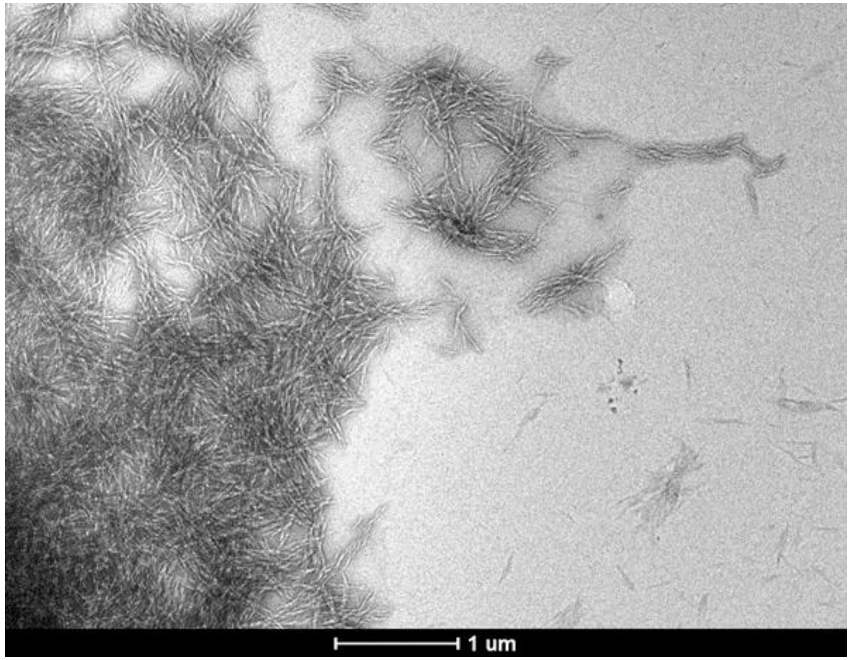
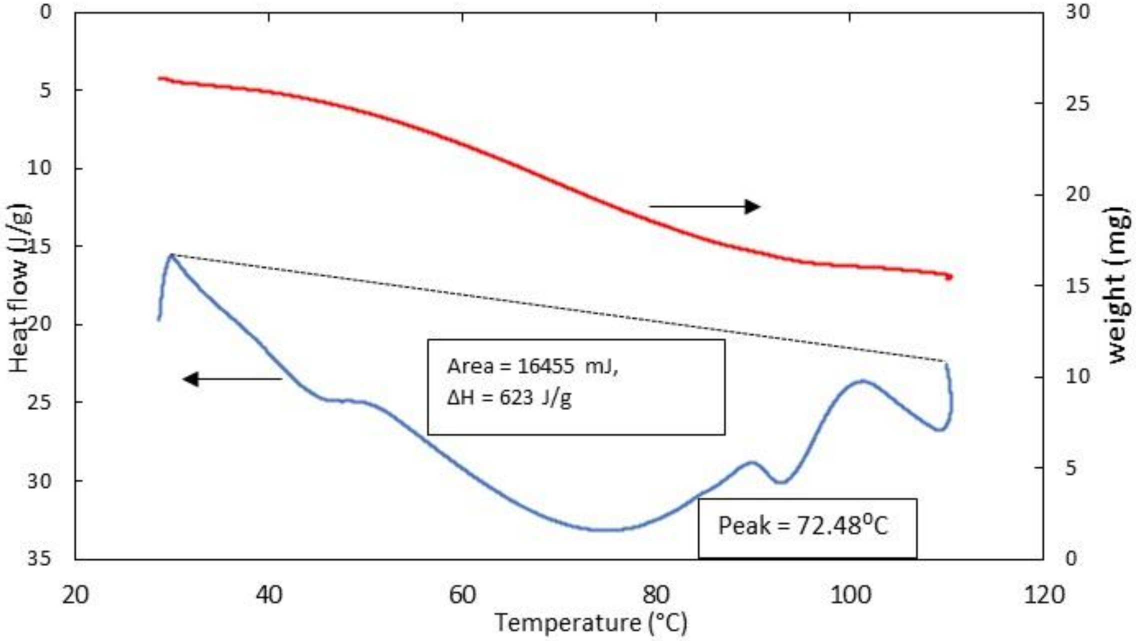
Development of a thermochemical, nanocellulose-based material for thermal energy storage





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DE – EE0009678

New Project

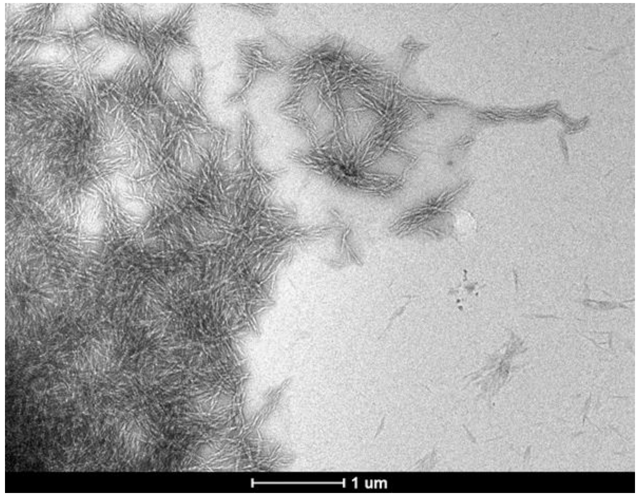
Project Summary – New Project

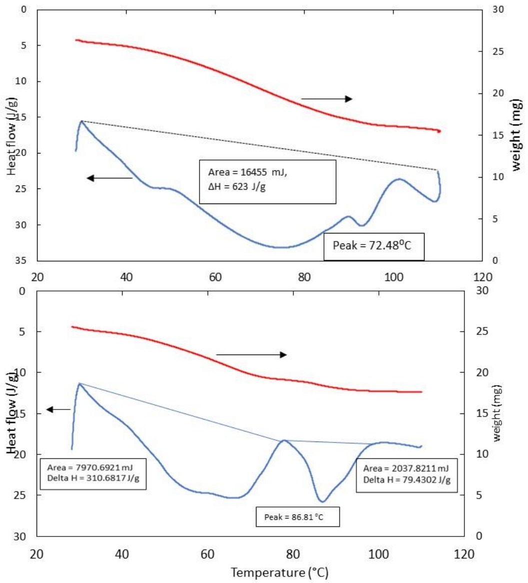
Objective and outcome

Objective – To develop and validate a cellulose nanocrystal (CNC)-based thermochemical, adsorption material for thermal energy storage

Outcome – A material capable of

- Material Energy Density ≥ 470 J/g
- Thermal reliability ≥ 90% after 5000 cycles
- Energy savings in the building energy simulation model for heating applications of ≥40%
- Predicted large-scale production material cost ≤$15/kW$_{th}$





Team and Partners

Institution	Lead	Role
North Dakota State University	Adam Gladen	Testing and Modeling
Montana State University	Dilpreet Bajwa	Material Synthesis
Oak Ridge National Lab	Tugba Turnaoglu & Kyle Gluesenkamp	Material Testing
Idaho National Lab	Neal Yancey	Material Testing

Stats

Performance Period: 10/2021 – 06/2025

DOE budget: $1,742k, Cost Share: $468k

Milestone 1: Identify two CNC-salt pairs that meet screening metrics for energy density, thermal reliability, thermal conductivity, and transition temperature

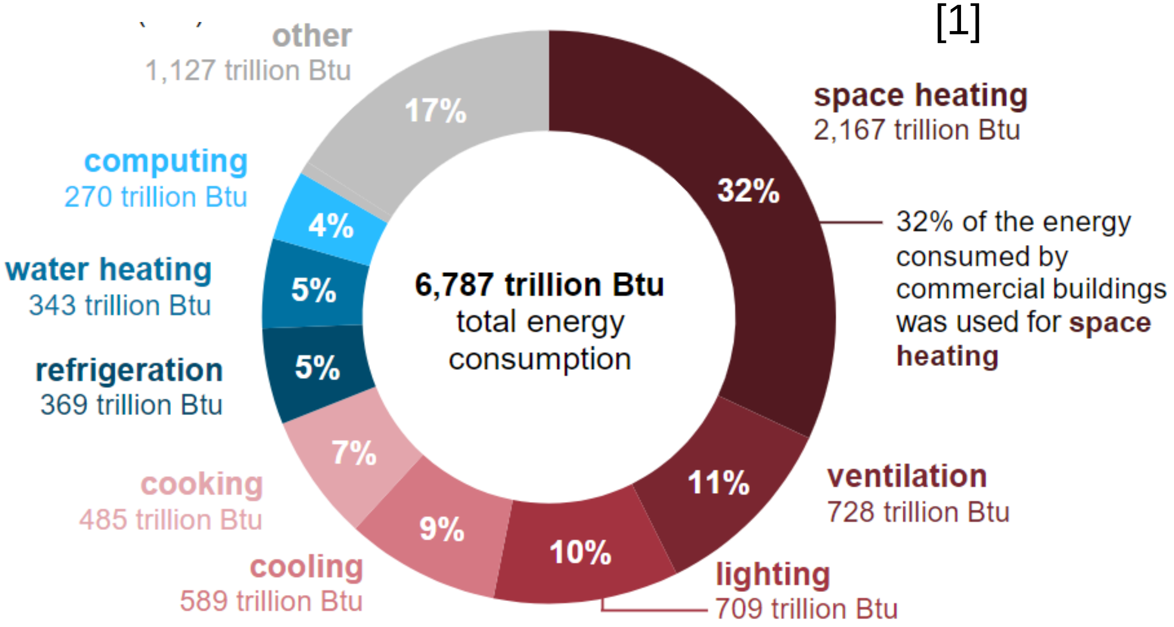
Milestone 2: Refine one CNC-salt pair to meet intermediate metrics for energy density, thermal reliability, thermal conductivity, and transition temperature, building energy savings, and predicted large-scale material costs

Milestone 3: Develop material to meet final metrics

Market Problem

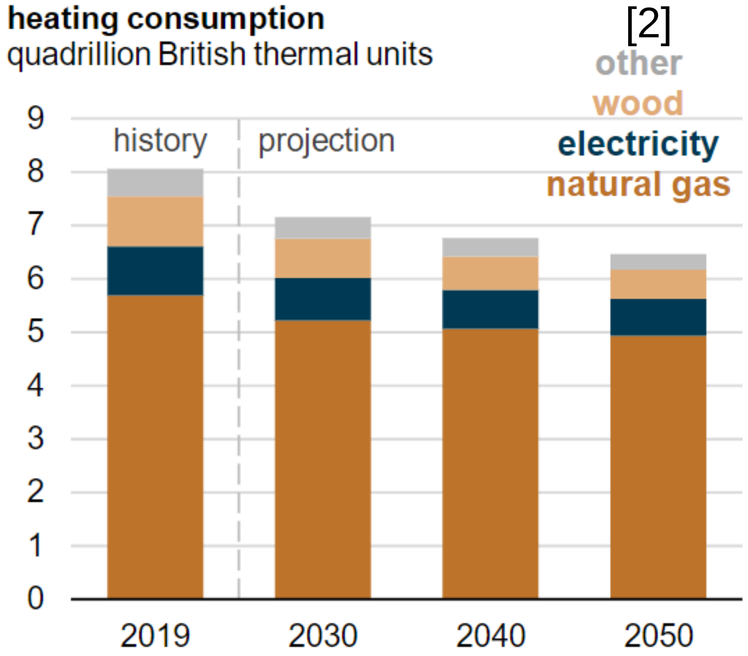
Energy end-use in Commercial Buildings

[1]



Energy Sources for Space Heating in Building Sector

[2]



- **<u>Problem:</u>** Thermal end uses (e.g. space and water heating) are the largest end-use of energy. Most energy for these uses are from fossil fuels. Energy sources not predicted to change significantly
  - Presents significant opportunity for decarbonization.
- Effective thermal storage is necessary to displace fossil fuels with other sources (e.g. solar thermal, waste heat, coupling with heat pumps).
- **<u>Issue to address:</u>** develop a high-energy density, thermal storage material with high cyclic stability

Alignment and Impact

- **<u>Motivation:</u> Help enable switch from fossil fuels to renewable energy for thermal needs. <u>Aligns</u> with National and BTO goals:**
  - National climate mitigation
    - Reduce greenhouse gas emission
    - Decarbonization
  - BTO vision for net zero U.S. Building sector
    - Reduce onsite fossil-based CO_2

Initial Energy Saving and on-site CO_2 Reduction Predictions

System Type:	HVAC w/o storage*	HVAC w/ CNC-salt storage*
Heating Energy Covered [%]	-	75%
% Energy Savings vs. Sys. 1	-	75%
Simple Payback vs. Sys. 1 [yrs]	-	8~10
Primary Energy [Quads]	9.2	2.3
CO2 Emissions [Mt]	457	111
CO_2 Emissions Savings vs. Sys. 1	-	75.7%

<u>Thermochemical storage advantages for decarbonization</u>:

- High theoretical energy density (gravimetric and volumetric)
- Flexible storage timeframe (short-to-long term)

*Initial, preliminary estimate using the BTO Baseline Energy Calculator tool

[1]https://www.energy.gov/eere/buildings/thermal-energy-storage

<u>Defining Success</u>: End-project Metrics

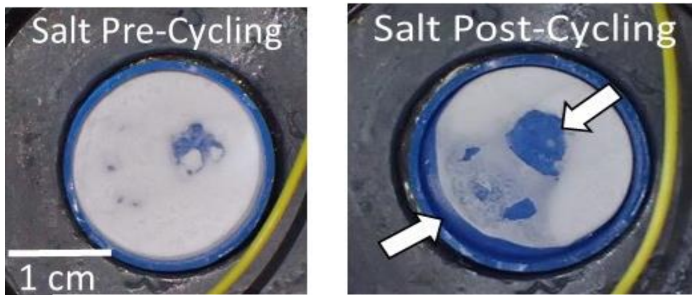
Metric	Project Goals (material-level)	FOA Goals[1] (system-level)
Energy Density	≥470 J/g (targeting ≥250 kWh/m^3)	≥80 kWh/m^3
Reliability and Cycles	≥ 90% after 5,000 cycles	≥ 10,000 cycles
Transition Temperature	Targeting ≤ 70 °C	--
Energy savings in building simulation model	≥40%	--
Predicted large-scale (25ton/day) material cost	≤ $15/kWh$_{thermal}$	System cost ≤ $15/kWh$_{thermal}$

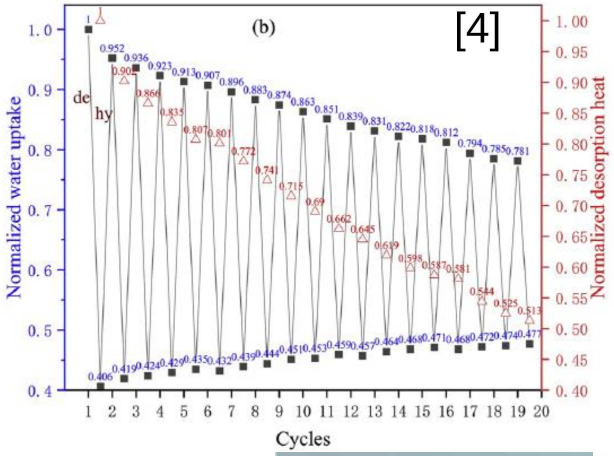
Technical background and problem

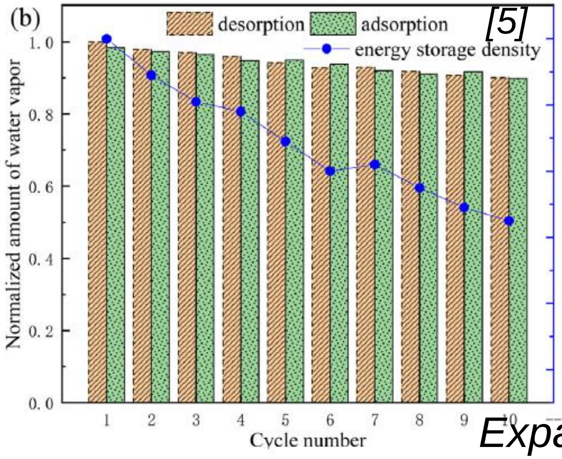
- Hydration-dehydration of salts active research interest due to:
  - Reaction occurs at temperature appropriate for buildings (Charge <150 ºC; Discharge at 30 - 60 ºC)
- **<u>Challenge:</u>** – pure salts have low stability even at low cycle numbers (e.g. <5 – 10)
- **<u>Current Solution:</u>** impregnate porous, host matrix (e.g. zeolites) with salt
- **<u>Issues with current solution:</u>**
  - Matrix often non-participating or require higher regeneration temperatures [6] than the salt
  - If matrix is foam – pores can become blocked and reduce surface area for reaction
  - Can still have loss of energy density with cycling

Theoretical energy density of two salt hydration reactions [3]

Reaction	Theoretical Energy Density (GJ/m^3)
$MgSO_4{\cdot}7H_2O(s) \leftrightarrow MgSO_4(s) + 7H_2O(g)$	2.80
$CaCl_2{\cdot}2H_2O \leftrightarrow CaCl_2(s) + 2H_2O(g)$	1.44
Sensible storage - water (ΔT = 60 °C)	0.25







Expanded Graphite-LiOH

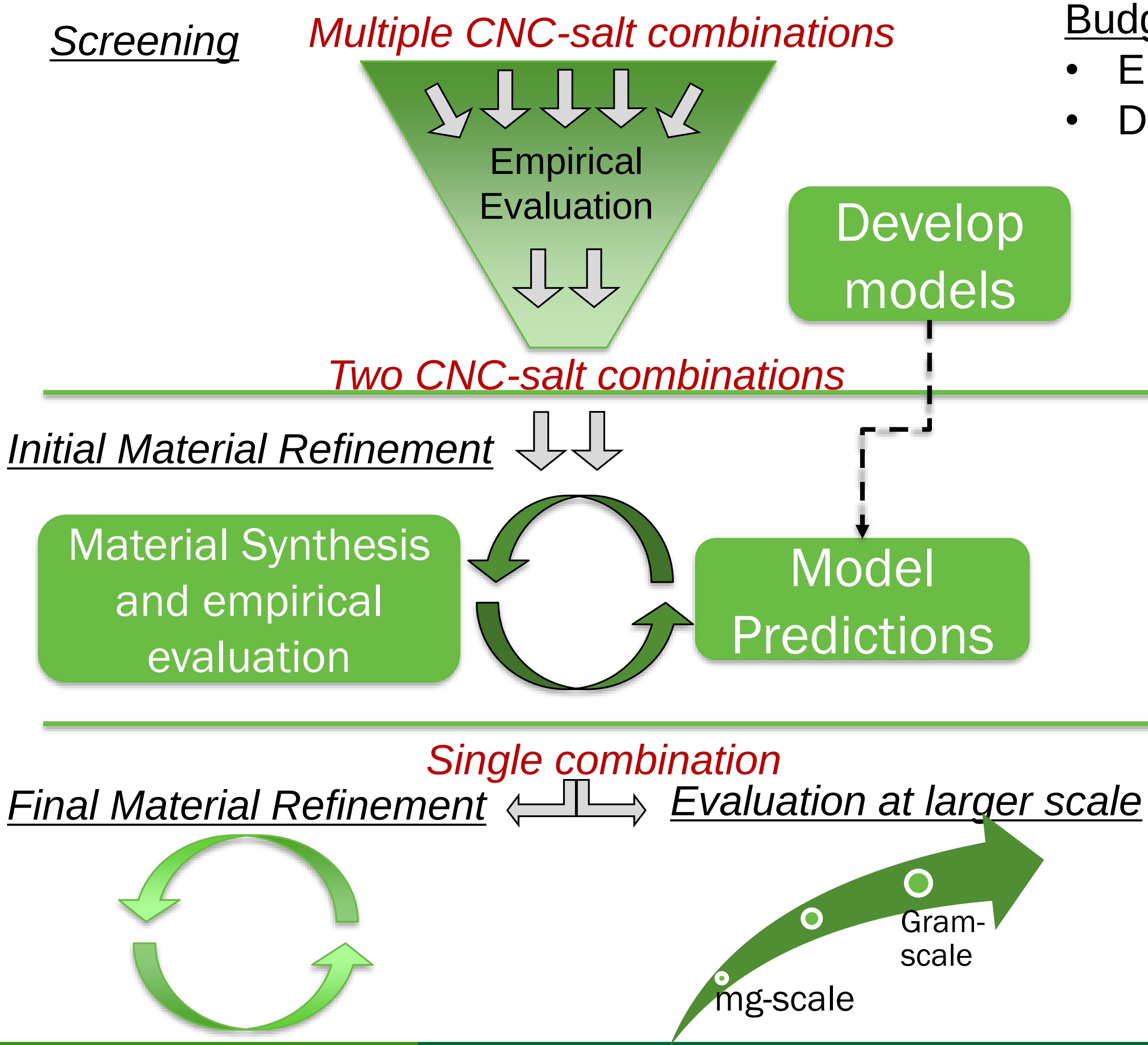
Proposed Solution

- **Proposed Solution:** Develop a composite material of a framework of cellulose nanocrystals (CNC) impregnated with salt
- **Novel aspects and advantages:**
  - Nanoscale, fiber-based stabilizing framework
    - Smaller (e.g. submicron) salt particles = increased surface area
    - Possibility for more flexibility during swelling
    - No potential for pore blockage
  - High surface area
  - Potential for Improved:
    - Salt utilization with stability
  - CNC is hygroscopic
    - Participate in hydration reaction
    - Expected to dehydrate at similar temperatures as salts
- **Demonstration of expected benefits:**
  - Empirical data demonstrating end-project achievement of material property metrics
  - Model simulations for material costs and performance in buildings based on measured properties

Cellulose nanocrystals (CNC) compared to other stabilizing agents

Stabilizing Material	Surface area	Stiffness	Affinity to moisture	Renewable	Conductivity
CNC	540 m^2/g	160 GPa	High	Yes	1 – 6 W/m·K
Clay	258 m^2/g	170 GPa	Medium	No	0.25 W/m·K
Expanded Graphite	17-27 m^2/g	1 TPa	Low	No	4 – 100 W/m·K
Activated Charcoal	500-708 m^2/g	-	Low	Yes	0.4 W/m·K

Plan – Entire project



Budget Period 1

- Empirically identify 2 promising CNC-salt pairs
- Develop Numerical Models:
  - Thermochemical material
  - Building energy simulations
  - Techno-economic analysis (TEA)
  - Life cycle assessment (LCA)

Budget Period 2

- Refine CNC-salt to intermediate metrics
- Design lab-scale reactor

Budget Period 3

- Refine CNC-salt to final metrics
- Long-term stability of CNC-salt
- Final Building energy simulations, LCA, TEA predictions
- Demonstrate lab-scale reactor

Stakeholder Engagement:

- Industrial Advisor Board
- Market survey and feedback

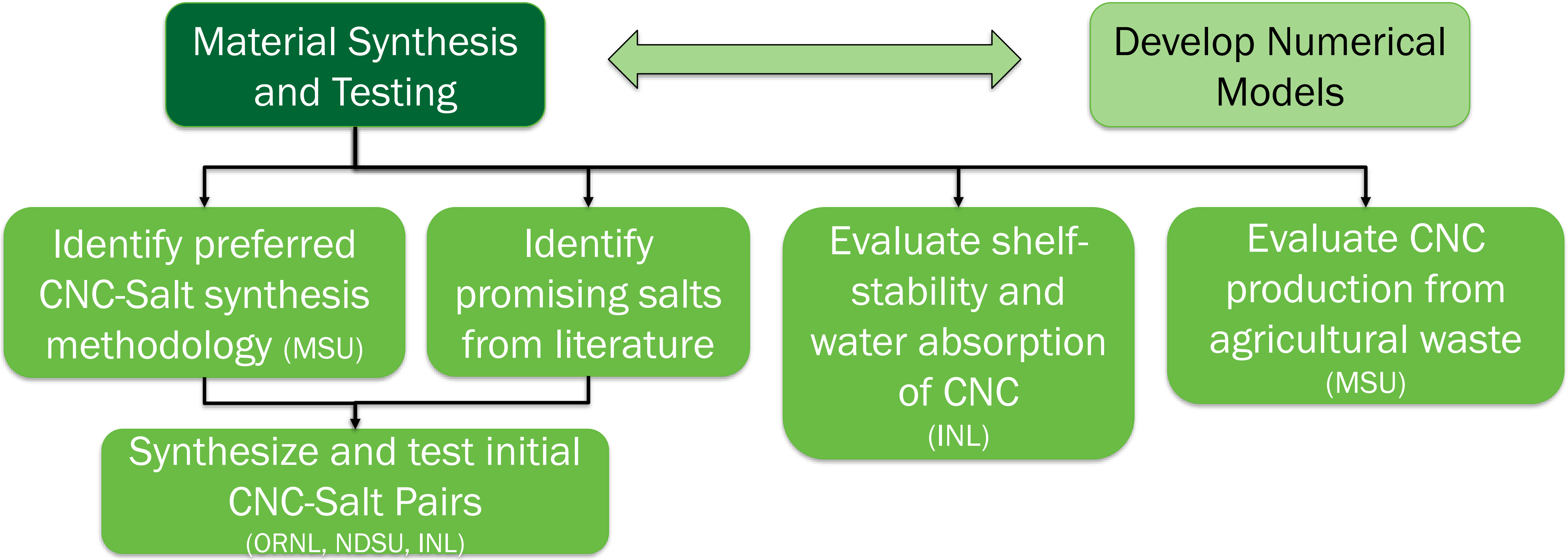
Barriers/Challenges

Barrier/Challenge	Mitigation
Inadequate salt impregnation	Prior experience of impregnating nanocellulose will guide a design of experiments to identify the impact of key processing variables and to improve the impregnation.
Competing effects of key variables on desired metrics (e.g. energy density vs conductivity)	The numerical models will be utilized to try to determine a balance point. The team will work with the advisory board to determine the priority of metrics desired by the stakeholders and thus will likely yield the most successful material. These characteristics will be emphasized.
High uncertainty in scaled production predictions due to lack of data on large-scale production	The experience and expertise of our industry partners and advisory board, who have expertise with new bio-based, products, industrial-scale beet processing and manufacturing, and of INL, leading experts in pilot scale bioprocessing, will be leveraged. The kg-scale testing will help refine the predictions.
Change in key personnel	On-board new personnel with training to help smooth transition
Analytical equipment breaks and requires repairs	Institutions have some duplicate equipment – temporarily shift experimentation to other equipment until repairs are made

- Risks are being mitigated through stakeholder engagement and overall approach:
  - Industrial Advisory board: representatives from sustainable building design and building company, bioprocessing companies, manufacturing company
  - Will conduct survey of various stakeholders (e.g. HVAC companies, building owners) to identify characteristics for thermochemical material and system
  - Overall approach: screening allows for alternate options, modeling provides guidance

Plan - Budget Period 1 – Material Testing

- Two-pronged, interrelated approach
  - Material synthesis and empirical evaluation
  - Model development to guide further material development



Plan - Budget Period 1 – Model Development Approach

Model Purpose/Outcomes:

Overall: Help guide material development and refinement by modeling material performance, production costs, and environmental impact. Use to help down-select combinations and reduce number of experiments for refinement

Develop Numerical Models

Thermochemical, material model
- Model material behavior
- Predict equilibrium and reaction rates CNC-Salt

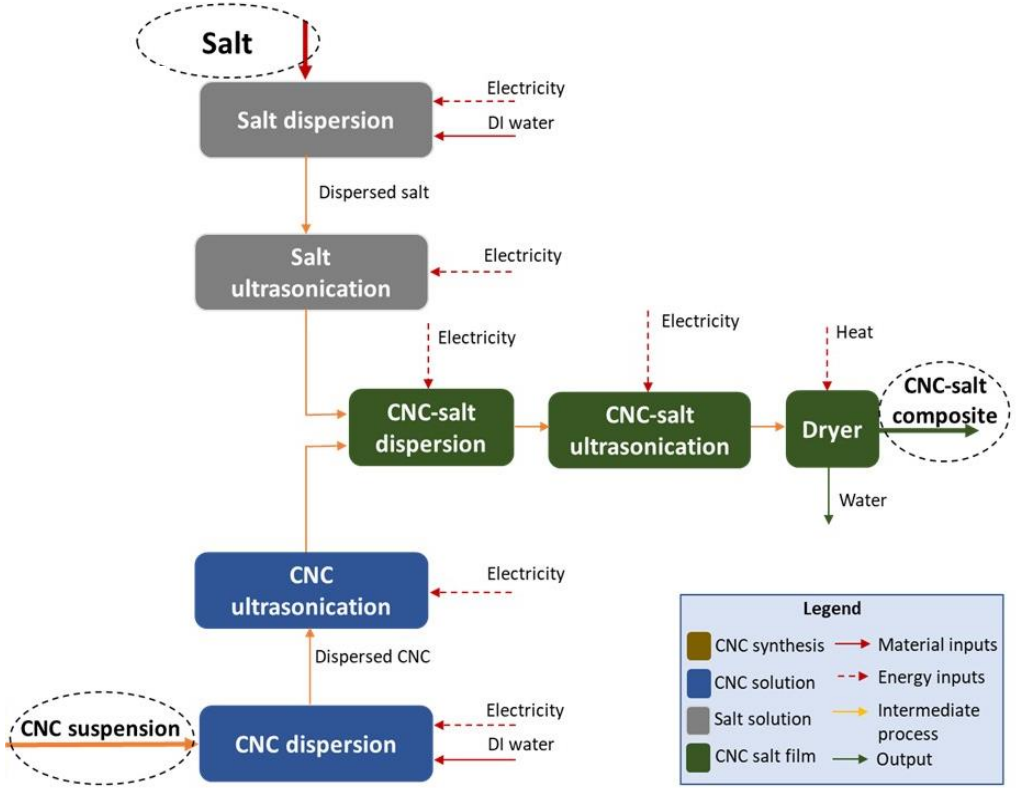
Building Simulation models
- Model building HVAC system using CNC-Salt
- Predict energy savings for various building types

Technoeconomic model (TEA)
- Model production of CNC-Salt Material
- Predict energetic and economic costs to produce material – help refine choice to ensure low cost

Life Cycle Assessment (LCA)
- Model production of CNC-Salt Material
- Predict environmental impact of production – help make choices to minimize environmental impact

Material Synthesis and Evaluation

Hypothesis: Synthesis method will impact microstructure and impregnation.
Approach: Conduct series of experiments to identify best methodology to impregnate CNC with salt



Flow Diagram of the CNC-salt synthesis process

- **Key Accomplishment:** Methodology identified

Conditions for combining CNC + Salt Hydrate:

CNC Addition	Salt Conc.	CNC Conc.	CNC Addition Rate
Dry	***10wt%*** ✓	***2.5wt%*** ✓	Steady Pour
Wet ✓	20wt%	5wt%	***Drop-wise*** ✓

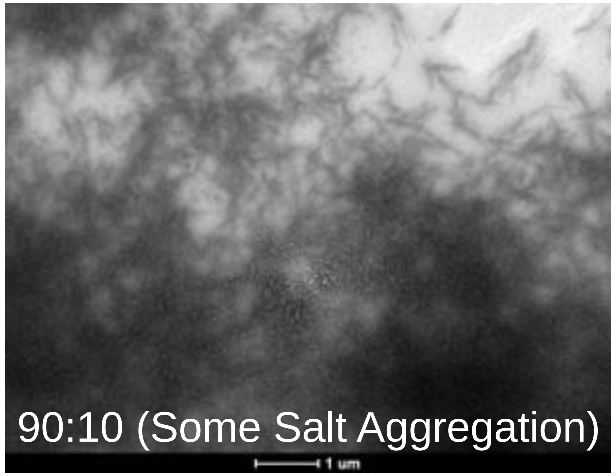
Hypothesis: Presences of CNC will affect the hydration behavior of salts compared to bulk
Approach: Identify promising salts from literature, combine with CNC, and conduct a series of screening experiments. Quantify CNC adsorption behavior

- **Key Accomplishment:** 12 Salt and Salt Blends Synthesized:
  - *Pure Salts:* $MgSO_4$, $CaCl_2$, $SrCl_2$, $ZnSO_4$, Na_2S, LiOH, $MgCl_2$
  - *Blends:* $MgSO_4$-$SrCl_2$, $MgSO_4$-$CaCl_2$, $SrCl_2$-$CaCl_2$, $CaCl_2$-$MgCl_2$, Na_2S-$CaCl_2$

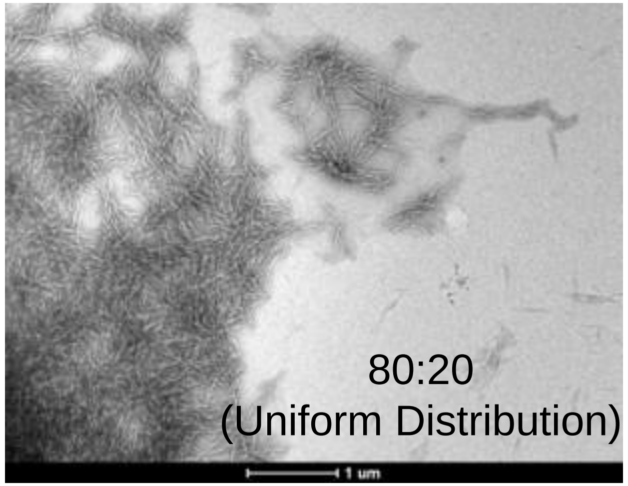
Material Characterization

Evidence of salt impregnation acquired via TEM imaging:

– TEM images for CNC-$MgCl_2$



90:10 (Some Salt Aggregation)



80:20 (Uniform Distribution)

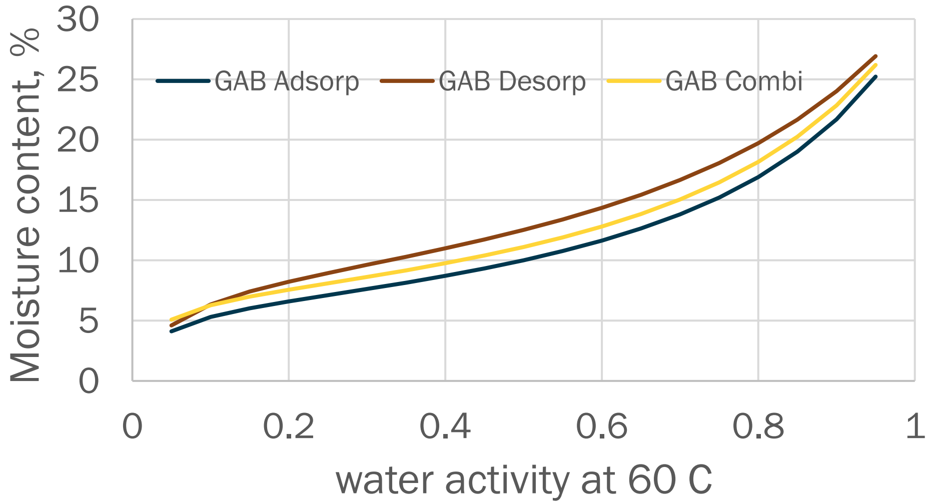
Moisture uptake and stability of pure CNC

– Measured adsorption isotherms at 30 and 60 °C

– Perform 2-week storage experiments on pure CNC at various water activity levels and temperatures

- ➢ Measured dry matter loss and imaged to detect biological degradation, and monitor turbidity for microbial growth
- ➢ Sub-saturated conditions (97% RH) was shown to cause highest dry matter losses at 45 °C
- ➢ **Key Accomplishment:** Bio-stable at 25 – 35 °C

Relative Humidity	Dry matter loss @ 45 °C
0% RH	1.7%±0.3%
97% RH	4.02%±2.46%
100% RH	2.7%±1.4%

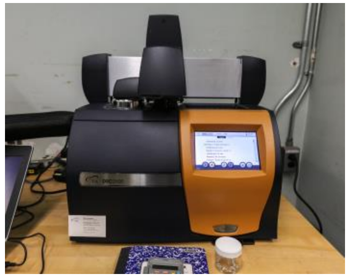
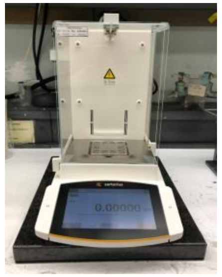


Evaluation of Energy Storage Properties

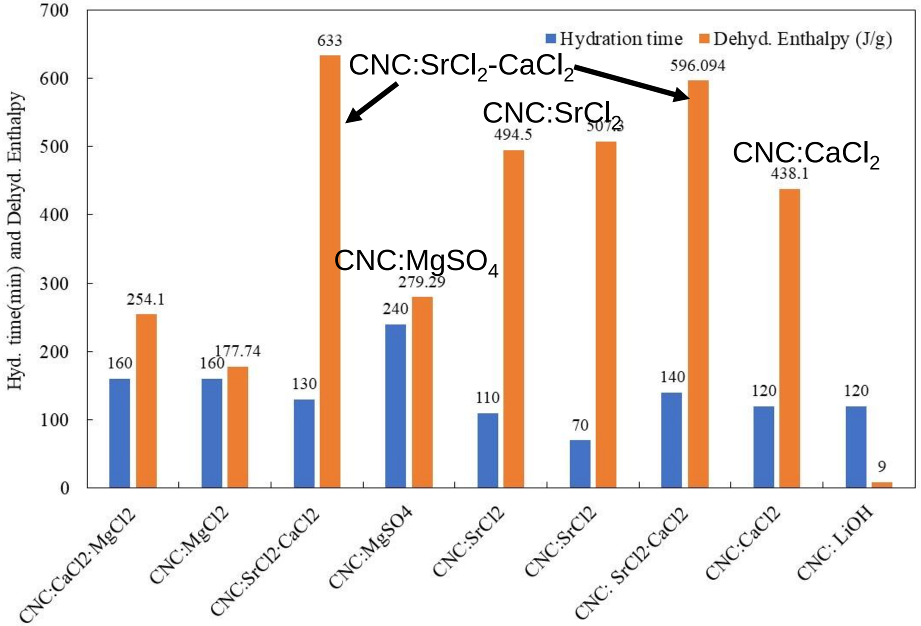
Initial Screening

- **Hydration:** ~85 mg, Room Temperature (~22 ^oC), 70% Relative Humidity
  - Hydration rates measured
- **Dehydration:** 2 ^oC/min to 110 ^oC, Dry Nitrogen

Cycling

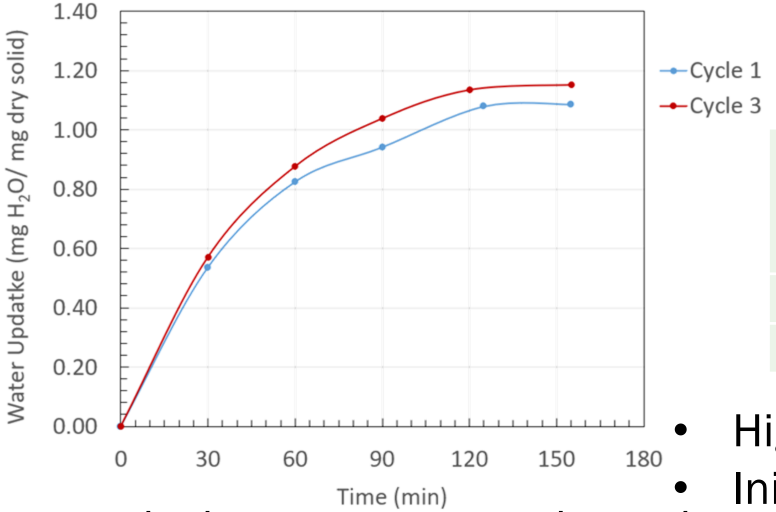




Dehydration ↔ Weighing ↔ Hydration



Hydrated $CaCl_2$

Hydrated CNC-$CaCl_2$



Hydration rates CNC:$SrCl_2$-$CaCl_2$

Cycle	Enthalpy of Desorption (J/g)	Energy Loss (%)
1	853.05	
3	850.85	0.3

- High dehydration enthalpy measured
- Initial cycling shows good stability

> **Key Accomplishment:** Promising CNC-Salt formulations ID thus far:
> - CNC:$SrCl_2$,
> - CNC:$CaCl_2$,
> - CNC:$SrCl_2$-$CaCl_2$,
> - CNC:$MgSO_4$-$SrCl_2$

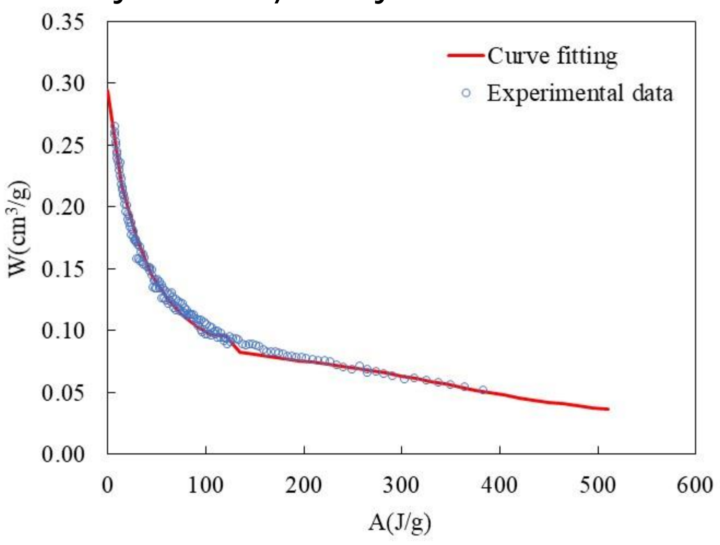
Modeling – Building Simulation and Thermochemical Models

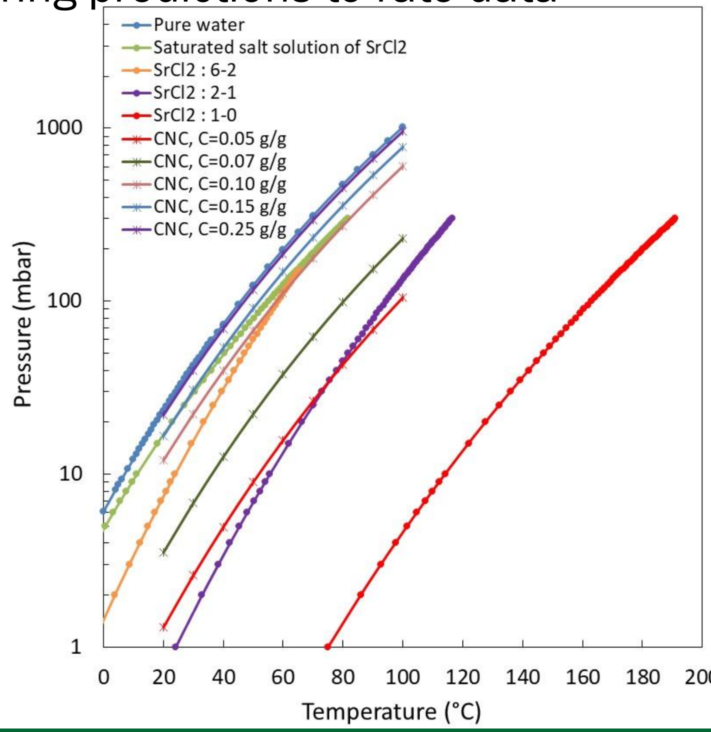
Purpose: predict behavior of composites to aid refinement and down-selection by modeling performance

Material Model Approach:

- Equilibrium and Reaction Enthalpy
  - Pure Salts: Clausius-Clapeyron Equation
  - Pure CNC: Dubinin-Polanyi model
- Reaction Kinetics
  - ID kinetic model and comparing predictions to rate data

➢ **Key Accomplishment:**
  - Models that predict hydration/dehydration behavior





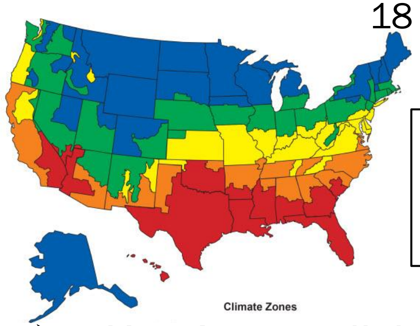
Building Simulations Approach:

Develop Baseline Building Energy Models

Calibrated TRNSYS Models (±5% for NMBE and <15% for CVRMSE per ASHRAE Guideline 14-2014)

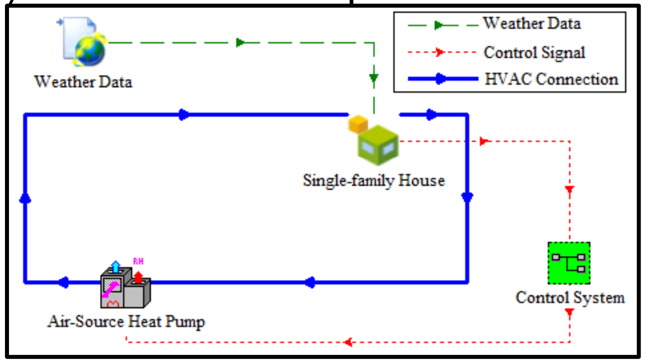
TRNSYS 18

18 Building Types



5 AIA Climate Zones across the US

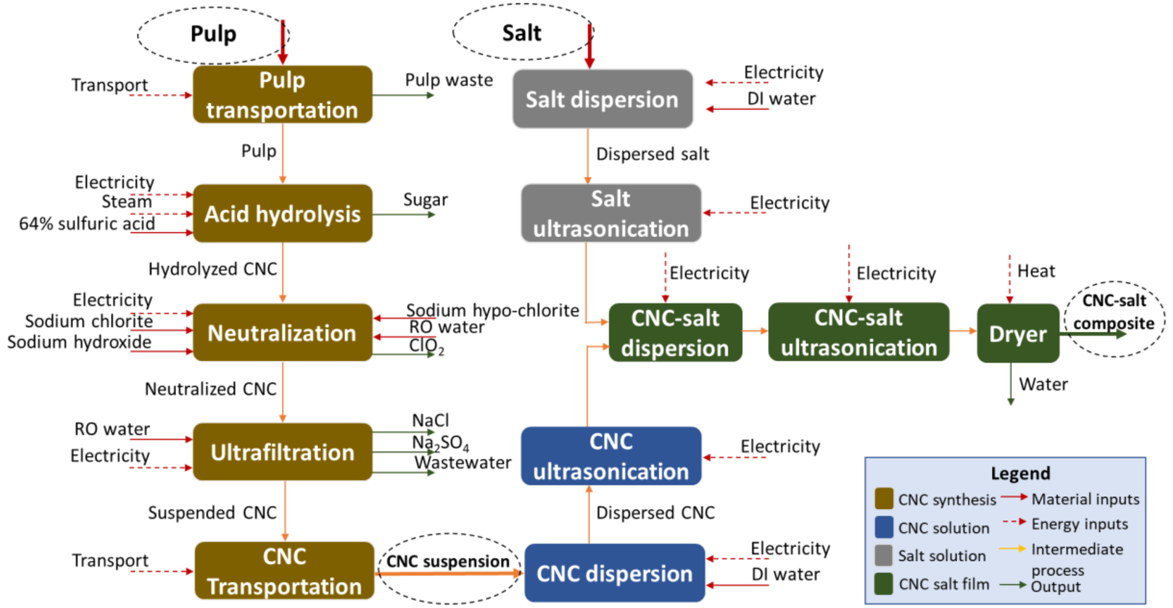
➢ **Key Accomplishment:**
  - 16/18 models complete



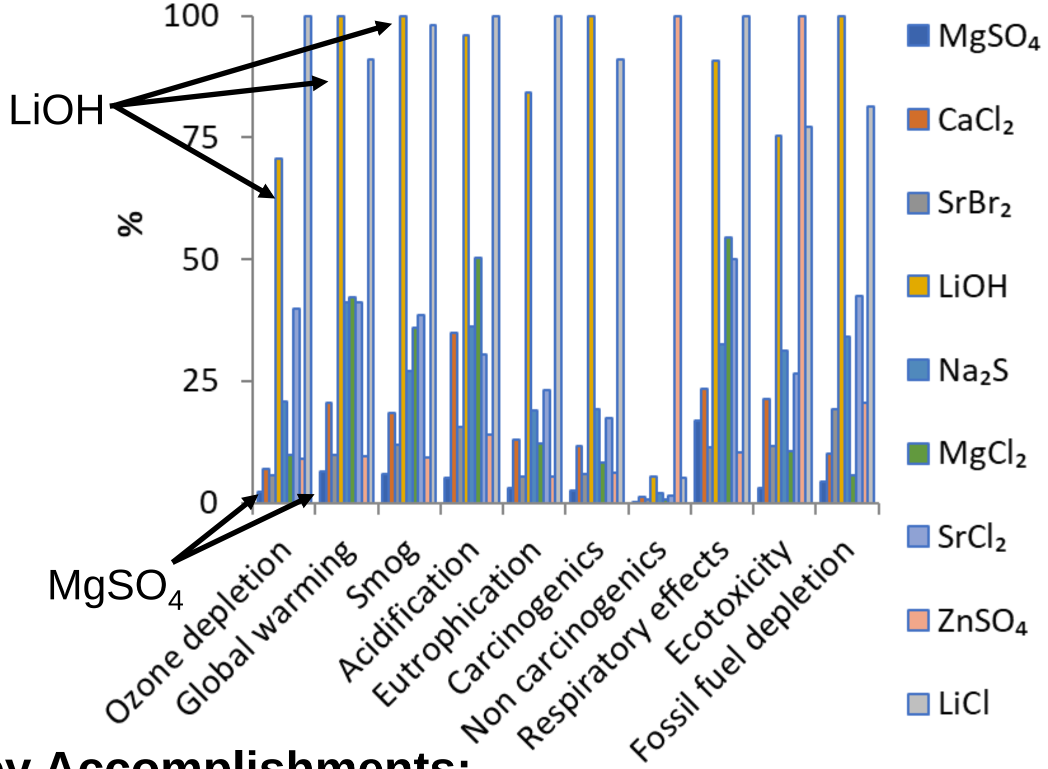
Process flow diagram of salt-CNC production

Purpose: screen salts on economic and environmental consideration. Model production of material to aid refinement process by identifying hot spots (in terms of cost and environmental impact) in production

Approach for LCA and TEA:



- Functional unit – 1 kg of CNC-salt or 1 MJ of energy provided
- Cradle to gate LCA in SimaPro software using TRACI 2.0 method
- All analysis based on 1:4 CNC:salt
- Process scale-up considerations: energy optimization for mixing, ultrasonication, and spray drying



Key Accomplishments:

- ➢ Hotspots: CNC use, drying step, and some salts
- ➢ Higher energy density salts have lower impact
- ➢ Sulphates tend to have lower environmental impacts – Lithium containing salts, higher impacts
- ➢ Environmentally LiOH and $LaCl_3$ are poor options

Accomplishments

Major Accomplishments

- Material Synthesis and Testing
  - Identified key variables affecting salt impregnation
    - CNC Concentration; Salt Concentration; Method of CNC Addition
  - Successfully impregnated CNC with 12 different salts and salt blends
  - Demonstrated salt impregnation at 3 CNC-salt ratios
  - Promising stability at low cycle numbers
  - Measured isotherms of pure CNC and developed adsorption models.
  - Quantified stability of pure CNC at various storage conditions
    - Identified recommended storage conditions
- Model Development
  - Established baseline building energy models for 16 building types at 5 different climate zones (80 models)
    - allNMBEs <2% and all CVRMSEs <7%
  - Developed models to predict equilibrium water uptake for CNC and salts, and reaction rates
  - Developed a model of HVAC system with salt storage
  - Developed LCA model for CNC-Salt production using lab-scale values. Evaluated environmental impact of various salts – eliminated $LiOH$ and $LaCl_3$

B.P. 1 Go/No-Go Metric	Status
Material Density ≥265 J/g	✓ - 6 Formulations
Transition temperature ≤100°C	✓- 10 Formulations
Thermal Reliability ≥80% after 50 cycles	In Progress
Thermal Conductivity ≥0.7 W/m·K	In Progress

Model	Status
Building Simulation Models	Near Completion (16/18 buildings complete)
Thermochemical material model	Framework complete – comparing to experimental data
Life Cycle Assessment	Completed using lab-scale values
Technoeconomic model	Initial Framework completed

Lessons learned so far:

- Precise methodology need for repeatable experimental data
- Synthesis methodology can be used to change behavior
- Anticipate slow reaction kinetics for planning experiments

Future Work

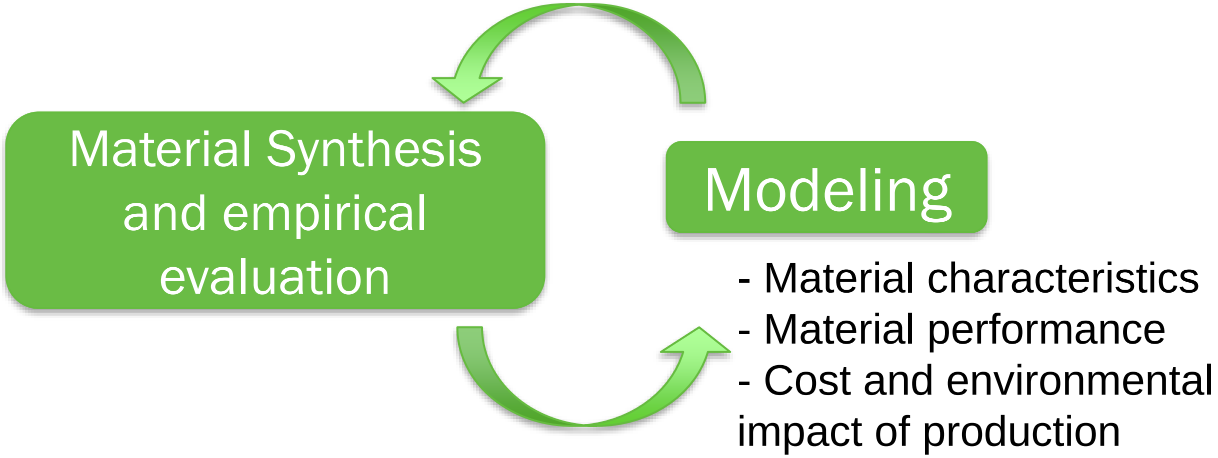
Near Term:

- **Material Synthesis and Testing**
  - Transition to freeze drying of samples to improve production efficiency (MSU)
  - Produce CNC from agricultural waste product (MSU)
  - Continue with screening, cycling experiments, material testing of of CNC-salt formulations (ORNL and NDSU)
  - Generate moisture isothermal of promising CNC-Salt pairs (INL)
  - Choose two combinations to refine in B.P.2

- **Model Development (NDSU)**
  - Integrate CNC and salt equilibrium and kinetic models to predict behavior of composites
  - Develop model of CNC-salt reactor for HVAC system with CNC-salt storage
  - Develop a model of an HVAC system with CNC-salt storage
  - Integrate CNC-salt HVAC System model with building simulation models
  - Further develop technoeconomic model of CNC-salt production

Longer Term:

- **Refine two CNC:salt pairs to achieve B.P. 2 metrics**



  - Use models to identify: improved formulations, predict performance in building HVAC systems, and evaluate environmental impact
  - Create and evaluate new samples based on model predictions
  - Develop reactor design to test CNC-salt materials at larger scale

Beyond end-of-project:

- Develop and test larger scale prototype system
- Partner with industry to investigate scale-up production

Thank You

North Dakota State University, Montana State University, Oak Ridge National Lab, Idaho National Lab
PI: Adam Gladen, Assistant Professor
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DE – EE0009678

REFERENCE SLIDES

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[5] Li, W., et al., 2020, "Development and characteristics analysis of salt-hydrate based composite sorbent for low-grade thermochemical energy storage," Renewable Energy, **157**, p. 920-940

[6] Xu, S.Z. et al., 2018, "A zeolite 13X/magnesium sulfate-water sorption thermal energy storage device for domestic heating", Energy Conversion and Management, **171**, p. 98-109

Project Execution – Budget Period 1

Task	Budget Period 1							Budget Period 2			
	Q0	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
0.0 Overall Project Management and Planning											
1.1 Production of submicron salt particles											
1.2 Identify key variables affecting salt impregnation											
1.3 Synthesis of salt-impregnated CNC											
1.4 Evaluation of energy storage properties for CNC-salt pairs											
1.5 Characterize the cycle stability of CNC-salt pair											
1.6 Testing the shelf life and storage stability of CNC											
1.7 Initial Market Evaluation											
2.1 Develop a thermochemical model of the CNC-salt material											
2.2 Development of baseline building energy simulation models											
2.3 Developing initial process simulations for salt-impregnated CNC											
2.4 Developing life cycle analysis (LCA) for salt-impregnated CNC											
2.5 Determine the material and chemical composition of the sugar beet pulp											
2.6 Development of the process to synthesize CNC from SBP											
2.7 Develop Techno-economic analysis (TEA) model for production of CNC from beet pulp											

Project Execution – Budget Period 2

Task	B.P. 1		Budget Period 2				Budget Period 3			
	Q5	Q6	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
2.8 Evaluation of CNC from beet pulp for CNC-salt material			■	■	■					
2.9 Analysis of CNC-salt pairs with thermochemical model			■	■	■	■				
2.10 Analysis of building energy savings			■	■	■	■				
2.11 Analysis of salt-impregnated CNC with LCA and TEA model					■	■				
2.12 Synthesis of CNC-salt formulations for refinement				■	■	■	■	■		
2.13 Evaluation of the material properties and cyclic stability				■	■	■	■	■	■	
3.1 Develop a model of a thermochemical lab-scale reactor	■	■	■	■						
3.2 Design of lab-scale experimental apparatus				■	■	■				
3.3 Cycle Stability Testing							■	■	■	■
3.4 Testing the shelf life and storage stability of CNC-salt								■	■	
3.5 Fabrication of the reactor and experimental apparatus							■			
3.6 CNC-salt material synthesis (500g batch)							■			
3.7 Lab-scale reactor testing of the refined CNC-salt material							■	■	■	
3.8 Analysis of lab-scale reactor performance									■	■
3.9 Final building energy simulations									■	■
3.10 Final LCA and TEA models for salt-impregnated CNC									■	■
3.11 Tech-to-market evaluation								■	■	■

Project Execution – Go/No-Go Decision Points

- Budget Period 1 Go/No-Go Decision Point
  - Identify two CNC-salt pairs that meet the screening metrics: Material energy density ≥265 J/g (volumetric energy density will also be reported with a secondary metric targeting ≥80 kWh/m3), thermal reliability ≥80% after 50 cycles, thermal conductivity ≥0.7 W/m·K, and a transition temperature ≤100 C.
- Budget period 2 Go/No-Go Decision Point
  - Refine one CNC-salt material to meet the intermediate metrics: Material energy density ≥390 J/g (volumetric energy density will also be reported with a secondary metric targeting ≥165 kWh/m3), thermal reliability ≥90% after 500 cycles, thermal conductivity ≥1 W/m·K, heating energy savings in the building energy simulation model of ≥30%, predicted large-scale (production of ~25 ton/day) material cost of ≤$30/kWh-thermal.
- End of Project Goal
  - The Recipient will deliver a material that meets the final energy storage, material metrics to maintain energy density, thermal conductivity, and transition temperature. Material energy density ≥470 J/g (volumetric energy density will also be reported with a secondary metric targeting ≥250 kWh/m3), transition temperature targeting ≤ 70 ° C, material thermal reliability ≥90% for ≥5000 cycles, a heating energy savings in the building energy model of ≥40%, and a predicted large-scale (production of ~25 ton/day) material cost of ≤$15/kWh-thermal. Reactor Targets: reactor size of approximately 500 grams, reactor-bed energy density ≥125 kWh/m3, demonstrate ≥80% retained energy density after 500 cycles charging-discharging cycles.
- Explanation for slippage
  - Nanomaterial approval at ORNL – prevented material testing
  - Personnel changes at NDSU, INL, and ORNL
  - Equipment issues needing repair

Team

NDSU NORTH DAKOTA STATE UNIVERSITY

Adam Gladen – PI
- Material modeling and evaluation
- Reactor design and testing

Yao Yu – co-PI
- Building model simulations

Ghasideh Pourhashem
- Life cycle assessment
- Technoeconomic analysis

MONTANA STATE UNIVERSITY

Dilpreet Bajwa – co-PI (MSU Lead)
- Material Synthesis and characterization

OAK RIDGE National Laboratory

Tugba Turnaoglu – co-PI (ORNL lead)

Kyle Gluesenkamp
- Material evaluation and assessment

INL Idaho National Laboratory

Neal Yancey– co-PI (INL lead)

William Smith

Damon Hartly
- Material evaluation (isotherms and shelf stability)
- LCA and TEA