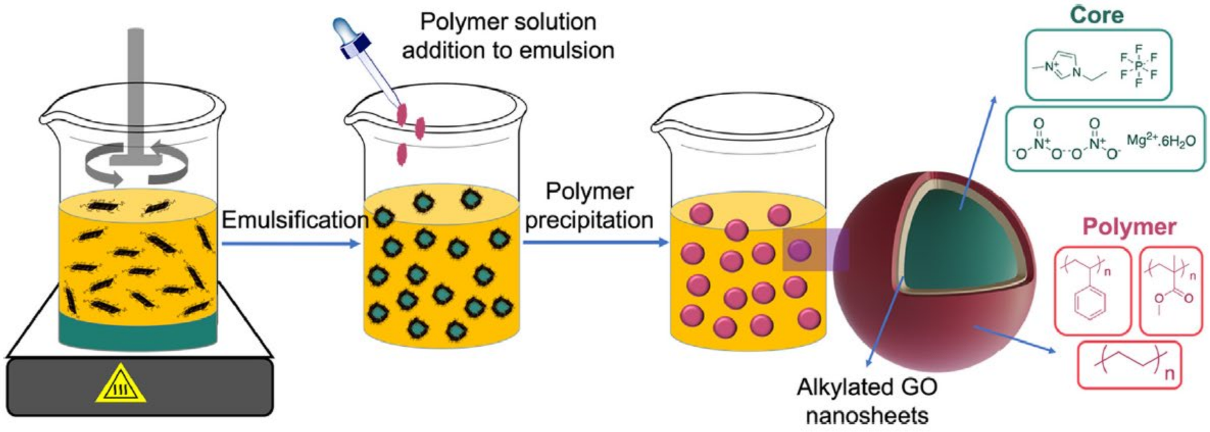
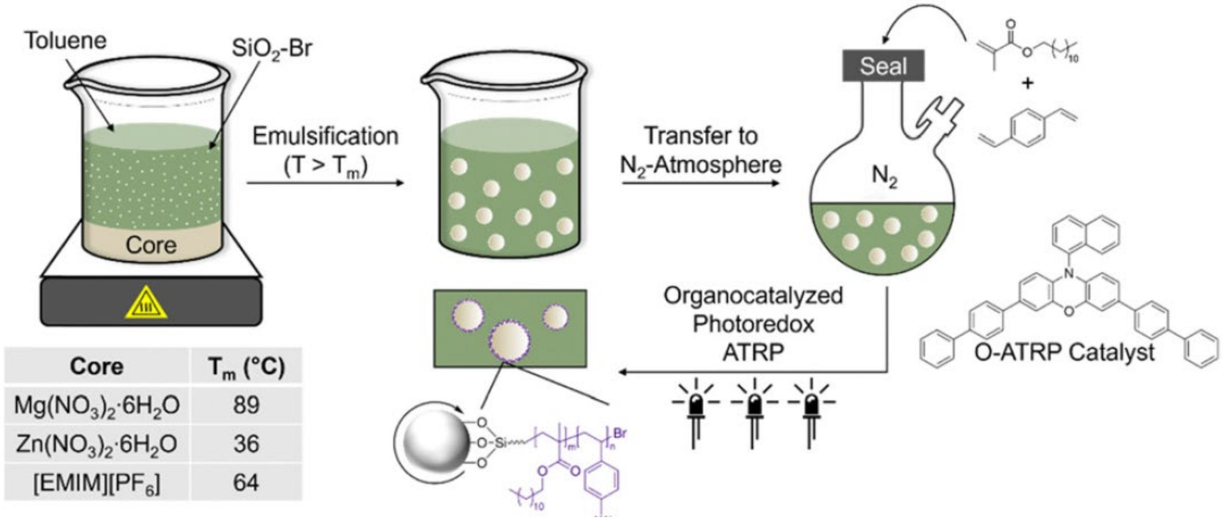


Fig. R4.1. Schematic of the new approach reported herein to encapsulation of sensitive core materials by preparation of a non-aqueous emulsion stabilized by alkylated graphene oxide nanosheets, then polymer precipitation onto the droplet surface. Both IL and PCM can be used as the core materials and commodity polymers are used as the shell. Figure reproduced from doi: 10.1016/j.jcis.2022.08.083

Related Manuscripts: S.N. Lak, S. Ahmed, **P.J. Shamberger**, **E.B. Pentzer**. Encapsulation of Hygroscopic Liquids via Polymer Precipitation in Non-aqueous Emulsions, *J Colloid Interface Sci.,* **628**(B), 605-613 (2022). doi: 10.1016/j.jcis.2022.08.083

Microcapsule Fabrication by ATRP

In this study, we report a new soft-template encapsulation method for water-sensitive materials with high core loading (>90%) via organocatalyzed photoredox ATRP using silica particle surfactants with surface-immobilized initiators. Silica particles were modified with ATRP initiators, and used to stabilize emulsions formed above the melting point of the desired core. ATRP of hydrophobic monomers in the continuous phase from the interfacially assembled particles produced microcapsules with rough surface morphology as visualized by SEM. FTIR analysis of the microcapsules pre- and post-core extraction indicates a PCM or IL core and silica/polymer composite shell. The core can undergo multiple melting-solidification cycles without leakage, and undercooling of the salt hydrate PCM was mitigated by addition of a co-surfactant, which served as a nucleating agent. Critically, this approach eliminates the need for monomer in the core and lays the foundation for tuning of the microcapsule shell composition. Our ongoing work addresses endowing the shell with specific properties for bespoke performance-related properties.



Core	T_m (°C)
$Mg(NO_3)_2 \cdot 6H_2O$	89
$Zn(NO_3)_2 \cdot 6H_2O$	36
$[EMIM][PF_6]$	64

Fig. R4.2. Overview of microcapsule fabrication method using silica particles modified with ATRP initiators as the surfactant. Figure reproduced from doi: 10.1016/j.jcis.2022.08.083

Related Manuscripts: N. Starvaggi, C. Somodi, E. Cruz-Barrios, **P.J. Shamberger**, **E. Pentzer**. Microcapsule Fabrication by ATRP at the Interface of Non-Aqueous Emulsions. *Chem. Commun.,* 60, 4346-4349 (2024). doi: 10.1039/d4cc00736k

3D Printing of Composites with Encapsulated Salt Hydrate PCMs

In this study, we report a facile formulation and 3D printing of inks composed of PCM particles and polymer by leveraging salt hydrate particles as rheology modifiers and DIW printing. Microscopic analysis of the printed and cured structures confirmed no phase separation and that the salt hydrate particles were dispersed through the PMMA matrix, even at salt hydrate content of up to 70 wt %. Thermal analyses validated the preservation of the salt hydrate composition and the reduction in undercooling in these printed polymeric composites. Moreover, these composites exhibit good thermal stability over at least 10 heating/cooling cycles without significant macroscopic changes in their structure. Notably, this approach eliminates the need for microencapsulation of salt hydrates prior to integration into the polymer composite. It further facilitates the incorporation of fillers such as carbon black, which resulted in a 33% enhancement in thermal conductivity. We demonstrate that this approach is adaptable to particles of different salt hydrates, and thus can be used to tailor the temperature at which thermal energy management can be performed. Our ongoing research focuses on expanding the range of matrix materials for DIW to optimize the stability and permeability of the composites. For instance, the use of non-solvent-based resins can reduce the formation of pores on the surface of the printed composites caused by solvent evaporation during the curing process. Overall, this new approach to formulate inks for 3D printing holds significant promise for manufacturing PCM composites with tailored properties, thus highlighting the potential of adopting salt hydrates in diverse thermal energy storage applications.

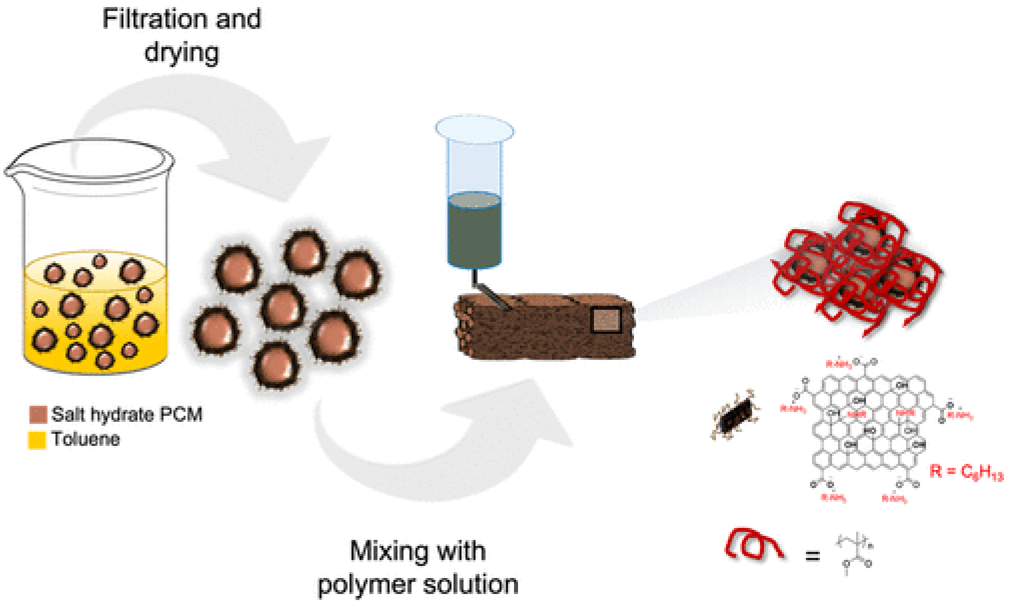


Fig. R4.3. Schematic illustrating the formulation of salt-hydrate-containing inks and direct ink write printing of salt hydrate phase change materials (PCMs). Salt hydrate particles coated with alkylated graphene oxide (GO) nanosheets are mixed with toluene dispersions in polymer, extruded, and the printed object cured by evaporation of toluene. Figure reproduced from doi: 10.1021/acsaenm.3c00324

Related Manuscripts: S. Lak, C.-M. Hsieh, L. Al Mahbobi, Y. Wang, A. Chakraborty, **C. Yu**, **E. Pentzer**. Printing Composites with Salt Hydrate Phase Change Materials for Thermal Energy Storage, *ACS Appl. Engineer. Mater*., 1(8), 2279-2287 (2023). doi: 10.1021/acsaenm.3c00324

Task R5. Shape stabilization of salt hydrate PCMs using thermo-reversible salogels

Thrust Lead: Sukhishvili

Milestone Number	Milestone Description	Result Presented
5.1	Demonstrate gelation temperature above the T_m for 2-5 nitrate and chloride eutectic systems. Measure preliminary data set of thermal, viscoelasticity and gelation of 2 to 5 candidate shape-stabilized nitrate hydrate eutectic PCMs (the same down-selected set used for nucleation catalyst efforts).	*K. Rajagopalan et al., doi: 10.1039/D2TA06183J* *K. Rajagopalan et al., doi: 10.1021/acsaenm.3c00522* *K. Rajagopalan et al., doi: 10.2139/ssrn.4752047*
5.2	Identify salogels for eutectic nitrate and chloride PCMs (*R1.1*) which maintain >90% of the PCM volumetric density, maintaining cost <$12/kWh of the composite PCM, while remaining shape-stable below T_g.	*K. Rajagopalan et al., doi: 10.1039/D2TA06183J* *K. Rajagopalan et al., doi: 10.1021/acsaenm.3c00522* *K. Rajagopalan et al., doi: 10.2139/ssrn.4752047*
5.3	Demonstrate the general ability to shape stabilize nitrate and chloride salt hydrates. *Demonstrate thermo-reversible gelation (up to 100 cycles) in salogel consisting of >90 vol.% PCM for both eutectic systems.*	*K. Rajagopalan et al., doi: 10.1039/D2TA06183J* *K. Rajagopalan et al., doi: 10.1021/acsaenm.3c00522* *K. Rajagopalan et al., doi: 10.2139/ssrn.4752047*
5.4	Validate long-term stability study of nucleation-catalyst-containing PCM salogels over >1yr, and 10^3 cooling/heating cycles (maintain ΔT < 2 C; maintain ΔH_{fus} > 95% after aging and cycling; change in T_{gel} < 5 C after aging and cycling).	*S. Ahmed et al., in prep.*

Technical Highlights:

Thermo-reversible Salogels with Boronate Ester Bonds as Thermal Energy Storage Materials

Inorganic salt hydrates are promising phase change materials (PCMs) but suffer from low viscosity at temperatures above their melting point resulting in leakage problems during thermal storage applications. To achieve shape stabilization of one type of molten inorganic PCM – calcium nitrate tetrahydrate (CNH) – this work explored gelation of polyvinyl alcohol (PVA) in this solvent and the effect of dynamic boronate ester bonds on salogel strength. The occurrence of gelation of PVA in molten CNH but not in water is rationalized by the extremely high salt content and scarcity of hydration water in CNH, enabling intermolecular hydrogen bonding between PVA chains. While neat PVA salogels in CNH were weak, with a gel-to-sol transition temperature (T_{gel}) below room temperature, the addition of small amounts of borax (<~0.3 wt%) introduced dynamic covalent crosslinks and yielded salogels with T_{gel} tunable over a wide temperature range from 7 to 70 °C. The PVA/borax salogels were about one order of magnitude stronger than their well-known PVA/borax hydrogel counterparts, and, unlike PVA/borax hydrogels, were capable of retaining their shape and preventing leakage of molten CNH. Moreover, the salogels exhibited reversible and repeatable temperature-triggered gel-to-sol transitions and the ability to self-heal. The low polymer and crosslinker concentration also ensured that more than 95% of the heat of fusion of neat CNH was maintained in the salogels and was retained after twenty cycles of melting and crystallization, demonstrating the robust nature of these energy storage materials.

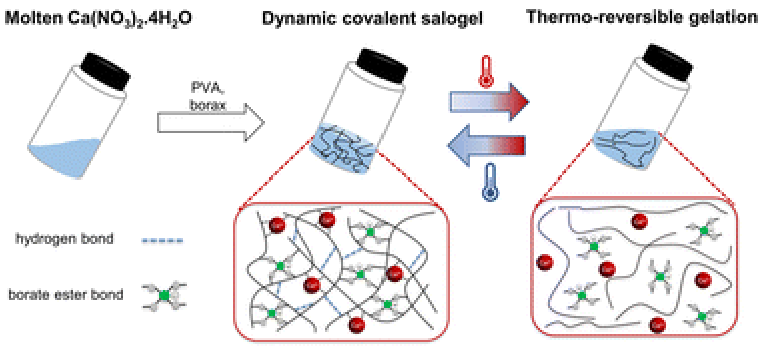


Fig. R5.1. Schematic representing dynamic covalent bonding with boronate ester bonds in a prototype salogel. Figure reproduced from doi: 10.1039/D2TA06183J

Related Manuscripts: K. Rajagopalan, X. Zhu, **S.A. Sukhishvili**, Strong, thermo-reversible salogels with boronate ester bonds as thermal energy storage materials, *J Mater. Chem, A,* **10**(40), 21622-21632 (2022). doi: 10.1039/D2TA06183J

Hybrid Polymer Salogels for Salt Hydrate-Based Thermal Energy Storage Materials

In this study, hybrid salogel design strategy was demonstrated based on a combination of physical entanglements and dynamic covalent cross-links to shape stabilize an inorganic PCM. The strategy was necessitated due to the significant effect of the anion type on gelation behavior of polymers in molten salt hydrates. The target PCM in this work was calcium chloride hexahydrate (CCH), an inexpensive and widely available salt hydrate PCM with a high heat of fusion and near ambient melting temperature. However, weaker PVA/borax gels with lower T_{gel} were formed in the chloride salt hydrate CCH in comparison to the previously studied nitrate salt hydrate, CNH, due to the strong salting-out effect of chloride ions. To achieve shape stabilization at low polymer concentration (<5 wt %) with thermo-reversible gelation and tunable T_{gel} in CCH, a combination of boronate ester crosslinks with physical entanglements was used in this work by introducing an ultrahigh molecular weight PAAm. Hydrogen bonding between PAAm and PVA within a joint, hybrid network supported a synergistic effect between the entanglements and dynamic covalent crosslinks to yield robust, shape stable yet temperature responsive salogels. The salogels formed using this strategy retained ~95% of the heat of fusion of CCH and only a small change in melting temperature while also providing shape stabilization above Tm of CCH and processability above T_{gel}, all at a low polymer and crosslinker concentration of ~4.8% that is essential for retention of high efficiency of this thermal energy storage materials. Finally, the hybrid salogels were easily moldable and retained their mechanical and thermal properties after 50 melting/crystallization cycles.

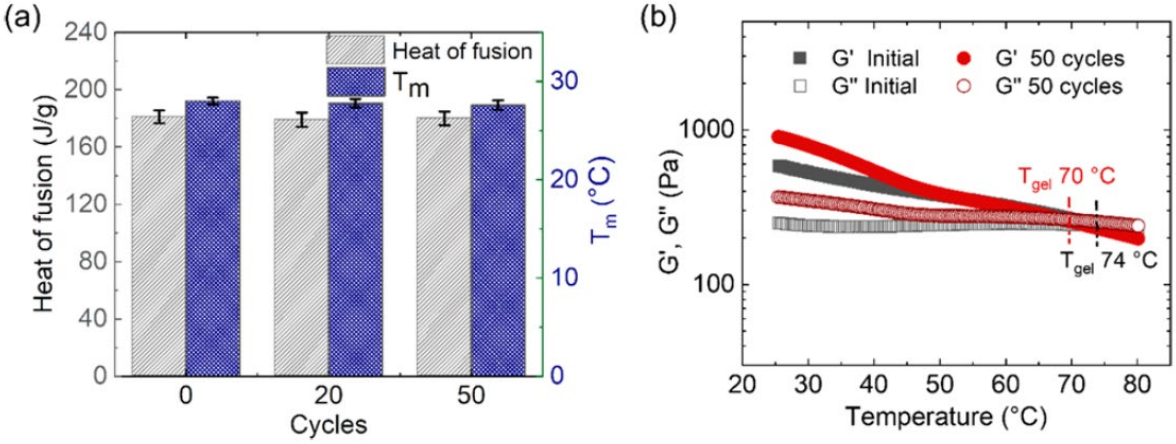


Fig. R5.2. (a) Heat of fusion and melting temperature for hybrid (2% PAAm/2% PVA/borax 10 mol %) salogel and (b) temperature sweep rheology experiments comparing G', G'', and T_{gel} of hybrid salogel before and after thermal cycling. Temperature sweep rheology experiments were performed at a frequency of 10 rad/s and 1% strain. Figure reproduced from doi: 10.1021/acsaenm.3c00522

Related Manuscripts: K. Rajagopalan, S. Haney, **P.J. Shamberger**, **S.A. Sukhishvili**. Hybrid Polymer Salogels for Reversible Entrapment of Salt-Hydrate-Based Thermal Energy Storage Materials, *ACS Appl. Engineer. Mater*., 2(3), 553-562 (2023). doi: 10.1021/acsaenm.3c00522

Diels-Alder Salogels for Shape Stabilization of Salt Hydrate Phase Change Materials

In this work, Diels-Alder (DA) crosslinks were used to create a shape stabilizing matrix for low-viscosity salt hydrate PCMs with widely ranging melting temperatures (room temperature to 89 °C). DA crosslinks formed robust salogels which could maintain their moduli over a broad temperature range up to the retro-DA reaction temperature (120 °C) allowing shape stabilization of a low melting lithium nitrate trihydrate (LNH) and a high melting magnesium nitrate trihydrate (MgNH) temperature PCM. Importantly, this work demonstrated the ability of the DA salogel to reversibly shape stabilize a salt hydrate PCM with a high melting temperature – a property not achievable with previously developed salogel materials. In addition, the low polymer concentration of 5 wt% in the DA salogels had effective energy storage capabilities, showing heat of fusion retention of the neat PCM during multiple melting and crystallization cycles. In comparison to the viscoelastic behavior of boronate ester salogels, the elastic nature of the DA salogels resulted in superior creep resistance and excellent strain recovery over a wide temperature range that are essential for the development of free-standing thermal energy storage materials.

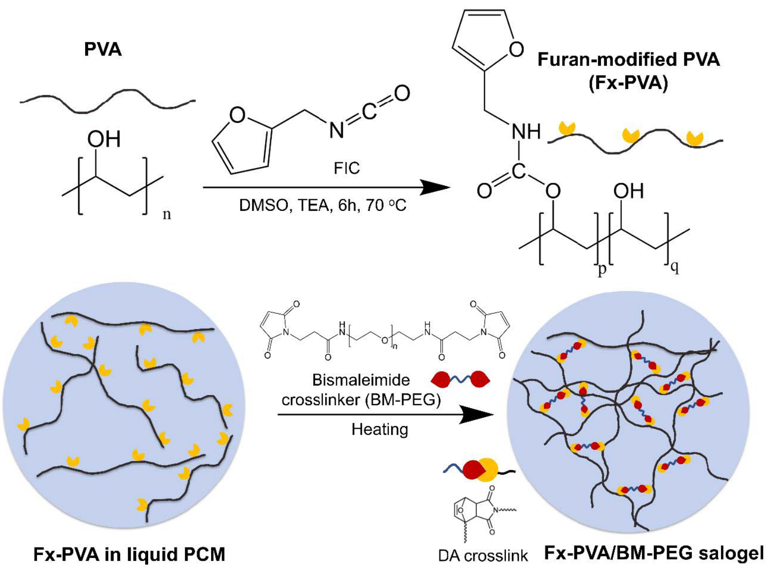


Fig. R5.3. Furan modification of PVA using furfuryl isocyanate (FIC) and crosslinking of furan-modified PVA with BM-PEG to form Diels-Alder salogels in salt hydrate PCMs. Figure reproduced from doi: 10.2139/ssrn.4752047

Related Manuscripts: K. Rajagopalan, **S.A. Sukhishvili**. Temperature- and Creep-Resistant Diels-Alder Salogels for Shape Stabilization of Salt Hydrate Phase Change Materials, *in review.* doi: *10.2139/ssrn.4752047*

Other Related Manuscripts Under this Task:

1. K. Rajagopalan, **P.J. Shamberger**, **S.A. Sukhishvili**. Polymer Salogels as Thermal Energy Storage Materials: Thermo-reversible vs Permanent Networks, *in prep.*
2. S. Ahmed, K. Rajagopalan, D. Ibbotson, **S.A. Sukhishvili, P.J. Shamberger**. Stability of Salt Hydrate Eutectic Salogels on Melt Crystallization Cycles*, in prep.*

Task R6. Building- and Component-level energy impact analysis

Thrust Lead: Felts, Culp

Milestone Number	Milestone Description	Result Presented
6.1	Develop a lumped system-level model and control scheme to determine most efficient peak load shifting method. Evaluate HVAC integrated energy storage embodiments. Identify two key temperature ranges (T_c* and T_h* +/- 5 C) that will be used to down-select PCMs.	Report model structure and prelim. validation results to EERE.
6.2	Develop test apparatus to assess the charge/ discharge rates of the proposed thermal storage solutions, and evaluate total energy stored, based on heat extraction from chilled/ heated air or water.	Report apparatus schematics plus test results on standard material to EERE.
6.3	Scale up synthesis techniques for a single down-selected salt hydrate system (including supporting technologies: gelling agents, nucleation agents, etc.) to 100 g to 1 kg level.	Report experimental results and comparison against simul. to EERE.

Technical Highlights:

Effectiveness of Heat Transfer in Eutectic Salt Hydrate PCM Slabs

In this work, we measured the time dependent rate of heat transfer into a composite PCM slab from a coolant, thereby evaluating the ability to absorb heat at a sufficient rate for an HVAC application. To this end, we developed a cooling loop apparatus to measure time dependent heat transfer from a coolant (water) into a PCM slab. We calibrated this system against a baseline paraffin that does not melt over the specified temperature range (octadecane) and paraffin PCM that does melt (hexadecane) to isolate the effect of latent heat of fusion. This system was used to evaluate a model salt hydrate system (zinc nitrate hexahydrate) and its eutectics, infiltrated into an expanded graphite matrix. We measured the rate of heat absorption under two different isothermal heating conditions, with temperatures of ΔT = 5 °C and 10 °C above the melting temperature of the salt hydrate, and compared these heat absorption rates against numerically predicted heat transfer rates using a 2D finite difference code. We demonstrate the ability to absorb heat at sufficient rates with moderate volume fractions of graphite (<10 vol.%). Additionally, we demonstrate very stable cycling behavior in scaled volumes (~100 mL) of salt hydrate eutectics over periods of up to 100 cycles, demonstrating the utility of these systems over long life spans.

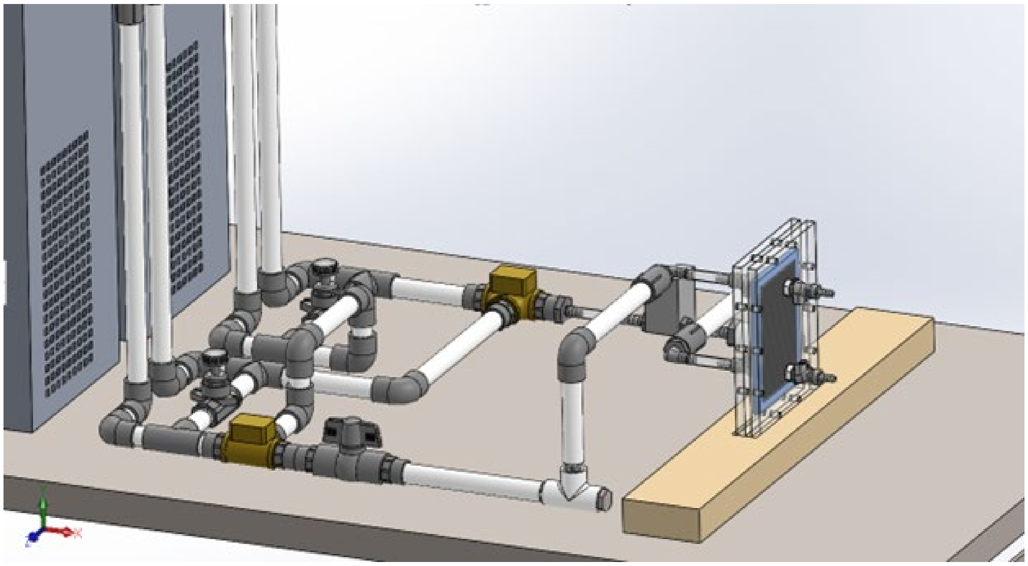


Fig. R6.1. Apparatus used to measure heat absorption rate in slab of composite PCM.

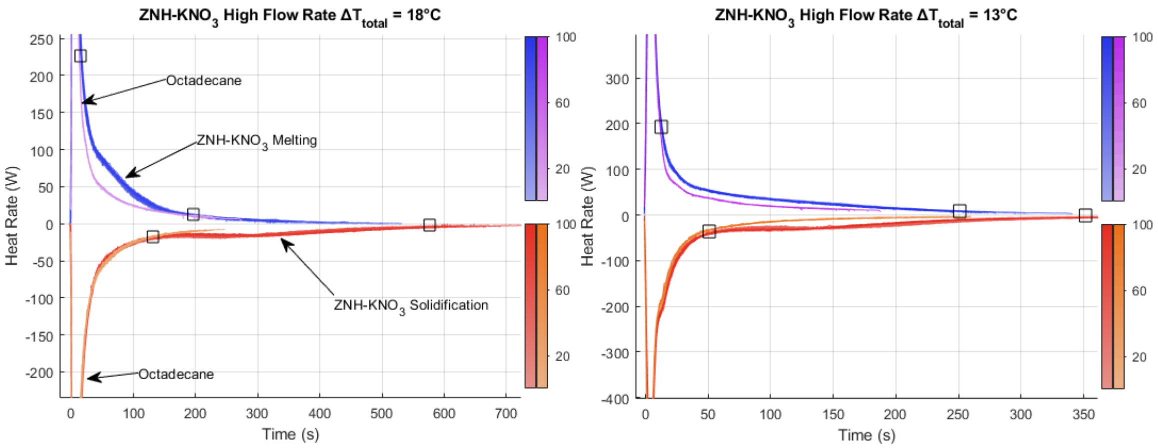


Fig. R6.2. Measured heat flow into a slab of zinc nitrate hexahydrate (ZNH) – KNO_3 eutectic infiltrated into an expanded graphite matrix under isothermal melting conditions held a) 10 °C above melting point, and b) 5 °C above melting point

Related Manuscripts: D. Morphew, **J. Felts**, **P.J. Shamberger**. Effectiveness of Heat Transfer of Phase Change Material-Expanded Graphite Composites in a Cold Plate Heat Exchanger, *in prep.*

PRODUCTS & DISSEMINATION

Below, we list the cumulative research output for this project.

1. Special Editions

ACS APPLIED ENGINEERING MATERIALS

S.A. Sukhishvili (Associate Editor), and **P.J. Shamberger** (Guest Editor) coordinated a special forum on Thermal Energy Storage materials, hosted by ACS Applied Engineering Materials: https://pubs.acs.org/toc/aaemdr/2/3

2. Papers (Cumulative)

In preparation

1. K. Rajagopalan, **P.J. Shamberger**, **S.A. Sukhishvili**. Polymer Salogels as Thermal Energy Storage Materials: Thermo-reversible vs Permanent Networks, *in prep.*
2. D. Morphew, **J. Felts**, **P.J. Shamberger**. Effectiveness of Heat Transfer of Phase Change Material-Expanded Graphite Composites in a Cold Plate Heat Exchanger, *in prep.*
3. D. Ibbotson, **P.J. Shamberger**. Evaluation of calcium chloride hexahydrate pseudo-binary eutectics, *in prep.*
4. D. Ibbotson, **P.J. Shamberger**. The degradation and rejuvenation of strontium chloride hexahydrate as a nucleation particle for calcium chloride hexahydrate, *in prep.*
5. S. Ahmed, K. Rajagopalan, D. Ibbotson, **S.A. Sukhishvili, P.J. Shamberger**. Stability of Salt Hydrate Eutectic Salogels on Melt Crystallization Cycles, *in prep.*
6. **P.J. Shamberger**, *et al.* Prediction and validation of eutectic nitrate salt hydrates, *in prep.*

In review

1. K. Rajagopalan, **S.A. Sukhishvili**. Temperature- and Creep-Resistant Diels-Alder Salogels for Shape Stabilization of Salt Hydrate Phase Change Materials, *in review.* doi: *10.2139/ssrn.4752047*
2. D. Ibbotson, S. Ahmed, **P.J. Shamberger**. Mutability of Nucleation Particles in Reactive Salt Hydrate Phase Change Materials, *in review.*

Published

1. N. Starvaggi, C. Somodi, E. Cruz-Barrios, **P.J. Shamberger**, **E. Pentzer**. Microcapsule Fabrication by ATRP at the Interface of Non-Aqueous Emulsions. *Chem. Commun.,* 60, 4346-4349 (2024). doi: 10.1039/d4cc00736k
2. **P.J. Shamberger**, **S.A. Sukhishvili**. Pathways toward Critical Advances in the Chemistry of Materials for Thermal Energy Storage, *ACS Appl. Engineer. Mater.*, 2(3), 501-502 (2024). doi: 10.1021/acsaenm.4c00148

3. K. Rajagopalan, S. Haney, **P.J. Shamberger**, **S.A. Sukhishvili**. Hybrid Polymer Salogels for Reversible Entrapment of Salt-Hydrate-Based Thermal Energy Storage Materials, *ACS Appl. Engineer. Mater*., 2(3), 553-562 (2023). doi: 10.1021/acsaenm.3c00522
4. S. Ahmed, D. Ibbotson, C. Somodi, **P.J. Shamberger**. Zinc Nitrate Hexahydrate Pseudobinary Eutectics for Near-Room Temperature Thermal Energy Storage, *ACS Appl. Engineer. Mater*., 2(3), 530-541 (2023). doi: 10.1021/acsaenm.3c00444
5. S. Lak, C.-M. Hsieh, L. Al Mahbobi, Y. Wang, A. Chakraborty, **C. Yu**, **E. Pentzer**. Printing Composites with Salt Hydrate Phase Change Materials for Thermal Energy Storage, *ACS Appl. Engineer. Mater*., 1(8), 2279-2287 (2023). doi: 10.1021/acsaenm.3c00324
3. A. Chakraborty, S. Ahmed, **P.J. Shamberger**, **C. Yu**. Achieving extraordinary thermal stability of salt hydrate eutectic composites by amending crystallization behaviour with thickener, *Composites Part B: Engineering,* 110877 (2023). doi: 10.1016/j.compositesb.2023.110877
4. K. Rajagopalan, X. Zhu, **S.A. Sukhishvili**, Strong, thermo-reversible salogels with boronate ester bonds as thermal energy storage materials, *J Mater. Chem, A,* **10**(40), 21622-21632 (2022). doi: 10.1039/D2TA06183J
5. A. Chakraborty, J. Noh, **P.J. Shamberger**, **C. Yu**. Unveiling Real-time Crystallization of Zinc Nitrate Hexahydrate Using Zinc Acetate Dihydrate Nucleator and Carboxymethyl Cellulose Thickener, *Energy Storage,* **e417**, (2022). doi: 10.1002/est2.417
6. A. Chakraborty, J. Noh, **P.J. Shamberger**, **C. Yu**. In-Operando Crystallization Study of Zinc Nitrate Hexahydrate Using Zinc Oxide Nucleators, *Energy Storage*, **e372**, (2022). doi: 10.1002/est2.372
7. A. Chakraborty, J. Noh, R. Mach, **P.J. Shamberger**, **C. Yu**. Thermal Energy Storage Composites with Preformed Expanded Graphite Matrix and Paraffin Wax for Long-term Cycling Stability and Tailored Thermal Properties, *J Energy Storage,* ***52****, 104856* (2022). doi: 10.1016/j.est.2022.104856
8. S.N. Lak, S. Ahmed, **P.J. Shamberger**, **E.B. Pentzer**. Encapsulation of Hygroscopic Liquids via Polymer Precipitation in Non-aqueous Emulsions, *J Colloid Interface Sci.,* **628**(B), 605-613 (2022). doi: 10.1016/j.jcis.2022.08.083
9. K. Rajagopalan, P. Karimineghlani, X. Zhu, **P.J. Shamberger**, and **S.A. Sukhishvili**, Polymers in Molten Inorganic Salt Hydrates: Solubility and Gelation, *J Mater. Chem, A,* **9**, 25892 (2021). doi: 10.1039/D1TA07842A

3. Theses / Dissertations

1. Temperature-Responsive Poly(Vinyl Alcohol)-Borax Salogels for Shape Stabilization of an Inorganic Phase Change Material (**X. Zhu**, M.S. Materials Sci. & Eng, 2021. Advisor: **S. A. Sukhishvili**)
2. Model and Simulation of a Vapor Compression Refrigeration System with Phase Change Materials for Thermal Energy Storage (**Z. Wilson**, M.S. Mech. Eng., 2022. Advisor: **J. Felts**)
3. Thermal Energy Storage Using Phase Change Materials and their Composites (**A. Chakraborty**, Ph.D. Materials Sci. & Eng., 2023. Advisor: **C. Yu**)
4. Encapsulation of Water-Sensitive Compositions Using Non-Aqueous Pickering Emulsions (**S. Lak,** Ph.D. Chemistry, anticipated 2024 Advisor: **E. Pentzer**)

5. Thermo-responsive salogels for shape stabilization of inorganic phase change materials (**K. Rajagopalan,** Ph.D. Materials Sci. & Eng., anticipated 2024 Advisor: **S. A. Sukhishvili**)
6. Eutectic salt hydrates for thermal energy storage (**S. Ahmed,** Ph.D. Materials Sci. & Eng., anticipated 2025 Advisor: **P. Shamberger**)
7. Solidification in Eutectic Salt Hydrates (**D. Ibbotson,** Ph.D. Materials Sci. & Eng., anticipated 2026 Advisor: **P. Shamberger**)

4. Refereed Conference Proceedings

1. S. Ahmed*, R. Mach*, H. Jones#, F. Alamo#, **P.J. Shamberger**, 'Solidification of Salt Hydrate Eutectics Using Multiple Nucleation Agents', in *REWAS 2022: Energy Technologies and CO2 Management (Volume II)*, ed. F. Tesfaye, L. Zhang, D. Post Guillen, Z. Sun, A. Abullahi Baba, N. R. Nellameggham, M. Zhang, D. E. Verhulst, S. Alam, (TMS, 2022), pp. 139-147. doi: /10.1007/978-3-030-92559-8

5. Presentations

1. K. Rajagopalan, S. Haney, **P.J. Shamberger**, **S.A. Sukhishvili**, Hybrid Polymer Salogels for Reversible Entrapment of Salt-Hydrate-Based Thermal Energy Storage Materials (**oral**), ACS Spring 2024 Meeting (March, 2024).
2. K. Rajagopalan, **S.A. Sukhishvili**, Diels-Alder Salogels for Shape Stabilization of Inorganic Salt Hydrate Phase Change Materials (**poster**), Materials Expo (Dec, 2023). (Best Poster Award)
3. K. Rajagopalan, **S.A. Sukhishvili**, Diels-Alder Salogels for Shape Stabilization of Inorganic Salt Hydrate Phase Change Materials (**oral**), Polymer Technology Industrial Consortium (Oct, 2023)
4. K. Rajagopalan, **S.A. Sukhishvili**, Shape Stabilization of Inorganic Salt Hydrate Phase Change Materials Using Thermo-reversible Salogels (**oral**), 11th Annual Texas Soft Matter Meeting (Aug, 2023)
5. S. Ahmed, D. Ibbotson, C. Somodi, **P.J. Shamberger**. Stability of salt hydrate eutectics for low-cost thermal energy storage (**oral**), ACS Fall Meeting 2023, San Francisco (Aug, 2023).
6. S. Lak, **P.J. Shamberger**, **E. Pentzer**, Encapsulation and 3D Printing of Salt Hydrates for Thermal Energy Storage (**poster**), MRS Spring 2023, San Francisco (Apr, 2023).
7. A. Chakraborty, **C. Yu**, **P.J. Shamberger**, S. Ahmed, Large-scale Fabrication and In-operando Crystallization Study of Expanded Graphite/Zinc Nitrate hexahydrate-Potassium Nitrate Eutectic Composites with Robust Thermal Properties (**virtual**), MRS Spring 2023, San Francisco (Apr, 2023).
8. D. Ibbotson, S. Ahmed, **P.J. Shamberger**, Role of Ba-containing Compounds in the Nucleation of Solid Calcium Chloride Hexahydrate (**poster**), MRS Spring 2023, San Francisco (Apr, 2023).
9. S. Ahmed, A. Chakraborty, D. Ibbotson, S. Lak, K. Rajagopalan, A. Tamraparni, **C. Culp**, **J. Felts**, **E. Pentzer**, **S. Sukhishvili**, **C. Yu**, **P.J. Shamberger,** Salt Hydrate Eutectics: Tailored Design of Equilibria, Reversibility, and Stability in Complex Phase Change Material Systems (**oral**), MRS Spring 2023, San Francisco (Apr, 2023).

10. **P.J. Shamberger,** S. Ahmed, D. Ibbotson, H. Jones, R. Mach, Salt Hydrate Eutectics: Expanding the Palette of Phase Change Materials for Thermal Energy Storage (**oral**), TMS Annual Meeting, San Diego, CA (Mar, 2023).
11. D. Ibbotson, S. Ahmed, **P.J. Shamberger**, Enhanced Reversibility in Calcium Chloride Hexahydrate with Nucleation Agents for Thermal Energy Storage Applications (**poster**), TMS Annual Meeting, San Diego, CA (Mar, 2023).
12. **P.J. Shamberger**, Nucleation Problems in Phase Change Materials (**invited oral**), Micro and Nanoscale Phase Change Phenomena, Gordon Research Conference, Lucca, Italy (Jan, 2023).
13. S. Ahmed, D. Ibbotson, **P.J. Shamberger**, Phase Stability of Zinc Nitrate Hexahydrate Eutectics for Low-Cost Thermal Energy Storage (**poster**), Society of Engineering Science Fall 2022, College Station, TX (Oct, 2022).
14. D. Ibbotson, S. Ahmed, **P.J. Shamberger**, Investigation into the Effects of Nucleation Agents in a Calcium Chloride Hexahydrate System for Thermal Energy Storage Applications (**poster**), Society of Engineering Science Fall 2022, College Station, TX (Oct, 2022). **Best Student Poster Award.**
15. K. Rajagopalan, X. Zhu, **S.A. Sukhishvili**, Thermo-responsive salogels with dynamic covalent crosslinks for shape stabilization of an inorganic salt hydrate phase change material (**poster**), Polymer Technology Industrial Consortium Student Poster Session, April 21-22, 2022.
16. K. Rajagopalan, X. Zhu, **S.A. Sukhishvili**, Thermo-responsive salogels with tunable gelation temperature for shape stabilization of inorganic salt hydrate phase change materials (**oral**), ACS Spring 2022 Meeting, March 23, 2022.
17. S. Ahmed, R. Mach, H. Jones, F. Alamo, **P.J. Shamberger**, Solidification of Salt Hydrate Eutectics Using Multiple Nucleation Agents (**oral**), TMS Annual Meeting, Anaheim, CA (Mar, 2022).
18. A. Hoe, A. Tamraparni, C. Zhang, A. Elwany, **J. Felts**, **P.J. Shamberger**, Design of Phase Change Material Composites for Efficient and Rapid Storage of Thermal Energy (**oral**), TMS Annual Meeting, Anaheim, CA (Mar, 2022).
19. **S.A. Sukhishvili**, Polymer Salogels for Shape Stabilization of Inorganic Phase Change Materials (**invited talk**), ACS Southeastern Regional Meeting, Birmingham, AL, (Nov. 2021).
20. X. Zhu, K. Rajagopalan, **S.A. Sukhishvili** "Temperature-Responsive, Tunable Poly(vinyl alcohol)-Borax Salogels for Shape Stabilization of an Inorganic Phase Change Material", poster presentation, ACS Spring 2021 Meeting (Apr, 2021). **Best Poster Award.**