

RELIABILITY ASSESSMENT OF PHASE CHANGE MATERIALS IN TES FOR RENEWABLE ENERGY SYSTEMS

G.K. Abdullayeva¹, A.L. Bakhtiyarov²

Azerbaijan State Oil and Industry University, Baku, Azerbaijan
¹gulshan.abdullayeva@asoiu.edu.az, ²bakhtiyarov.aliashraf@asoiu.edu.az

Abstract

The reliability of phase change materials (PCMs) in thermal energy storage (TES) systems is crucial for the stable and efficient operation of renewable energy infrastructures. This study presents a comprehensive methodology for assessing PCM reliability under repeated thermal cycling, focusing on degradation mechanisms such as latent heat reduction, phase change temperature shifts, and decreased thermal conductivity. Experimental characterization using techniques like Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) provides data on property evolution over thousands of heating–cooling cycles. Failure thresholds for critical parameters are established to define functional limits. An exponential decay model is proposed to quantify degradation kinetics and predict the effective service life of different PCM types, including paraffins, salt hydrates, and eutectic mixtures. Comparative analysis reveals distinct degradation behaviors and informs material selection for TES applications. The integration of empirical data, failure criteria, and predictive modeling supports reliability-centered design and maintenance planning, ultimately enhancing TES system durability and performance in renewable energy applications.

Keywords: Reliability modeling; Phase change materials (PCMs); Thermal degradation; Latent heat loss; Failure thresholds; Thermal energy storage (TES);

I. Introduction

Modern energy systems are undergoing a fundamental transformation, shifting from centralized generation based on fossil fuels to decentralized, sustainable, and environmentally friendly solutions. In this paradigm, renewable energy sources (RES) — such as solar, wind, geothermal, and biomass — play a key role. Despite their obvious advantages, including sustainability, zero carbon emissions, and reduced dependence on conventional fuels, RES are inherently intermittent and unstable, which necessitates the development of efficient and reliable energy storage systems.

One of the most promising approaches to thermal energy storage (TES) involves the use of phase change materials (PCMs), which can absorb and release significant amounts of energy during phase transitions, primarily between solid and liquid states [1]. PCMs are increasingly used in solar thermal systems, industrial heat recovery, building heating and cooling, and in emerging smart energy networks.

The main advantage of PCMs over traditional sensible heat storage materials (such as water, gravel, or oils) is their ability to store heat at an almost constant temperature with a high energy density, due to the latent heat of fusion. However, under real operating conditions involving repeated heating and cooling cycles, the thermal, chemical, and mechanical properties of PCMs can degrade, reducing system performance and potentially leading to premature failure.

The reliability of PCMs is therefore a critical factor in the long-term, safe, and cost-effective operation of TES systems, especially in applications where regular replacement of storage media is impractical or economically unfeasible [2]. In this context, reliability refers to the ability of the PCM to maintain its essential functional properties — such as phase transition temperature, latent heat, thermal conductivity, and thermal stability — over a large number of thermal cycles and under varying thermal loads.

Despite extensive research on the thermophysical and thermochemical properties of PCMs, a standardized methodology for quantitatively assessing their reliability and residual service life under cyclic thermal conditions has not yet been established. Most existing studies focus on isolated property changes without integrating them into a comprehensive assessment of system reliability.

Therefore, the purpose of this paper is to develop a structured approach for evaluating the reliability of phase change materials by analyzing the evolution of their thermophysical characteristics during thermal cycling. This study reviews the main degradation mechanisms of PCMs, presents experimental and modeled dependencies of key parameters as functions of cycle number, and proposes failure criteria applicable to real-world TES systems.

From the standpoint of reliability engineering, the performance degradation of phase change materials (PCMs) can be analyzed using established metrics such as the mean time to failure (MTTF), failure rate functions, and reliability functions $R(t)$ or $R(N)$, where N represents the number of thermal cycles. In many material fatigue and degradation processes, the Weibull distribution is commonly employed to statistically model the time (or cycles) to failure, allowing estimation of characteristic life and failure probabilities under varying conditions [3-5]. Although deterministic degradation models (e.g., exponential decay) are useful for capturing average behavior, integrating probabilistic methods provides a more robust foundation for service life prediction, risk assessment, and maintenance planning. This approach is particularly relevant for TES systems in renewable energy infrastructure, where component longevity and system-level reliability are critical. Therefore, combining empirical degradation modeling with classical reliability concepts enables a comprehensive evaluation of PCM performance throughout its operational lifecycle.

This research aims to establish a scientific foundation for the development of more durable PCMs and to enhance the operational stability and energy efficiency of TES systems integrated into renewable energy infrastructures.

II. Formulation of the problem

Thermal energy storage (TES) plays a pivotal role in balancing the intermittent nature of renewable energy sources (RES), such as solar and geothermal systems. Among TES methods, latent heat storage using phase change materials (PCMs) is especially attractive due to its high energy density and the ability to operate near-isothermally during phase transitions. However, the long-term viability of PCMs is strongly affected by their degradation under cyclic thermal loading, which directly impacts system performance and reliability (table 1).

In real-world applications, PCMs are subjected to thousands of heating and cooling cycles, which gradually alter their thermophysical, chemical, and mechanical properties. The most significant degradation mechanisms include: reduction in latent heat of fusion (ΔH_f), drift in phase change temperature (T_f), decreased thermal conductivity (λ), increased supercooling, and structural or chemical instability. These changes can be critical, especially in TES systems designed for maintenance-free operation over a lifespan of 10–20 years.

Table 1: *Classification of PCMs Based on Composition and Properties*

Type	Advantages	Limitations	Examples
Paraffins	Chemically stable, inexpensive, non-corrosive	Low thermal conductivity, flammable	Octadecane, RT42, n-docosane
Salt Hydrates	High latent heat, good thermal conductivity	Phase segregation, water loss, supercooling	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
Eutectic Mixtures	Sharp melting point, design flexibility	Complex preparation, limited long-term data	NaNO_3 - KNO_3 , organic eutectics
Inorganic Compounds	High temperature range, non-flammable	Corrosiveness, structural expansion	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Experimental evidence demonstrates varying degradation behavior among PCM types. For example, salt hydrates can lose up to 25–40% of ΔH_f within 500 cycles due to dehydration and phase segregation. In contrast, paraffins often retain over 90% of their thermal storage capacity after 1000 cycles, but their performance is limited by low thermal conductivity and the development of supercooling over time. Eutectic mixtures show intermediate behavior, though they are highly dependent on formulation and purity.

Despite their wide adoption, PCM-based TES systems still lack a standardized reliability evaluation framework [6]. Most current studies focus on individual properties (e.g., ΔH_f or T_f) without defining clear criteria for functional failure. As a result, engineers and designers are left without actionable thresholds for predicting PCM end-of-life or planning preventive maintenance.

III. Problem solution

Reliable operation of thermal energy storage (TES) systems using phase change materials (PCMs) requires a systematic approach to evaluating their long-term performance under cyclic thermal loading [7]. This section outlines the combined experimental, analytical, and empirical modeling framework used to assess PCM reliability based on thermophysical degradation.

A central aspect of the methodology is the characterization of key thermal properties over a representative number of heating–cooling cycles, typically ranging from hundreds to several thousand. The primary parameters of interest include:

- Latent heat of fusion (ΔH_f)
- Phase change temperature (T_f)
- Thermal conductivity (λ)
- Supercooling behavior and crystallization hysteresis
- Visual and structural integrity (leakage, volume change)

These properties are measured using standardized thermal analysis techniques, such as:

- Differential Scanning Calorimetry (DSC) — to determine ΔH_f and T_f ;
- Thermogravimetric Analysis (TGA) — for assessing thermal stability and mass loss;
- Hot Disk or Laser Flash Analysis — for measuring λ ;
- Infrared spectroscopy and microscopy — to detect chemical or morphological changes;
- Visual inspection — to detect encapsulation failure or leakage.

To address this gap, we propose a set of practical failure thresholds (Table 2), which aggregate key performance indicators across thermophysical and structural domains. These thresholds can be used to define when a PCM has degraded beyond acceptable limits for safe and efficient TES operation.

Table 2.: Failure Criteria for PCM in TES Systems

Parameter	Failure Threshold	Effect on System Performance
Latent heat of fusion (ΔH_f)	>20% reduction from initial value	Reduced energy storage capacity
Phase change temperature (T_f)	$\pm 2^\circ\text{C}$ deviation from nominal value	Incompatible thermal integration, control instability
Thermal conductivity (λ)	>15% reduction	Lower heat exchange efficiency
Supercooling tendency	$\Delta T_f > 5^\circ\text{C}$ compared to initial	Delayed heat release, hysteresis
Visual integrity / leakage	Encapsulation rupture or PCM leakage	Risk of mechanical failure, safety hazard
Mass loss (evaporation/chem. loss)	>10% mass loss	Altered material balance, chemical instability

To illustrate the rate of thermal degradation in different PCM types, Figure 1 presents the relative latent heat retention (ΔH_f) as a function of the number of thermal cycles. The data reflects typical experimental trends for three common PCM categories.

As shown, paraffins exhibit a gradual and relatively linear degradation profile, remaining functionally stable over long durations. Salt hydrates, by contrast, suffer steep performance drops due to material stratification and water migration. Eutectic mixtures offer more stable melting points but demonstrate moderate degradation depending on formulation and phase compatibility.

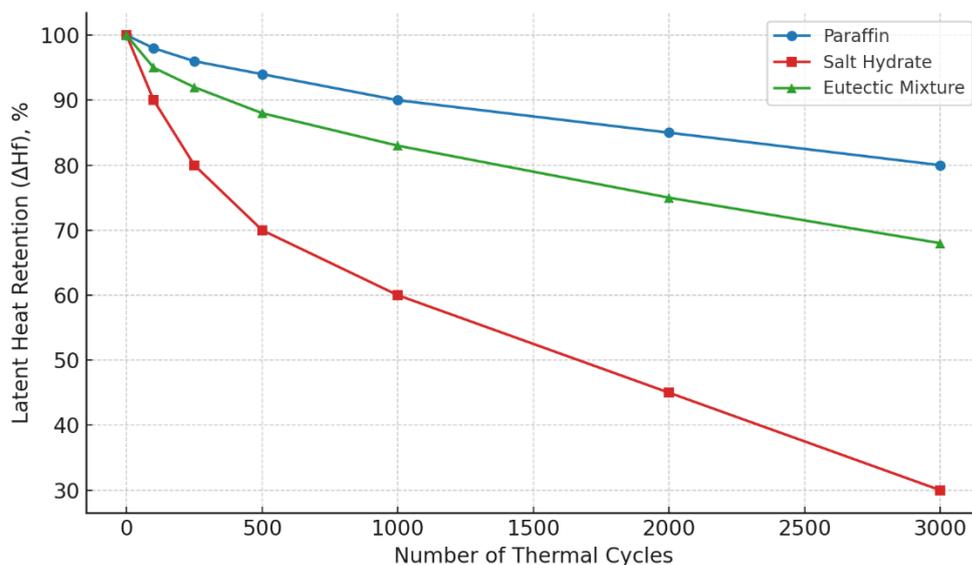


Figure 1.: Latent Heat Retention of PCMs Over Thermal Cycling

In summary, the challenge of PCM degradation poses a significant barrier to the long-term reliability of TES systems. The absence of clear, quantifiable failure metrics complicates material selection and lifecycle planning [8-10]. Therefore, it is essential to establish comprehensive reliability models that integrate experimental degradation data, mechanistic understanding, and failure thresholds. This will facilitate the design of robust, high-performance TES systems aligned with the reliability requirements of renewable energy infrastructures.

As evident, paraffins show relatively stable performance over 1000–3000 cycles, while salt hydrates degrade rapidly due to phase segregation and water loss. Eutectic mixtures demonstrate intermediate behavior.

To quantitatively describe the degradation behavior of PCM under repeated thermal cycling, empirical models are frequently employed. One of the most widely used expressions for latent heat degradation is based on exponential decay, assuming that the reduction in thermal storage capacity follows a first-order degradation process:

$$\Delta H_f(N) = \Delta H_{f0} \cdot e^{-kN}$$

where: $\Delta H_f(N)$ is the latent heat of fusion after N thermal cycles, ΔH_{f0} is the initial latent heat (at $N=0$), k is the degradation rate constant (cycle^{-1}), N is the number of completed thermal cycles.

This model effectively captures the observed exponential trend in latent heat degradation, particularly in salt hydrates and eutectic materials. The parameter k can be experimentally identified via least squares fitting of DSC (Differential Scanning Calorimetry) data obtained after controlled cyclic aging tests.

For example, a PCM with an initial latent heat of 200 kJ/kg and a degradation constant $k=2.5 \times 10^{-4}$ will retain approximately 78% of its capacity after 1000 thermal cycles:

$$\Delta H_f(1000) = 200 \cdot e^{-0.00025 \cdot 1000} \approx 156.8 \text{ kJ/kg}$$

This corresponds closely with experimental trends observed in Figure 1, particularly for salt hydrates. For paraffins, the value of k is typically an order of magnitude lower, reflecting their higher thermal stability but lower thermal conductivity.

By integrating such empirical models into PCM reliability assessment, it becomes possible to:

- estimate the service life of a material under a given cycling regime;
- compare degradation rates across material types and compositions;
- establish predictive maintenance schedules based on thermal performance decay;
- and develop design margins for TES system capacity to compensate for gradual loss of storage efficiency.

Ultimately, combining experimental degradation profiles (as shown in Figure 1), failure thresholds (Table 2), and predictive models like the one above provides a robust foundation for engineering PCM-based TES systems with quantified reliability.

IV. Conclusions

The presented analysis highlights the dynamic degradation behavior of phase change materials (PCMs) under thermal cycling and provides a quantitative foundation for predicting their end-of-life based on latent heat retention. The empirical model, described by the exponential decay function $\Delta H_f(N) = \Delta H_{f0} \cdot e^{-kN}$, demonstrates good agreement with experimental trends for various PCM classes.

As observed in the experimental graph and model curves (see Figure 2), different PCM types exhibit distinct degradation profiles.

This radar chart provides a comparative assessment of three main classes of phase change materials (PCMs)—Paraffin, Salt Hydrate, and Eutectic Mixture—based on three key reliability-related criteria: thermal stability, heat storage capacity, and cycle life. Each axis represents a normalized score (0–10 scale), where higher values indicate superior performance.

- Paraffin shows strong thermal stability and long cycle life, making it a preferred choice for applications requiring durability, albeit with moderate latent heat.
- Salt Hydrate exhibits high heat capacity but suffers from poor stability and reduced cycle life due to issues like phase separation and supercooling.
- Eutectic Mixture offers a balanced profile, performing moderately well across all criteria, which makes it suitable for systems that require a compromise between capacity and longevity.

The diagram serves as a visual decision-making tool for selecting PCMs in reliability-critical thermal energy storage applications.

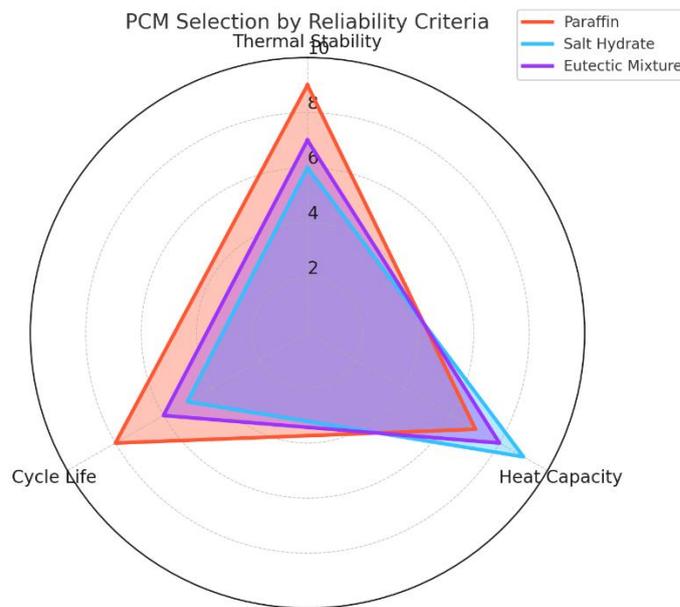


Figure 2.: Reliability-Based Comparison of PCM Types Using Radar Diagram.

These differences are also summarized in Table 2 (Failure Criteria for PCMs), which outlines key indicators such as melting point shift, phase separation, and heat capacity loss. Understanding these failure modes is essential for selecting the appropriate PCM for specific operational regimes.

Furthermore, the integration of the empirical degradation model allows for predictive maintenance and design optimization. By establishing a threshold (e.g., $\Delta H \leq 160$ kJ/kg) and solving for the corresponding cycle limit, engineers can define the effective service life of thermal energy storage units. For instance, with $k=2.5 \times 10^{-4}$, the material reaches this limit after approximately 892 cycles, enabling scheduling of inspections or replacements before functional failure occurs.

This modeling approach not only enhances the reliability-based design of PCM systems but also supports life-cycle cost analysis by quantifying degradation rates. Future studies may incorporate temperature-dependent $k(T)$, multi-cycle hysteresis, or mechanical fatigue for more comprehensive assessment.

In summary, the combination of empirical data, analytical modeling, and visual representation provides a robust methodology for evaluating and improving PCM reliability in long-term thermal applications.

This study integrates empirical degradation data with analytical reliability modeling, providing a robust framework for predicting the service life of phase change materials in thermal energy storage systems. By establishing failure thresholds and modeling degradation kinetics, the approach supports reliability-centered design, predictive maintenance, and lifecycle cost optimization. This contribution advances the reliability engineering of TES materials, facilitating more durable and efficient renewable energy storage solutions.

References

- [1] Prieto, C., & Cabeza, L. F. (2019). Thermal energy storage (TES) with phase change materials (PCM) in solar power plants (CSP). Concept and plant performance. *Applied Energy*, 254, 113646.
- [2] Elkhatat, A., & Al-Muhtaseb, S. A. (2023). Combined “renewable energy–thermal energy storage (RE–TES)” systems: a review. *Energies*, 16(11), 4471.

- [3] Piriyeva, N. M., Karimova, R. K., & Abdullayeva, G. K. (2025, June). *High-temperature heat-insulating materials: A compromise between thermal conductivity and reliability*. *Reliability: Theory & Applications*, 2(84), 408–413. <https://doi.org/10.24412/1932-2321-2025-284-408-413>
- [4] Kerimzade, G. S. (2025, March). *Features of hanging the parameters of induction control support*. *IJ TPE Journal*, 1, 69–80.
- [5] Kerimzade, G. S. (2024). *Structure of the monitoring and tracking electromechanical control system*. *Przeglad Elektrotechniczny*, 100(7), 295–297.
- [6] Rzayeva, S. V., Piriyeva, N. M., & Guseynova, I. A. (2024). *Analysis of reliability of typical power supply circuits*. *Reliability: Theory & Applications*, 19(3), 173–178.
- [7] Piriyeva, N. M., Abdullayeva, G. K., & Bakhtiyarov, A. A. (2024). *Engineering approaches to minimizing environmental impact of thermal power plants*. *International Journal on Technical and Physical Problems of Engineering*, 16(4), 231–243.
- [8] Safiyev, E., Rzayeva, S., & Karimova, R. (2024). *The importance of diagnostics of electrical equipment at thermal power plants for ensuring the reliability of power systems*. *Przeglad Elektrotechniczny*, 9, 127–130.
- [9] Karimova, R. K., & Rzayeva, S. V. (2023). *Comparison of thermal conductivity of aqueous and formamide solutions (BeCl₂) at high temperatures*. *International Journal on Technical and Physical Problems of Engineering*, 15(3), 156–159.
- [10] Sharma, R. K., Ganesan, P., & Tyagi, V. V. (2016). *Long-term thermal and chemical reliability study of different organic phase change materials for thermal energy storage applications*. *Journal of Thermal Analysis and Calorimetry*, 124(3), 1357-1366.