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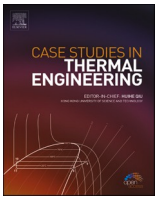

Thermal performance evaluation of recycled salt hydrates through T-history

Charles A. Wesemann [a,b,*], Tessa Junggeburth [a], H.J.H. Brouwers [a]

[a] Department of the Built Environment, Eindhoven University of Technology, P. O. Box 513, 5600, Eindhoven, the Netherlands
[b] Eindhoven Institute for Renewable Energy Systems (EIRES), Eindhoven University of Technology, P. O. Box 513, 5600, Eindhoven, the Netherlands

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ABSTRACT

Recycled magnesium sulfate heptahydrate, sourced from chemical byproducts in the nano-silica extraction from olivine, exhibits unique minor phases and reduced purity compared to analytical-grade counterparts. This study investigates phase stabilizer usage, titania as a nucleating agent, and carboxymethyl cellulose (CMC) as a stabilizing gel, to enhance the functionality of recycled salt hydrates for thermal energy storage applications. Thermocouple measurements over ten heating and cooling cycles reveal distinct thermal characteristics, with observable latent heat manifesting as a critical indicator for melting-crystallization cycling. The addition of titania increases the number of functional cycles of recycled samples but diminishes performance in analytical samples. Suggesting it provides another function other than nucleation. Statistical analysis shows an exponential decay in thermal cycles ($R^2 > 0.84$) with increased cycles. While titania shows promise, gel stabilizers like CMC did not yield meaningful results. The average latent heat storage of the recycled epsomite was 285.4 ± 37.1 J/g. This study addresses a previously unexplored area and highlights the potential of nucleating agents in improving the functionality of recycled salt hydrates for sustainable thermal energy storage.

1. Introduction

Heating is one of the major contributors to the energy demands of a building, motivating researchers to find ways to reduce, store, or substitute thermal energy [1]. One of the technologies that could enable thermal energy storage (TES) is employing phase-changing materials (PCMs) [2–7]. These materials use latent heat storage, that occurs when the material undergoes a phase change [7–17]. The advantages of PCMs compared to sensible heat storage methods are 1) higher energy density (thus requiring a smaller volume), 2) minimal maintenance costs, and 3) they can be safer to manage [18–20]. PCMs may play a crucial role in regulating temperature fluctuations within buildings, offering a unique solution to thermal management [21] by strategically incorporating them into walls and ceilings within closed containers. Unlike traditional insulation materials, PCMs provide insulation, and absorb and release heat, effectively buffering indoor temperature fluctuations [22].

Inorganic PCMs, such as hydrated salts, are usually preferred over organic alternatives (e.g. paraffin waxes) in the build environment. These materials, on average, offer higher volumetric storage density (e.g. 367 MJ/m^3 for Glauber salt, compared to 180 MJ/m^3 for paraffin wax), increased thermal conductivity (1.02 W/mK for Glauber salt, compared to 0.3 W/mK for paraffin wax), and greater fire resistance, as documented in several studies [18,23,24]. Their superior thermal conductivity enables more efficient

* Corresponding author. Department of the Built Environment, Eindhoven University of Technology, P. O. Box 513, 5600, Eindhoven, the Netherlands.c.a.wesemann@tue.nl

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thermal discharging and charging, ensuring effective internal building temperature regulation.

However, salt hydrates present some practical challenges [25], particularly in maintaining their energy storage density (performance) over multiple heating and cooling cycles [26]. This can be caused by incongruent melting, which occurs when a salt hydrate phase does not melt directly but instead forms another phase containing less or no water, alongside a liquid phase. Due to volumetric density differences, the remaining solid phase tends to settle at the bottom of its container causing clumps that are challenging to rehydrate completely [18]. This way incongruent melting can create a mixture that contains various hydrated material phases and reduce the overall efficiency of latent heat storage. Additionally, salt hydrates may encounter supercooling. Supercooling occurs when the temperature of the salt drops below its solidification temperature, yet the salt remains in a liquid state due to a lack of nucleation. Understanding how phase separations and supercooling affect salt hydrate efficiency requires researching their behavior under various heating and cooling rates [27].

Heating and cooling rates significantly impact the thermal behavior of materials [28–30]. While current rates typically average between 5 and 10 °C/min [28–30], the standard heating rate for salt hydrates is generally lower, usually performed in the range of 1–5 °C/min [27]. Higher heating rates can accelerate detrimental processes in salt hydrates, potentially leading to phase separation or supercooling [8,9,31].

To improve thermal cycling for salt hydrates, various techniques are implemented to prevent phase separation and supercooling. A common solution for phase separation is the thickening agent usage such as carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), bentonite, or comparable viscous material. By increasing the viscosity of the salt hydrate, these agents hinder the solid crystals from settling at the bottom of the container and ensure they remain suspended in the liquid, facilitating the recrystallization process when the temperature is lowered again [31–33]. Supercooling prevention is more challenging. Dynamic solutions, such as ultrasonic vibrations, shockwaves, or electro-freezing, can help crystallization [34,35]. However, they are non-practical when a salt hydrate is incorporated as a passive buffer in a building. In such a case passive nucleating agents such as copper, borax, or titanium oxide can be added to stimulate crystallization [31,33,36]. The function of nucleating agents is primarily to disrupt the effects of supercooling by providing a solid surface for crystallization to grow from, thereby reducing the surface energy required for crystallization [37–39].

Such an inorganic phase change material example is magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, epsomite). It has a thermal storage energy density of 287 kJ/kg if applied as a PCM [20,27,40–42]. Epsomite can be obtained through various methods such as mining, desalination from ocean regions, or as a byproduct from nano-silica production [43]. The magnesium sulfate from nano-silica production contains contaminants that can influence the thermal behaviour. However, despite its potential, epsomite poses challenges because its phase changes can be kinetically hindered, resulting in increased phase separation and diminished performance over repeated cycles [44]. The cyclability of magnesium sulfate heptahydrate can be evaluated by subjecting recycled epsomite to multiple cycles of heating and cooling of 40–55 °C to investigate the phase change from epsomite to hexahydrate that occurs at 49.2 ± 0.3 °C [45,46].

In this study, the thermal performance of pure epsomite and epsomite derived from olivine-based nano-silica extraction was evaluated through the use of the T-history method, with the effectiveness of titania and carboxymethyl cellulose in enhancing their efficiency and stability being investigated. The primary motivation for selecting these additives was their safety, cost-effectiveness, and compatibility with practical thermal energy storage applications. While previous research has explored salt hydrates as PCMs, the thermal behavior and cyclability of recycled magnesium sulfate heptahydrate remain largely unexplored [47]. This study addresses this gap by optimizing the thermal stability and energy storage performance of recycled epsomite, demonstrating that, with the appropriate stabilizing agents, it can achieve performance comparable to its virgin/analytical-grade counterpart. Unlike conventional approaches, which focus solely on analytical-grade materials, this work provides valuable insights into the viability of upcycled salt hydrates as a sustainable alternative for thermal energy storage. To our knowledge, this is the first study to systematically investigate and optimize the phase change behavior and long-term thermal cycling performance of recycled magnesium sulfate heptahydrate, using T-history analysis [31,41,48], paving the way for its practical implementation in sustainable thermal energy storage systems.

2. Materials and methods

2.1. Materials

Recycled epsomite was obtained as a byproduct of the production of nano-silica from olivine as described in the work of Lazaro [43,49,50]:

$$(Mg,Fe,Ni)_2SiO_{4\ (s)} + 2H_2SO_{4\ (l)} \rightarrow Si(OH)_{4\ (aq)} + 2(Mg,Fe,Ni)^{2+}_{(aq)} + 2SO^{2-}_{(aq)} \quad (1)$$

$$Mg^{2+}_{(aq)} + SO^{2-}_{(aq)} + 7H_2O_{(l)} \rightarrow MgSO_4 \cdot 7H_2O_{\ (s)} \quad (2)$$

Initially, olivine undergoes dissolution through treatment with sulfuric acid (Eq. (1)), followed by an oxidation process to remove iron and other heavy metals. Subsequently, the remaining liquid undergoes air drying for 24 h (Eq. (2)) and is further dried using a 1:2 ratio of ethanol to salt solution [47].

A comprehensive characterization of the recycled epsomite is discussed in Wesemann et al. (2024) [47], It contained traces of Fe, Ni and Si and exhibited distinct thermal behavior compared to analytical grade epsomite, such as delayed melting and cold crystallization. Cold crystallization is a phenomenon in thermal testing where energy is released just before melting as the material is heated [51]. This generally occurs due to rapid improper crystallization, pollutants, and other effects that interfere with proper crystallization

of material.

To investigate the thermal performance of the recycled epsomite, analytical magnesium sulfate heptahydrate (99.5 % Acros Organics) was used as a reference material. CMC (Sigma-Aldrich) was used as a thickening agent and titanium (IV) oxide (Ph. Eur. BP USP 99–100.5 % Sigma-Aldrich) was used as a nucleating agent.

The process for incorporating CMC began by dissolving it in distilled water at a ratio of 1:15 at 80 °C. Once fully dissolved, the solution was cooled to 40 °C. Mechanical mixing ensued until the PCM was thoroughly integrated with the CMC solution.

To determine the effect of the gel on the salt performance, additional CMC mixes containing 0.03 % %, 0.05 %, and 0.25 % by weight of the CMC powder into water were evaluated (Table 1) [38,52,53]. Each mixture underwent the same process of dissolution and mechanical mixing as described. Similarly, 5 wt% of titanium oxide were added to the epsomite, which is a standard amount (0.5-5 wt%) commonly used for nucleating agents [39]. To comprehend the impact of these additives, mixtures without salts were also evaluated for their thermal performance. Furthermore, standalone experiments were conducted with individual additives, such as CMC and titania to discern their behavior in isolation. For a detailed breakdown of materials and sample sets, refer to Table 1.

2.2. Methods

The experimental set-up consisted of a rack with six test tubes containing 15–30 mL of material, which were placed in a climate chamber (Memmert UF160 Plus) with an accuracy of $\pm 0.1°C$ and ±0.5%RH, as depicted in Fig. 1. The tubes were closed off with parafilm, to prevent water escaping. Despite the sealing of the salt samples, dehydration was still observed. Consequently, all samples were tested at a relative humidity (RH) of 80 % inside the climate chamber [54]. The material underwent 10 rounds of thermal cycling while maintaining constant humidity, resulting in a total of 11 heating and cooling cycles. The first cycle was excluded to avoid irregular values, and cycles 2 to 11 were analyzed. The temperature range spanned between 40 °C and 55 °C and was selected to be slightly above the melting point of Epsomite (49.2 ± 0.3 °C) to ensure phase transformation, from solid to a liquid + solid (slurry).

The cycling procedure involved several steps: The temperature was raised from 40 °C to 55 °C at a heating rate of either 0.1 °C/min or 0.5 °C/min. Upon reaching the maximum temperature of 55 °C, the material was held at that temperature for an additional 2 h. Subsequently, the temperature decreased to 40 °C using the same heating rate (0.1 °C/min or 0.5 °C/min). The material remained at 40 °C for another 2 h. This entire process was repeated ten times (as shown in Fig. 1). The cooling curve data is not included as the recrystallization could not be observed with the chosen method.

Appendix 1 shows a slight temperature overshoot during heating in the control materials (air, dH_2O, and standalone additives). However, this is not considered to have any influence due to the 2-h waiting time.

The temperature of the materials during the experiments was measured with six thermocouples that lay in the tubes enclosed by the material. The thermocouples Pt100 A, which have an accuracy of $\pm 0.15°C$, measured the temperature every 30 s using the Eltek Squirrel 1000 Series Data Logger, which has an accuracy reading of ±0.1 %. XRD measurement determined the crystalline structure of the materials after cycling. After grinding the materials for 15 min using the XRD Mill McCrone, XRD was performed with the Bruker D2 Phaser with a Co-Anode (Kα1: 1.7901 Å and Kα2: 1.7929 Å) from 2 Theta of 5–60° using a LynxEye detector [47]. The uncertainty in the enthalpy of fusion (J/g) measurements was primarily evaluated using standard deviation (S), as shown in Table 2, following the method described in Ref. [55]. A detailed uncertainty analysis of the measured values used for statistical evaluation is provided in Appendix 5.

Table 1
Overview of materials and samples.

Measurement Group	Sample ID	Analytical Epsomite (wt%)	Recycled Epsomite (wt%)	Water (wt%)	Titania (wt%)	CMC (wt%)
Control	CA	100	0	0	0	0
	CR	0	100	0	0	0
	C1	0	0	100	0	0
	C2	0	0	0	0	0
	C3	0	0	0	100	0
	C4	0	0	0	0	100
Nucleating Agent	NA	95	0	0	5	0
	NR	0	95	0	5	0
Thickening Agent	GA1	95	0	4.97	0	0.03
	GA2	95	0	4.95	0	0.05
	GA3	95	0	4.75	0	0.25
	GR1	0	95	4.97	0	0.03
	GR2	0	95	4.95	0	0.05
	GR3	0	95	4.75	0	0.25
Nucleating and Thickening Agent	NGA	85	0	9.9	5	0.1
	NGR	0	85	9.9	5	0.1

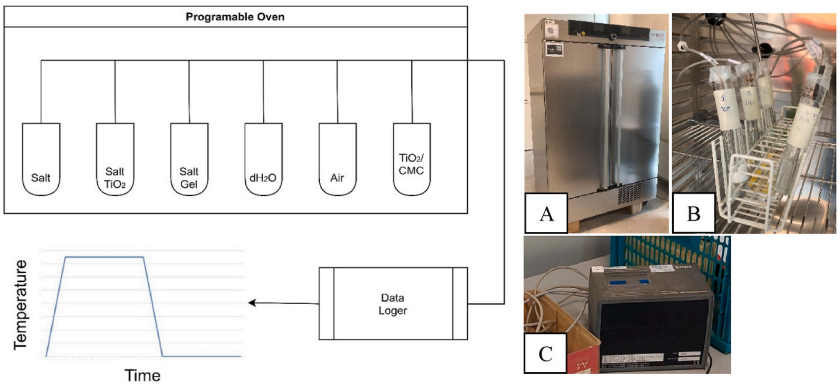


Fig. 1. Experimental setup: Samples were placed in test tubes and subjected to controlled heating and cooling cycles in a programmable climate chamber (A). Thermocouples (B) were positioned inside the sample to measure and record temperature data with a data logger (C). This temperature data was utilized to plot the T-history of the experiment. To the left is the schematic overview of the setup, while on the right shows the real world components of the setup.

Table 2
Overview of the area under the curve of the first melt of five different CA samples, the mean value of these five runs, standard deviation, and theoretical latent heat of fusion of epsomite.

Run		AUC $\int$
1)		298
2)		253
3)		335
4)		244
5)		297
Mean $\overline{x}$	Standard Deviation S	Theoretical value μ (J/g)
285.4	37.14	287.85

3. Results and discussion

3.1. Phase change

In Fig. 2, the plateau corresponds to the measured phase change of epsomite from solid to liquid slurry of hexahydrite with water,

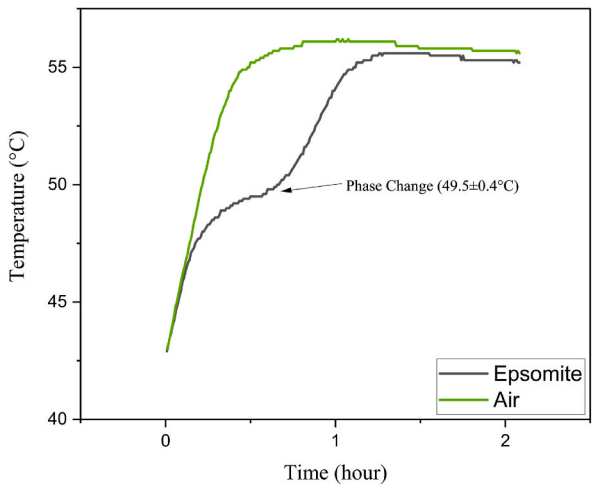


Fig. 2. Measured sample of analytical quality epsomite, at a heating rate 0.5 °C/min, compared to an empty test tube to highlight the phase change.

occurring around 49.5 ± 0.4 °C. The melting temperature was determined by identifying the intersection point of the tangential line drawn from the plateau of the measured curve and the tangential line of the heating curve. This value was then compared across multiple measurements and averaged to obtain the final melting temperature. This is the key feature of interest and outlines latent heat absorption during the phase transition. The plateau remains until the phase change ends, as depicted in Fig. 2. The temperature then continues to increase. The mechanism of this phase change is presented in the subsequent chemical equation [56]:

$$MgSO_4 \bullet 7H_2O \xrightarrow{\Delta} MgSO_4 \bullet 6H_2O + H_2O$$

However, it is important to note that the precise mechanism of salt hydrate melt is not comprehensively understood, and various scholarly sources present differing perspectives on its precise mechanism [57–59].

3.2. Heating rates

The purpose of testing different heating rates, specifically 0.5 °C/min and 0.1 °C/min, using the T-History methodology in a programmable climate chamber is to evaluate how these rates influence the thermal behavior and phase change characteristics of the materials. As noted by Yan et al. [27] and Yang et al. [56], the phase change of epsomite is best observed at heating rates below 1 °C/min. Therefore, a heating rate of 0.5 °C/min and 0.1 °C/min were tested to understand the effects of slower versus faster thermal transitions on material stability, energy storage capacity, and the accuracy of phase change measurements. This investigation is critical for optimizing the T-History method and ensuring that the selected heating rate accurately reflects the material's performance.

The results are shown in Fig. 3, and make it evident that the phase change plateau obtained at 0.1 °C/min heating rate (depicted as the top two graphs of Fig. 3), is indistinct and challenging to interpret for both the CA and CR samples. Conversely, when the heating rate was increased to 0.5 °C/min, a clear plateauing was observed corresponding to the phase change discussed previously. Therefore all further experiments were conducted using the 0.5 °C/min rate. The observed plateau appears to decrease over time, demonstrating an increasing lack of phase change taking place. In the recycled salt sample heated at 0.1 °C/min, the phase change is evident for a few cycles but quickly disappears. Based on these raw material measurements, of the need for thermostabilizing agents is evident.

3.3. Performance of nucleating agent

Testing of the nucleating agent, titania, is crucial for enhancing the phase change performance of materials like CA and CR. By investigating how a nucleating agent affects the phase change stability and duration, improvements in material behavior are aimed to be identified. The goal is to determine how this agent can reduce inconsistencies, extend phase change cycles, and enhance the overall reliability of phase transitions. This approach is intended to optimize the performance of phase change materials, ensuring more predictable and effective thermal energy storage.

Fig. 4 illustrates the influence of titania on the phase change behaviour of both NA and NR samples, which were tested in a programmable climate chamber. The NA sample exhibited a consistent phase change over 8 cycles, whereas the CA sample demonstrated a slightly longer duration with phase changes observed across 10 cycles. In contrast, the NR sample showed a significant improvement when titania was added, sustaining a clear phase change over 7 cycles. This is notably better than the CR sample, which only exhibited phase change for 2 cycles before the effect diminished.

The addition of titania to NR resulted in a more stable and predictable phase change behaviour, marked by a sustained plateau, compared to the erratic and short-lived phase changes seen in CR. Specifically, while CR showed considerable fluctuations and a rapid loss of phase change capability, NR with titania maintained a consistent performance throughout the testing period. This enhanced stability underscores the beneficial role of titania in improving the reliability and longevity of phase change behaviour in NR, in stark contrast to the performance observed with the untreated CR sample.

A continual and inconsistent decrease in performance was observed during the thermal cycling of the materials. To investigate this issue, the samples were weighed before and after a full test run of 10 cycles. A notable decrease in weight, amounting to 5.7 wt%, was

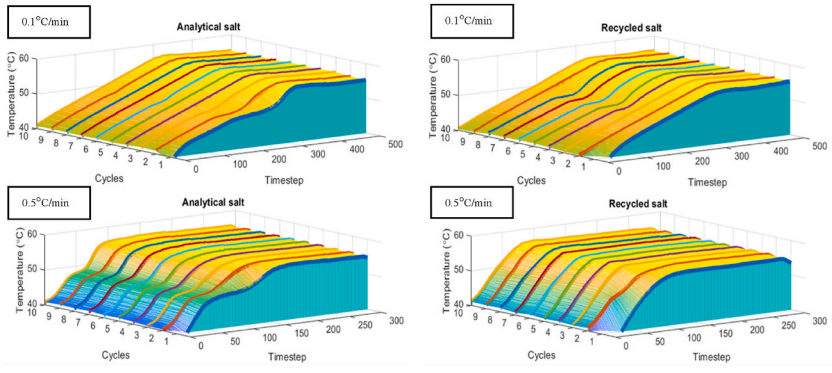


Fig. 3. Comparison of heating rates of analytical epsomite CA (left) vs recycled epsomite CR (right) at 0.1 °C/min (top) vs 0.5 °C/min (bottom).

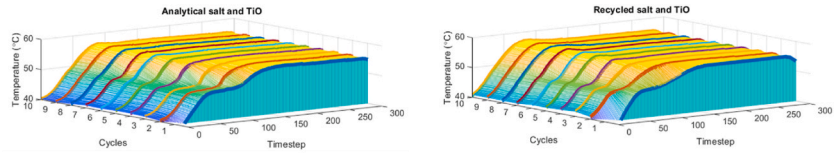


Fig. 4. Analytical NA (left) and Recycled NR (right) epsomite salt with the titania mix at 0.5 °C/min.

observed, which was attributed to water loss corresponding to the dehydration of epsomite from 7 to 6 water molecules. XRD analysis confirmed that the material was no longer epsomite.

To address this problem, initial tests involved rehydrating the samples with the equivalent amount of water lost and then running them through 10 additional cycles. However, the results showed no significant improvement in performance. This lack of improvement may be due to the slow hydration kinetics of epsomite and possibly the formation of titanium hydroxide from the reaction of water with titania [60].

As a result, it was decided to conduct all subsequent tests at a relative humidity (RH) of 80 % to prevent water loss. The effects of this adjustment are illustrated in Fig. 5, showing the performance of fresh NA and NR samples.

Although maintaining a RH appeared to benefit the cycling of the material, the inability of the material to consistently achieve 10 full cycles prompted a closer examination of the nucleating agent. Fig. 6 reveals that after several cycles, the salt mixture containing titania separated into two distinct layers: titania settled at the bottom, while the salt remained above.

This separation into distinct phases can be explained by the difference in density between the epsomite (1.67 g/cm^3) and the titanium oxide (4.23 g/cm^3). To ascertain whether the settling and therefore separation of the titania was the underlying cause of the observed phenomenon of decreasing performance after multiple phase changes, the separated analytical and recycled epsomite salt samples were subjected to mechanical remixing and retested. Fig. 7 indicates that the density hypothesis alone can be ruled out, as the mechanical remixing of the material failed to induce thermal cycling for either the analytical or recycled salt.

Despite remixing with titania, the material continued to exhibit a loss of performance, as verified by XRD analysis, which showed that dehydration persisted regardless of high (+80%RH) humidity. This indicates that while maintaining humidity helps, it does not fully prevent the dehydration of the samples. Further research into hydration mechanisms, as detailed by Clark et al. [44] and Rehman et al. [61], highlights the limitations of magnesium sulfate in rehydrating to its heptahydrate form regardless of humidity; they were only able to achieve the hexahydrate form. The likely explanation lies in the crystal structure of epsomite, where six water molecules are bound to the cation, with one unbound water molecule that is easily lost during heating. The most probable way for the hexahydrite to rehydrate into epsomite is through a process of deliquescence.

It can be concluded that titania likely did not serve effectively as a nucleating agent for epsomite. However, the marked improvement observed in NR samples suggests that titania may have functioned as a conductive agent, with a thermal conductivity of 7–10 W/m·K. This conductivity likely enhanced the thermal performance of CR samples but had limited impact on CA samples. This can be explained by the presence of minor contaminants in the recycled epsomite, which disrupt the material's thermal conductivity. This issue can be mitigated by adding a conductive agent. However, in the case of CA, the addition of the conductive material appears to have disrupted the heating and cooling rates, causing the material to lose water and form hexahydrite more readily. The observed improvement in NR samples highlights the potential for enhancing the thermal performance of recycled salt hydrates by incorporating conductive materials. This suggests that further research into materials with high thermal conductivity and density compatibility could lead to more effective thermal energy storage solutions.

3.4. Performance of thickening agent

Fig. 8 presents the results of epsomite with CMC gel. As clearly observed neither analytical or GR3 show any phase change in the presence of CMC. There are two explanations for this observation: the salt dissolved entirely into the gel, preventing phase change, or the gel is significantly more hydrophilic than the hexahydrate. In the latter case, the gel could bind a substantial amount of water, which is released during phase change from heptahydrate to hexahydrate, making a rehydration impossible. As discussed in the previous section, the dehydration of epsomite to hexahydrate is notably easier than its rehydration. Consequently, if dehydration occurs, the likelihood of maintaining effective thermal cycling performance becomes negligible.

A short experiment was conducted to determine the relative hydrophilicity of the thickening agent (CMC [0.25g]) compared to the salts. A closed container with open bottles of H_2O, CR, CA, and CMC was weighed after one week. The results, presented in Fig. 9, revealing a decrease in the weight of H_2O over time, while the weight of CMC increased. However, the weights of the salts remained

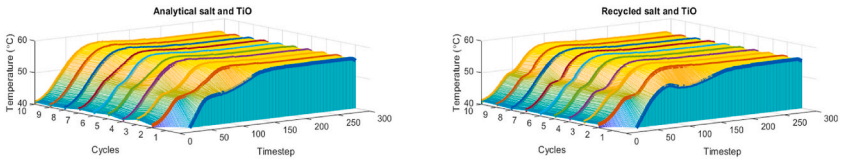


Fig. 5. Thermal cycling of fresh NA and NR mixture with Titania in humid environment.

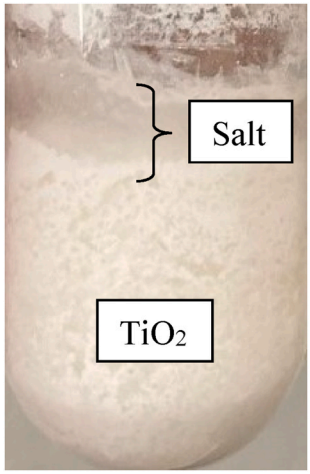


Fig. 6. Overview of phase separation of titanium oxide and salt.

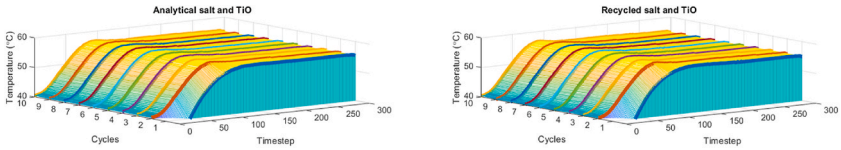


Fig. 7. The figure illustrates the results of re-mixing NA and NR samples that had already undergone 10 cycles of thermal cycling. Both samples were subjected to 10 cycles of heating and cooling prior to re-mixing. The purpose of this experiment was to assess whether physically re-mixing the salt samples with titania would induce a phase change in the epsomite.

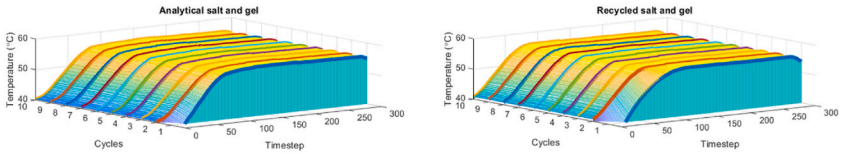


Fig. 8. GA3 (left) and GR3 (right) epsomite salt mixtures of CMC gel with salt at 0.5 °C/min.

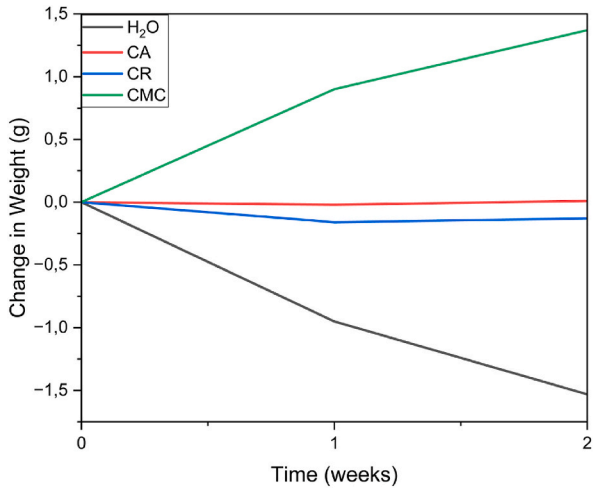


Fig. 9. Weight change of CMC, recycled salt, analytical salt, and H_2O.

relatively constant. This confirms the hydrophilic nature of CMC. However, the salt's minimal water absorption indicates a less hydrophilic nature than anticipated. It was initially expected that the salt hydrates would exhibit a level of hydrophilicity similar to that of CMC, ensuring that the two would not compete for moisture. Additional experimentation, particularly including reducing gel concentrations, could provide additional insights into the interaction between CMC and CA/CR.

To address this issue, the ratio of gel to salt in subsequent experiments was adjusted, resulting in different lesser ratios of GA1/GR1 (0.03g of CMC) and GA2/GR2 (0.05g of CMC). The hypothesis that epsomite might dissolve in the gel solutions was tested by experimenting with varying concentrations of CMC gel (G1, G2, and G3). The results, presented in Fig. 10, revealed different levels of latent heat storage based on the CMC concentration. Samples with the lowest CMC concentration (G1) showed no PCM performance in both analytical and recycled salts. When the CMC concentration was increased to GA2, limited latent heat storage was observed. Further increasing the concentration to G3 led to some improvement in latent heat storage for both analytical and recycled materials, but performance remained suboptimal.

When comparing these results with those from samples that did not contain CMC gel, no phase transition was observed in the samples with CMC gel. For the GA samples, the phase change plateau is consistently visible throughout the 10 cycles without gel (as observed in samples CA, CR, NA, and NR). However, with the addition of gel, the plateau becomes barely discernible after the second cycle at the GA2 concentration and diminishes even further at GA3. In contrast, for GR, there is no significant performance improvement when comparing with samples without gel (as observed in samples CA, CR, NA, and NR). However, a sharper plateau is observed at the GR3 CMC gel concentration, although it only lasts for a shorter duration.

The data indicate that incorporating CMC gel into salt hydrates does not inherently offer beneficial effects. The gel's pronounced hydrophilicity appears to interfere with phase change measurements, regardless of its concentration, as observed through T-history analysis. Given the ease with which the material dehydrates, it is recommended to explore alternatives that may perform better. Potential alternatives include using hydrogels (eg. polymers from acrylics, ethylenes, styrenes, or esters) with hydrophobic properties or experimenting with gels that have a lower Log S (solubility) and higher Log P (partition coefficient). Additionally, the implementation of a porous medium, such as mica, clays, or aerogels, could provide a more stable environment, potentially enhancing the material's phase change behavior and overall performance. The use of porous materials allows for capillary force to absorb and retain water in the system causing focal areas of deliquescence that would be ideal in the rehydration of salt hydrates like hexaydrite into epsomite.

3.5. Combined performance of titania and thickening agent with PCM

Ideally, both titania and thickening agents should work synergistically to enhance the properties of epsomite during thermal cycling. While the gels alone did not yield promising results when used with the salts, there was potential that their combination with titania as a conductivity agent could improve overall performance. In the final experiment, mixtures labeled NGA and NGR were prepared, consisting of 5 wt% titania and 10 wt% of the G2 gel. The results, presented in Fig. 11, indicate no significant reaction, suggesting that the gel may have diminished the beneficial properties of titania rather than enhancing them.

3.6. Determining heat of fusion

An effective way to study the thermal properties of materials is primarily to determine the heat of fusion. To evaluate the effectiveness of the additive, it is crucial to quantify its impact. "Area Under the Curve" (AUC) was used to measure the salts mixed with titania to analyze their melting behavior. This analysis was conducted to determine the heat of fusion of the material, which is the amount of energy required to change the material from solid to liquid at its melting point. The AUC is used in this context as a way to

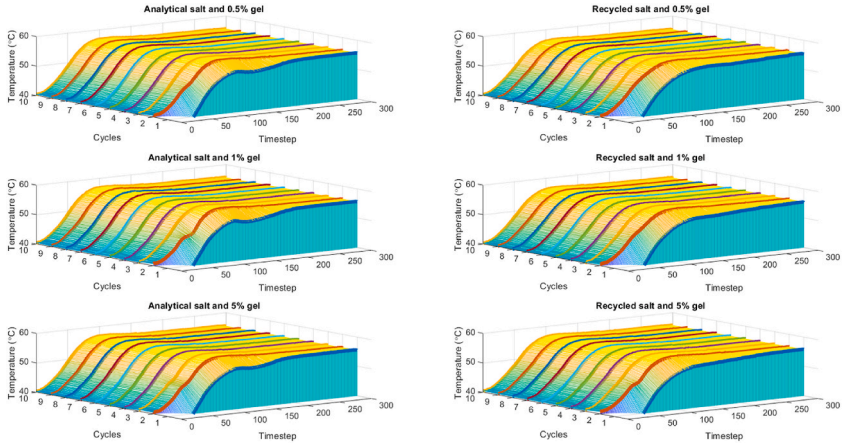


Fig. 10. Analytical and recycled mixture with different gel ratios. 0.5 % refers to the G1, 1 % refers to the G2 and 5 % refers to the G3 mixture all after combining with water.

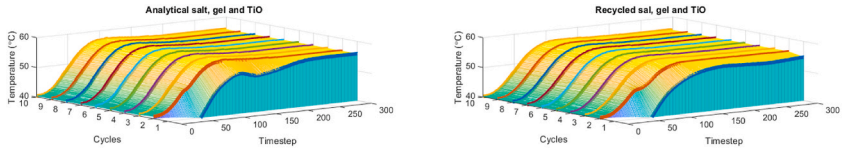


Fig. 11. Performance of NGA (left) and NGR (right) samples.

quantify the thermal energy involved in the phase change during melting. The conventional approach involves performing DSC on samples; however, this method imposes a limitation on the total material quantity that can be used (typically <10 mg), which can make the result unrepresentative. Additionally, several challenges were encountered, particularly in maintaining proper humidity levels for the samples. The perforations in the hermetically sealed lid allowed steam to escape, resulting in the loss of water. Another observation when conducting DSC measurements on the samples, it was observed that the titania had settled to the bottom of the pan, interfering with the measurement.

The method utilizing the T-History of samples, as demonstrated in previous figures similar to Figs. 3 and 5, was evaluated and quantified. This methodology involved integrating the area difference between the control (ambient) and the measured samples. The resulting measurement was then compared to theoretical values. Subsequently, the AUC was determined and compared to literature standards to assess the validity of the approach. The reported heat of fusion (ΔH_f) for the transformation from epsomite to hexahydrate ranges between 54.3 kJ/mol [62] and 84.6 kJ/mol [42]. The wide range in these values is primarily due to the fact that they are estimations based on simulations. These values are highly dependent on the specific variables and constraints applied in the modeling of such samples. Converting the average of these values to J/g, the heat of fusion is calculated to be approximately 287.85 J/g. The units of J/g are standard units for heat of fusion, commonly used in DSC, hence the conversion from kJ/mol to J/g for consistent values to be compared to literature.

Table 2 presents the values from five different runs of CA, which were used to obtain a robust dataset for statistical analysis. The values are based on the material's second cycle, aligning with the methodology used in DSC analysis. As previously noted, the first heating cycle was disregarded due to the significant noise associated with the initial cycle of the sample, similar to the observations made in DSC measurements. Similar values were observed in CR within normality of values of CA.

A one-sample T-test was conducted to assess if the obtained values were statistically comparable to the theoretical ones. This analysis was performed under the assumption of normality, which was confirmed by the Shapiro-Wilk test ($p = 0.69$) and visual inspection of the Q-Q plot. Based on this T-test, the p-value equals 0.89, thus, there is no statistical difference ($\alpha = 0.05$), between the measured values and the theoretical one. The obtained values align well with theoretical measurements, indicating that the experimental setup manifests a valid alternative to DSC measurements for larger samples than those typically accommodated by DSC. However, like any rudimentary setup, it is not without limitations and potential sources of error. A significant limitation may be the sensitivity and accuracy of the thermocouples, which might not detect subtle changes effectively. Additionally, the data collection did not occur at every second. To address these issues, ensuring repeatability in testing is essential to minimize erroneous values.

After noting that the initial cycle's values were comparable to theoretically provided values, the analysis was extended to include 10 cycles to assess the overall behavior. Fig. 12 illustrates the complete data comparison of CA and CR relative to NA and NR (left side of Fig. 12). Additionally, further samples were tested at a lower maximum temperature, just above the melting point, adjusting the range from 55 °C to 50 °C (right side of Fig. 12), while all other parameters were kept the same. The term used for identifying these samples was Lt, which stands for low temperature. This approach allowed for a more comprehensive understanding of the materials' performance across varying conditions.

Fig. 12 compares non-linear regression behavior (Exponential Decay) applied to four samples over ten cycles. These models did not adequately capture latent heat storage behavior over time in the samples. However, the analysis revealed that the exponential decay

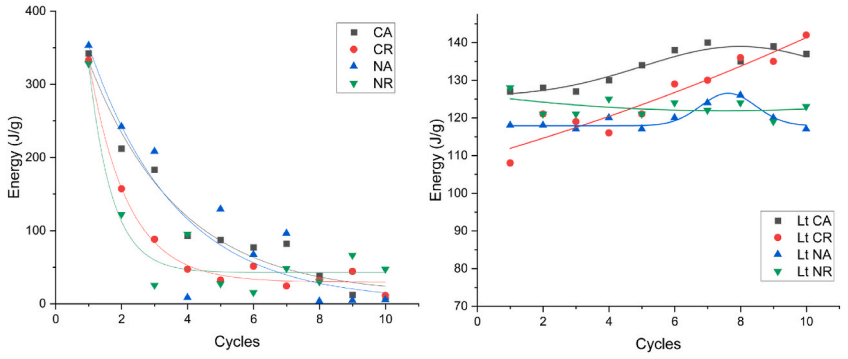


Fig. 12. Non-Linear Regression [Exponential Decay], Non-Linear Regression of four samples for ten runs, heated to 55 °C (Left), Non-Linear behavior of four samples for ten runs heated up to 50 °C (Right).

model, $y = y_0 + A_1 e^{-\frac{x-x_0}{t_1}}$, provided the best fit for humid (H) climate chamber conditions. The equation components appear as follows: y_0 represents the offset, x_0 denotes the center of the curve, A_1 stands for the amplitude, and t_1 represents the decay constant. These parameters imply the existence of a consistent baseline energy level, y_0, which the material attains across different cycles.

A higher R-squared (R^2) value indicates a stronger correlation between the regression model and the data. Table 3 shows that most models had R^2 values around 0.85 or higher. The exception was the NR samples at a lower temperature, where the Exponential Decay had an R^2 of only 0.504.

These findings suggest that when reaching 55 °C, the samples exhibit the maximum energy output consistent with theoretical values of epsomite PCM behavior. However, the observed exponential decay at 55 °C indicates the presence of multiple contributing factors, such as low discharge, phase separation, and a lack of nucleating agent sites, which impede an effective material's cycling. Conversely, heating the samples to a lower temperature (50 °C) resulted in greater stability in cycling behavior. This stability may be attributed to the material not being thermally fully charged at this temperature, allowing for a more consistent energy storage and release per cycle. The lower temperature likely enables the material to store more thermal energy per cycle, as it has not reached full latent heat storage capacity and facilitates easier charging and discharging over time.

Measuring and determining the heat of fusion of the samples using T-history methods allows for comparing the thermal energy storage capacity of both analytical and recycled salt hydrates. The results provide comparable numerical values that fall within statistical normalcy. Practically, this indicates that recycled salt hydrates, when used in this manner for thermal energy storage, can potentially be implemented in various beneficial TES applications.

4. Conclusion

This study assessed the thermal stability of recycled epsomite compared to its analytical-grade counterpart using the T-History method. Despite containing minor impurities, such as brine (Appendix 4), the recycled material exhibited comparable thermal cycling performance, demonstrating its viability as a sustainable thermal energy storage material. The addition of titania improved performance in recycled samples, likely by enhancing thermal conductivity rather than acting as a nucleating agent. However, the use of CMC as a thickening agent failed to prevent phase separation, emphasizing the need for alternative stabilization strategies.

The measured heat of fusion (285.4 ± 37.1 J/g) aligned with theoretical values, validating the T-History method as a large-scale alternative to DSC for evaluating salt hydrate PCMs. While heating samples to 55 °C maximized energy storage, it also accelerated performance degradation, whereas heating to 50 °C resulted in more stable long-term cycling. Statistical analysis ($R^2 > 0.84$) indicated an exponential decay in thermal performance, highlighting the challenges in rehydrating $MgSO_4{\cdot}6H_2O$ back to its heptahydrate form. The most likely cause for this difficulty is the melting of the epsomite, which reduces bed porosity and, in turn, hampers the vapor transport necessary for water reuptake, which is consistent with the findings reported by Zondag et al. [63].

Future improvements could focus on integrating lower-density conductive agents or porous materials to enhance stability and promote rehydration through deliquescence. These findings confirm the potential of recycled salt hydrates as an alternative to virgin PCMs, offering a sustainable pathway for reducing CO_2 emissions and advancing TES applications.

CRediT authorship contribution statement

Charles A. Wesemann: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Tessa Junggeburth:** Writing – original draft, Visualization, Investigation. **H.J.H. Brouwers:** Supervision, Resources, Project administration.

Declaration of Generative AI and AI-assisted technologies in the writing process

During this work preparation, the authors used Chat GTP 3.5 to improve the clarity and readability of the material. After using this tool/service, the authors reviewed and edited the content as needed and took full responsibility for the publishing content.

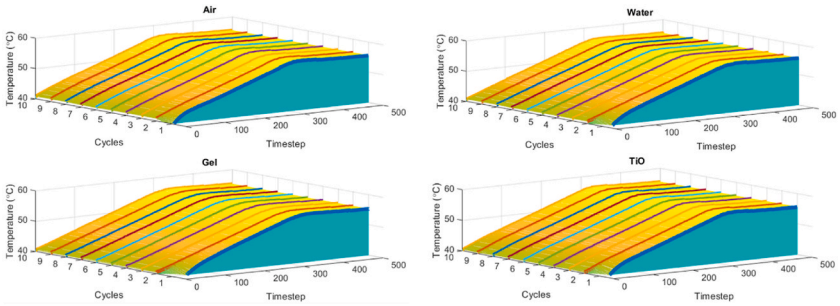
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

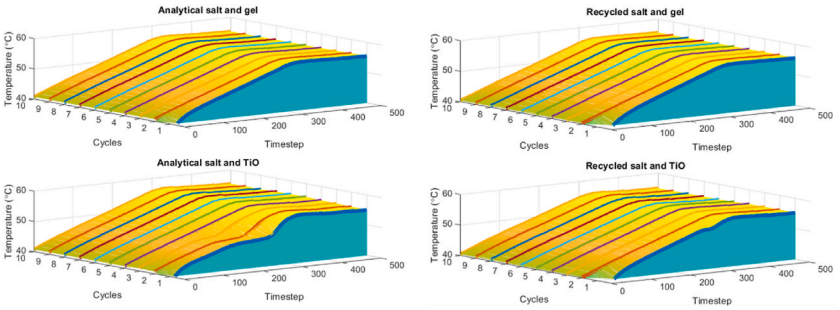
Table 3
Statistical R^2 values of four samples.

	Analytical Ref	Recycled Ref	Ana + TiO_2	Rec + TiO_2
R^2 Exponential Decay	0.943	0.854	0.850	0.989

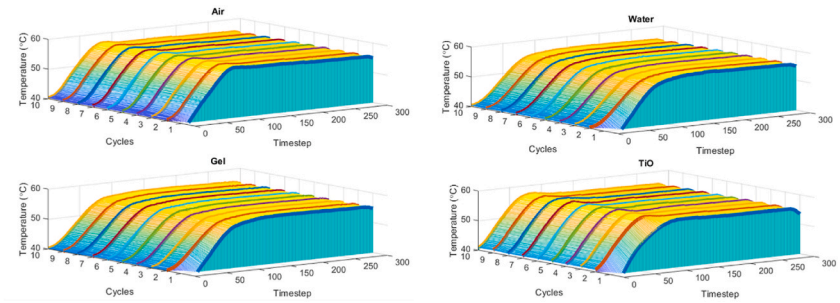
APPENDICES



Appendix 1. Standardized material mixtures at 0.1 °C/min.



Appendix 2. Analytical (left) and Recycled (right) epsomite salt mixtures of CMC gel with salt (top) and the titania mix (bottom) at 0.1 °C/min.



Appendix 3. Standardized materials mixtures at 0.5 °C/min.

Appendix 4. Microscopy of recycled Epsomite with observable water/brine bubbles trapped.

Appendix 5
Uncertainty analysis results of the measured values

Uncertainty Parameter	Unit	Uncertainty (S)
Temperature	(°C)	±0.15
Rate of Heating	(°C/min)	±0.1
Enthalpy of Fusion	(J/g)	±1 %

Data availability

Data will be made available on request.

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