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A Review on High-Temperature Phase-Change Materials for Waste Heat Recovery: Advances in Materials, System Integration, and Industrial Sustainability

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ABSTRACT

This paper reviews recent advances in high-temperature phase-change materials (PCMs) for waste heat recovery (WHR), focusing on applications above 150°C, which have received less attention than low-temperature systems. It critically examines material developments, system integration strategies, and sector-specific uses, aiming to identify pathways for broader industrial adoption. The study uses a systematic approach that combines analysis of thermophysical properties, stability, and thermal conductivity with evaluation of system designs such as cascaded storage, segmented heat exchangers, hybrid configurations, and techno-economic performance. Findings show notable progress in metallic alloys, molten salts, and composite and nano-enhanced PCMs, each offering benefits in energy density, responsiveness, and stability. Case studies demonstrate that integrating high-temperature PCMs into WHR systems can improve energy recovery efficiency by 20%–40%, reduce thermal variability, increase usable energy output, and achieve payback periods of 3–5 years in some applications. However, trade-offs between cost, durability, and performance remain significant, and no single PCM meets all industrial requirements. The review emphasizes that optimal results depend on codesigning materials and system architecture rather than isolated improvements. Future work should prioritize standardized testing, scalable and corrosion-resistant encapsulation, and sustainable composite materials to support wider deployment and industrial decarbonization.

1 | Introduction

Improving energy efficiency has highlighted the crucial role of waste heat recovery (WHR) in driving sustainable innovation [1, 2]. Phase-change materials (PCMs) are gaining attention for their capacity to manage fluctuating thermal loads, balance supply and demand mismatches, and store a large amount of latent heat [3]. In particular, high-temperature PCMs are suited for high-enthalpy WHR in energy-intensive sectors such as steelmaking, ceramic processing, and concentrated solar power (CSP), where conventional systems often fall short in efficiency and flexibility [4–6]. Despite their potential, the widespread use of PCMs in energy-intensive industries such as steel production, automotive, along with ceramic kilns, foundries, internal combustion engines and maritime applications remains limited. This is largely due to challenges in aligning material properties with specific application needs and ensuring economic feasibility. This article examines the latest advancements in PCM-based technologies designed for recovering waste heat above 150°C, aiming to provide insights into how material advancements

and system integration can effectively utilize the intermittent nature of waste heat sources. The high variability of temperature and flow rate makes traditional recovery systems either inefficient or undersized. However, recent innovations in materials such as metallic alloys like Al-12%Si [4], advanced molten salts like H500 and H885 [7] and composite PCMs incorporating waste foundry sand (WFS) [8] show that PCMs can do more than just store heat. They act as dynamic thermal buffers, capable of reshaping fluctuating heat profiles [9] especially when integrated with advanced system designs such as modular latent heat storage units, cascade thermal configurations [10], or nano-enhanced heat exchangers [11]. These materials help stabilize steam production, improve turbine performance, and reduce emissions during cold starts. This demonstrates that PCMs can transform thermal variability from a limitation into a valuable resource.

This review evaluates recent developments in PCMs across three core dimensions: material innovation, system-level design, and sector-specific integration. It focuses on how key PCM properties, such as melting temperature, thermal conductivity, and cyclic stability, interact with operational constraints, including spatial limitations in shipboard systems or transient thermal profiles in engine exhausts. Recent advancements in encapsulation methods, such as alumina-coated Al–Si alloys for capturing heat from steel production gases [12] and chloride salt-based nanocomposites for CSP [13] applications, illustrate how material development is being customized to meet the thermal demands of different sectors. For instance, Al-12%Si's high thermal conductivity is ideal for handling steelmaking exhaust at around 600°C [4], while maritime systems benefit from compact, corrosion-resistant materials like $LiNO_3$–NaCl cascades [14]. Similarly, in the automotive field, nano-enhanced paraffins are used for quick preheating of intake air [11], whereas PCMs integrated with ORC require carefully selected melting temperature to manage general variable heat inputs [15]. In addition to the advancements reported, this study critically evaluates the trade-off that influences the real-world implementation of PCMs. Key considerations include the balance between energy density and thermal response, the cost-to-durability ratio and the scalability potential, particularly in the context of bio-derived[1] and metal–organic framework (MOF) enhanced composites [16]. The experimental findings are discussed alongside techno-economic and deployment metrics, including payback periods for steel billet heating applications [15], and volumetric efficiency in naval energy storage [17].

Recent studies highlight the importance of adopting a systematic and structured approach [18] to embedding thermal characteristics of PCMs into the design of thermal systems [19]. In particular, the development of high-temperature PCMs for WHR demands a complex synergy between material properties and engineering constraints. This integration is not merely additive but synergistic, requiring that thermophysical properties such as melting point, thermal conductivity, and latent heat be tailored to match system architectures and operational conditions, including cyclic durability, spatial constraints, and fluctuating thermal loads. Only through such a targeted integration strategy can high-temperature PCMs realize their full potential in real-world WHR system applications. This ensures that the materials' heat storage capabilities match the fluctuating profile of waste heat in real-world applications [20]. This is especially critical in sectors like steelmaking and maritime operations, where temperature changes are significant. Ultimately, this review presents high-temperature PCMs as flexible tools that can support decarbonization across different sectors. Waste heat should be viewed as a valuable energy source; when combined with PCMs, it can be both stabilized and enhanced to improve energy use. Section 2 discusses the physical properties that are most relevant when assessing high-temperature PCMs for WHR, providing the basis for comparing different material solutions. It further classifies state-of-the-art PCM materials, including metallic alloys, molten salts, composites, and advanced formulations, while critically examining their thermophysical behaviour and inherent trade-offs. Section 3 looks at real use cases across different industrial sectors, such as steelmaking, ceramics, automotive systems, ORC, CSP, and maritime applications showing what benefits high-temperature PCMs deliver in practice and what typically limits their adoption. Section 4 shifts the focus from individual applications to system integration, discussing how advanced layouts (e.g., cascaded storage and segmented heat exchangers (SHE)) and hybrid configurations (e.g., PCM coupled with TEGs or sCO_2 cycles) can improve performance. It also summarizes the main economic drivers behind deployment, payback time and cost-performance trade-offs. Section 5 then outlines the key barriers and research needs, such as degradation, limited heat transfer, encapsulation, standardized testing and scalable manufacturing, together with emerging directions such as AI-assisted design and sustainable composites.

1.1 | Review Approach

The review adopts a structured and multidimensional methodology to ensure a comprehensive and unbiased assessment of high-temperature PCMs and WHR system designs.

The selection of studies followed explicit inclusion criteria to ensure consistency and relevance. Only works reporting operating temperatures above 150°C, with a clear link to WHR applications, and providing quantitative thermophysical and/or performance data (e.g., melting temperature, latent heat, thermal conductivity, cyclic stability, energy output, efficiency, or payback period) were retained. Studies focused solely on low-temperature PCMs, purely theoretical concepts without validation, or applications unrelated to WHR were excluded. This filtering step ensured that the reviewed materials and systems are directly comparable in the context of high-temperature industrial WHR.

Materials are systematically classified into four main categories: (i) metallic alloys, (ii) molten salts and inorganic eutectics, (iii) composite and bio-derived PCMs, and (iv) advanced multifunctional formulations. This classification combines compositional aspects with functional performance, allowing a consistent comparison across studies. In parallel, WHR systems are grouped according to their integration strategy (packed beds, cascaded latent storage, SHE, hybrid sensible–latent configurations) and application domain (steelmaking, ceramics, automotive and internal combustion engines, CSP, ORC, maritime and other energy-intensive sectors).

To compare materials and systems, the present review uses a unified evaluation approach that links material-level evidence

(thermophysical properties, degradation behaviour and energy density) to system-level considerations (heat exchanger design, storage configuration and operational constraints), complemented by application-driven criteria across temperature ranges and industrial sectors. Techno-economic indicators are included to support deployment-oriented comparisons (e.g., payback time, levelized cost of storage (LCOS) and scalability). To minimise selection bias, the review covers both established and emerging PCM families and draws on experimental, simulation and techno-economic studies, critically discussing reported benefits alongside limitations, while cross-sector comparisons and multicriteria evaluation approaches improve objectivity and help identify gaps such as the lack of standardized testing protocols. To address these gaps, this review focuses on high-temperature PCMs (melting temperature higher than 150°C) for WHR in energy-intensive industrial sectors, with particular emphasis on steelmaking and high-temperature thermal storage systems such as CSP and thermocline-based units. The paper is structured around four guiding research questions:

RQ1. Which classes of high-temperature PCMs (metallic alloys, molten salts, composite, and advanced formulations) are most suitable for WHR above 150°C in terms of thermophysical properties and stability?

RQ2. How do different system-integration strategies (packed beds, cascaded latent storage, HE, and hybrid sensible–latent configurations) shape material requirements and the performance of PCM-based WHR systems?

RQ3. What energy and operational benefits have been demonstrated by high-temperature PCMs in key energy-intensive sectors (e.g., steelmaking, ceramics, CSP, and maritime), and what limitations emerge under realistic operating conditions?

RQ4. Which techno-economic trade-offs and standardization issues currently limit the large-scale deployment of PCM-based WHR technologies, and which directions appear most promising to overcome them?

Completeness and minimisation of selection bias are addressed by including a broad range of PCM families (from well-established Al–Si alloys and nitrate salts to emerging nano-enhanced and bio-derived composites) and by covering multiple industrial sectors with different waste-heat profiles (steelmaking, ceramics, automotive, CSP, ORC, maritime). The review deliberately reports both successful implementations and documented limitations (e.g., degradation, corrosion, cost barriers, and scalability issues), thus avoiding an overemphasis on positive results. Cross-sector comparisons and the use of multicriteria decision analysis studies further reduce the risk of bias by providing a structured basis for weighing performance, cost, and retrofit constraints across different materials and applications.

2 | High-Temperature PCM Materials

High-temperature WHR systems are highly dependent on the development of PCMs that can operate reliably under extreme thermal conditions while maintaining thermodynamic efficiency, cost-effectiveness, and scalability for industrial deployment[2]. High-temperature PCMs are commonly defined as those with melting points above 150°C [21], serving as a critical interface between material innovation and energy systems engineering. Their development must address competing performance demands: high energy density to maximize storage capacity, rapid thermal response to match fluctuating waste heat profiles, and structural durability to withstand corrosive environments and repeated phase transitions. This section traces the evolution of PCMs from conventional metallic and salt-based materials to advanced composites[3] and novel formulations, critically examining the thermophysical trade-offs that influence their practical viability. Recent developments indicate a shift from single-component PCMs to hybrid systems tailored for high-temperature applications. As industries such as steel manufacturing to CSP increasingly require customized thermal management solutions, PCMs are being engineered as integrated systems combining alloys, salts, and bio-derived or synthetic matrices to overcome inherent limitations. The following analysis categorizes PCMs by their operational temperature thresholds, explores the interrelated properties of melting point, latent heat, thermal conductivity, and cyclic stability, and evaluates sector-specific barriers to adoption in different sectors. To compare materials and systems in a unified way, the review employs an evaluation framework that links material-level metrics (thermophysical properties, degradation behaviour, energy density) with system-level parameters (temperature gradients, HTF inlet temperature and flow rate, storage configuration, heat exchanger geometry) and techno-economic indicators (payback period, LCOS, and scalability). Rather than listing parameters in isolation, this framework considers their combined influence on thermal performance, durability and economic feasibility, reflecting the multiscale nature of real WHR systems.

2.1 | State-of-the-Art PCM Materials

The development of high-temperature PCMs for WHR represents a sophisticated intersection of material science and application-oriented engineering. These materials are typically categorized into four primary categories, such as organic PCMs, salt hydrates, eutectic PCMs and high-temperature salts. Each address unique thermal, economic, and operational challenges. Their practical implementation is governed by a delicate interplay of thermophysical properties, including melting temperature, latent heat capacity, thermal conductivity, cyclic stability, and volumetric energy density, which collectively define their industrial applicability. This comprehensive analysis explores each category, emphasizing both classification frameworks and strategies for optimizing key performance parameters.

2.1.1 | Metallic Alloys and Eutectics Systems

Metals and metal-based alloys (such as Al–Si, Mg–Cu binary systems, Zn/Al/Mg) are characterized by their high thermal conductivity, often exceeding 100 W/m·K and well-defined melting points, which facilitate fast thermal charging and discharging as well as high volumetric energy storage. Despite these advantages, their application is limited by issues related to corrosion at elevated temperatures, necessitating the use of durable

encapsulation strategies. The thermophysical properties of selected high-temperature alloys, Al-12%Si, $Mg_{84}Cu_{16}$, and Zn/Al/Mg, are summarized in Table 1. The selection of Al-12%Si, $Mg_{84}Cu_{16}$, and Zn/Al/Mg alloys is based on their favourable thermophysical characteristics, which are essential for effective performance as PCMs in WHR systems. Al-12%Si, a eutectic aluminium-silicon alloy, offers high thermal conductivity and a sharply defined melting point, enabling rapid and reliable thermal cycling. $Mg_{84}Cu_{16}$ benefits from the lightweight nature of magnesium and the thermal efficiency of copper, providing a tuneable melting range and good energy storage potential. The Zn/Al/Mg ternary system combines the strengths of its constituent metals, delivering enhanced corrosion resistance, stable thermal behaviour, and efficient heat transfer. These properties collectively support the fast thermal charging and discharging required in WHR applications, while also contributing to high volumetric energy storage capacity.

- ***Melting Temperature and Thermal Source Alignment***: The Al-12%Si alloy, with a melting point (T_{melt}) of 576°C, exhibits strong thermal compatibility with steelmaking off-gases, which typically reach around 600°C. This compatibility contributes to a 34% reduction in thermal fluctuations and a 22% enhancement of arc furnace power generation [4, 15]. In contrast, $Mg_{84}Cu_{16}$ (melting at 488°C) and Zn/Al/Mg alloys (melting between 370°C–390°C) show potential for use in thermocline-based thermal energy storage systems. However, their behaviour under thermal shock conditions has not been thoroughly investigated [5, 22, 23].
- ***Volumetric Energy Density***: $Mg_{84}Cu_{16}$ demonstrates a high volumetric energy density of ≈571 MJ/m^3, attributed to its substantial density and latent heat of fusion (ΔH = 232 kJ/kg). However, to prevent interfacial degradation, the use of advanced encapsulation materials, such as titanium or ceramic, is required, which significantly increases system costs [22–25].
- ***Thermal Conductivity and System Design***: Although the intrinsic thermal conductivity exceeds 100 W/(m·K), integrating hybrid configurations, such as Al-12%Si combined with finned heat exchangers, enables efficient heat transfer. These designs have demonstrated up to 79.5% charging efficiency in packed bed systems by offsetting the inherent thermal limitations of PCMs [4, 8].
- ***Cyclic Stability***: To counteract oxidation-induced degradation, advanced encapsulation strategies such as fluidized-bed-deposited PyC/SiC coatings on aluminium spheres are employed. These protective layers maintain structural and thermal integrity over 10 thermal cycles between 300°C and 850°C, preserving a latent heat capacity of 293.3 J/g and accommodating up to 14.5% volumetric expansion [26, 27].

2.1.2 | Molten Salts and Inorganic PCMs

Salt-based PCMs, such as chlorides, nitrates, and carbonates, are effective within intermediate to high temperature ranges (200°C–900°C). they are relatively moderate costs, offer adjustable melting points, and maintain stability over repeated thermal cycles. However, their practical use is hindered by issues like moisture absorption, subcooling, and inherently low thermal conductivity (0.5–2 W/m·K), which often require the use of additives or geometric enhancements to improve the performance. Table 2 presents thermophysical properties of selected inorganic PCM mixtures, including H500, H885, $MgCl_2$–KCl–NaCl, and $LiNO_3$–KCl–$NaNO_3$.

TABLE 1 | Key thermophysical properties and enthalpy retention of Al-12%Si, $Mg_{84}Cu_{16}$, and Zn/Al/Mg alloys.

Material	T_{melt}, °C	ΔH, kJ/kg	K, W/m·K	Reported ΔH retention	Notes
Al-12%Si	576	560	160	95% (100 cycles)	High conductivity; corrosion issues with steel; 3-year payback in steelmaking [4, 15].[4]
$Mg_{84}Cu_{16}$	488	232	97	88% (50 cycles)	High volumetric energy density (571 MJ/m^3); requires titanium encapsulation [22]
Zn/Al/Mg alloys	370–390	—	50–80	—	Potential for CSP; unstable under thermal shock [5]

TABLE 2 | Thermophysical properties of selected inorganic PCM mixtures: H500, H885, $MgCl_2$–KCl–NaCl, and $LiNO_3$–KCl–$NaNO_3$.

Material	T_{melt}, °C	ΔH, kJ/kg	K, W/m·K	Reported ΔH retention	Notes
H500 ($NaNO_3$–KNO_3)	509	260	1.5	88% (20 cycles)	Corrosion-resistant; steel industry retrofits [28].
H885 (KCl–$MgCl_2$)	888–891	191–212	1.5	96.3% (20 cycles)	Stable in ceramic kilns; 15–20% cost increase [5, 28].
$MgCl_2$–KCl–NaCl	380	198	0.5	50% (20 cycles)	Hygroscopic decomposition; HCl release [29].
$LiNO_3$–KCl–$NaNO_3$	350	300	1.5	85% (30 cycles)	Requires graphite foam hybridization [30].

- ***Melting Temperature and Application-Specific Tuning***: Binary eutectic salt like KNO_3–$NaNO_3$ ($T_{melt} = 222°C$) is well-suited for CSP systems, while $MgCl_2$–KCl–NaCl ($T_{melt} = 380°C$) enables stable isothermal operation in industrial furnaces [29]. Customized salt blends are also developed for sector-specific needs, such as H500 ($T_{melt} = 509°C$) for retrofitting steel processes, and H885 ($T_{melt} = 888°C–891°C$) for ceramic kiln operations. Although H885's narrow melting range minimizes thermal inertia, it introduces corrosion challenges that necessitate the use of alumina-based containment materials [28, 29, 31]. High-temperature PCMs like H500 and H885 are designed for efficient performance in environments with thermal loads beyond conventional PCMs limits. H500, with a melting point around 500°C, is typically made from inorganic salts or eutectic mixtures (e.g., sodium or potassium-based), offering high latent heat, thermal stability, and high thermal conductivity. Its physical resilience and nonflammable nature make it suitable for industrial heat recovery. In contrast, H885 is designed for ultra-high-temperature scenarios, with a melting point of ≈885°C. This is composed of metallic alloys or high-temperature eutectic mixtures, such as aluminium-silicon or other refractory compounds. This is enabling it to withstand extreme thermal conditions without degradation. Both PCMs exhibit excellent energy density and thermal conductivity, characteristics that support their integration into advanced thermal management systems in sectors such as steel production, ceramics, and CSP. These may require special encapsulation or containment due to operating temperatures.
- ***Latent Heat and Real-World Performance***: In practical applications, the latent heat of salt-based PCMs often underperforms compared to theoretical predictions due to factors impurities and moisture-induced degradation. In real-world applications, salt-based PCMs often deliver less latent heat than expected due to impurities and moisture-induced degradation over time. This means the actual energy stored and released during phase change is lower than the theoretical values. For example, nitrate salts such as KNO_3-$NaNO_3$ ($\Delta H = 360$ kJ/kg) are prone to subcooling, which reduces their discharge effectiveness, i.e., the fraction of stored latent heat that can be released within the required temperature and time window of the application. Chloride-based mixtures like $MgCl_2$–KCl can experience up to a 50% reduction in latent heat capacity due to moisture absorption [29, 32–34]. Although LiF-KF mixtures offer a high latent heat ($\Delta H = 618$ kJ/kg), their low thermal conductivity (3.98 W/m·K) limits broader use, confining them to niche CSP applications [22]. Despite their dominance in CSP, nitrate eutectics like KNO_3-$NaNO_3$ continue to face unresolved subcooling challenges that hinder discharge efficiency [32], while chloride salts suffer significant energy losses (ΔH by 50%) from moisture-driven decomposition compared to theoretical values [33, 34]. These deviations indicate that latent heat and stability values reported for salt-based PCMs are often test-condition-dependent rather than fixed material constants. Therefore, high nominal ΔH values alone are insufficient for material selection unless cycling protocol, atmosphere, moisture-control procedure, and postcycling phase composition/stability are also reported.
- ***Thermal Conductivity Enhancement:*** To overcome the inherently low thermal conductivity of salt-based PCMs, hybrid strategies have been developed. Incorporating 30 wt% graphite flakes into $NaLiCO_3$ significantly reduces internal temperature gradients through thermal percolation [35]. Similarly, integrating highly porous (85%) silicon carbide (SiC) foams into solar salt formulation boosts thermal conductivity threefold, reaching 1.49 W/m·K, and shortens solidification time by 52% [36]. In another approach, the eutectic mixture $LiNO_3$–KCl–$NaNO_3$ ($\Delta H = 300$ kJ/kg) is combined with graphite foam structures to extend discharge duration while compensating for its low thermal conductivity (1.5 W/m·K) [30, 37].
- ***Cyclic Stability and Degradation Mechanisms***: H885 salt formulation demonstrates remarkable thermal reliability, retaining 96.3% of its latent heat after 20 thermal cycles (3.7% loss) under the reported test conditions; however, this value should be compared cautiously with chloride-based salts which degrade due to hydrogen chloride (HCl) off-gassing [28, 29]. While encapsulation techniques, such as nickel-coated ceramic shells, can extend material lifespan, they introduce additional design and manufacturing complexity.
- ***Chloride-Fluoride Configurations***: Layered salt systems (as shown in Figure 1) can improve thermal energy output. Chloride-fluoride configurations show up to 20% gain annually. This is due to better heat transfer and stability. However, their long-term use faces material degradation. High temperatures (higher than 600°C) accelerate corrosion [38].

Vacuum drying reduces moisture-related risks. Corrosion-resistant alloys are essential for containment. Impurity control remains a key challenge. Future work must focus on system durability. Operational safety and cost effectiveness are also critical.

2.1.3 | Composite and Bio-Derived PCMs

Composite materials are engineered to overcome inherent limitations of base PCMs, such as low thermal conductivity and phase separation, by incorporating them into porous supports like graphite, industrial residues, or bio-derived organics. These structures enhance energy storage capacity, structural integrity, mechanical stability and environmental sustainability, although their mechanical strength may diminish at temperatures exceeding the melting point. Table 3 presents the thermophysical properties of selected composite and carbon-based PCMs, including WFS-CPCM, Dynalene MS-XTT, popcorn-carbon/adipic acid, and silicon. These materials demonstrated diverse thermal behaviors and storage capacities, offering promising alternatives for high-temperature thermal energy storage applications, particularly where enhanced conductivity and structural stability are required.

- ***Volumetric Energy Density and Waste Valorization***: In terms of volumetric energy density and waste utilization, composites using WFS with $NaNO_3$ or solar salt

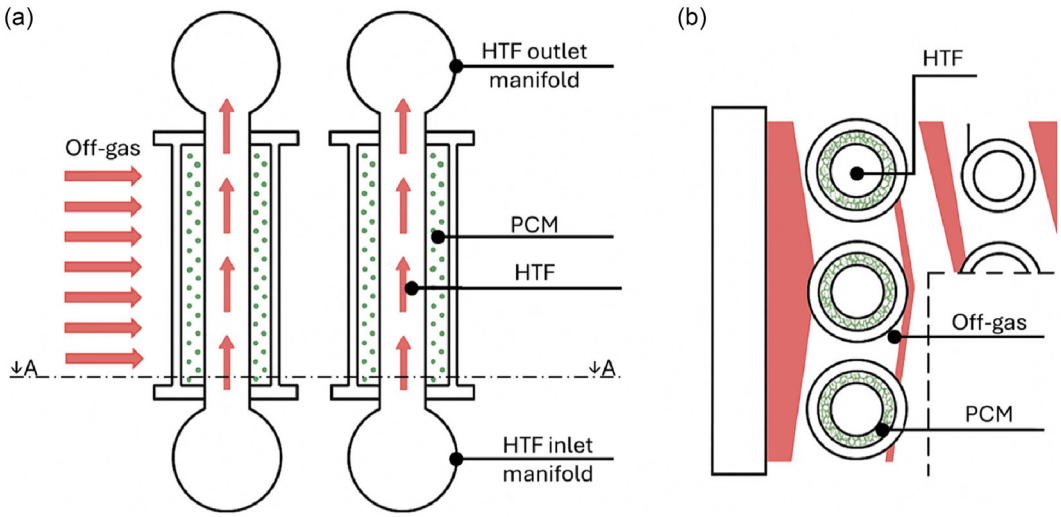

FIGURE 1 | Geometrical configuration of HESU (a) lateral and (b) A–A section view (adapted from [4].

TABLE 3 | Thermophysical properties of selected composites and carbon-based PCMs: WFS-CPCM, Dynalene MS-XTT, popcorn-carbon/adipic acid, and silicon, MOF-stabilized mannitol, and NaCl–Na_2CO_3/okra-derived SiC composite.

Material	T_{melt}, °C	ΔH, kJ/kg	K, W/m·K	Reported ΔH retention	Notes
WFS-CPCM ($NaNO_3$/solar salt)	308	542	1.2	90% (100 cycles)	Volumetric energy: 1,074–1,117 MJ/m; mechanical degradation [8].
Dynalene MS-XTT/ graphite foam	355	200	110	92% (50 cycles)	30% PCM volume sacrificed for conductivity [37].
Popcorn-carbon/ adipic acid	160	195	1.18	93.83% (100 cycles)	93.83% photothermal efficiency; hygroscopic [39].
Silicon	1414	1800	148	—	Ultra-high energy density; vacuum containment required [40].
MOF-stabilized mannitol	—	193.45	1.17	ΔH_m change: 8.1% (200 cycles)	Supercooling reduced by 18.42%; leakage rate 4.98% after 24 h [16].
NaCl–Na_2CO_3 in okra-derived SiC skeleton	630	186–207	17.4–30.5	From 192.56–165.68 kJ/kg after 500 cycles)	Bio-derived/biomimetic SiC skeleton; thermal storage density 422 J/g; thermal storage power density 101% greater than pure h-PCMs [41]

achieve energy densities between 1,074 and 1,117 MJ/m^3, while accommodating up to 9.7% volumetric expansion during phase change [8, 14, 42]. Similarly, steel slag porous ceramics (SSPC) infused with $NaNO_3$ can hold up to 77.32 wt% PCM loading and retain 96% of their latent heat after 50 thermal cycles [43].

- ***Thermal Conductivity Enhancement Strategies in PCMs:*** A bio-based composite made from okra-derived SiC and NaCl-Na_2CO_3 shows high thermal conductivity (17–31 W/m·K) and latent heat of 207 J/g [41]. This bio-derived/biomimetic approach is particularly relevant because the okra-derived SiC skeleton provides continuous heat-transfer pathways while preserving high PCM loading, although long-term deployment still requires further validation under realistic operating conditions. Graphite foam filled with Dynalene MS-XTT increases conductivity to 110 W/m·K, (40 times higher than pure salts), though it reduces PCM volume by 30% [37]. This trade-off indicates that a higher effective thermal conductivity does not necessarily translate into a better storage system. In highly conductive porous matrices, faster charging and discharging may be obtained at the expense of active PCM content, reducing the effective latent storage density. Therefore, conductivity-enhancement strategies should be assessed together with usable stored energy, charging/discharging time, cost, scalability, and system compactness. Furthermore, carbon from popcorn combined with adipic acid achieves 93.83% photothermal efficiency in solar-WHR systems [39]. Hybrid mixtures like Solar Salt with Al–Cu-Si microencapsulated PCMs improve thermal conductivity by 380%, reaching to 2.27 W/m·K, by eliminating air gaps through salt infiltration [44].

- ***Cyclic Stability and Microstructural Evolution***: Mannitol stabilized with MOF shows promising results, reducing supercooling by 18% and maintaining 97% of its latent heat after 200 cycles thanks to its hierarchical pore structures. However, the complexity of MOF synthesis limits its scalability. This material illustrates the potential of MOF-derived porous scaffolds to improve shape stability, leakage control, and heat transfer, although scalability remains an open issue [16]. In another case, $NaLiCO_3$ combined with MgO and graphite improves thermal uniformity over 50 cycles, with radial temperature differences decreasing from 62°C to 29°C due to internal salt redistribution [35]. On the other hand, biomimetic NaCl-Na_2CO_3/SiC composites experience a 14% loss in latent heat after 500 cycles, primarily due to volatilization, highlighting the need for controlled atmospheric conditions [41]. Unprotected $NaNO_3$ also shows degradation, with a 12% reduction in latent heat over cycles [7]. In contrast, shape-stabilized composites like Al-25Si embedded in Al_2O_3 retain over 95% of their latent heat after 50 cycles, demonstrating strong thermal durability [45].

2.1.4 | Advanced and Multifunctional Formulations

Emerging PCMs incorporate nanomaterials, doped ceramics, or pure elements to achieve rapid thermal responses, broader operating temperature ranges, and multifunctional capabilities such as combined heat and data storage. Although these materials are often expensive, they offer significant advantages in extreme environments. Table 4 summarizes the thermophysical properties of SiC-doped Sb_2Te, soda-lime glass, and Zn/Al/Mg alloys. These materials exhibit distinct thermal characteristics that influence their performance as PCMs in high-temperature energy storage systems, particularly in applications requiring stability, durability, and efficient heat transfer.

- ***Ultra-High-Temperature Performance***: For ultra-high temperature applications, silicon stands out with a melting point of 1414°C, and a high latent heat of $1.8{\cdot}10^6$ J/kg. However, its use is limited to CSP cogeneration due to the unmatched energy density and complex containment needs [40]. Soda-lime glass, with a melting point of nearly 1000°C, and latent heat of ≈2740 kJ/kg, respectively, maintains thermal stability up to 970°C when paired with graphite conductors in Stirling engines [31].
- ***Multifunctionality and Encapsulation***: In multifunctional systems, SiC-doped Sb_2Te nanomaterials deliver ultrafast thermal response (7 ns) and stable crystallization at 251°C, making them suitable for both thermal management and memory technologies [23]. Preoxidized Al-graphite composites achieve high PCM loading (80 wt%) and a ΔH of 188.2 kJ/kg, overcoming previous encapsulation challenges [27]. Microstructural reorganization during cycling improves material uniformity. However, some systems like NaCl-Na_2CO_3/SiC still suffer from volatilization, leading to a 14% loss in latent heat after 500 cycles, which highlights the need for controlled operating conditions [34, 41].
- ***Thermal conductivity trade-offs***: Thermal conductivity trade-offs are often addressed through structural design. For example, ribbed Al channels in diesel heat exchangers reduce the melting time of PCMs by 29.54%, improving heat transfer efficiency [46]. Similarly, adding 0.5 mm-thick transverse stainless-steel fins to hydroquinone-based systems increases effective thermal conductivity (k) by 25.83% [47].

2.1.5 | Synthesis: Balancing Properties for System Integration

Selecting an appropriate PCM involves balancing multiple interrelated properties. The melting point must match the thermal profile of the target system, for example, $LiNO_3$–KCl–$NaNO_3$ suits a 350°C exhaust stream, while Al-12%Si is better for 576°C furnace applications. Latent heat determines storage capacity but can be reduced by impurities, as seen in stearic acid contaminated with palmitic acid [48]. Volumetric energy density, calculated as the product of density and latent heat ($E_v = \rho{\cdot}\Delta H$), influences system compactness. Composites like WFS-CPCMs reach up to 1,117 MJ/m^3, outperforming traditional salts that range between 350 and 550 MJ/m^3 [14, 46, 49, 50]. Stability over repeated cyclic varies depending upon the degradation pathway. H885 suffers from oxidative losses, chlorides degrade through HCl release [28, 29], while MOF-stabilized mannitol maintains 97% of its latent heat after 200 cycles [16]. No single PCM material optimizes across all metrics, making integrated design essential. Innovations in multifunctional composites, hybrid configurations, and advanced encapsulation are helping to resolve these trade-offs. Moving forward, standardize testing, prototype validation, and impurity control will be key to unlocking the full potential of high-temperature PCMs in industrial applications.

2.2 | Application-Driven Selection Criteria

Selecting a suitable PCM involves a complex multidimensional optimization process. It requires precise balancing of melting

TABLE 4 | Thermophysical properties of SiC-Doped Sb_2Te, soda-lime glass, and Zn/Al/Mg alloys.

Material	T_{melt}, °C	ΔH, kJ/kg	K, W/m·K	Reported ΔH retention	Notes
SiC-doped Sb_2Te	251	—	4.2	99% (1,000 cycles)	Dual-use in thermal management/memory tech [23].
Soda-lime glass	~1000	2740	0.79 (graphite-enhanced)	88% (50 cycles)	Brittle; paired with graphite conductors [31].
Zn/Al/Mg alloys	370–390	—	50–80	—	Potential for CSP thermoclines; unstable under thermal shock [5].

point, latent heat, thermal conductivity, volumetric energy density, chemical stability, and cost, all while meeting the specific needs of each application. Newer systems also demand fast thermal response, resistance to corrosion, and durability under frequent cycling.

- ***Low-Temperature Applications Below 200°C:*** For low temperature applications below 200°C, such as maritime systems or cold-start emission control in automotive applications, tailored solutions are essential. In maritime settings, $LiNO_3$-NaCl cascades ($T_{melt} = 208°C$) and pillow-plate latent heat storage like PlusICE A82 (89 kWh/m^3) offer compact designs and corrosion resistance, delivering up to 19% net power gains onboard [14, 17]. For preheating during cold-start, $Na_2SO_4 \cdot 10H_2O$ ($T_{melt} = 32°C$, $\Delta H = 254$ kJ/kg) helps to reduce CO emissions by 64%. However, its performance declines in humid environments due to hydration stability [49].
- ***Temperature Range 200°C–500°C:*** In this range, PCMs are used in different sectors: automotive systems, ceramics processing, and organic Rankine cycles (ORC). Automotive exhaust gas WHR, eutectics like $LiNO_3$–KCl–$NaNO_3$ ($\Delta H = 300$ kJ/kg) and NaOH/$NaNO_3$ ($T_{melt} = 237°C$) help reduce temperature gradients in catalytic converters by 80%. However, their low thermal conductivity (1.5 W/m·K) requires enhancement, such as adding Al_2O_3 nanoparticles, which ca improve charging rate by +34% [11, 24]. In ceramics kilns, H885 remains stable at 888°C–891°C and supports heat recovery from 1100°C exhaust gases. Yet, its use in encapsulation in double-concentric tube systems increases overall cost by 15% [5, 28]. For ORC applications, $LiNO_3$–KCl–$NaNO_3$ ($T_{melt} = 350°C$, $\Delta H = 300$ kJ/kg) enables extended discharge times of up to 51 min at 400°C. Al-12%Si with a high thermal conductivity of 160 W/m·K and a melting point of 576°C, improves ORC capacity factors by 14% through thermal buffering.
- ***Temperature Higher than 500°C:*** For applications above 500°C, PCMs are used in heavy industry and advanced energy systems. In steelmaking, Al-12%Si stand out due to its high thermal conductivity ($k = 160$ W/m·K) and latent heat ($\Delta H = 560$ kJ/kg). It effectively stabilizes off gases at 600°C. However, its economic return depends on benefits like turbine downsizing, with a typical payback period of 3 years [4, 15]. In CSP and nuclear systems, materials such as Mg–Cu eutectics ($\Delta H = 232$–571 MJ/m^3) and silicon ($\Delta H = 1.8 \cdot 10^6$ J/kg) offer extremely high energy densities. Despite their potential, these materials require major system redesigns to manage challenges like containment and corrosion at extreme temperatures [22, 40].

Key challenges and perspectives in PCM development highlight the need for balanced performance across durability, cost, and standardization. While materials like H885 and MOF-based composites show strong cyclic stability, others, such as $MgCl_2$–KCl–NaCl, and low-cost organics like paraffin, degrade rapidly under repeated thermal cycling. This necessitates the importance of accelerated ageing tests for industrial validation [28, 29]. High-performance metallic PCMs like Al-12%Si offer excellent thermal properties and performance but remain limited to specialized applications due to high production costs. In contrast, bio-based composites such as WFS-CPCMs are more affordable but sacrifice some performance, requiring policy supports to encourage adoption [8, 15]. A major barrier to progress is the lack of standardized testing methods, especially for hybrid PCMs. For example, EG/PCM composites report thermal conductivity values ranging from 3 to 20 W/m·K, depending on graphite orientation, making comparisons difficult [32, 37].

The development of high-temperature PCMs is shifting from material-centric innovation to system-integrated design. While molten salts and metallic alloys continue to dominate industrial WHR, newer composites and advanced formulations are gaining ground by emphasizing sustainability and multifunctionality. Bio-derived scaffolds and MOF-enhanced systems are examples of this trend. To move forward, the field must address the gap in cyclic stability testing and scalable encapsulation. Collaborations across disciplines, supported by AI-driven design tools and policy frameworks, will be essential for translating lab-scale advances into industrial solutions. As sectors like CSP, maritime, and aerospace push thermal limits, PCMs are evolving from passive storage materials into active components of decarbonization, turning waste heat into a valuable resource for circular energy systems.

2.3 | Assessment Criteria and Key Operating Parameters

To clarify how the reviewed materials and systems are compared, this review adopts an integrated evaluation framework based on three interconnected levels: material properties, system operating conditions, and techno-economic deployment indicators. Material-level parameters, such as melting temperature, latent heat, thermal conductivity, specific heat capacity, cyclic stability, and corrosion behaviour, determine whether a PCM can operate within the temperature range and durability requirements of a given WHR application. System-level parameters, including HTF inlet temperature, flow rate, temperature gradient, heat-exchanger geometry, PCM arrangement, and storage configuration, control charging/discharging rates, exergy performance, and the ability to buffer transient heat sources. Finally, techno-economic indicators, such as capital cost, encapsulation cost, energy recovery efficiency, LCOS, scalability, and payback period, determine whether the proposed solution can be realistically deployed. These parameters are strongly coupled: improving one aspect often introduces penalties elsewhere. For example, conductivity enhancement may reduce active PCM fraction or increase pumping requirements, while high-temperature metallic PCMs improve heat transfer but require more expensive corrosion-resistant containment. Therefore, the review does not treat operating parameters as isolated variables but uses them to interpret the trade-offs between material selection, system integration, durability, and economic feasibility. Table 5 summarizes the main parameter categories considered throughout the manuscript and indicates their relevance for PCM-based WHR systems. 'Energy density' is used in the present work to indicate volumetric storage capacity when expressed in MJ/m^3, whereas latent heat is reported on a mass basis in kJ/kg. Similarly, cyclic stability refers to the reported retention of latent heat after a specified number of thermal cycles under the testing conditions described in the cited study.

TABLE 5 | Key operating parameters and their roles in PCM-based WHR systems.

Category	Operating parameters	Role/Significance	Main implication/trade-off
Thermophysical properties	Melting temperature (T_m)	Determines compatibility with heat source temperature	Affects energy recovery efficiency and system integration
	Latent heat (ΔH)	Governs energy storage capacity	Higher $\Delta H \rightarrow$ higher storage density
	Thermal conductivity (k)	Controls heat transfer rate	Low thermal conductivity limits charging/discharging rate
	Specific heat capacity (C_p)	Influences sensible heat storage	Affects total thermal storage capacity
Operational parameters	Temperature gradient (ΔT)	Drives heat transfer between HTF and PCM	Higher ΔT improves heat exchange but may increase losses
	HTF flow rate/velocity	Controls convective heat transfer	Excess flow may lead to diminishing return
	Inlet temperature (HTF)	Defines charging/discharging conditions	Affects phase change dynamics
	System geometry (e.g., shell-and-tube, H/R ratio)	Determines heat transfer area and flow distribution	Influences melting/solidification rates
System design parameters	PCM arrangement (e.g., cascaded systems)	Matches OCM melting points with temperature profile	Improves exergy efficiency and reduces entropy loss
	Heat exchanger configuration (segmented vs. conventional)	Control thermal management strategy	Enhances uniformity and heat transfer efficiency
Durability and stability	Thermal cycling stability	Measures long-term performance	Degradation reduces latent heat over time
	Supercooling degree	Affects phase transition reliability	Delays heat release during discharge
	Phase segregation	Causes material instability	Reduces effective storage capacity
	Corrosion compatibility	Interaction with containment materials	Impacts system lifespan and safety
Mechanical and structural	Thermal expansion mismatch	Stress between PCM and container	May cause structural failure
	Encapsulation integrity	Prevents leakage and degradation	Critical for long-term reliability
Techno-economic parameters	LCOS	Measures economic feasibility	Key for industrial adoption
	Capital and encapsulation cost	Initial investment requirement	High-cost limits scalability
	Payback period	Time to recover investment	Determines commercial viability
	Energy recovery efficiency	Measures system effectiveness	Higher efficiency improves return on investment

3 | Sector-Specific Applications of High-Temperature PCMs in WHR

The application of high-temperature PCMs in WHR systems varies significantly across industrial sectors due to differences in thermal profiles, operational constraints, and economic considerations. From high-grade heat streams in steelmaking and ceramics to transient thermal loads in automotive and maritime systems, PCMs must be carefully tailored to meet sector-specific requirements. This section examines how material properties and system designs are adapted in practice, highlighting both performance benefits and integration challenges. The following subsections provide a detailed overview of PCM deployment across key industries, emphasizing real-world applications and technological limitations.

3.1 | Heavy Industry (Steelmaking and Ceramics)

The steel and ceramics industries together account for nearly 8%–10% of global CO_2 emissions [51, 52]. These sectors release a large amount of high-grade waste heat (500°C–1100°C), much of which remains untapped due to technical and economic constraints. In steelmaking, Al-12%Si alloys, whose thermophysical properties and material-level trade-offs have been discussed in Section 2 have become a benchmark material. When used in modular heat exchange and storage units (HESUs), they help in reducing thermal fluctuations in electric arc furnace off-gases from 12.7% to 32.4% [4].

This thermal stabilization approach enables a 41% reduction in steam generator size and improves turbine efficiency by 22%. In

industrial trials, this translates to annual savings of 48.166 MWh and a payback period of 3 years [4, 15]. However, Al–Si alloys remain expensive and are prone to oxidation above 600°C, promoting interest in alternatives. One such option is molten salt H500 ($T_{melt} = 509°C$, $\Delta H = 260$ kJ/kg), which delivers similar performance in retrofitted billet reheating systems. Yet, its low thermal conductivity (1.5 W/m·K) requires graphite-enhanced encapsulation for effective heat transfer [15, 28]. Another promising development is the use of WFS composites, such as $NaNO_3$-based CPCMs ($T_{melt} = 308°C$, $\Delta H = 542$ kJ/kg). These materials repurpose industrial waste and reach volumetric energy densities of 1,074 MJ/m^3 with a charging efficiency of 79.5%. However, their mechanical strength drops below 1 MPa above the melting point, requiring external structural support [7, 8].

In ceramics manufacturing, kiln exhaust temperatures often exceed 800°C. H885 molten salt whose thermophysical properties and cycling behaviour are summarized in Section 2, is mainly discussed here in terms of its integration into packed-bed latent heat storage systems subjected to daily heating and cooling cycles [5, 28]. Simulations of vertical shell-and-tube systems using 4,700 kg of H885 indicate that 90% melting can be achieved in 16 h through conduction and natural convection. These systems can preheat combustion air from 650°C to 865°C, saving up to 570 MWh annually [5]. However, integrating PCMs like H885 into existing kiln designs can increase capital costs by 15%–20%, slowing adoption despite long-term benefits [5]. Carbonate-salt composites offer alternative solutions for ceramics kilns. Packed-bed systems using $NaLiCO_3$–MgO–graphite bricks deliver 41% higher charging power (296.3 W) compared to sensible storage, and extend isothermal discharge times crucial for recovering heat from 800°C–1100°C exhaust [6]. Another approach uses macroencapsulated ternary carbonate salts (Li_2CO_3–K_2CO_3–Na_2CO_3) in stainless steel spheres. These systems reach 83.6% efficiency under optimized flow conditions, though uneven radial temperature requires improved insulation [53].

The preference for metallic PCMs in steelmaking and salt-based PCMs in ceramics reflects a broader trend: materials are chosen not only for their thermophysical properties but also for how well they fit into existing systems. Al-12%Si is widely adopted because it integrates easily into modular HESUs. In contrast, H885 has seen slower adoption due to the need for custom-designed containment systems. This highlights a gap in retrofit-friendly PCM options that can integrate seamlessly with legacy industrial setups.

Packed-bed systems using microencapsulated Al-25Si MEPCM pellets (1–5 mm in diameter) show strong performance, with a round-trip efficiency of 0.93 and volumetric heat exchange rate of 0.67 kW·L^{-1}. However, these systems require improved insulation to reduce convective heat losses at high airflow rates [54].

3.2 | Automotive and Internal Combustion Engines

The stricter emission standards have increased interest in PCMs for two key automotive applications: recovering exhaust heat (300°C–600°C) to improve fuel economy and mitigating cold-start emissions through rapid thermal buffering. Latent heat storage systems used for storing the exhaust waste heat energy of SI engines have been explored with low melting temperature [55]. Cascade PCM systems are advanced thermal energy storage configurations designed to recover and utilize waste heat across a broad temperature spectrum in automotive applications. By layering PCMs in a cascade structure as shown in Figure 2, high-temperature material absorbs heat from exhaust gases, while medium- and low-temperature PCMs capture residual heat from other subsystems. This system reduces pressure fluctuations by 42%, allowing 15%–20% higher thermal tolerance [10, 15]. Despite these benefits, challenges remain. Nitrate salts still suffer from low conductivity (1.5 W/m·K), often requiring graphite-based composites, while chloride salts degrade over time, retaining only about 50% of their original latent heat [30, 46]. This staged approach enhances thermal efficiency, minimizes energy loss, and enables continuous heat recovery during dynamic driving conditions.

By cascading two PCMs with different melting points (D-sorbitol and paraffin wax), the system can recover and store waste heat more effectively across a wider temperature range, instead of losing low-grade heat. First, the waste heat from the automotive engine enters the system, and D-sorbitol (i.e., high melting point) absorbs the high-grade waste heat and stores it through a solid–liquid phase change. Once D-sorbitol is saturated, the remaining

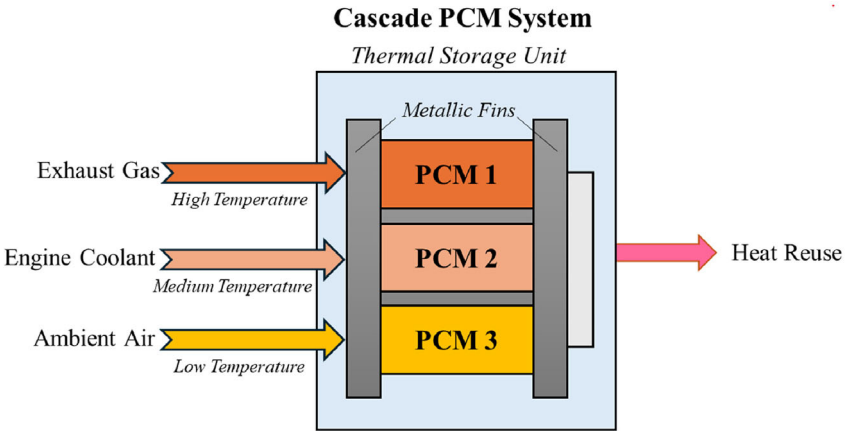

FIGURE 2 | Schematic of a cascade PCM system for automotive applications.

heat is passed on to the paraffin wax (i.e., lower melting point). Paraffin wax captures and stores the lower-temperature heat that remains after D-sorbitol. After both cascaded PCMs absorb heat, the residual heat is released to the ambient. D-sorbitol ($\Delta H = 339.8$ kJ/kg) and paraffin wax ($\Delta H = 243$ kJ/kg) have shown 20% higher energy recovery in diesel engines compared to single-PCM configurations [24]. D-sorbitol captures high-temperature exhaust heat during peak loads, while paraffin wax stores lower-temperature heat during idle. Together, they stabilize catalytic converter temperatures within ±50°C using 19–20 kg of PCM [24, 49]. Paraffin wax is a widely adopted PCM due to its high latent heat (243 kJ/kg) of fusion and excellent chemical stability. It has been effectively integrated into diesel engine air preheating systems to enhance thermal energy utilization. Numerical simulations incorporating the RNG k-ε turbulence model and phase-change dynamics have demonstrated that ribbed heat exchangers significantly improve PCM charging performance. Specifically, a rib spacing of 90 mm and rig height of 7.5 mm were identified as optimal, resulting in a reduction of charging time by ≈23%–29%. This configuration promotes enhanced convective heat transfer while maintaining manageable flow resistance, thereby improving the overall efficiency of the thermal storage system. This enabling rapid intake air preheating from 273 to 302 K within 1 min, storing up to 582.84 kJ/kg at 3000 rpm, and effectively lowering cold-start emissions [46].

A sodium nitrate PCM unit coupled to the exhaust line of a twin-cylinder four-stroke diesel engine, was able to store about 5.5% of the total fuel energy that would otherwise be lost with the exhaust gases. Integrating this thermal energy storage system reduced the share of exhaust energy directly rejected to the atmosphere from 45.1% to 39.5% and enabled on-demand steam generation for auxiliary uses, while also lowering the exhaust gas temperature and associated harmful emissions compared with the reference configuration without PCM [56] (Figure 3).

Nano-enhanced PCMs offer further improvements. Adding 5 wt% SiO_2 nanoparticles in paraffin wax reduces melting times by 34.88% in ribbed aluminium heat exchangers. This enables fast air preheating and reduces CO and HC emissions by 64% and 15%, respectively [11, 49]. However, higher nanoparticle concentrations (higher than 5 wt%) lead to agglomeration, increasing viscosity and reducing heat transfer efficiency [11]. Hybrid

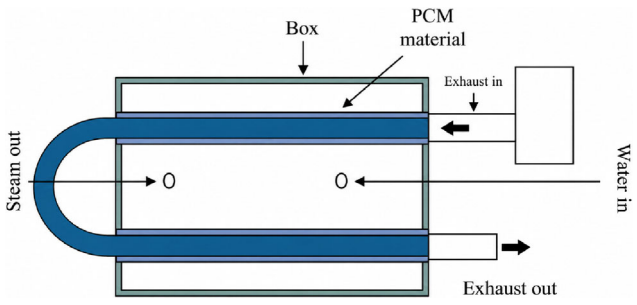

FIGURE 3 | Experimental setup of the PCM unit coupled to the exhaust line of a twin-cylinder four-stroke diesel engine (adapted from [56]).

systems integrating PCMs with thermoelectric generators (TEGs) are also being explored. For example, RT55 paraffin used in propane-fuelled engines recovered 1.66% fuel energy through separate heat transfer loops. However, TEG power output dropped by 10% due to reduced exhaust heat availability [25].

Although nano-enhanced PCMs and cascaded systems show strong technical performance, their cost-effectiveness remains uncertain. Nanoparticles like SiO_2 are expensive, typically ranging from $50 to $100 per kilogram [11]. Additionally, advanced heat exchanger designs such as ribbed channels or segmented designs add manufacturing complexity and cost. These factors offset the fuel savings, especially in cost-sensitive automotive markets. Another concern is the limited long-term durability of organic PCMs like paraffin. Their behaviour under extended thermal cycling beyond 1000 cycles is still not well understood, raising concerns about long-term durability [24, 57].

3.3 | Organic Rankine Cycle System

PCMs play a dual role in ORC systems by stabilizing fluctuating heat inputs and providing additional energy storage capacity. ORC units are widely used to convert low- and medium-grade waste heat into power, but their performance is strongly affected by fluctuations in thermal input, which can reduce stable evaporator operation, capacity factor, and net power output [58]. PCM-based latent storage is therefore introduced not only to increase stored energy, but also to decouple the transient heat source from the power cycle [59]. In steel plants retrofits, Al-12%Si-based heat storage units 2,916 kg of PCM) increased ORC capacity factors from 38% to 52%. This resulted in an additional 583 MWh of annual output, with a return on investment achieved in 3–5 years at electricity prices of 83–120 €/MWh [14]. For engine-exhaust WHR, Figure 4 illustrates the same temperature-buffering principle applied to the exhaust-side thermal input. Engine exhaust recovery using $LiNO_3$–KCl–$NaNO_3$ ($T_{melt} = 350$°C, $\Delta H = 300$ kJ/kg) extended discharge durations to 51 min at 400°C but required hybrid sensible-latent systems to overcome low conductivity (1.5 W/m·K) [30].

Cascaded PCMs like KNO_3-$NaNO_3$ ($T_{melt} = 221$°C) in TES-RORC systems, added 17.5 min of thermal inertia during heat-source interruptions, enabling smoother shutdowns in industrial WHR [60]. D-Mannitol-based LTES reduced thermal fluctuations by 60.5% under transient ORC loads, increasing net power output by 23.5% [61]. Figure 5 illustrates the complete schematic of PCM integration in the CSP system. In advanced thermal energy systems, the integration of two boilers serves a strategic purpose to enhance operational flexibility, reliability, and energy efficiency. The primary boiler is directly connected to the main heat source, such as solar collectors in a CSP system, and is responsible for generating steam during peak energy availability. However, due to the intermittent nature of solar radiation, a secondary boiler is incorporated to ensure continuity of operation. This auxiliary boiler is often coupled with a PCM thermal storage unit, which absorbs excess heat during high solar flux periods and releases it during low or no solar input conditions. This configuration improves load balancing, system resilience, and facilitates better integration of thermal storage technologies.

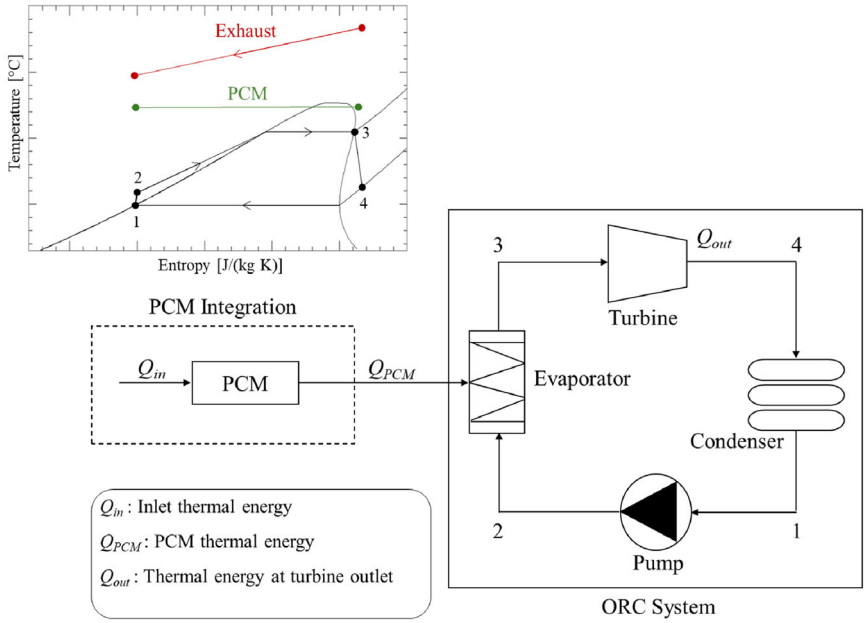

FIGURE 4 | Schematic of PCM integration into the ORC system.

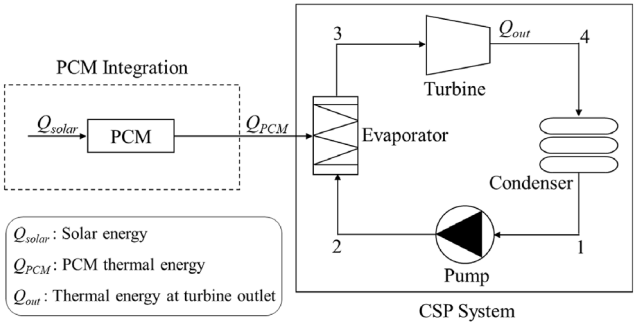

FIGURE 5 | Schematic of PCM integration into CSP system.

3.4 | Solar Power (CSP)

In CSP, the pursuit for higher operating temperatures (higher than 500°C) has led to interest in ultra-high-temperature PCMs. Silicon ($T_{melt} = 1414$°C, $\Delta H = 1.8{\cdot}10^6$ J/kg) and Mg–Cu eutectics (e.g., $Mg_{84}Cu_{16}$, $T_{melt} = 488$°C, $\Delta H = 232$ kJ/kg) offer higher energy density. However, silicon's reactivity with oxygen requires vacuum-sealed graphite containers for supercritical CO_2 cycles, increasing system costs by 30%–40% [22, 40]. Chloride salts like $MgCl_2$–KCl–NaCl ($T_{melt} = 380$°C, $\Delta H = 198$ kJ/kg) face decomposition and release corrosive HCl gas, limiting them to 50% of the theoretical latent heat in practice [29]. Graphite foam infiltrated with Dynalene MS-XTT ($T_{melt} = 355$°C, $\Delta H = 200$ kJ/kg) improves conductivity to 110 W/(m·K), but reduces PCM volume by 30%, highlighting the trade-off between thermal kinetics and energy density [37].

At temperatures above 550°C, radiative heat transfer becomes the dominant mechanism in packed beds. Increasing the emissivity of $NaLiCO_3$–MgO–graphite composite PCMs from 0 to 1 and reduces charging time by 25.7%, outperforming cylindrical alloy-based PCMs through combined radiation and conduction [6]. Ceramic foams (SiC, 10–20 PPI) added to solar salt improve melting rates by 39%–51% and raise exergy efficiency by up to 54%–57%, supporting economic feasibility [62].

CSP systems predominantly utilize molten salts for thermal energy storage due to their commercial maturity and operational reliability. However, advanced PCMs, such as silicon and Mg–Cu eutectics, offer higher energy densities and thermal conductivities, making them promising candidates for next-generation CSP applications. For instance, the Mg-25%Cu-15%Zn eutectic alloy exhibits a stable phase change temperature of ≈452.6°C and maintains thermal reliability over 500 heating/cooling cycles, with minimal degradation in enthalpy and structural integrity. Despite these advantages, several technical barriers hinder their deployment. High-temperature PCMs often require expensive, corrosion-resistant containment materials. Stainless steel 304L has shown relative compatibility with Mg-based alloys, but aluminium-based PCMs remain highly corrosive to iron-based containers, limiting their long-term use [63]. Moreover, the absence of standardized testing protocols for ultra-high-temperature cycling complicates performance validation and cross-study comparisons, impeding material qualification for industrial use. System integration also presents challenges. Many PCMs suffer from low thermal conductivity, necessitating complex heat exchanger designs to ensure efficient energy transfer. Packed-bed and shell-and-tube configurations have been explored to address this issue. For example, a moving packed-bed heat exchanger integrated into a CSP facility demonstrated improved heat transfer coefficients, reaching up to 150 W/(m^2·K), by optimizing particle flow and tube arrangements [64]. Pilot-scale systems like the cascade PCM proposed by Prieto and Cabeza improve heat transfer fluid (HTF) profiles and exergy efficiency by layering PCMs by melting point. However, transient phase changes require iterative sizing and advanced modelling tools [65]. To advance the adoption of these materials, the CSP sector must prioritize pilot-scale demonstrations that validate laboratory findings under real-world conditions. Furthermore, the development of standardized testing protocols for thermal cycling, corrosion

resistance, and long-term performance is essential. Material innovation aimed at reducing containment costs and improving compatibility with existing CSP infrastructure will also be critical to overcome current limitations and enable broader commercialization.

3.5 | Maritime and Naval Applications

Maritime WHR systems require PCMs that are compact, corrosion-resistant, and responsive to variable thermal loads. Cascaded latent storage using $LiNO_3$-NaCl ($T_{melt} = 208°C$), D-Mannitol ($T_{melt} = 165°C$), and oxalic acid ($T_{melt} = 105°C$) improved net power output by 19.1% in shipboard systems. However, cost constraints led to the use of Group II PCMs over higher-performing Group I materials, reducing storage volume by 27.3% and cutting costs by 52.5% [14]. SHE with copper foam-PCM composites (97% porosity) shortened melting times by 34% by aligning flow and temperature gradients. A reduced-order model validated these results, predicting phase change with less than 20% error in under 0.1 s [66]. Marine WHR systems, especially those targeting exhaust gases (which account for 20%–30% of engine power), benefit from the high energy density of PCM. Turbo compounding systems using PCMs can recover 3%–11% of the engine. Latent heat storage also buffers thermal fluctuations, improves fuel efficiency and reduces emissions. Still, Challenges remain, including material degradation at high temperatures and integration with existing ship infrastructure. Corrosion-resistant salts, such as chlorides, are under investigation to address these issues [50].

Sustainable PCM options are also emerging. Bio-derived PCMs are gaining attention for their sustainability and potential in medium-temperature thermal energy storage. One such innovation is popcorn-derived porous carbon with adipic acid ($\Delta H = 195$ kJ/kg, $k = 1.18$ W/m·K), synthesized via precarbonization at 600°C and alkali activation at 700°C. This material exhibits a high surface area of 2361.25 m^2/g and a nitrogen content of 1.8%, making it suitable for encapsulating organic PCMs or enhancing thermal conductivity in composite systems [67]. Although primarily explored for supercapacitor electrodes, its thermal insulation and shape-stabilizing properties suggest potential for PCM applications. However, these systems remain at the laboratory scale, with no reported integration into marine or field-scale thermal energy storage systems. Their development focuses on enhancing shape stability and thermal cycling durability through surface functionalization and composite integration. Another promising candidate is D-mannitol, a sugar alcohol with a high latent heat of fusion, ranging from 246 to 338 kJ/kg, and a melting point around 165°C-168°C. Despite its favourable energy density, D-mannitol suffers from severe supercooling (up to 60°C) and thermal degradation when exposed to air at elevated temperatures. For instance, after 120 h at 180°C, its enthalpy dropped from 280 to 95 kJ/kg, and the material transformed into a resinous paste, indicating significant chemical breakdown [68]. To mitigate these issues, researchers have developed shape-stable PCMs (ss-PCMs) by embedding D-mannitol into expanded vermiculite (CV). The resulting composite achieved a melting enthalpy of 205.1 J/kg, crystallization enthalpy of 174.1 J/kg, and reduced supercooling to 45.6°C, while maintaining structural integrity over multiple cycles [69]. Similarly, researchers have embedded mannitol with MOF matrices, which act as a nano-confinement structure to stabilize the PCM and suppress crystallization irregularities. MOF-stabilized mannitol ($\Delta H = 193$ kJ/kg) shows promise, achieving 93.83% photothermal efficiency and 97% cyclic retention, respectively [16, 39]. However, these systems are also limited to lab-scale experimentation, with no evidence of deployment in real-world settings or maritime. Popcorn-carbon is hygroscopic, which reduces performance in humid environments, while MOF synthesis remains costly and complex [9, 35]. Direct-contact heat exchangers using adipic acid/SnBi58 MEPCM composites reach storage densities of 1,391 MJ/m^3 and a heat transfer rate of 198 W. Under staggered configurations, they reduce melting time by 12% [70]. Overall, while bio-derived PCMs offer significant sustainability advantages, most, including popcorn-carbon and MOF-stabilized mannitol, remain in the experimental phase. Further work is needed to assess their long-term stability, scalability, and compatibility with existing thermal storage infrastructure.

In maritime applications, the focus on corrosion resistance has limited material choices to a few groups of salts, such as $LiNO_3$-NaCl, and selected eutectics. This has slowed progress in bio-based composites and metallic PCMs. A lack of standardized testing further complicates development. For example, studies use different leakage thresholds, 5% weight loss in [16] and 10% in [17], making comparisons difficult.

4 | System Level Integration of PCMs

Beyond material development, the successful implementation of PCMs in WHR depends on effective system-level integration. Advanced thermal storage architectures, optimized heat exchanger designs, and hybrid energy system play a critical role in maximizing performance and ensuring operational reliability. However, these innovations also introduce complexity in design, cost, and scalability. This section explores how recent engineering approaches, including cascaded storage systems, SHE, and hybrid configurations, enhance thermal management while addressing practical constraints. It also evaluates techno-economic factors that influence industrial adoption, bridging the gap between laboratory-scale innovation and real-world deployment.

4.1 | Thermal Storage Architectures

Both cascaded thermal storage systems (CTSS) and SHE demonstrate that optimizing thermal performance in high-temperature PCM systems requires a careful balance between efficiency and practical feasibility. While cascaded configuration enhances energy recovery across wide temperature ranges, segmented designs improve real-time heat transfer through localized control. However, both approaches introduce additional design complexity and cost, highlighting the importance of application-specific optimization. These considerations underscore the need to integrate advanced storage architectures with complementary technologies, as discussed in the following section on hybrid energy systems.

4.2 | Cascaded Thermal Storage System and Segmented Heat Exchangers

Both CTSS and SHE are presented together because they address the common challenges of managing large temperature gradients in high-temperature energy systems. CTSS focuses on storing thermal energy across multiple temperature levels using a series of PCMs, which enhances exergy efficiency and reduces entropy generation during heat storage and recovery. While SHE is designed for real-time heat transfer optimization, it divides the heat exchange surface into zones tailored to specific thermal conditions to maximize heat transfer rates. Reporting these systems together highlights their shared goal of improving thermal performance while clarifying their distinct operational roles, summarized in Table 6.

Thermal energy management is a cornerstone of modern energy systems, particularly in applications involving renewable energy integration and WHR. Two distinct approaches, CTSS and SHE, offer a unique solution to thermal changes, each with its own design philosophy and operational focus. Cascaded thermal storage systems are engineered to store heat across multiple temperature levels using a series of PCMs. Each PCM is selected based on its melting point, allowing the system to absorb and release heat in a staged manner. This configuration enhances the efficiency of thermal energy storage by aligning the temperature gradient with the melting behaviour of the materials. The cascading configuration minimizes entropy generation and enhances exergy efficiency, making CTSS well-suited for storing and recovering heat across broad temperature ranges. In contrast, SHE are designed to optimize the transfer of thermal energy rather than store it. These systems divide the heat exchange surface into multiple zones; each zone tailored to specific thermal conditions. Segmentation may involve variations in geometry, flow configuration, or material properties, all aimed at maximizing heat transfer efficiency. The fluid passing through the exchanger experience controlled temperature changes across each segment, which allows for precise thermal management. For example, cylindrical exchangers split into 10 parts (height-to-radius ratios, $H/R = 1$) improve heat transfer by aligning flow and temperature near the melting point. While both systems contribute to improved thermal performance, their roles are fundamentally different. CTSS focuses on retaining thermal energy for later use, whereas SHE is concentrated on transferring heat efficiently in real-time. The choice between these technologies depends on the specific requirements of the application, whether the goal is to store energy for future use or to manage heat flow dynamically during operation.

1. ***Cascaded thermal storage systems***: The thermophysical properties of the individual PCMs are discussed in Section 2; here, the focus is on how their arrangement within cascaded architectures affects system-level performance. In steel billet reheating furnaces, a three-layer PCM system (Al-12%Si, H500 molten salt, and $NaNO_3$) reduces evaporator pressure fluctuations by 42% during step-changes. This enables the ORC system to sustain 15%–20% higher thermal amplitude tolerance compared to single-PCM configurations [10, 15]. Al-12%Si absorbs high-temperature heat quickly, while H500 and $NaNO_3$ store lower-temperature energy. This setup reached 68.5% recovery efficiency [8, 15]. Similarly, marine systems using $LiNO_3$-NaCl ($T_{melt} = 208°C$), D-Mannitol ($T_{melt} = 165°C$), and Oxalic acid ($T_{melt} = 105°C$) increased power output by 19.1% by matching PCM melting points to exhaust temperature [14]. In CHEST systems with cascaded PCMs at 107°C, 119°C, and 132°C, doubled energy density (6.9 MWh/m^3) and improved round-trip efficiency by 13% [71]. Solar ORC systems use acetamide (82°C) and salt hydrates (117°C) to balance collector efficiency and power generation [72]. However, cascaded systems are complex. They need precise thermal matching and often rely on AI-driven algorithms to manage PCM charging and discharging in response to load fluctuations [73]. Shell-and-tube configurations with high-temperature salts like LiF-KF (melting point ≈500°C) show that tank shape affects charging efficiency. A COMSOL-based 2D axisymmetric model found that optimized designs reduce charging time by 60%. But increasing fluid speed beyond 0.07 m/s gave little benefit due to convective limits [34]. This highlights the need to match PCM properties with tank design for best performance [74].
2. ***Segmented heat exchangers***: A key study using copper foam-PCM composites ($\Delta H = 199.424$ J/kg) demonstrated that splitting a cylindrical unit into 10 parts ($H/R = 1$) reduced melting time by 34%. This phase change was 31%–38% faster than in conventional designs [66]. This improvement is due to better alignment of flow and temperature gradients. The synergy angle cosine increases from 0.65 to 0.82, boosting heat transfer [66]. In CSP systems, segmented shell-and-tube units with soda-lime glass ($T_{melt} \approx 1000°C$, $\Delta H = 2740$ kJ/kg) and graphite maintained 970°C operation. However, repeated cycling caused a 12% loss in latent heat after 50 cycles due to subcooling [31]. While segmentation improves performance, it raises cost. Precision manufacturing, such as thin-slicing and copper foam use, increases capital costs by 10%–15%. This is a challenge for cost-sensitive sectors like maritime and automotive [17, 66].

TABLE 6 | Comparison of CTSS and SHE systems.

Feature	CTSS	SHE
Primary function	Storage of thermal energy for later use	Transfers heat efficiently in real time
Design principle	Multiple PCMs arranged by melting point	The heat exchange surface is divided into zones
Operational focus	Staged heat absorption and release	Controlled temperature change across segments
Efficiency benefit	Minimizes entropy generation, improves exergy efficiency	Maximizes heat transfer rate and uniformity
Typical application	WHR, renewable energy storage	Dynamic thermal management in industrial processes

Placement of thermal enhancers also matters. Inserting ceramic foam in the upper half of a shell-and-tube unit reduced solidification time by 34% compared to lower placement. This takes advantage of natural convection, where hot liquid rises and cold flow accelerates solidification in pure-PCM zones [36]. For $NaLiCO_3$–graphite composites, cold compression-sintering creates stable modules at 500°C. Although early cycles show nonuniform temperature distribution ($\Delta T \leq 62$°C), the structure self-adjusts over time, leading to more uniform heat distribution after 50 cycles via microstructural reorganization [35].

There is a trade-off between heat-recovery performance and economic feasibility. High-performance systems often involve higher upfront costs. For example, cascaded LTES systems used in steel plants, the staged heat recovery enables more consistent temperature delivery to downstream processes. This allows for the use of smaller or lower capacity steam turbines in ORC systems, as the thermal input is better matched to the turbine operating range. As a result, the overall system cost is reduced, leading to a payback period of ≈3 years [15]. In contrast, marine applications face a longer payback period, typically five to 7 years, due to the high cost of encapsulating PCMs in corrosion-resistant alloys [14]. Similarly, segmented exchangers, while demonstrating strong performance in a laboratory setting, face economic barriers in industrial deployment. Their 15% cost premium is difficult to justify in sectors like ceramics, where existing kiln infrastructure is not easily adaptable [5].

4.3 | Hybrid Energy Systems

High-temperature PCMs play a key role in linking thermal energy storage with advanced systems like supercritical CO_2 cycles and WHR systems. Their latent heat helps smooth out temperature fluctuations in hybrid setups such as TEG-PCM and supports flexible operations in CSP plants. However, several issues limit their use. These include material breakdown at interfaces, trade-offs between thermal conductivity and viscosity when using nano-additives (e.g., SiO_2, Al_2O_3), and the high costs of containers for extreme temperatures (e.g., Mg–Cu eutectics, silicon). In one case, RT55 paraffin-PCM improved fuel recovery in TEG by 61% (2559 kJ stored), but heat losses reduced the net benefits to just 1.66% [25]. Similarly, nano-enhanced PCMs reduced diesel engine cold-start time by 34.88%. However, the high cost of nanoparticles ($50–100/kg) limited their practical value, resulting in only 8.2% TEG efficiency gains [11]. Silicon-based PCMs combined with sCO_2 turbines achieved 32% electrical efficiency. But they required vacuum-sealed graphite, which raised system costs by 30% [40]. The goal is to identify PCM solutions that strike a balance between strong thermal performance and economic feasibility.

Hybrid TEG-PCM systems help stabilize temperature differences across TEG modules. This improves power generation during load fluctuations. A propane engine using RT55 paraffin ($T_{melt} = 55$°C, $\Delta H = 175$ kJ/kg) stored 2559 kJ of heat energy through separate HTF loops. It recovered 1.66% of fuel energy, 61% more than a TEG-only systems [25]. However, the diversion of exhaust heat to the PCM lowered the TEG's temperature gradient by 10%. This limited the overall efficiency, revealing a key trade-off in hybrid designs [25]. In diesel engines, paraffin with 5% SiO_2 nanoparticles shortened cold-start time by 34.88%. Yet, the 8.2% increase in TEG output did not justify the high nanoparticle cost ($50–100/kg), making it impractical for widespread use [11].

Supercritical CO_2 systems offer 40–50% higher thermal efficiency than steam cycles. They require PCMs that can operate above 500°C with minimal delay in heat transfer. Silicon ($T_{melt} =$ 1414°C, $\Delta H = 1.8 \cdot 10^6$ J/kg) used in residential cogeneration reached 32% electrical efficiency. However, it required vacuum-sealed graphite containment, which raised system costs by 30% [40]. Hybrid designs combining sensible and latent storage, like solar salt with Al–Cu-Si MEPCM, boosted volumetric storage density by 154% (1.09 GJ/m^3) and remained stable over 100 thermal cycles. These systems also fit well with existing molten salt setups [44]. In CSP applications, Mg–Cu eutectics ($Mg_{59}Cu_{41}$: $T_{melt} = 550$°C, $k = 97$ W/m·K) provided 48.8-minutes of discharge at 325°C. But corrosion at stainless steel interfaces limited their durability to less than 50 cycles. This highlights the need for better containment materials, such as titanium or ceramics [22].

Adding nanoparticles like SiO_2 or Al_2O_3 to PCMs improves thermal conductivity but can increase viscosity. In diesel exhaust heat exchangers, paraffin with 5% SiO_2 melted 34.88% faster, cutting time from 43 to 28 min. However, it raised pumping power by 18% due to nanoparticle agglomeration [11]. In contrast, CuO-enhanced erythritol ($T_{melt} = 118$°C, $\Delta H = 339.8$ kJ/kg) improved thermal conductivity by 80% from 0.73 to 1.32 W/(m·K) without significantly affecting viscosity. This makes it suitable for medium-temperature ORC systems [24]. Despite these benefits, large-scale use remains difficult. Inconsistent nanoparticle dispersion, varying by ±15%, creates challenges for industrial-scale production and quality control [11].

Hybrid systems highlight the gap between innovation and real-world application. TEG-PCM configurations and sCO_2 cycles show strong theoretical potential. However, issues like corrosion at material interfaces, such as SS316 corrosion in Mg–Cu systems [22] and the lack of testing standards for nanoparticle-enhanced PCMs [11, 29]. Furthermore, ultra-high-temperature PCMs such as silicon offer decarbonization potential, but their containment costs up to 30–40% of total expenses, remain a major hurdle. Solutions may lie in advanced manufacturing or targeted subsidies [40].

5 | Challenges and Future Developments

High-temperature PCMs for WHR face a range of interconnected challenges that span material performance, system integration, and economic feasibility. While significant progress has been made in enhancing thermal conductivity, cyclic stability, and energy density, critical issues such as material degradation, corrosion, supercooling, and scalability continue to limit widespread industrial adoption. In addition, the lack of standardized testing protocols and reliable long-term performance and complicates cross study comparisons and technology validation. Addressing these challenges requires a multidisciplinary approach that combines material innovation, advanced encapsulation techniques, system-level optimization, and supportive policy frameworks. The following

subsections examine these challenges in detail, along with emerging strategies and future research directions aimed at enabling robust, cost-effective, and scalable PCM-based WHR systems.

5.1 | Real World Performance and Deployment Gaps

The reviewed high-temperature PCMs demonstrate strong potential under controlled and application-specific conditions. However, their performance under realistic industrial environments remains constrained by several interrelated factors. As outlined in Section 2, although many materials exhibit favourable thermophysical properties, such as high latent heat and thermal conductivity, their long-term reliability under repeated thermal cycling remain a critical limitation. Materials such as H885 molten salts and MOF-stabilized composites show relatively high stability, retaining over 90%–96% of latent heat across tens to hundred of cycles. In contrast, chloride-based salts and some low cost or organic composites exhibit significant degradation, with latent heat losses reaching up to 50% due to moisture absorption, volatilization, or chemical decomposition. Similarly, while metallic alloys such Al-12%Si offer excellent thermal conductivity and stable melting behaviour. Their susceptibility to oxidation and corrosion above 600 C necessitates advanced encapsulation strategies, increasing system complexity.

Chemical stability and compatibility with containment materials remain critical challenges. As discussed in Section 2.2 and Section 4, many high temperature PCMs, particularly chloride salts and Mg-based eutectics, interact aggressively with conventional structural materials such as stainless steel, leading to corrosion, intermetallic formation, or gas release (e.g., HCl). Although protective coatings, such as SiC or Al_2O_3, and alternative containment materials, including ceramics or nickel-based alloys, can mitigate these effects, they introduce additional cost and manufacturing complexity, limiting large-scale deployment. From a techno-economic perspective, several PCM systems demonstrate promising feasibility at the industrial level when integrated into optimized system architectures (Section 4). For example, Al-12%Si-based WHR systems in steelmaking achieve payback periods of ≈3–5 years due to improved energy recovery and turbine efficiency. However, in sectors such as maritime and hybrid automotive systems, high material and encapsulation costs extend payback period to 5–8 years or more, reducing economic attractiveness. Advanced configurations, including nano-enhanced PCMs and hybrid TEG-PCM systems discussed in Section 4.2, often show strong laboratory performance but fail to deliver proportional economic benefits due to high material costs, increased system complexity, or efficiency trade-offs.

A key gap between laboratory-scale results and industrial deployment lies in the limited consideration of real-world operating conditions in experimental studies. While the evaluation framework in Section 2 provides a basis for material comparison, many studies focus on short-term cycling, idealized boundary conditions, and small-scale systems, without accounting for thermal gradients, long duration operation, mechanical stresses, impurity effects, and integration with existing industrial infrastructure. In addition, inconsistencies in testing protocols, particularly for thermal cycling, leakage, and corrosion resistance, higher cross-study comparability and material benchmarking, as highlighted in Section 5. Emerging materials, such as bio-derived and nano-enhanced PCMs, further suffer from a lack of large-scale validation and long-term performance data.

5.2 | Material Challenges: Degradation, Conductivity, and Stability

Integrating high-temperature PCMs into WHR systems presents complex thermal, chemical, and mechanical issues. A major challenge across most PCM types, metallic, salt-based, or composite, is low thermal conductivity, which slows heat transfer during charging and discharging. For example, inorganic salts like $NaNO_3$ are affordable and offer moderate latent heat (175–260 kJ/kg) [8, 29, 75], but their thermal conductivity is low (0.45–0.69 W/m·K) [8, 29], leading to longer phase change durations. In packed-bed systems using WFS-PCM composites [8], thermal conductivity drops further in the liquid state (1.17–1.45 W/m·K), worsening thermal stratification. Similarly, soda-lime glass, considered for ultra-high-temperature storage ($T_{melt} = 1414$°C) [31], also suffers from poor thermal conductivity (0.79 W/m·K). Graphite additives improve performance but increase system complexity and cost. Even advanced chloride salts like $MgCl_2$–KCl–NaCl, which offer high latent heat ($\Delta H = 198$ J/g) [29], face stability issues due to moisture absorption and corrosive HCL release.

5.2.1 | Cyclic Degradation and Structural Challenges

Repeated thermal cycling exacerbates these problems. Molten salts such as H500 and H885, used in the steel and ceramic industries [28], lose 12% and 3.7% of latent heat, respectively, over 20 cycles. Metallic alloys PCMs, such as Al-12%Si, also face corrosion when in contact with stainless steel heat exchangers. Chloride-based PCMs are especially problematic; Mg–Cu eutectics [22] form brittle intermetallic compounds (e.g., Mg_2Cu, $MgCu_2$) when exposed to steel, requiring costly ceramic or nickel-alloy containment. Mechanical failure is another concern. Composites made with $NaNO_3$- or solar salt in WFS lose up to 90% tensile strength above melting temperatures [8]. Even bio-based PCMs such as popcorn-carbon/adipic acid composites improve thermal conductivity by 150%, but reduce latent heat by 17% compared to pure PCMs [39]. Encapsulated Al–Si PCMs remain stable after 1,300 cycles due to protective Al_2O_3 shells [12], while chloride salt-nanoparticle composites maintain stability up to 820°C with less than 3% mass loss [13].

5.2.2 | Halide Salt Decomposition and Supercooling Challenges

Decomposition of halide salts remains a critical. $MgCl_2$–KCl–NaCl mixtures release corrosive HCl gas during thermal cycling, damaging containment materials and reducing latent heat by up to 50% [76]. Encapsulation methods like SiO_2-coated microcapsules or SiC/PyC layers suppress corrosion. For example, SiC forms a protective SiO_2 layer in molten chlorides at 700°C, but fails above 800°C unless upgraded with robust alloys [26]. Supercooling and phase segregation also reduce reliability. Sodium sulfate decahydrate, a low-cost PCM for engine preheating, shows supercooling of up to 3.9°C, delaying heat release during cold starts [49]. Nitrate salts ($LiNO_3$–KCl–$NaNO_3$) in

cascaded ORC systems, like melt unevenly due to thermal conductivity differences between solid (0.5 W/m·K) and liquid (0.3 W/m·K) phases [30]. Thermocline storage systems using molten salts also develop inactive thermal zones during partial charging [77]. Managing subcooling is essential for consistent discharge. Ternary carbonate salts show 2°C–4°C supercooling during solidification [53], while adipic acid exhibits 4°C–5°C hysteresis due to delayed nucleation [78]. Composite materials like $NaNO_3$ embedded in SSPC reduce supercooling by 5.47°C. Their rough surfaces act as nucleation sites, improving heat release timing [62].

5.2.3 | Future Directions: Emerging PCMs and Standardization Needs

Overcoming these limitations requires multidisciplinary innovations. Hybrid PCMs combining materials at different scales are gaining interest. Nano-enhanced PCMs, such as paraffin-SiO_2 and erythritol-Al_2O_3, reduce melting times by 25%–35% through improved nanoparticle-driven heat conduction [79]. Porous scaffolds, such as MOF-derived yeast carbon and graphite foam, improve both thermal conductivity and leakage control [37]. For example, mannitol encapsulated in yeast-templated ZIF-8 carbon reaches 1.17 W/m·K, nearly double that of pure mannitol and reduces supercooling by 18% [16]. Metal-based PCMs such as $AlSi_{12}$ and Mg–Cu eutectics offer high thermal conductivity (97–160 W/m·K) but require advanced containment [80]. Solutions like Haynes alloy shells [5] and refractory concrete vessels [31] show promise for high-temperature containment, though costs limit large-scale use. Sustainable options are emerging. Bio-inspired and waste-derived materials offer both performance and cost benefits. Okra-templated SiC skeletons provide adjustable porosity (76%–85%) for NaCl-Na_2CO_3 salts, increasing thermal storage power by 101% through directional heat flow [41]. SSPC reduce raw material costs by over 90%, while delivering 1.13 W/m·K thermal conductivity and 96% stability over cycles [43].

5.2.4 | Standardization: A Critical Need

Without unified testing protocols for latent heat, conductivity, and leakage, it is difficult to benchmark new materials, especially emerging composites. PCM research lacks consistent testing methods [81]. Studies use different DSC protocols and cycling criteria, making comparisons difficult. $NaNO_3$/BFS composites retain about 96% latent heat after 100 cycles [82], whereas $MgCl_2$–KCl–NaCl formulations exhibit moisture-sensitive decomposition and HCl-related degradation under the conditions reported in [29]. These cases should not be interpreted as directly conflicting results, but as evidence that stability metrics depend strongly on PCM chemistry, pretreatment, atmosphere, and cycling protocol. Universal standards like ASTM guidelines are needed, defining benchmarks for cyclic stability (e.g., ≤5% latent heat loss over 1000 cycles) and corrosion resistance (e.g., mass loss under 1% after 500 h at increased temperature). EN 12 977 standards for solar thermal systems offer a model, focusing on reproducibility in encapsulation and thermal properties. Unified criteria for leakage and degradation are also overdue. H885 allows 5.5% weight loss in ceramic systems [28], while marine bio-composites require <3% [41]. Corrosion rates in chloride salts vary depending on impurity control [76]. Establishment of ASTM-like standards for thermal cycling (e.g., ≤5%, ΔH loss/1000 cycles) and corrosion (mass loss < 1%/500 h) are essential for cross-sector comparisons [83].

5.2.5 | Artificial Intelligence and Modelling: Accelerating PCM System Design

Artificial intelligence (AI) and computational modelling tools are reshaping PCM development. ROMs simulate melting behaviour in milliseconds with <20% error [66], enabling rapid design iterations. Dynamic simulations of cascaded PCMs reveal uneven heat release, emphasizing the need for nano-enhanced materials to improve thermal conductivity in transient WHR conditions [72]. Machine learning can optimize cascaded PCM configuration. In ORC-integrated systems, $LiNO_3$–KCl–$NaNO_3$ extended the discharge time by 48% compared to single-PCM setups [30]. Digital twins of packed-bed systems can dynamically adjust HTF flow and capsule size in real time to reduce thermal stratification [77]. Generative AI may also help in designing new eutectic composites with melting points such as 550–600°C for CSP applications [73]. However, these tools rely on accurate data. Current data sets are limited, making it difficult to train reliable models. Open-access PCM databases are urgently needed to support AI-driven design.

5.2.6 | Industrial Decarbonization Potential

High-temperature PCMs offer significant potential for reducing industrial emissions, but success depends on overcoming technical and cost-related challenges. In heavy industries, PCM-based WHR systems can cut energy losses by 20%–40%. For example, using Al-12%Si in steelmaking stabilizes exhaust heat from electric arc furnaces [3, 6]. This is enabling 41% reduction in turbine size and generating an additional 48.166 MWh of electricity annually, equivalent to avoiding 28,000 tons of CO_2 emissions. Similarly, in maritime applications, cascaded LTES systems improve transcritical CO_2 cycle efficiency by 19.1%, supporting the International Maritime Organization's (IMO) target of reducing shipping emissions by 50% by 2050 [14].

5.2.7 | Economic Outlook and Scalability Challenges

Despite strong environmental benefits, PCM retrofits face scalability hurdles. In billet reheating, PCM-integrated ORC systems offer a 3–5-year payback when electricity prices range from 83 to 120 €/MWh [15]. Ceramic furnaces equipped with thermal storage systems can reduce natural gas consumption by 570 MWh annually [7]. However, cost remains a major barrier. Nickel-coated salt capsules cost around 60 €/kWh at the lab scale [5], while metallic PCM systems exceed 400 €/kWh due to specialized containment materials requirements [22]. Emerging low-cost alternatives, such as composites supported by blast furnace slag (BFS), reuse industrial waste and cost less than 10 €/kWh [82], making PCM technologies more accessible, especially in developing economies.

5.2.8 | Policy Support and Data Standardization

Policy frameworks are critical to accelerate PCM adoption. The EU's Energy Efficiency Directive (EED), mandating WHR in high-energy industries, could drive PCM use in ceramics [28] and glass production [31]. Financial incentives, such as tax

TABLE 7 | Challenges and solutions for high-temperature PCM integration in WHR systems.

Challenge	Solution
Low thermal conductivity of PCMs	Additives such as graphite, nanoparticle enhancements (e.g., paraffin–SiO_2, erythritol–Al_2O_3), and porous scaffolds (graphite foam, MOF–derived carbon) can be used to improve heat transfer.
Thermal stratification and slow phase change	Use composite materials and hybrid PCMs to enhance uniformity and speed of phase change.
Stability issue (e.g., moisture absorption, gas release)	Encapsulation (e.g., SiO_2-coated microcapsules, SiC/PyC layers), use of robust containment materials (Haynes alloy, refractory concrete).
Cyclic degradation (loss of latent heat over cycles)	Use encapsulated PCMs (e.g., Al–Si with Al_2O_3 shells), chloride salt-nanoparticle composites, and bio-based composites for improved cycle stability.
Corrosion of containment materials	Switch to ceramic or nickel-alloy containers, use protective coatings (SiO_2, SiC), or encapsulate PCMs.
Mechanical failure at high temperatures	Provide external support for composites, utilize advanced containment methods (e.g., refractory concrete vessels), and optimize the composite structure.
Supercooling and phase segregation	Embed PCMs in porous ceramics (e.g., steel slag porous ceramics), use rough surfaces for nucleation, and develop composite PCMs to reduce supercooling.
Halide salt decomposition (corrosive gas release)	Encapsulation, use of protective layers (SiO_2, SiC), and selection of more stable salt mixtures.
High cost of advanced materials	Employ waste-derived and bio-derived materials (e.g., okra-templated SiC, steel slag ceramics) to reduce costs and support sustainability.
Need for standardization and material optimization	Develop hybrid and nano-enhanced PCMs, standardize testing, and tailor materials for specific operational environments.
Lack of standardized testing methods and criteria	Develop and adopt universal standards (e.g., ASTM-like, EN 12 977) for cyclic stability, corrosion resistance, leakage, and degradation.
Inconsistent data and limited comparability	Establish an open-access PCM database and unified testing protocols for reproducible, comparable results.
Limited reliable data for AI/modelling	Create and maintain comprehensive, open-access datasets to support AI-driven PCM design and modelling.
Scalability issues and high costs	Use low-cost, waste-driven composites (e.g., BFS-supported PCMs), and develop scalable manufacturing processes.
Technical and cost barriers for industrial decarbonization	Integrate PCMs with other storage types (sensible, thermochemical) and use hybrid/multistage systems for higher efficiency.
Policy and financial support gap	Implement stronger policy frameworks (e.g., EDD), provide financial incentives (tax credits), and promote global collaboration.
Overlooked real-world limitations in lab studies	Encourage replication studies, honest reporting (including negative results), and focus on system-level integration.
Agglomeration and instability in nano-enhanced PCMs	Optimize nanoparticle concentration and dispersion; combine with other storage types to mitigate limitations.
Corrosion and instability in harsh environments	Use advanced encapsulation, impurity control, and robust containment materials; tailor PCMs for specific applications.
Lack of holistic, interdisciplinary approaches	Foster cross-disciplinary collaboration and integrate PCMs with broader energy storage strategies for the net-zero transition.

credits, would further support hybrid systems like TEG-PCM units in aviation [79] and sCO_2-PCM cycles in CSP [37]. Global initiatives, such as IEA's Annexe 34 on PCMs, should prioritize knowledge sharing to bridge the gap between academic research and industrial implementation. A major barrier remains the lack of reliable data on temperature-dependent properties and inconsistent testing methods for alloys. Establishing a unified open-access database is urgently needed to standardize performance metrics and enable cross-sector comparisons [84].

5.3 | Key Challenges and Perspectives

Table 7 summarizes the principal challenges and corresponding solutions for integrating high-temperature PCMs into WHR systems.

6 | Findings, Discussion, and Recommendations

The review highlights three main findings and provides the basis for the following discussion and recommendations:

1. ***Material-system compatibility***: High-conductivity metals like Al-12%Si perform best in modular, retrofit-friendly systems. In contrast, salts and composites are preferred where corrosion resistance or sustainability is a priority.
2. ***Hybrid systems are standard***: Cascaded PCMs, nanoparticle additives, and TEG integrations are now common, reflecting a shift toward multifunctional thermal solutions.
3. ***Economic constraints***: Payback periods ranging from 3 to 5 years for steel applications to 5–7 years in maritime systems. High encapsulation costs, such as 60 €/kWh for Ni-coated salts [37], remain a major barrier, necessitating policy support to de-risk PCM adoption.

These observations indicate that future research should move beyond material-level optimization alone and focus on the co-design of PCM properties, heat exchanger architecture, containment strategy, and sector-specific operating conditions.

PCMs hold potential, but progress may stall without addressing deeper issues. Many studies, especially on nano-enhanced PCMs [11, 39], focus on lab-scale performance and overlook scalability. For example, SiO_2 nanoparticles improve paraffin's thermal conductivity, but agglomerate at concentrations above 5 wt.%, nullifying its benefits, an issue often ignored in optimistic reports. Similarly, claims of high stability in Mg–Cu eutectics often omit their rapid corrosion in humid conditions, making them unsuitable for marine applications [14, 22]. These oversights limit real-world applicability. Another concern is the lack of consistent comparisons. Differences in composition, sample preparation, cycling protocol, atmosphere, and reporting criteria often make direct comparison between studies difficult, especially when pure salts, composites, and multicomponent formulations are discussed together. This confuses end-users and highlights the need for replication studies and publication of negative outcomes. PCMs are not a universal solution. Their role in decarbonization will depend on integration with other storage types. Combining PCMs with sensible or thermochemical storage can overcome their limitations. For instance, multistage PCM systems in CSP plants improve efficiency by 44% over single PCM systems [73]. This shows that system-level integration is more effective than isolated solutions. To move forward, the field must adopt a holistic approach. Collaboration across disciplines and honest reporting are essential to make PCMs a core part of the net-zero transition. Future work should prioritize standardized durability testing, scalable encapsulation strategies, and pilot-scale demonstrations under realistic WHR conditions, so that material-level advances can be translated into reliable and economically viable system-level solutions.

Nomenclature

ASTM	American Society for Testing and Materials
BFS	Blast furnace slag
CHEST	Compressed heat energy storage
CHEST	Cascaded heat energy storage technique
CPCM	Composite phase change materials
CSP	Concentrated solar power
CTSS	Cascaded thermal storage system
ΔH	Latent heat
DSC methods	Differential scanning calorimetry
Dynalene MS-XTT	Chloride-based molten salt heat-transfer fluid/PCM
EG/PCM	Expanded graphite/phase change material
EU-EED	European Union Energy Efficiency Directive
Ev	Volumetric energy density
H/R	Height-to-radius ratio
H500	High-temperature inorganic PCM / heat-transfer salt grade (designation code)
H885	High-temperature inorganic PCM grade (designation code)
HC	Hydrocarbon
HCl	Hydrogen chloride
HESU	Heat exchange and storage unit
HTF	Heat transfer fluid
IEA	International Energy Agency
IMO	International Maritime Organization
k	Thermal conductivity
LCOS	Levelized cost of storage
LTES	Latent thermal energy storage
MCDA	Multicriteria decision analysis
MEPCM	Microencapsulated phase change material
NEPCM	Nano-enhanced phase change material
ORC	Organic Rankine cycle
PBLHS	Packed-bed latent heat storage
PCM	Phase change material
PPI	Pores Per Inch
PyC	Pyrolytic Carbon
RNG	Renormalization Group
ROM	Reduced-order model
RORC	Regenerative Organic Rankine Cycle
ρ	density
sCO_2	Supercritical carbon dioxide
SHE	Segmented heat exchanger
SSPC	Steel slag porous ceramics
TEG	Thermoelectric generators
TES	Thermal energy storage
T_{melt}	Melting point temperature
WFS	Waste foundry sand
WHR	Waste heat recovery

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Conflicts of Interest

The authors declare no conflicts of interest.

Endnotes

[1] A bio-derived phase-change material is a thermal energy storage medium whose latent-heat storage capacity arises from phase transitions of organic compounds sourced from renewable biomass (e.g., vegetable oils, fatty acids, or esters). Such materials combine high energy density with reduced environmental impact, making them ideal for sustainable high-temperature waste-heat recovery systems.

[2] The ability to scale a phase-change material process from laboratory to commercial volumes while preserving thermodynamic performance, cost-effectiveness, and quality consistency.

[3] Composite PCMs are phase-change materials obtained by combining a traditional PCM (organic, inorganic, or eutectic) with another material, typically a solid matrix or support material, with the aim of improving certain key properties such as mechanical stability, thermal conductivity, resistance to phase separation, and durability. In practice, the PCM is embedded, encapsulated or dispersed within a matrix (e.g., polymeric, ceramic, metallic, or porous), thus forming a composite material that combines the latent heat storage capacity of the PCM with the physical and mechanical properties of the host material. This strategy overcomes certain limitations of pure PCMs, such as low thermal conductivity, loss of material during melting/solidification cycles and difficulty of integration.

[4] Macroencapsulation via DPF/IPF methods enhances cyclic durability (1,300 cycles) and volumetric stability (5%–7% void ratio) for Al–Si alloys [12].

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