Final Report – SMARTHEAT

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1 Project Information

- **Project Title:** SMARTHEAT- Smart Supercooled PCM Heat Battery for Long-term Storage
- **Project number:** TKITOE1821202
- **Partners: University of Twente (UT), Mesa+(UT), De Ridder BV (Coolpack), Geotherm E.S.**
- **Project period: 22/05/2020- 12-11-2023**

2 Abbreviations

FO	Fundamental Research
PCM	Phase Change Material
SAT	Sodium Acetate Trihydrate
GELSAT	Gel Salt
UT	University of Twente
DSC	Differential Scanning Calorimetry
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared
TGA	Thermogravimetric Analysis
LFA	Laser Flash Analysis
POM	Polarized Optical Microscopy

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3.1 Summery

The aim of this project was to design and implement a breakthrough salt hydrate composite to address the challenges associated with an innovative thermal battery. This battery needed to provide both short and long term storage, high energy storage density, high flexibility and cyclability, while being integrated with local renewable energy generation.

The SmartHeat project presented a lightweight hybrid material consisting of salt hydrate and a compatible polymer network. This material can be strategically used in large-scale seasonal energy storage systems, with the following key results:

- **Polymer modification for SAT (GELSAT):**

- Successfully addressed phase separation issues in SAT.

- Retained over 80% of the latent heat of pure SAT.
- GELSAT demonstrated a supercooled liquid state without phase separation.
- Demonstrated remarkable supercooling stability for over six months after charging.
- Allowed the release of thermal energy at any time during this period.

- **Electrical nucleation of supercooled GELSAT:**

- Established a stable supercooling capability in GELSAT.
- Developed an electrical triggering method using silver electrodes.
- Achieved instantaneous triggering with a response time of less than one second.
- Investigated different electrode placements to regulate the crystallisation rate.

- **Validated GELSAT at laboratory scale:**

- Designed and implemented a single cell heat storage setup for laboratory scale testing.
- Used a spiral heat exchanger and multiple triggering locations for optimal heat distribution.
- Performed simulations to fine-tune heat exchanger parameters.
- Expected the observed thermal performance to be indicative of practical applications.

The successful outcomes of the project not only effectively addressed the inherent challenges of SAT, but also introduced an innovative solution with potential applications in various fields requiring efficient thermal energy management. The transparent and supercooled nature of GELSAT, coupled with controllable discharge through electrical triggering, opens up avenues for practical implementation and further exploration across a range of industries.

3.2 Introduction

Thermal energy storage (TES) plays a crucial role in enabling 100% renewable heating and cooling (RHC) in individual buildings. It facilitates the optimal use of different renewable energy sources (RES) throughout the day or even the year. Hybridization and thermal storage offer effective solutions to the challenges associated with the intermittency of variable RES, such as solar thermal. As a result, there is an increased focus on advancing thermal storage technologies. Innovative compact thermal energy storage technologies exploit the physical principles and properties of phase change materials (PCMs) to store heat in a denser form with lower losses compared to conventional systems such as hot water storage tanks.

However, there is a need for further development or improvement of large-scale TES technologies to achieve the following objectives.

- Simultaneous provision of short and long term storage.
- Utilization of liner materials with high energy density, very long lifetime and acceptable cost.
- Reduce heat losses and improve storage efficiency.
- Implementing intelligent, optimized and modular thermal battery integration to improve overall system performance.

To overcome the above limitations, an interesting concept is to develop a novel material capable of providing highly competitive energy storage. This material should be able to meet the significant heat demand while providing flexibility in the charging and discharging processes.

3.3 Objective

The objective of this project is to develop and implement novel salt hydrate composite to address the challenges for innovative heat battery capable of short and long-term storage with high energy storage density and great flexibility and cyclability, paired with local renewable energy generation. The fully controllable PCM based heat battery with capability of heat storage for more than 90 days with high energy density and discharge temperature of 58°C was desired as this project outcome.

3.4 Methodology

This project focuses on the creation of an innovative flexible composite phase change gel designed to meet the demands of long-term heat storage. The formulation of this gel integrates plymer supporting matrix for the salt hydrate Phase Change Material (PCM), SAT. The synthesis process employs a one-pot, environmentally friendly method, emphasizing a holistic approach. Following tasks were followed to successfully prepare and study the performance of GELSAT for heat storage applications:

Task 1: Materials Development and Characterization:

- Identifying an optimal polymer matrix to prevent phase separation and producing metastable supercooled SAT with the highest energy density.
- Conducting crystal and chemical structure analysis of the synthesized GELSAT, incorporating XRD and FTIR techniques.
- Comprehensive thermal and physical analysis of GELSAT through techniques such as

DSC, TGA, T-history method, thermal conductivity assessment (LFA), POM, IR imaging, and rheology measurements.

- Investigating the cyclic performance of GELSAT during the charging and discharging processes.

Task 2: The electrical nucleation triggering of the supercooled GELSAT

- Engineering an electrical triggering method using proper electrodes.
- Meticulous study of electrode spacing and voltage for instantaneous triggering.
- Exploration of various electrode placements to regulate crystallization speed.
- Evaluation of response time and crystal growth speed at different activation temperatures.

Task 3: Laboratory-scale verification of heat storage cell's performance based on GELSAT.

- Setup Design: Creation of a specialized experimental arrangement for validating the heat storage cell based on GELSAT.
- Equipment Utilization: Deployment of a custom-designed setup involving a spiral heat exchanger and two thermostats for controlled testing.
- Simulation: Conducted simulations before fabrication to refine heat exchanger parameters and ensure optimal heat distribution.
- Fabrication: Construction of the experimental setup according to the designed specifications.
- Performance Evaluation: Execution of tests to observe and analyze the thermal properties of GELSAT on a larger scale.
- Indicator of Practical Application: Expectation that the observed thermal performance in the lab-scale setup provides insights into how the GELSAT-based Phase Change Material (PCM) performs in practical applications.

3.5 Results

3.5.1 Modification of SAT with Polymers

The presence of liquid-solid phase separation in sodium acetate trihydrate (SAT) can result in an uneven distribution of energy density, exacerbating with prolonged cycling. In this project, we addressed this issue by modifying SAT through the synthesis and polymerization of an acrylic acid-based copolymer. The resulting GELSAT, containing 4 wt% polymers, effectively eliminated phase separation concerns while retaining over 80% of the latent heat found in pure SAT. This advanced Phase Change Material (PCM) boasts a transparent appearance and undergoes transitions between a soft gel state (supercooled) and a solid state (crystallized) during its melting-solidification cycles (Figure 1(a)). The crosslinked polymer within GELSAT slows down the heat release rate compared to pure SAT, optimizing the discharging profile.

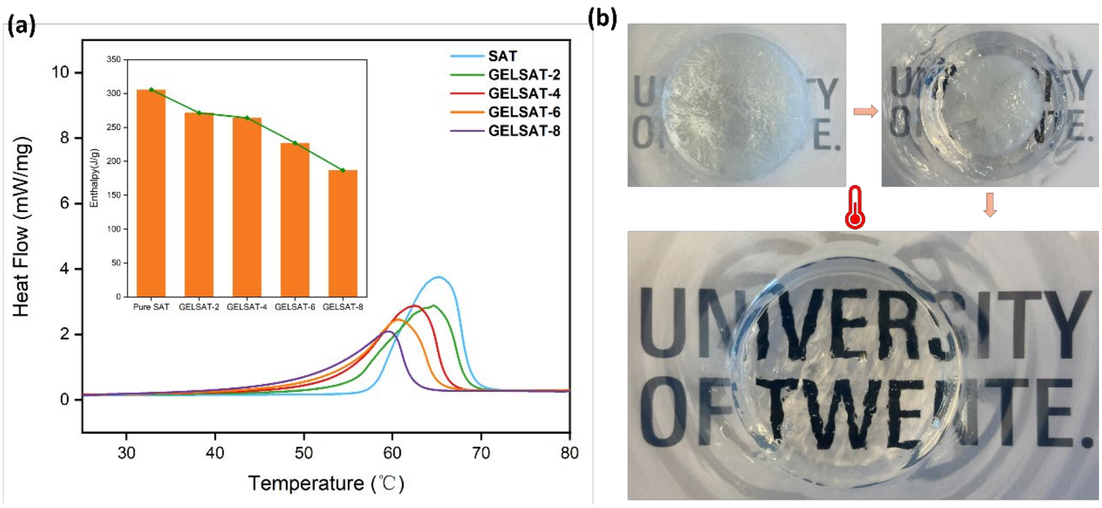

Figure 1- (a) Differential Scanning Calorimetry (DSC) curves and latent heat of GELSAT and pure SAT. (b) Melting process of GELSAT.

In Figure 2, samples exhibit characteristic peaks corresponding to sodium acetate trihydrate. The absence of the 2θ = 8.7° (010) peak in X-ray Diffraction (XRD) patterns of GELSAT indicates a lack of crystalline structure, showcasing its supercooled liquid state without phase separation. GELSAT not only overcomes phase separation but also demonstrates remarkable supercooling stability, maintaining its supercooled state for over six months post-charging and allowing thermal energy discharge at any point during this period.

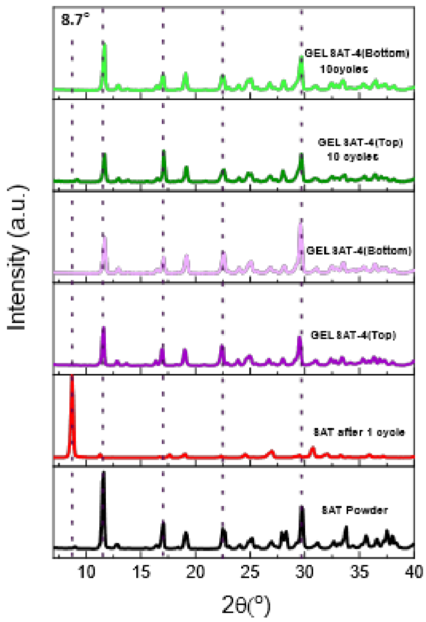

Figure 2- XRD results of SAT and GELSAT-4 before and after cycles.

3.5.2 Electrical Nucleation Triggering of Supercooled GELSAT

Our newly developed GELSAT exhibits stable supercooling post-charging, enabling users to control heat release by initiating nucleation. For efficient discharge, an electrical triggering method was engineered using pure silver electrodes. Upon activation, these electrodes release silver ions into the PCM, dehydrating SAT molecules and inducing crystallization. Meticulous studies on electrode spacing and voltage achieved instantaneous triggering with a response time of less than one second. Various electrode placements were explored to regulate crystallization speed (Figure 3).

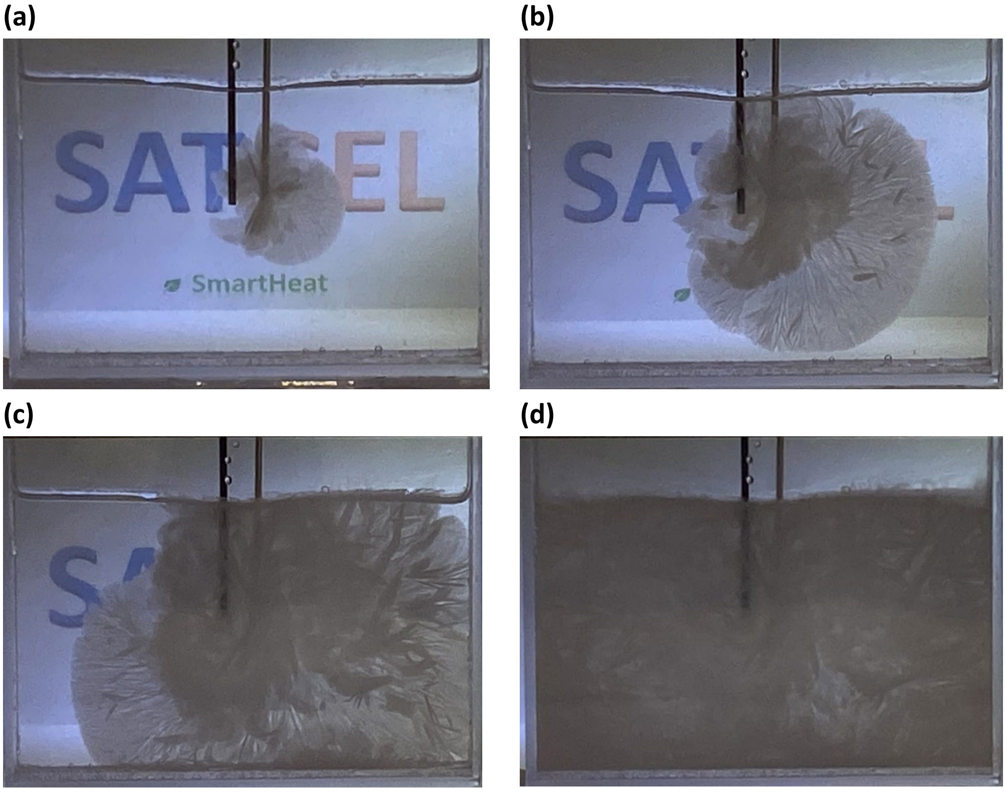

Figure 3: Electrical nucleation triggering of supercooled GELSAT.

3.5.3 Lab-Scale Validation of GELSAT

The lab-scale validation of GELSAT was conducted with meticulous attention to detail, employing a specialized setup designed to mirror practical applications on a larger scale. The configuration, depicted in Figure 4, incorporated a spiral heat exchanger and two thermostats, ensuring precise control over thermal conditions. Before fabrication, extensive simulations were undertaken to fine-tune the parameters of the heat exchanger, enhancing its efficiency for optimal heat distribution as illustrated in Figure 5. This rigorous preparation aimed to emulate real-world scenarios and evaluate the performance of the novel Phase Change Material (PCM) under diverse conditions.

Figure 4: Lab-scale testing setup for GELSAT.

The observations derived from this sophisticated setup go beyond mere thermal measurements, offering valuable insights into how GELSAT interacts with larger systems and performs over extended periods. By scrutinizing the thermal behavior in this controlled environment, we gain a comprehensive understanding of the practical implications of GELSAT's application, laying the groundwork for potential advancements in thermal energy management and storage solutions across various industries. This methodical approach ensures that the innovative PCM is not only effective at a smaller scale but also scalable for broader, real-world applications.

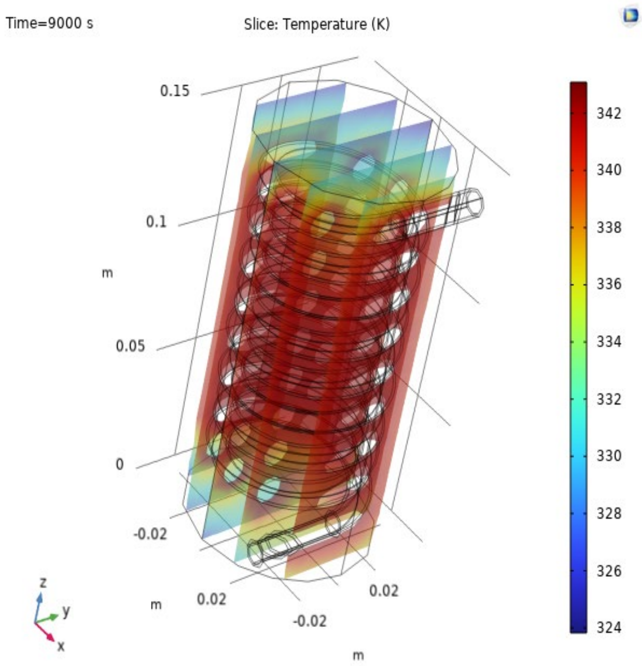

Figure 5- The simulation of the spiral heat exchanger

The successful development of GELSAT, coupled with the patent application, opens up exciting opportunities for spin-off companies and follow-on activities. Here are some potential avenues to explore:

Diversification into different PCMs:

Leverage the patented technology to explore applications beyond sodium acetate trihydrate (SAT). Investigate the adaptation of the GELSAT polymer modification approach to other salt PCMs, extending its utility to different temperature ranges and enabling cold storage solutions.

Collaborative research and licensing:

Establish collaborations with research institutions, industry or potential partners to further enhance the adaptability of GELSAT. Consider licensing the technology to interested parties for specific applications, fostering a collaborative environment for ongoing research and development.

Commercialization for cold storage solutions:

Explore opportunities in the cold storage industry, capitalizing on GELSAT's ability to address phase separation issues and provide stable thermal performance. Develop tailored solutions for refrigeration and cold chain applications where maintaining specific temperature ranges is critical.

Temperature specific variants:

Investigate the modification of GELSAT for different temperature ranges, creating specialized variants for applications such as temporary storage of heat or cold. This could cater for different industries such as pharmaceuticals, food storage and climate-controlled environments.

Pilot projects and field trials:

Initiate pilot projects or field trials in collaboration with potential end users. This can provide real-world data on GELSAT's performance and build a robust case for its adoption in specific industries.

Ongoing research and development:

Provide resources for ongoing research and development to improve the performance of GELSAT, taking into account advances in materials science, polymer technology and energy storage. Stay at the forefront of innovation to maintain a competitive edge.

By strategically exploring these opportunities, spin-off activities and follow-on initiatives for GELSAT can extend its impact across multiple industries and temperature ranges, establishing it as a versatile and commercially viable solution.

3.6 Conclusion and Recommendations

The completion of the project marks a significant milestone in the field of thermal energy storage, particularly with the successful development of GELSAT, a flexible composite phase-change gel. Through a meticulous process of polymer modification for sodium acetate trihydrate (SAT), GELSAT demonstrates remarkable thermal properties, overcoming challenges associated with phase separation and presenting an innovative solution for long-term heat storage. The extensive characterization, including crystal and chemical structure analysis, showcases its suitability for various applications.

The electrical nucleation triggering method introduces a new dimension to heat release control, enhancing the efficiency of GELSAT. The lab-scale validation further reinforces its practical viability, indicating potential real-world applications.

Recommendations:

1. **Further Optimization:**
    - Continue research efforts to optimize GELSAT's composition for enhanced performance. Explore variations in polymer concentrations and types to fine-tune its thermal characteristics, ensuring versatility across different temperature ranges.
2. **Scale-Up and Industrial Collaboration:**
    - Initiate efforts to scale up GELSAT production for larger applications. Collaborate with industrial partners for mass production, ensuring seamless integration into various sectors requiring efficient thermal energy storage solutions.
3. **Pilot Projects by developing SMARTHEAT heat battery:**
    - Implement pilot projects in collaboration with end-users to gather real-world performance data. Use these projects to validate GELSAT's efficacy in diverse environments and applications, providing valuable insights for further improvements.

In summary, the GELSAT project establishes the groundwork for a transformative era in thermal energy storage. Guided by strategic recommendations, this initiative has the potential to extend beyond laboratory boundaries, leaving a lasting imprint on various industries and fostering sustainable and efficient energy management practices.

Moving forward, we are committed to sustaining this research momentum and actively pursuing new funding opportunities. Our goal is to persist in advancing this project and constructing a heat battery based on the innovative technology developed, further contributing to the evolution of energy storage solutions.

4 Execution of the project

4.1 Technical and Organizational Problems

There were no significant technical or organizational problems during the project. The only problem was the effect of the corona pandemic on the progress of the project, which was solved by extending and changing some tasks within the project.

4.2 Changes in the Project Plan

Throughout the SMARTHEAT project, we have encountered valuable insights and breakthroughs that have necessitated adjustments to our original plan. These changes, driven by the pursuit of optimal performance and efficiency, are outlined below:

Improvement in polymer selection:

In response to promising developments in polymer technology, we decided to adjust our polymer selection. Initially, some polysaccharides additives were proposed . However, recent advances in polymer research have introduced a superior alternative that has improved compatibility with the salt hydrate PCM (SAT) and contributes to improved performance characteristics. This strategic shift is in line with our commitment to bring the most advanced elements to the project to ensure optimal results.

Re-evaluation of additives:

The original plan was to include Mxene as an additive in the GELSAT composition. However, after thorough evaluation and experimentation, it was determined that a simpler modification of the electrodes could achieve the desired results without the need for Mxene. This modification streamlines the production process and eliminates the use of additional materials, contributing to a simpler and more efficient methodology.

These adjustments to our project plan underline our commitment to staying at the forefront of technological advances and refining our methodologies based on new knowledge. By incorporating these changes, we aim to optimize the performance of GELSAT and take the project to new heights of innovation in thermal energy storage.

4.3 Knowledge Dissemination

The GELSAT, created during this project, has been patented and filed. Ongoing discussions with partners aim to explore the development of similar products tailored for different temperature ranges, applicable in both heat and cold storage applications. The project had a Fundamental Research (FO) character. Hence, knowledge dissemination occurs through various scientific channels, including publications in professional journals and presentations at scientific conferences. The following publications are currently in preparation or submitted to the journals :

- S. Peng[a], J. E. ten Elshof, G. Brem ,M. Mehrali (Unveiling the Potential of GELSAT: A Meta Stable Supercooled Salt Hydrate Hydrogel with Superior Heat Storage Capacity and Structural Integrity) Under review in Chemical Engineering Journal.
- Efficient Induction of Metastable Supercooled Salt Hydrates through Modified Electrode Techniques (in preparation)
- Controlling the Speed of Charging and Discharging in Supercooled Salt Hydrates through Polymer Matrix Manipulation (in preparation)
- Evaluation of Heat Battery Cell Performance Utilizing Metastable Supercooled GELSAT

(in preparation)

The project has been previously presented and deliberated during a scientific community:

- 3rd Edition of LTES2023, 4th - 8th September, 2023, International Summer School on Latent Thermal Energy Storage. (Oral presentation)

In addition to the upcoming publications mentioned earlier, S.Peng will compile a PhD dissertation that incorporates the findings of the SMARTHEAT project, highlighting the role of meta stable supercooled GELSAT on future of PCM based heat batteries .

Beyond the distribution of knowledge via scientific channels, such as publications in professional journals and presentations at scientific conferences, alternative dissemination channels have been and continue to be employed.

4.4 Further Project Continuation

The Ph.D. candidate and postdoctoral researcher are expected to play a key role in the Smartheat project through their collaboration with project partner De Ridder. Their primary focus will involve progressing and implementing material development concepts and solutions. De Ridder intends to broaden its engagement by incorporating additional heat storage products through the commercialization of GELSAT products. This extended collaboration is anticipated to amplify the overall impact of the project's outcomes. There are also plans to write future proposals for continuation of the project to build future PCM based Heat battery based on GELSAT.

4.5 Financial Report

The presented table offers a summarized overview with approximate figures. Subsequent to the table, an elucidation is provided regarding the disparities between the initial budget and the actual expenditures.

Partner	Budget (€)	Actual Costs (€)
University of Twente	538,326	290,000
COOLPACK (De Ridder)	30,000	7,000
GEOTHERM	11,325	3,000

As a consortium partner, COOLPACK (De Ridder) actively contributed to the project by providing valuable assistance in material development and upscaling processes. Their expertise played a crucial role in advancing the development of the heat battery technology. On the other hand, GEOTHERM contributed through consultations, offering insights into the application of the developed battery technology with different home technologies. Their input provided a comprehensive understanding of the potential integration of the heat battery in various home systems.