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A comprehensive review of thermal energy storage technologies and their applications: Creation of a database

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ABSTRACT

Thermal energy storage (TES) stands out as a key solution for advancing energy conservation and enhancing system efficiency, especially when paired with local renewable energy sources (RES). As the global shift toward sustainability accelerates, TES technologies hold the potential to play a central role in mitigating the challenges posed by increasing energy demands. However, despite its demonstrated efficacy and promise, TES has not yet achieved widespread adoption. This gap underscores the need for greater collaboration among experts, coupled with initiatives to raise public awareness and enhance education on the benefits and applications of TES. In this review, we take a comprehensive approach to explore the latest developments in TES systems, with a specific focus on their integration with renewable energy and HVAC&R applications. In addition, this review includes a comparative analysis of TES technologies focusing on costs, environmental aspects and selection criteria. This work's main objective is to provide an in-depth analysis of TES technologies and to create a valuable resource for the renewable energy community. To this end, we have compiled a detailed and structured dataset that categorizes TES technologies by type and forms the foundation of a unique, user-friendly database. A key innovation of this review is the creation of a dynamic online platform that offers free and open access to this database. Built using "Looker Studio," the platform provides a seamless, interactive experience where users can easily search and filter information based on TES type, application, temperature range, efficiency, lifetime, and other relevant parameters. This continuously updated database addresses the long-standing need for a centralized, accessible repository of TES information, offering researchers, industry professionals, and stakeholders a powerful tool for informed decision-making. This novel platform distinguishes our review from previous studies by making the vast landscape of TES technologies not only more accessible but also adaptable to the specific needs of users. By offering this free, searchable resource to the renewable energy community, we aim to facilitate the adoption of TES technologies and support the global transition toward sustainable energy solutions.

Abbreviations

AHU	Air Handling Unit

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ASV	Above Sheathing Ventilation
ATES	Aquifer Thermal Energy Storage

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Table 1
Past TES review papers.

Title	Author	Year (Published)	Type of TES Technology Covered	Reference
Thermal Energy Storage in Energy Communities: A Perspective Overview through a Bibliometric Analysis	Brunelli et al.	2024	Bibliometric analysis: integration of TES in renewable energy communities (RECs)	[22]
A review of borehole thermal energy storage and its integration into district heating systems	Sadeghi et al.	2024	Integration of the BTES systems into DHC	[23]
Progress on rock thermal energy storage (RTES): A state of the art review	Amiri et al.	2024	Rock thermal energy storage (RTES)	[24]
Phase change material (PCM) candidates for latent heat thermal energy storage (LHTES) in concentrated solar power (CSP) based thermal applications - A review	Jayathunga et al.	2024	Latent heat	[25]
Integration of solar thermal collectors and heat pumps with thermal energy storage systems for building energy demand reduction: A comprehensive review	Vahidhosseini et al.	2024	Sensible heat, latent heat, thermochemical	[26]
Effect of nano-enhanced phase change materials on performance of cool thermal energy storage system: A review	Sathishkumaret al.	2024	Cool Thermal Energy Storage (CTES), latent heat	[27]
Hybrid nano-fluid for solar collector based thermal energy storage and heat transmission systems: A review	Kalbande et al.	2024	Solar-based thermal energy storage (TES), latent heat	[28]
Advances in thermal energy storage: Fundamentals and applications	Ali et al.	2024	Sensible heat, latent heat, thermo-chemical	[29]
Potential applications of phase change materials for batteries' thermal management systems in electric vehicles	Alami et al.	2022	Latent heat. Focus on battery thermal management	[16]
A review of thermal energy storage technologies for seasonal loops	Mahon et al.	2022	Seasonal heat	[18]
Energy storage on demand: Thermal energy storage development, materials, design, and integration challenges	Sadeghi	2022	Sensible heat, latent heat, thermochemical. Focus on design and integration	[8]
Solid-liquid phase change materials for the battery thermal management systems in electric vehicles and hybrid electric vehicles – A systematic review	Zare et al.	2022	Latent heat. Focus on battery thermal management	[17]
Advanced/hybrid thermal energy storage technology: material, cycle, system and perspective	Ding et al.	2021	Sensible, latent, thermochemical	[30]
Thermal energy storage technologies for concentrated solar power – A review from a materials perspective	Palacios et al.	2020	Sensible, latent, thermochemical	[31]
Latent thermal energy storage technologies and applications: A review	Jouhara et al.	2020	Latent heat	[10]
Thermal Energy Storage for Grid Applications: Current Status and Emerging Trends	Enescu et al.	2020	Applications for systems connected to the electrical grid	[1]
Latest developments on TES and CSP technologies – Energy and environmental issues, applications and research trends	Achkari et al.	2020	Sensible heat, latent heat, thermochemical for CSP	[15]
Where is Thermal Energy Storage (TES) research going? – A bibliometric analysis	Calderón et al.	2020	Sensible heat, latent heat, thermochemical	[32]
Review on sensible thermal energy storage for industrial solar applications and sustainability aspects	Koçak et al.	2020	Sensible heat	[33]
A review on sensible heat based packed bed solar thermal energy storage system for low temperature applications	Gautam et al.	2020	Sensible heat	[34]
Advances in seasonal thermal energy storage for solar district heating applications: A critical review on large-scale hot-water tank and pit thermal energy storage systems	Dahash et al.	2019	Seasonal TES for DH applications: Aquifer thermal energy storage (ATES) Borehole thermal energy storage (BTES) Tank thermal energy storage (TTES) Pit thermal energy storage (PTES)	[19]
A Comprehensive Review of Thermal Energy Storage	Sarbu et al.	2018	Sensible heat, latent heat, thermochemical	[21]
An overview of thermal energy storage systems	Alva et al.	2018	Materials, cycle frequency, delivery scheme, mechanism, operating temperature	[7]
High temperature systems using solid particles as TES and HTF material: A review	Calderón et al.	2018	Solid particle storage for CSP	[14]
Thermal energy storage systems for concentrated solar power plants	Pelay et al.	2017	Thermochemical materials for CSP	[13]
Thermal Energy Storage: A Review	Avghad et al.	2016	Sensible heat, latent heat, thermochemical	[35]
Thermal energy storage: Recent developments and practical aspects	Zhang et al.	2016	Sensible heat, latent heat, thermochemical	[20]
Thermal energy storage (TES) for industrial waste heat (IWH) recovery: A review	Miró et al.	2016	Industrial waste heat recovery	[12]
Combining thermal energy storage with buildings – a review	Heier et al.	2015	Sensible heat, latent heat, thermochemical. Building applications.	[11]
A Critical Review of Thermochemical Energy Storage Systems	Abedin et al.	2011	Thermochemical	[9]

(*continued*)

BHE	Borehole Heat Exchanger
BTES	Borehole Thermal Energy Storage
CHP	Combined Heat and Power
COP	Coefficient of Performance
CSP	Concentrating Solar Power
CST	Concentrating Solar Thermal
CTES	Cold Thermal Energy Storage
DCS	District Cooling System
DHC	District Heating and Cooling
DNI	Direct Normal Irradiance
EPS	Expanded Polystyrene
ETES	Electric Thermal Energy Storage
EU	European Union
GCHP	Ground Coupled Heat Pump

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GHE	Ground Heat Exchanger
GHG	Greenhouse Gases
GSHP	Ground Source Heat Pump
GWP	Global Warming Potential
HDPE	High Density Polyethylene
HP	Heat Pump
HTF	Heat Transfer Fluid
HVAC&R	Heating, Ventilating, Air Conditioning and Refrigeration
IWH	Industrial Waste Heat
LHTES	Latent Heat Thermal Energy Storage
LTES	Latent Thermal Energy Storage
PCM	Phase Change Material
PTES	Pit Thermal Energy Storage
PV/T	Photovoltaic/Thermal

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REC	Renewable Energy Community
RES	Renewable Energy Sources
RTES	Rock Thermal Energy Storage
SHIP	Solar Heat for Industrial Processes
SIM	Salt In Matrix
STES	Sensible Thermal Energy Storage
TCES	Thermochemical Energy Storage
TCM	Thermochemical Material
TES	Thermal Energy Storage
TMS	Thermal Management System
TRL	Technology Readiness Level
TTES	Tank Thermal Energy Storage
UNIFE	University of Ferrara
UOIT	University of Ontario Institute of Technology

1. Introduction

The growing global energy demand, predominantly met by fossil fuels, is a critical challenge for our shared planet. These non-renewable resources are unevenly distributed, with a small percentage of the global population consuming a disproportionate share, leading to their rapid depletion. This unsustainable reliance on fossil fuels necessitates an urgent transition to sustainable energy systems to ensure resource security. Additionally, mounting concerns about climate change, highlighted by recent extreme weather events, underscore the pressing need for change.

In this context, energy storage plays a crucial role within the contemporary landscape of energy systems. Serving as a linchpin, energy storage addresses the inherent variability and intermittency of RES, such as solar and wind power [1]. By storing excess energy during periods of high renewable energy production and releasing it during high-demand or low-generation periods, energy storage technologies significantly enhance grid stability, reliability, and flexibility. This allows the seamless integration of RES into existing power grids, fostering the transition towards a sustainable and low-carbon energy landscape [2]. Various possibilities are available or under development to store energy in different forms. The most relevant are pumped-hydro and thermal energy storage for large-scale applications, batteries for high power and energy requirements, supercapacitors when short duration and fast response are needed [3].

Considering that almost half of the global energy consumption is attributed to heat, which is responsible for 38 % of the energy-related greenhouse gases (GHG) emissions [4], thermal energy storage technologies assume a paramount role in helping decarbonization. Indeed, TES systems facilitate the coupling between the electricity and the heating/cooling sector, thus enhancing the integration of RES. TES not only aids in balancing energy supply and demand but also contributes to a more efficient and robust energy infrastructure. Other advantages include lower energy consumption and costs, reduced initial and maintenance expenses, smaller equipment sizes, operational flexibility, improved indoor air quality, enhanced energy efficiency and substitution of fossil fuels, lower emissions of pollutants or GHG gases [5,6].

Diverse TES technologies exist, each meticulously designed to suit specific applications and operational demands. Their categorization can be approached from multiple perspectives, including the nature of the storage medium or material, the storage process, the intended application and operating temperature range, the heat source, the storage cycle frequency [7].

The most common classification is related to the storage process or mechanism. Prominent among these are sensible heat storage, which involves harnessing heat through changes in the storage material temperature, latent heat storage, which employs phase change materials (PCMs) for energy storage and release, and thermochemical storage relying on reversible chemical reactions, including sorption mechanisms such as the adsorption and desorption of gases on solid surfaces [8]. A more specific classification includes the storage mediums or materials, such as water, concrete, salt hydrates, organic phase change materials or thermochemical materials. Furthermore, TES can be categorized by application, such as residential, industrial, or grid-scale energy storage.

1.1. Survey of TES review papers

Review papers concerning TES technologies published over the past 10 years are compiled in Table 1. Several papers have focused on specific types of TES, including thermochemical storage [9] and latent heat storage [10]. Others have addressed particular applications such as integration into buildings [11], systems connected to the electric grid [1], industrial waste heat (IWH) recovery [12], concentrated solar power (CSP) plants [13–15], and thermal management systems (TMSs) for electric batteries [16,17]. Seasonal heat storage has been reviewed in two publications [18,19]. A comprehensive review of high-temperature TES is provided by Ref. [20], where systems are categorized based on working temperatures (heat transfer fluids), mechanisms (sensible heat storage, latent heat storage, thermochemical storage), and storage concepts (active, passive, hybrid). Solar heat and its application in reducing energy demand in buildings are discussed by Sarbu et al. [21]. In the review by Brunelli et al. [22], emphasis is placed on identifying key networks and institutions involved in TES within Renewable Energy Communities (RECs), with significant gaps in research being highlighted to encourage further studies. Sadeghi et al. [23] offer a detailed examination of Borehole Thermal Energy Storage (BTES) systems integrated into District Heating and Cooling (DHC) networks. Various aspects such as technical design, environmental impact, and economic feasibility are analyzed, aiming to provide valuable insights for policymakers, engineers, and regulators. A review by Amiri et al. [24] explores recent advancements in Rock Thermal Energy Storage (RTES), identifying challenges and proposing potential solutions for future research. Non-technical factors such as policy, regulations, and community awareness are also considered, offering a comprehensive view of the subject. Jayathunga et al. [25] provide a historical analysis of Phase Change Materials (PCM) used in Latent Heat Thermal Energy Storage (LHTES) systems for CSP plants. The review highlights technological advancements, economic considerations, and current trends in the field. Vahidhosseini et al. [26] categorize TES materials into sensible heat, latent heat, and thermochemical energy storage (TCES), offering a comparative analysis of the benefits and limitations of each type. A comparison of open and closed systems for TCHS is also provided. Sathishkumar et al. [27] offer an in-depth review of PCMs applied in Cold Thermal Energy Storage (CTES) for low-temperature applications. A comprehensive overview of techniques and methods is presented. Kalbande et al. [28] explore hybrid nanofluids used in solar thermal energy storage systems, providing detailed insights into emerging applications and innovative methods within the field.

Despite the numerous review papers on TES, few studies provide a cross-sectional, comparative overview of all TES types, focusing on real-world applications. This review aims to fill these research gaps through a comprehensive analysis of TES technologies, covering all major categories—sensible heat, latent heat, and thermochemical storage— and the related employed materials, as well as a wide range of applications and emerging technologies, with emphasis on real case studies. Indeed, research on TES often lacks field demonstrations and real-world integration with buildings, industry and renewables [36]. Moreover, this study introduces a comparative analysis of the considered TES technologies from different perspectives, rarely addressed collectively in past reviews: technological maturity and development, economic feasibility, environmental impact and selection criteria. As a culmination and practical outcome of this review, an open-access online database has been developed for researchers, industry professionals, and stakeholders. Unlike previous reviews, which often provide static or fragmented data, this database offers a thorough, up-to-date resource

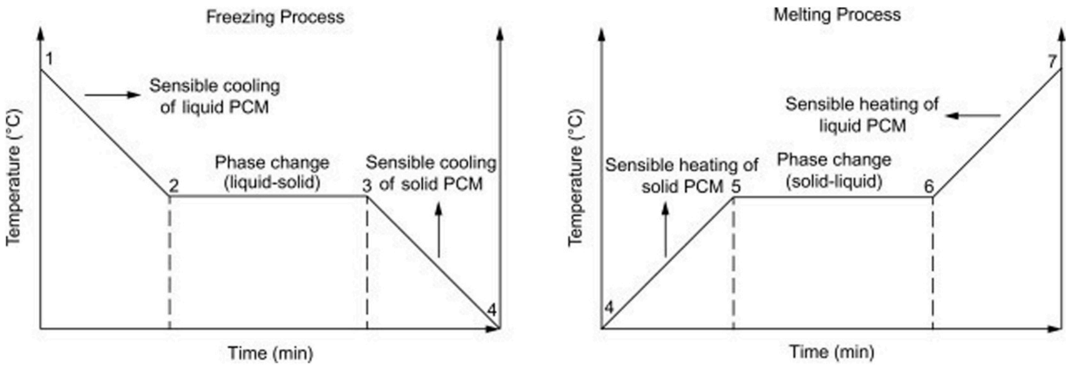

Fig. 1. Trend of PCM's temperature during phase change processes. Reprinted from S. Kalaiselvam,R. Parameshwaran, "Thermal Energy Storage Technologies for Sustainability", "Chapter 5 – Latent Thermal Energy Storage", Pages 83–126, Copyright (2014), with permission from Elsevier.

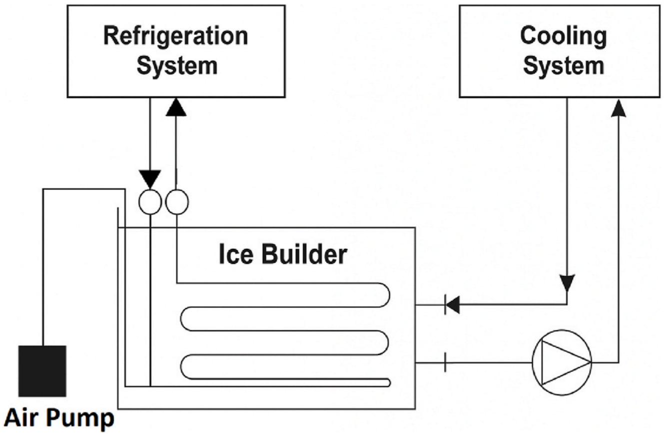

Fig. 2. Ice builder concept [38].

where users can filter information by TES type, application, temperature range, lifetime, efficiency, and other relevant criteria. The user-friendly interface supports smooth navigation and enables users to obtain the latest technical and economic data in a centralized location. By making this database freely accessible, this work facilitates more efficient research, accelerating progress in TES technology development and adoption.

2. Latent Thermal Energy Storage (LTES)

2.1. Functioning of LTES

Latent Thermal Energy Storage (LTES) operates through the use of diverse storage materials, including aqueous solutions (like salt hydrates), ice, and paraffins. All these substances fall under the category of PCMs, utilizing the same phase change process. In LTES systems, these materials enable the capture and release of thermal energy by undergoing transitions between solid and liquid phases [10]. These processes are displayed in Fig. 1 and the stored heat is described by Eq. (1).

$$\Delta Q = \Delta H = m\Delta h \tag{1}$$

where ΔH is the enthalpy variation between the solid and liquid phases, Δh is its specific value, and m is the mass of PCM.

Most PCMs store latent heat in the process of shifting from solid to liquid state, and transition back to their solid state when energy is discharged. They are able to absorb and release large amounts of heat with only slight temperature variations. Including different types of storage materials, LTES offers an efficient way to handle energy fluctuations and improve energy use in various settings, such as solar power plants or heating and cooling systems in buildings.

2.2. LTES medium

2.2.1. Ice

Several techniques for ice production have been developed [37]. Direct applications are primarily employed in the food industry, where ice is utilized to chill and preserve items such as fish, vegetables, meat, and poultry. Indirect applications, on the other hand, make use of ice for its latent heat, implementing it in process cooling, including ice storage, TES systems for air conditioning, and as a secondary cooling medium in industrial processes.

2.2.1.1. Static ice production systems. Static ice production systems are among the earliest used techniques, where ice forms and melts without being physically removed. Key methods include:

Ice on Coil: A refrigerant or glycol solution (−4 °C to −10 °C) circulates through coils in an insulated water tank, forming ice. Stirring mechanisms ensure uniform ice distribution, while sensors monitor thickness to regulate operations (Fig. 2). This stored ice is then used during peak cooling demand periods, where the cooling system circulates warmer fluid through the same coils, allowing the ice to absorb heat and cool the fluid without engaging the refrigeration system, thus shifting energy use to off-peak hours and improving overall system efficiency.

Ice Banks: Heat exchangers with pressurized polyethylene tubes consist of a low-temperature glycol solution which freezes surrounding water. Ice level sensors control the process, with water circulated to meet cooling demands (Fig. 3). During operation, as the glycol solution extracts heat from the water, ice forms around the tubes, storing thermal energy. When cooling is required, warm water is passed through the system and cooled by the melting ice, effectively delivering chilled water to the cooling load. This configuration permits the system to defer energy consumption to off-peak periods, resulting in improved energy efficiency.

Encapsulated Ice Modules: High density polyethylene (HDPE) or steel containers are filled with water as a PCM to store and release thermal energy [39]. Some examples are illustrated in Fig. 4.

2.2.1.2. Dynamic ice production systems. Dynamic ice production systems involve collecting ice from the freezing unit and transferring it to a storage container, where its energy is utilized by circulating chilled water for cooling needs. Common techniques include:

Ice Harvester: Ice forms on vertical evaporator plates, with water pumped over them until 8–10 mm thick ice layers develop in about 20 min. Ice is released using a hot gas bypass, melting the contact layer and depositing the ice into a tank (Fig. 5).

Tubular Ice: The working principle is similar to the ice harvester method, but ice forms inside tubes rather than on plates, with

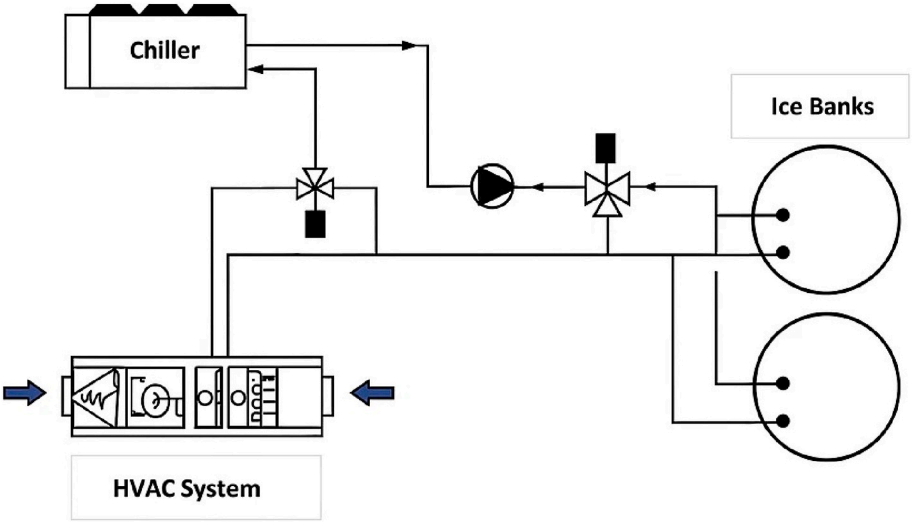

Fig. 3. Ice bank systems encapsulated ice storage [38].

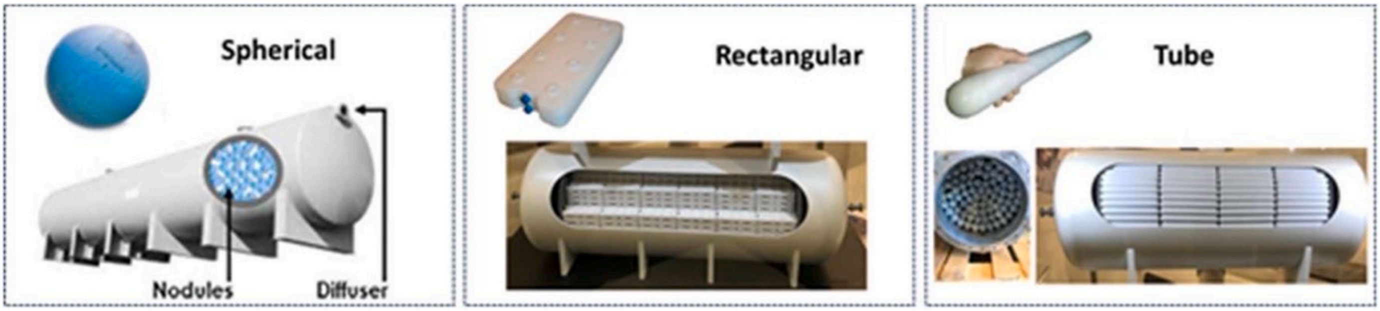

Fig. 4. Encapsulated ice TES modules [38].

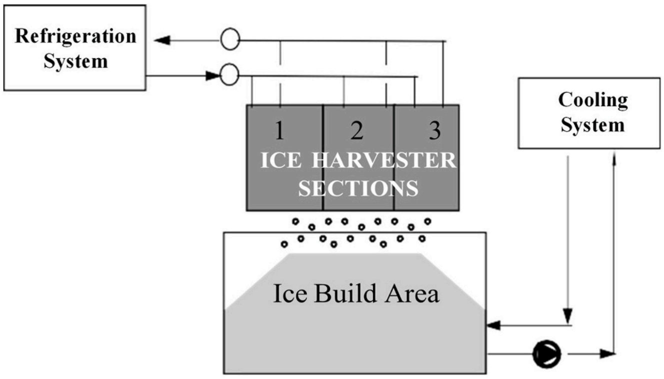

Fig. 5. Ice harvester [38].

comparable applications and storage techniques.

Ice Flakes: A rotating freezing apparatus continuously produces ice flakes, which are collected in a drum for cooling applications.

Slurry Ice: A binary solution is supercooled using heat exchangers (e.g., falling film, scraper, or vacuum), producing fine ice crystals. These can be stored or used directly, with the warm solution cooled by the slurry before entering the chilled water circuit for air conditioning.

2.2.2. Phase change materials (PCMs)

PCMs are essential in LTES systems, offering versatile energy storage through phase transitions that maintain constant temperatures while absorbing and releasing significant thermal energy. This makes them ideal for applications requiring precise temperature control, such as building systems, solar TES, borehole TES, and electronic devices [40]. Moreover, PCMs' ability to store and release energy within specific temperature ranges enhances their adaptability across industries. The most common PCM utilizes the heat of fusion during solid-liquid transitions, though solid/solid and liquid/gas changes are also possible. However, materials with liquid/gas transition are difficult to handle due to the required gas-tight confinement. Effective PCMs must absorb and release large amounts of energy, have a defined phase change temperature, minimize subcooling, and offer stability, non-toxicity, affordability and preserve their thermal and chemical properties after prolonged thermal cycles [41].

Water is the best-known and the oldest PCM for cold storage. It has been used for preserving food and cooling beverages since ancient times. Owing to its harmless and vital properties for life, it is directly used as ice cubes in contact with food and beverages. It is also used in encapsulated forms for temperature control where direct contact or mixing is undesired. However, the main drawback of water is its phase change temperature of 0 °C, which does not satisfy the required temperature levels of different applications of cooling and heating. At this point, other PCMs, such as eutectic salt-water mixtures [42], salt hydrates [43], fatty acid esters [44–51], fatty acids [52,53] or paraffins [54–56], provide latent heat storage via phase change in the range of −70 up to several hundred degrees for cooling applications well below freezing point of water as well as for extreme heating applications.

2.2.2.1. Inorganic PCMs. Inorganic PCMs include salts and salt hydrates on the one hand, and metals and their alloys on the other. Compared to organic PCMs, they are characterized by high volumetric heat storage

Table 2
Candidate salts and hydrated salts [57].

Salts	Melting point [°C]	Latent heat of fusion [kJ/kg]
$AlCl_3$	192	280
$LiNO_3$	250	370
$NaNO_3$	307	172
KNO_3	333	266
KOH	380	150
$KClO_4$	527	1253
LiH	699	2678
$MgCl_2$	714	452
Salt hydrates		
$Na_2P2O_7\cdot 10H_2O$	70	184
$Ba(OH)_2\cdot 8H_2O$	78	266
$(NH_4)Al(SO_4)2\cdot 12H_2O$	95	269
$MgCl_2\cdot 6H_2O$	117	169
$Mg(NO_3)2\cdot 6H2O$	89.3	150

Table 3
Melting and latent heat of fusion values of some fatty acids [56].

Material	Carbon numbers	Melting point (°C)	Latent heat (kJ/kg)
Acetic acid	2	16.7	184
Capric acid	10	36	152
Lauric acid	12	49	178
Myristic acid	14	58	199
Palmitic acid	16	55	163
Stearic acid	18	69.4	199

Table 4
Melting and latent heat of fusion values of some high-chain fatty acid esters and dicarboxylic acid diesters.

Material	Carbon numbers	Melting point (°C)	Latent heat (kJ/kg)[a]	Reference
Tetradecyl tetradecanoate (Myristyl myristate)	14–14	41.60	210.43 ± 2.39	[44]
Tetradecyl pentadecanoate	14–15	45.43	214.81 ± 3.49	[44]
Tetradecyl hexadecanoate (Myrsityl palmitate)	14–16	48.03	213.85 ± 2.07	[44]
Tetradecyl heptadecanoate	14–17	46.68	217.19 ± 2.67	[44]
Tetradecyl octadecenoate (Myristyl stearate)	14–18	49.58	221.80 ± 2.34	[44]
Hexadecyl decanoate (Cetyl caprate)	16–10	29.38	186.36 ± 3.86	[46]
Hexadecyl eicosanoate (Cetyl arcihidate)	16–20	59.32	226.47 ± 2.27	[46]
Octadecyl tetradecanoate (Stearyl myristate)	18–14	48.86	203.53 ± 2.04	[47]
Octadecyl eicosanoate (Stearyl archidate)	18–20	64.96	226.12 ± 3.58	[47]
Ditetradecyl-1,14-tetradecanedioate	14-14-14	57.36	207.07 ± 2.92	[49]
Dihexadecyl-1,8-octanedioate	16-8-16	54.95	213.92 ± 2.96	[51]
Dihexadecyl-1,10-decanedioate	16-10-16	57.61	214.84 ± 2.10	[50]

[a] ± 95 % confidence interval.

capacity, thermal conductivity, operating temperatures, and low cost [57]. However, salt hydrates exhibit high latent heat of fusion due to their significant water content but face challenges such as phase segregation during charging and discharging, which reduces TES capacity over time and is an irreversible phenomenon [58]. These hydrates, classified as hydrous compounds, incorporate water into their crystalline structure through bonds with cations, forming water of crystallization [43,58]. Many aqueous salt-based PCMs are hygroscopic or prone to evaporation, requiring encapsulation in airtight containers [59]. The most common salt hydrates include sulfates, phosphates, nitrates, acetates, carbonates, alkaline earth metal halides and alkali hydrates [60]. In contrast, anhydrous compounds, formed by removing water from hydrates through heating or suction, serve as drying agents in applications like paper, food, and tobacco products [61]. Some salt and salt hydrate candidates are listed in Table 2.

Although metals overcome some of the drawbacks of salt hydrates, their weight and low heat of fusion hinders their applicability [57].

2.2.2.2. Organic PCMs. Organic materials are noted for their thermal and chemical stability, negligible super-cooling, non-corrosive and non-toxic behavior and environmentally friendly nature compared to inorganic PCMs. However, they have lower density and thermal conductivity, higher flammability and cost. Paraffins, fatty acids and fatty acid esters are the most deeply investigated organic PCM groups in literature [44–56,62].

Paraffins consist of mostly n-alkanes, which are saturated linear hydrocarbons. They exhibit congruent melting and freezing with high latent heat during phase transition. Their melting point and latent heat of fusion increase with increasing alkyl carbon chain length. Since pure paraffins are expensive materials, only technical grade paraffin wax can be used for thermal applications, due to cost constraints. Paraffins are chemically inert and stable up to several hundred degrees with low vapor pressure in liquid state.

Similar to paraffins, fatty acids also have high heat of fusion values. They exhibit reproducible melting and freezing cycles without any super-cooling, which prove advantages for thermal energy storage applications. However, they are more expensive than technical grade paraffin wax. Due to the carboxylic acid group in the chemical structure, they have a mild corrosive behavior and might undergo chemical interactions during polymeric coacervation processes. As is clearly seen in Table 3, fatty acids cover a broad temperature interval for both cooling and heating applications with latent heat of fusion values up to 200 kJ/kg.

Fatty acid esters are derived from the esterification reaction between carboxylic acid and hydroxyl groups with the release of water under specific reaction conditions. High-chain fatty acid esters and dicarboxylic acid diesters of higher carbon alcohols are robust organic PCMs with desired thermal and chemical properties. They offer excellent thermal and chemical stability after thermal aging, as well as high latent heat of fusion without any super-cooling [44–51]. They have latent heat of fusion up to 230 kJ/kg at melting onset temperatures in the range of 29–65 °C (Table 4).

Compared to the n-alkanes with the same number of carbons on the backbone, high-chain fatty acid esters and dicarboxylic acid diesters of higher alcohols exhibit single phase changes as a consequence of the chemical modification by the ester bond. Hence, the total latent heat capacity of the material is utilized in a single step at a lower phase change temperature than that of the corresponding n-alkane [44], i.e., structural modifications play a vital role in development of organic PCMs with desired properties. High-chain fatty acid esters and dicarboxylic acid diesters are chemically inert materials without any corrosive behavior, which provide an advantage not only for polymeric coacervation, but also for functional composite development in thermal energy storage applications. Mathematical correlations have been generated for estimation of the phase change temperature and enthalpy of the high-chain fatty acid esters based on the position of the ester bond on the carbon backbone and the carbon chain length of the fatty acid and alcohol moieties, which enlightens the relation between the chemical structure of the material and its thermal properties [47].

2.2.2.3. Eutectic PCMs. Eutectics consist of combinations of two or more substances that are blended to achieve a specific melting or

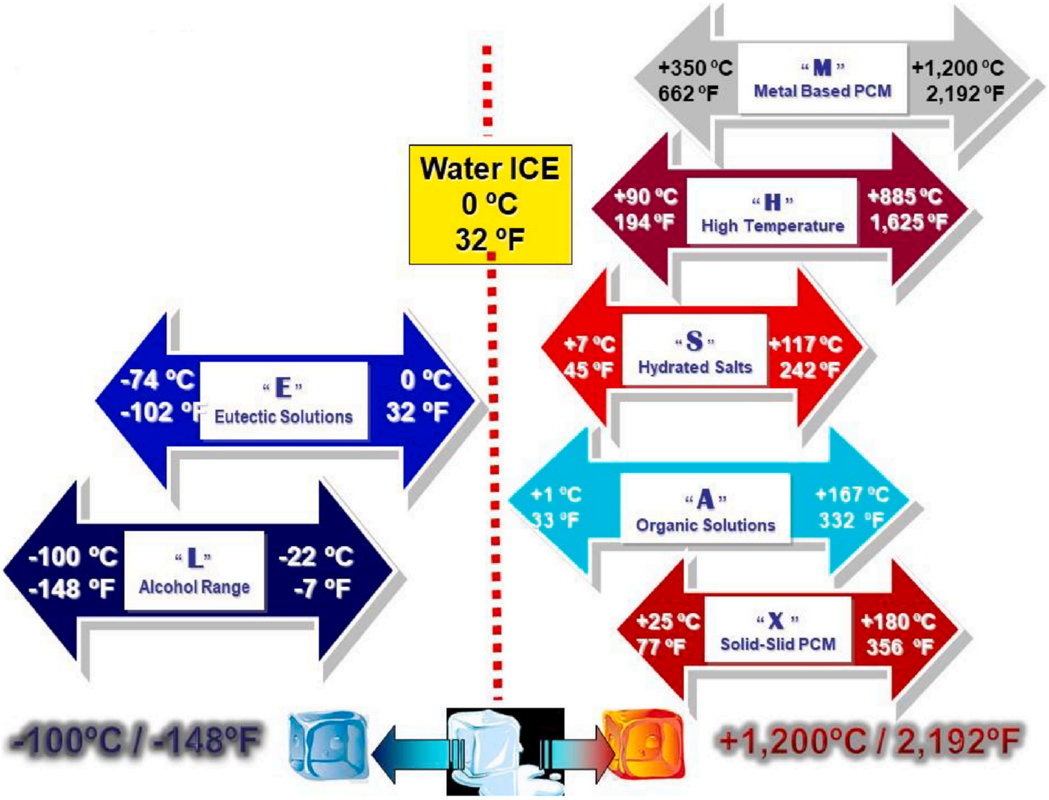

Fig. 6. Commercially available PCM products [38].

freezing point [63]. Eutectic mixtures are mixtures of two or more constituents, which solidify simultaneously out of the liquid at a minimum freezing point. This temperature receives the name of eutectic point temperature and corresponds to the minimum melting temperature of the different possible compositions. At the eutectic point, the liquid reacts to a solid that is composed of two or more solid phases with different composition; however, the overall composition is still the same as in the liquid, i.e., eutectic compositions are mixtures of two or more constituents, which solidify simultaneously out of the liquid at a minimum freezing point. Therefore, none of the phases can sink down due to density difference. Besides, eutectic compositions show a specific melting temperature and good storage density. At the designated temperature, these mixtures are completely liquefied, exhibiting a consistent composition in both their liquid and solid forms, thus fulfilling the primary requirement of a PCM.

For temperatures below 0 °C, usually water-salt solutions with a eutectic composition are used. Eutectic water-salt solutions have melting temperatures below 0 °C, because the addition of the salt reduces the melting temperature, and they usually have good storage density. A good example of eutectic water-salt solution is $NaCl/H_2O$. At the eutectic composition of 22.4 wt% NaCl, the system has 222 kJ/kg of melting enthalpy at −21.2 °C melting temperature. Another interesting example is KCl/H_2O system, which has 283 kJ/kg melting enthalpy at −10.7 °C melting temperature when the KCl concentration is 19.5 wt% in water.

In addition to the eutectic water-salt solutions at sub-zero temperatures, different eutectic organic-organic, organic-inorganic or inorganic-inorganic PCM compositions are available in literature for applications where higher temperatures are required for different purposes [64–67]. While the majority of the reported studies include paraffin, fatty acid and fatty acid-fatty alcohol-based compositions for organic-organic eutectic PCMs, salt hydrate and metal-based compositions dominate the inorganic-inorganic eutectic PCM studies. The binary eutectics n-heptadecane (C17), n-octadecane (C18), n-nonadecane (C19), n-eicosane (C20), and n-tetracosane (C24) developed by Sari et al. [68] exhibit phase change above 19 °C with phase change enthalpy in the range of 170–270 kJ/kg. The eutectic compositions are 90/10, 5/95, 95/5 and 90/10 (wt.%) for C17-C24, C19-C18, C19-C24, C20-C24, respectively. The determined eutectic compositions of lauric acid (LA)-stearic acid (SA) (75.5/24.5, wt.%), myristic acid (MA)-palmitic acid (PA) (58/42, wt.%) and palmitic acid (PA)-stearic acid (SA) (64.2/35.8, wt.%) provided eutectic PCMs, which have melting temperatures at 37.0 °C, 42.60 °C, and 52.30 °C with phase change enthalpy 182.7 kJ/kg, 169.7 kJ/kg, and 181.7 kJ/kg, respectively [69]. Zhang et al. [70] investigated the ternary eutectic composition of LA-MA-PA and determined the eutectic composition as 55.24/29.74/15.02 (wt. %). The melting point and phase change enthalpy for this ternary composition is 31.41 °C and 145.80 kJ/kg, respectively.

For salt hydrate-based inorganic-inorganic eutectic PCMs, different salt combinations are found in literature [71–75]. For instance, Kazemi et al. [74] developed an inorganic-inorganic eutectic PCM employing $Na_2HPO_4.10H_2O$ and $Na_2CO_3.10H_2O$ for thermo-regulating textiles that can provide insulation. The eutectic PCM comprised 15 % Na_2HPO_4, 17 % Na_2CO_3, and 68 % distilled water. The eutectic had melting point and phase change enthalpy of 28.90 °C and 14.90 kJ/kg for the treated coated fabric, respectively.

2.2.2.4. Clathrates. Clathrates, commonly referred to as gas hydrates, comprise mixtures where one substance is encapsulated within another, creating a cage-like structure. In TES applications, water forms the bonding framework for these clathrates, with alternative refrigerants being the most widely employed variants. Indeed, clathrate hydrates are mostly employed for cold storage, since their melting temperature ranges between 0 and 30 °C. The most employed substances include hydrofluorocarbon (HFC), CO_2, tetra-n-butylammonium bromide (TBAB), tetrabutyl ammonium chloride (TBAC) and tetrahydrofuran (THF). On the other hand, clathrates of organic compounds are suitable for shifting the peak load in buildings. Research has particularly focused

Table 5
Comparison of organic and inorganic PCMs [38].

Type	Advantages	Disadvantages
Organic	Simple to use Non-corrosive No supercooling No nucleating agent	Generally, more expensive Lower latent heat/density Often give quite broad melting range Can be flammable
Salt-Based	Generally cheap Good latent heat/density Well defined phase change temperature Non-flammable	Need careful preparation Need additives to stabilize for long term use Prone to supercooling Can be corrosive to some metals

on quaternary ammonium halides, quaternary ammonium fluorides, bolaform salts, tetrabutylammonium carboxylates and tetrabutylammonium alkane-sulfonates. They are generally characterized by high latent heat of fusion, ranging between 270 and 430 kJ/kg [76].

2.2.2.5. Solid-solid PCMs. Solid-solid PCMs are a recent innovation, transitioning between solid forms while absorbing and releasing substantial heat. They change crystalline structures at specific temperatures, with latent heats similar to efficient solid-liquid PCMs. These materials avoid the nucleation process needed to prevent supercooling in solid-liquid PCMs. Additionally, the solid-to-solid phase change results in minimal visual changes, eliminating issues like containment and leakage associated with liquid PCMs. They are more durable thanks to the smaller changes of volume and limited phase segregation. A broad range of enthalpy, thermal conductivity and transition temperature is available, depending on the material [77]. Solid-solid PCMs can be classified as organic, inorganic and hybrid. The first group includes a variety of materials, such as polyalchohols, polymerics and organic salts. Ceramics and metallics are inorganic, while the hybrid solid-solid PCMs include organometallics and perovskites [78]. The applications of these PCMs include solar TES, cold storage, building applications, thermal management of electronic devices, aerospace thermal systems, textiles, automobiles, and medical applications [79].

Fig. 7. PCM encapsulation examples [38].

Fig. 8. PCM variations and application formats [38].

Currently, the available range of commercially offered PCMs spans temperatures from −100 °C to 1200 °C, as illustrated in Fig. 6.

A comparison of benefits and drawbacks between organic and salt-based PCMs is outlined in Table 5.

2.2.2.6. Encapsulated PCMs. Encapsulated PCM products require secure containment to maintain their functionality and safety. Aqueous salt-based PCMs, being hygroscopic, must be stored in airtight containers to prevent moisture absorption or water evaporation [80]. Organic PCMs, though non-aqueous, also need secure encapsulation to avoid contamination and fire risks due to low flash points. Salt-based PCMs are typically stored in plastic vessels for cost-effectiveness, but their use is limited to temperatures below 80–90 °C as plastic softens above 50 °C. Flexible pouches made from thin films provide economical options with efficient heat transfer but are prone to punctures. Organic PCMs can be integrated into construction materials such as concrete, mortar, or plastics to enhance thermal performance [81]. They are available in various physical formats including powders, granules, and thermo-formed solid sheets, and can be exposed to air depending on the application [82]. For improved heat transfer efficiency or higher temperature applications, metal containers are often preferred. Examples of PCM encapsulation methods are illustrated in Fig. 7, while various physical

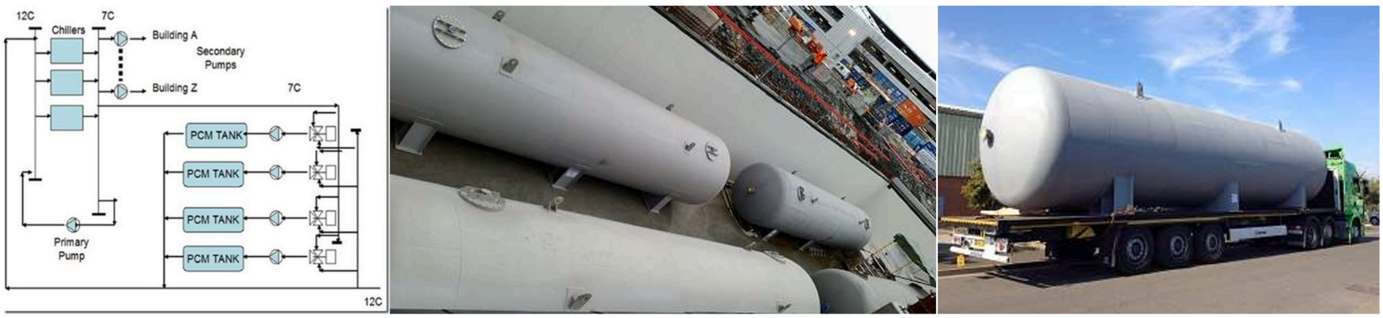

Fig. 9. Installed TES capacity 4 × 60 m3 + 13 °C PCM solution providing total 10,000 kWh [38].

Fig. 10. Installed TES capacity, 8 storage tanks each with 8 m3 + 8 °C PCM solution providing total 2000 kWh [38].

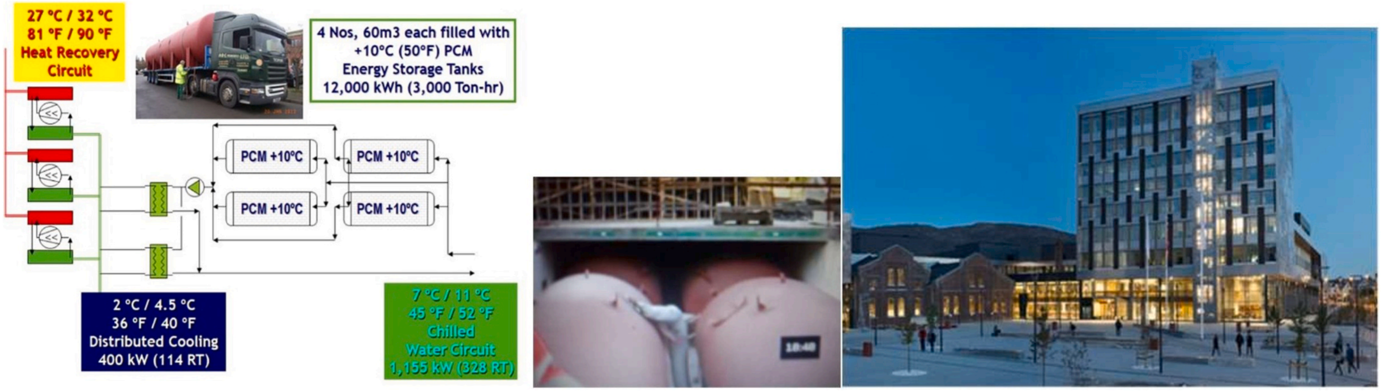

Fig. 11. Installed TES capacity, 4 storage tanks each with 60 m3 + 10 °C PCM solution providing total 12,000 kWh [38].

forms of organic PCMs are shown in Fig. 8.

2.3. Case studies

2.3.1. Building and HVAC systems

2.3.1.1. Bergen airport, T3 energy Centre (Norway). Bergen airport adopted a solution for storing 30–40 % of the daily cooling demand in PCM tanks, operating chillers during night, when flights are stopped due to noise restrictions [83]. This approach reduced the required number of chillers by up to 50 %, effectively spreading the cooling load over 24 h (Fig. 9).

2.3.1.2. Dekra HQ (Germany). An office building in Stuttgart (Germany) with a 62,000 m^2 floor area and high cooling demand, integrated a TES system designed by the Fraunhofer Institute for Solar Energy Systems ISE [84]. The design is based on a combined heat and power (CHP) system for self-supply of electricity, enhancing renewable energy integration and managing supply and demand fluctuations. Electricity from the CHP powers mechanical cooling for the A/C system, with surplus cooling stored in PCM tanks to prevent energy waste.

2.3.1.3. National theatre (UK). The National Theatre in London underwent renovations to reduce CO$_2$ emissions, including a 400 kWh CHP system [83]. The building hosts evening shows but also includes offices requiring year-round services like water, electricity, cooling, and heating during office hours. The CHP plant was sized primarily based on electricity demand. Waste energy from the CHP is used to charge PCM tanks via absorption chillers (when heat is available) or electric chillers (when excess electricity is generated). The stored cooling energy powers the theatre's A/C for 2–3 h without any additional cost, utilizing the reclaimed waste energy (Fig. 10).

2.3.1.4. University of Bergen (Norway). The Bergen University College campus renovation, completed in 2014, covered 50,983 m^2 and aimed to provide an annual heating capacity of 2600 MWh and cooling capacity

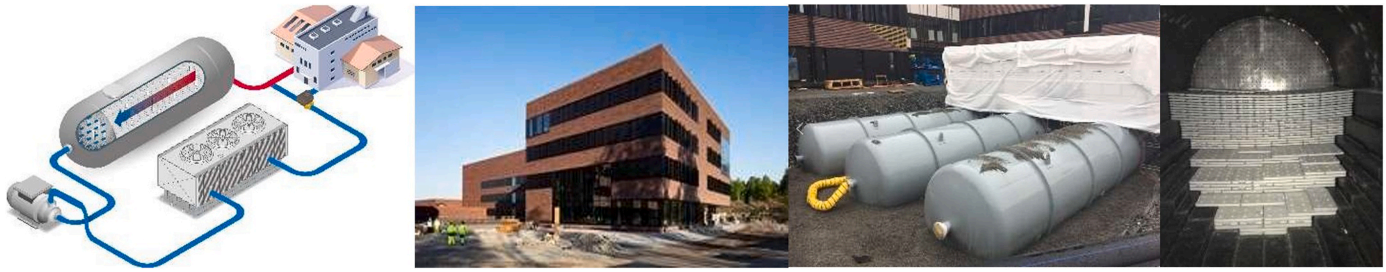

Fig. 12. PCM-TES campus installation near Oslo, Norway [38].

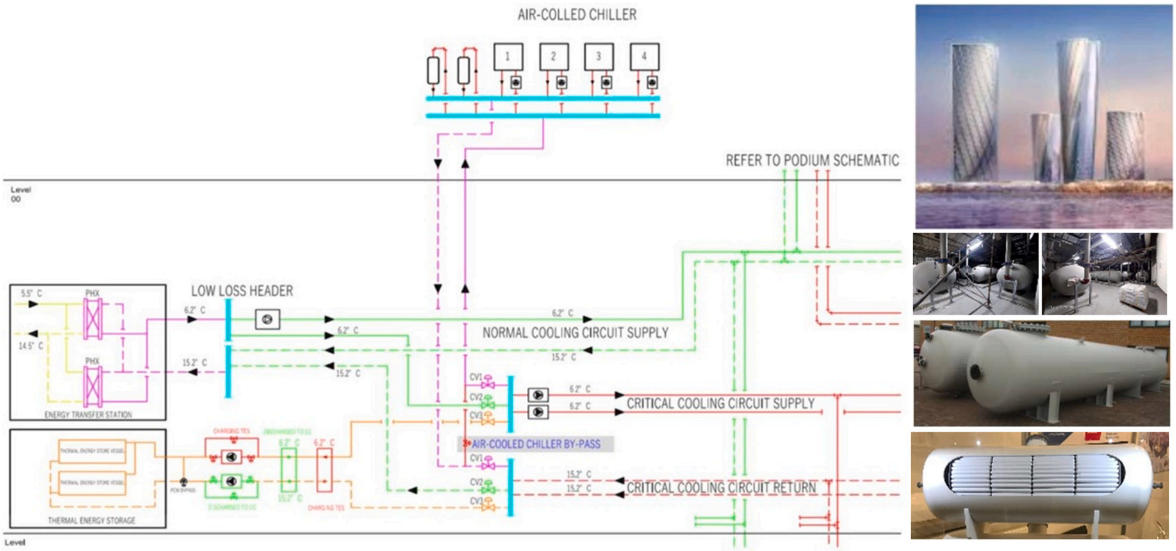

Fig. 13. PCM-TES system installed in Qatar [38].

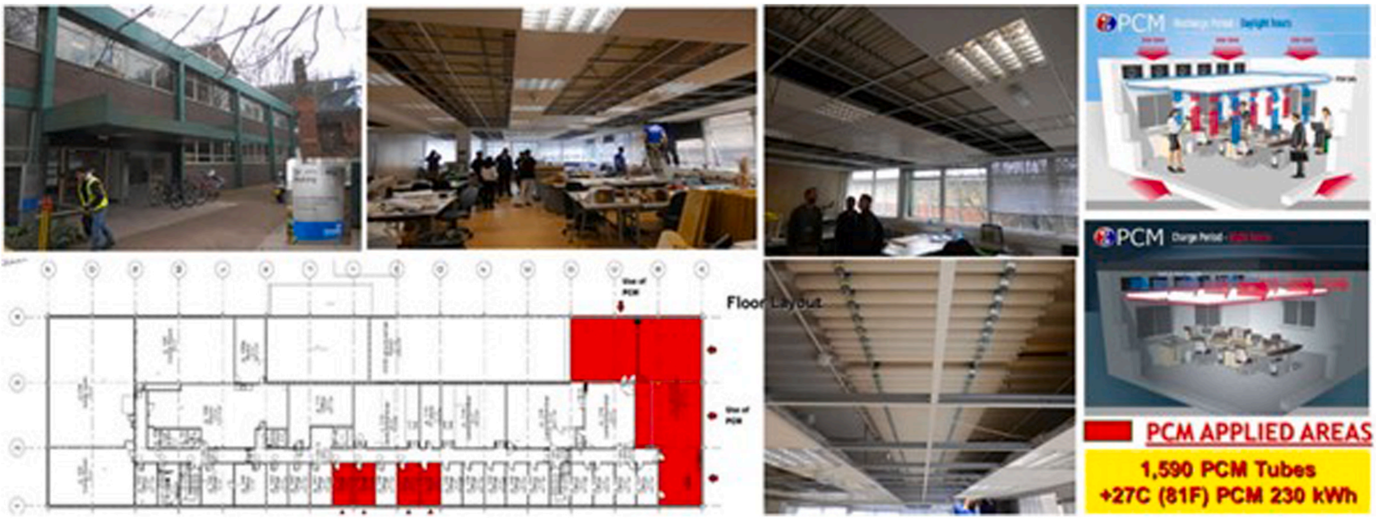

Fig. 14. Sir John Laing building passive cooling in the UK [38].

of 1060 MWh [85]. The system is designed for peak loads of 2830 kW for heating and 3000 kW for cooling, and is supported by a combined heat pump and chiller system with PCM storage. The PCM storage includes 47,000 encapsulated salt-hydrate elements (FlatICE®), each 500 x 250 × 32 mm, stacked in four cylindrical tanks with a total storage volume of 228 m^3. These elements, resembling plate heat exchangers, facilitate water flow and maximize heat transfer. The system can store 12 MWh, delivering 1600 kW of cooling over 7 h. At night, heat pumps provide heating to student accommodations while storing waste cooling energy in the PCM units. By day, the PCM TES integrates with the chilled-water loop, reducing chiller capacity needs by 53 % (Fig. 11).

2.3.1.5. Norwegian University of life sciences (Norway). At a campus near Oslo, Norway, a PCM-TES system was incorporated into the

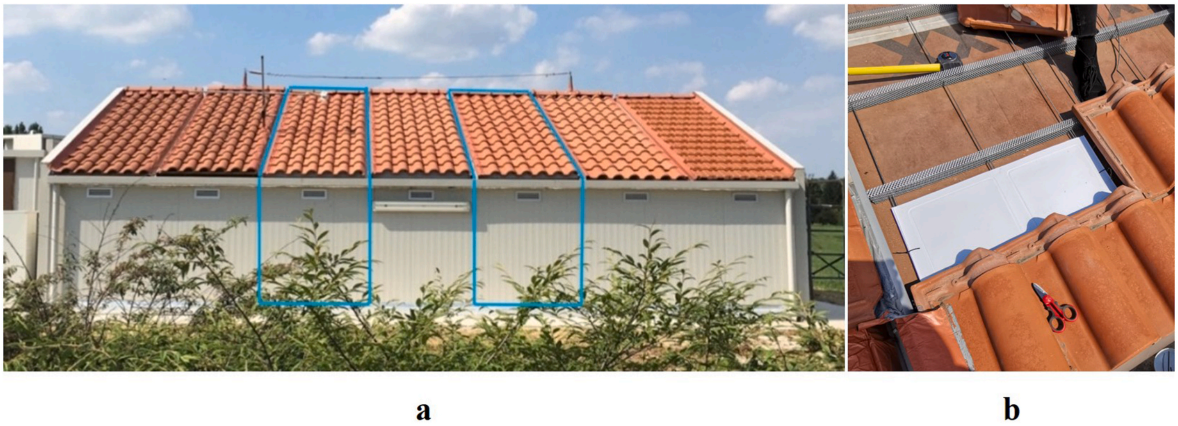

Fig. 15. Mock-up building (a); arrangement of PCM containers in the ASV layer of the roof (b). Reprinted from Bottarelli, Michele; Baccega, Eleonora, "Improving thermal performance of a ventilated tiled roof by using phase change materials", International Journal of Low Carbon Technologies (2023), under the terms of the Creative Commons CC BY license.

Table 6
Thermophysical properties of the selected PCM.

Melting temperature °C	Thickness m	Density kg/m^3	Latent heat kJ/kg	Specific heat kJ/(kg·K)	Thermal conductivity W/(m·K)
25	0.007	600	100	1.80	0.60

existing infrastructure, enabling the cooling load to be spread across a 24-h period [38]. This method reduces by half the number of mechanical cooling units required while still meeting peak cooling loads. The PCM-based energy storage system is able to balance the cooling load throughout the day, leading to lower initial installation costs and ongoing operational savings (Fig. 12).

2.3.1.6. Lusail Towers (Qatar). Lusail Towers (Qatar) are equipped with a backup system, which remains operational during District Cooling System (DCS) disruptions and ensures critical services, like IT rooms. Eleven PCM-filled storage tanks (18 m^3 each) were installed to store cold water at 40 °C, delivered by the DCS [38]. The PCM, encapsulated in 50 mm × 1 m HDPE TubeICE® containers, is set at 6.5 °C and provides a standby cooling capacity of 7920 kWh. This reserve supports backup chillers during the 15–30 min needed to reach full capacity, absorbing transient cooling loads and preventing thermal inertia in the DCS. The LTES maintains supply temperature stability during emergencies, ensuring uninterrupted cooling performance (Fig. 13).

2.3.1.7. Sir John Laing building (UK). The Sir John Laing building (UK) adopted a passive cooling solution, which relies on natural temperature fluctuations, storing coolness in PCM during night for release during the day, absorbing internal heat and solar gains. TubeICE® containers were suspended from the ceiling with 50 mm pipe brackets to capture rising warmth [86]. At maximum density, they could deliver 1.7–2.2 kWh/m^2 of cooling energy, depending on the PCM type (Fig. 14).

2.3.1.8. Ventilated roof enhanced with PCM, mock-up building (Italy). The University of Ferrara's TekneHub Laboratory explored the integration of PCMs into a ventilated roof system to improve energy efficiency [87]. Two identical pitched roofs to cover two rooms of a mock-up building (Fig. 15) were compared: one included a 0.007 m thick PCM layer within the air cavity of the above sheathing ventilation (ASV) channel. The thermophysical properties of the PCM are listed in Table 6. The PCM reduced peak daytime temperatures within the ASV channel by up to 5 °C (11.4 %) and lowered temperatures above the wooden deck by 2 °C (5.2 %), with nighttime temperatures being up to 3 °C higher. Energy input was reduced by an average of 8 % daily, reaching 15 % during the hottest periods. The air velocity below the PCM layer was not affected, while airflow above the PCM layer more than doubled. These findings confirm the potential of PCM-enhanced ventilated roofs for reducing heat flux and improving thermal performance in buildings.

2.3.1.9. PCM integrated Plasters, mock-up building (Italy). A study by UNIFE, in collaboration with Fassa S.r.l. [88], evaluated the thermal performance of lime-based plaster mixed with PCM granules for energy refurbishment, aiming at reducing cooling energy consumption in warm climates, focusing on historical buildings [89]. The investigation, conducted on the southern façade of a mock-up building at the TekneHub Laboratory (Fig. 16-a), tested four wall samples: a reference without PCM, and three PCM-enhanced configurations (10TK27 with 10 % PCM granules' mass at 27 °C, 10AS28 with 10 % at 28 °C, and 30AS28 with 30 % at 28 °C). Each 0.30 m × 0.30 m sample featured a 0.06 m masonry tile layer and 0.03 m plaster layers, secured in frames to ensure one-dimensional heat transfer (Fig. 16-b, c). The thermophysical properties of the PCM samples are detailed in Table 7. Results showed that 10AS28 and 30AS28 configurations provided the best energy savings. The 10AS28 reduced incoming energy by 10.6 % at room temperature >25 °C, 12.6 % at temperatures <25 °C, and 9.9 % during peak hours. Outdoor energy reduction averaged 67.1 %. The 30AS28 offered higher reductions of 28.4 % (>25 °C), 29 % (<25 °C), and 42 % (peak hours), with a significant 95.6 % reduction in outgoing energy.

2.3.1.10. PCMs enhanced radiant floor (Italy). UNIFE investigated a PCM-enhanced hydronic radiant floor system as part of the H2020 IDEAS project (GA 815271) [90]. The study involved a progressive scale approach: lab-scale, small-scale, and full-scale implementations. Hydrated salts encapsulated in HDPE containers (ThinICE) provided by PCM Products Ltd [38] were used, with thermophysical properties listed in Table 8.

2.3.1.10.1. Laboratory-scale installation. Lab-scale investigations focused on heating mode, testing wet and dry sand conditions and PCM placement (above or below pipes) on a 0.6 × 0.6 m setup (Fig. 17) [91]. Wet sand significantly improved thermal performance, increasing heat flux by up to 100 % during transient operation. The best positioning of the PCM was below pipes, yielding a 1.5 °C higher surface temperature and slower phase change.

2.3.1.10.2. Small-scale installation in mock-up. The small-scale prototype was installed in a 10 m^2 mock-up building at UNIFE's TekneHub laboratory to further evaluate the under-piping configuration from lab-scale tests [92]. The building featured a 5 kW multi-source (ground, sun,

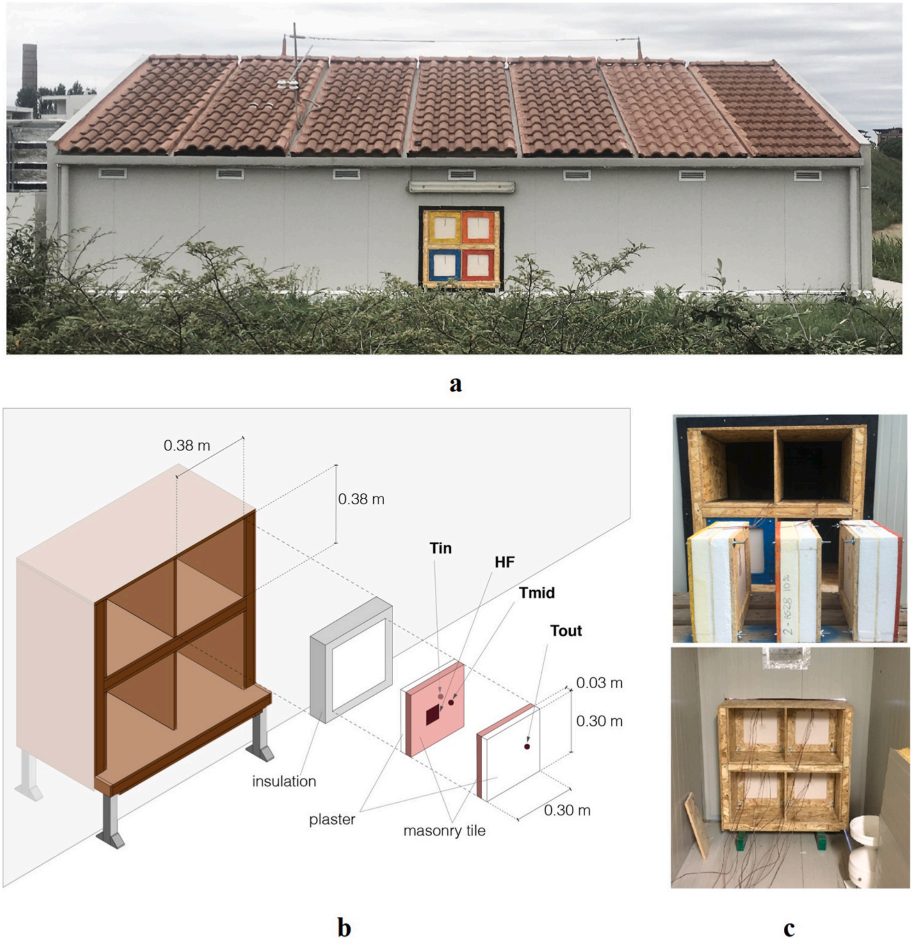

Fig. 16. Axonometric scheme of the set-up (a), view of the samples (b) and installation in the mock-up building (c). Reprinted from Baccega, Eleonora, “Thermo-physical Characterisation of Plasters Containing Phase Change Materials (PCMs)”, International Journal of Thermophysics (2024), under the terms of the Creative Commons CC BY license.

Table 7
Thermophysical properties of the samples.

	Density kg/m^3	Latent heat kJ/kg	Specific heat kJ/(kg·K)	Thermal conductivity W/(m·K)
Reference	1646	–	895	0.31
10TK27	1365	14.5	1100	0.24
10AS28	1522	9.2	1100	0.28
30AS28	1321	27.6	1280	0.24

Table 8
Thermophysical properties of the selected PCMs [38].

PCM	Melting temperature °C	Density kg/m3	Latent heat kJ/kg	Specific heat kJ/(kg·K)	Thermal conductivity W/(m·K)
S17	17	1525	155	1.90	0.43
S21	21	1530	220	2.20	0.54
S27	27	1530	185	2.20	0.54

and air) water-to-water heat pump connected to two 100-L tanks. The main room (26 m^3), where the PCM-enhanced radiant floor was installed, was flanked by two smaller guard rooms (6.24 m^3 each), all equipped with fan coils (Fig. 18-a). The radiant floor was divided into three zones to separate PCMs with melting points of 27 °C (S27, for winter) and 21 °C (S21, for summer). The northern zone contained 12 ThinICE containers with S27, the southern zone held 12 with S21, and the central zone combined 15 containers of both types. Layers of the floor assembly included a 7 mm laminate finish, wet sand embedding the PCM containers, a mortar layer with LDPE pipes, and expanded polystyrene (EPS) insulation, as detailed in Fig. 18-b,c. Wet sand improved inspection and enhanced thermal properties of the system. Cooling period results were less significant due to prototype startup issues, including non-homogeneous slab conditions, low building envelope performance, and limited system control expertise. For heating, after the installation of roof insulation, the radiant floor consistently achieved the setpoint temperature but exhibited thermal inertia, leading to overheating on sunny days due to slow PCM heat flux reduction. This aspect can be optimized with automation leveraging weather forecasts and electricity costs. The system demonstrated 12–18 h of thermal storage, enhancing heat pump flexibility by allowing extended off/on cycles.

2.3.1.10.3. *Full-scale installation.* The full-scale prototype was installed in a 100 m^2 snack bar at UNIFE’s Department of Biomedical and Specialties Surgical Sciences, replacing the existing 20–22 cm thick floor with a new floor of matching thickness to integrate TES into a space-constrained building [93]. The radiant floor incorporated 420 ThinICE units filled with PCMs melting at 27 °C for winter (S27) and 17 °C for summer (S17), as shown in Table 8. The air handling unit (AHU) was modified to operate independently or alongside the radiant floor. The radiant floor setup, depicted in Fig. 19-a, included a vinyl surface over a 50 mm dry-set mortar layer reinforced with macro-synthetic fibers for high thermal conductivity. Ø16 × 2 mm pipes

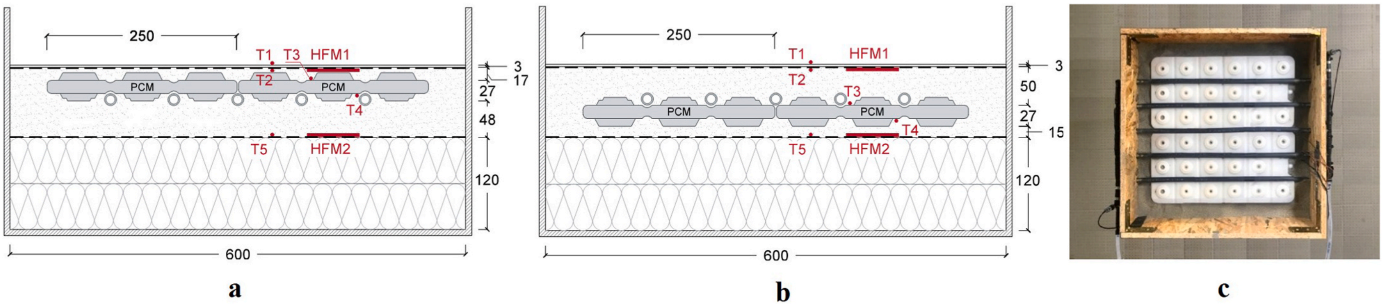

Fig. 17. Radiant floor structure with PCM above (a) and under (b) piping; view of the lab-scale set-up (c). Reprinted from Barbara Larwa, Silvia Cesari, Michele Bottarelli, "Study on thermal performance of a PCM enhanced hydronic radiant floor heating system", Energy (2021), under the terms of the Creative Commons CC BY license.

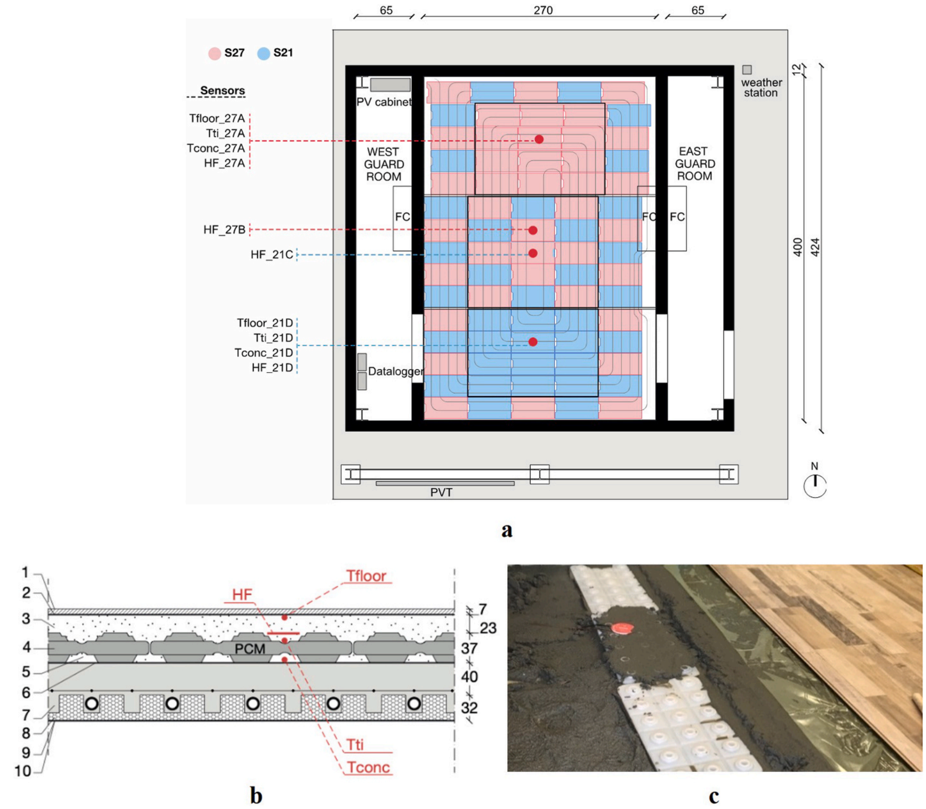

Fig. 18. Radiant floor structure (a) and its installation (b); plan of the mock-up building with the distribution of PCM containers and sensors (c). Reprinted from Silvia Cesari, Giuseppe Emmi, Michele Bottarelli, "A weather forecast-based control for the improvement of PCM enhanced radiant floors", Applied Thermal Engineering (2022), under the terms of the Creative Commons CC BY license.

(spaced 80 mm apart) were placed above the ThinICE units, which alternated between S27 and S17 (Fig. 19-b). Beneath the PCMs, a vapor barrier, a 40 mm high-density XPS insulation panel, and an 80 mm concrete slab reinforced with a metal mesh were layered, with system details in Fig. 19-c,d. During summer, PCM units absorbed heat during the day, reducing AHU cooling demand, and released stored heat at night to stabilize indoor temperatures. In winter, the integration of the radiant floor with the AHU achieved 13 % energy savings compared to the AHU alone, reducing AHU operation by 70 % while maintaining a 20 °C setpoint for up to 9 h post-shutdown. When operating independently, the radiant floor maintained the setpoint for nearly 30 h. Despite the building's poor envelope performance, the system demonstrated significant energy savings potential.

2.3.2. *Radiant floor mortar integrated with PCM-graphene (Italy)*

UNIFE explored integrating PCMs into cement-based mortar to improve its TES capacity, addressing the inherently low thermal conductivity of paraffin PCMs [94]. Laboratory tests and numerical simulations compared two radiant floor systems: a reference mortar (REF) and a modified mortar (MIX) containing 10 % granular paraffin PCM and 0.2 % hydrophobic graphene. These systems were tested in a 0.6 m × 0.6 m wooden box at UNIFE's TekneHub Laboratory, separated by 0.06 m of EPS insulation (Fig. 20). Both systems had similar structures, including polyethylene pipes embedded in 0.08 m of mortar. Results showed that PCM integration enhanced TES capacity, with graphene accelerating the PCM's phase change, narrowing its melting/solidification range to 1 K. In steady-state tests, the MIX system had a maximum temperature 0.5 K lower and a heat flux 15 W/m^2 less than the REF system. In unsteady-state tests, the MIX system exhibited slower cooling, delaying thermal equilibrium by over 9 h, demonstrating its superior thermal inertia.

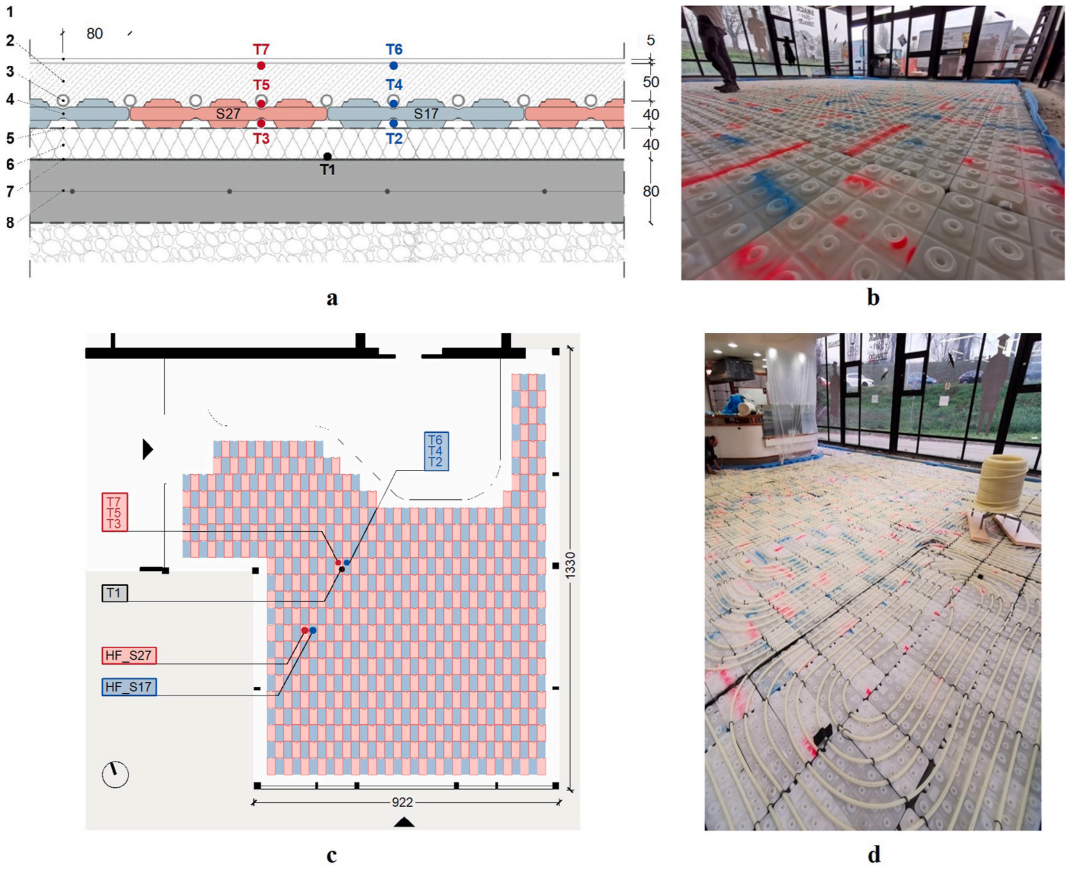

Fig. 19. Radiant floor structure (a); ThinICE S27 (marked in red) alternated to ThinICE S17 (marked in blue) (b); plan of the demo-building with the distribution of PCM containers and sensors (c); Installation of the piping over PCMs (d). Reprinted from Silvia Cesari, Eleonora Baccega, Giuseppe Emmi, Michele Bottarelli, “Enhancement of a radiant floor with a checkerboard pattern of two PCMs for heating and cooling: Results of a real-scale monitoring campaign”, Applied Thermal Engineering (2024), under the terms of the Creative Commons CC BY license.

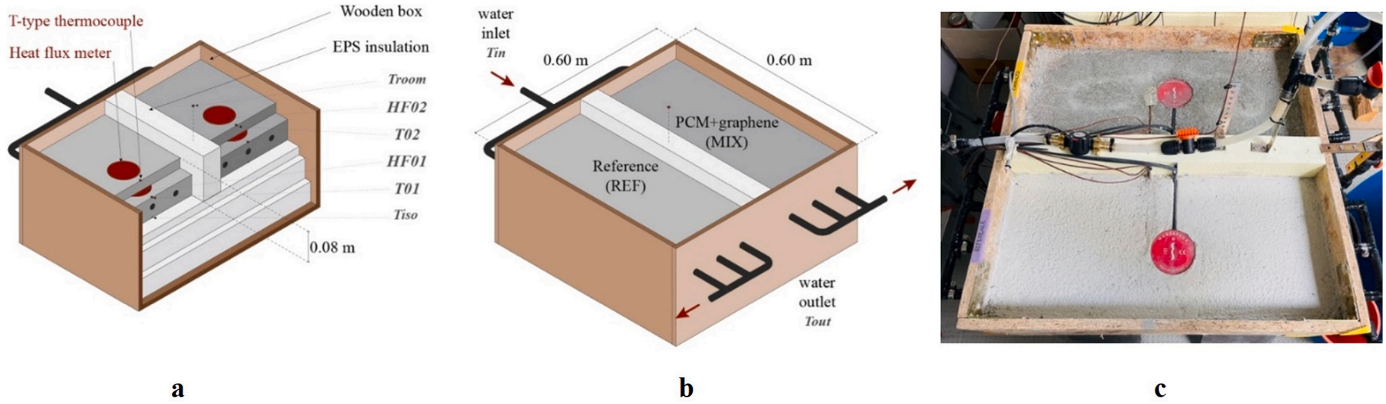

Fig. 20. Experimental set-up: axonometric section (a) and axonometric view (b); reference mortar on the lower side, enhanced mortar on the upper side (c). Reprinted from Eleonora Baccega, Michele Bottarelli, Silvia Cesari, “Addition of granular phase change materials (PCMs) and graphene to a cement-based mortar to improve its thermal performances”, Applied Thermal Engineering (2023), under the terms of the Creative Commons CC BY license.

2.3.3. Water storage tank enhanced with PCM-graphene (Italy)

At UNIFE’s TekneHub Laboratory, the thermal performance of a PCM-based LTES enhanced with graphene oxide was studied to improve thermal conductivity and system efficiency [95]. The system featured two coaxial PVC cylinders, with a smooth stainless-steel helical heat exchanger placed in the smaller cylinder, immersed in a commercial paraffin PCM with a melting point of approximately 28 °C (Fig. 21). Hot and cold water circulated through the heat exchanger to induce the PCM’s phase change. Thermal measurements were taken using thermocouples at various heights and radial distances from the heat exchanger to monitor PCM temperature. Initially, pure paraffin was used, followed by the addition of graphene oxide (mass concentrations of 1.5 % and 3 %) to enhance the PCM’s thermal conductivity. The system was tested in three configurations: pure paraffin, paraffin with graphene oxide, and a reference setup with pure water. Results showed that adding graphene oxide improved the heat flux, with up to 24 % enhancement during heating and 31 % improvement during cooling compared to the pure paraffin setup.

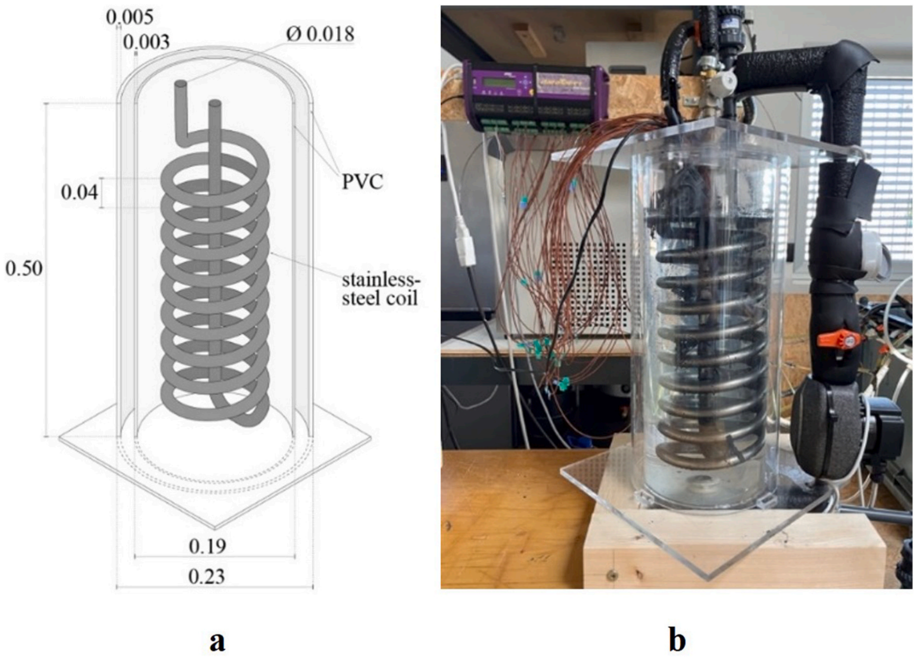

Fig. 21. Experimental set-up: axonometric view reporting the main dimensions (a) and picture of the system with the recirculation circuit on the right side (b). Reprinted from G Emmi, E Baccega, S Cesari, L Giacon, A Zarrella and M Bottarelli, “Experimental analysis of a graphene oxide-enhanced paraffin PCM”, Journal of Physics: Conference series (2023), under the terms of the Creative Commons Attribution 3.0 license.

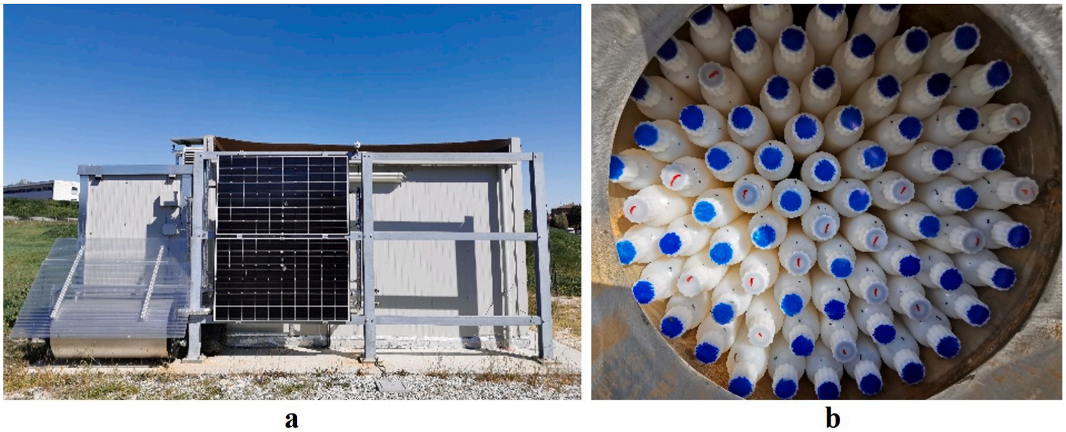

Fig. 22. PV/T panels installed on the south facade of the mock-up with the PCM-tank on the left (a); detail of TubeICE S10 (marked in blue) and S32 (marked in red) filling the storage tank (b). Reprinted from Barbara Larwa, Silvia Cesari, Michele Bottarelli, “Study on thermal performance of a PCM enhanced hydronic radiant floor heating system”, Energy (2021), under the terms of the Creative Commons CC BY license.

Table 9
Thermophysical properties of the selected PCMs.

PCM	Melting temperature °C	Density kg/m^3	Latent heat kJ/kg	Specific heat kJ/(kg·K)	Thermal conductivity W/(m·K)
S10	10	1470	170	1.90	0.43
S32	32	1460	220	1.90	0.51

2.3.4. *Water storage tank enhanced with PCM (Italy)*

As part of the H2020 IDEAS project (GA 815271) [90], UNIFE set up a small-scale prototype in a 38 m^3 mock-up building at their TekneHub Laboratory. The system’s core consisted of a 5 kW multi-source (ground, sun, and air) water-to-water heat pump (HP) connected to two 100-L tanks. The prototype comprised also two commercial PV panels (2 × 1.6 m^2, 300 Wp) with an integrated PCM 200-l buffer tank filled with 76 cylindrical HDPE PCM containers (TubeICE from PCM Products Ltd [38]), laid horizontally (Fig. 22-a). The containers were filled with two types of PCMs (Table 9): 17 containers with a melting point of 32 °C for summer use (S32), and 59 containers with a melting point of 10 °C for winter (S10). The tank had a total water volume of around 60 L. An additional circulator was installed to enable the PV/T loop to operate independently and store thermal energy in the tank (Fig. 22-b).

2.3.5. *Shallow geothermal energy*

2.3.5.1. Enhanced borehole heat exchangers (BHEs) with integrated PCM (Cyrpus). The EU Horizon project TESSe2b investigated advanced borehole heat exchangers (BHEs) with PCMs to enhance underground thermal storage and boost the efficiency of ground-coupled heat pumps (GCHPs) [96]. Traditional BHEs rely on conductive heat transfer, resulting in low thermal diffusivity and slower ground thermal response,

Fig. 23. PCM addition for geothermal borehole grout for a small building in Cyprus [96].

Table 10
Thermophysical properties of GHX1 backfilling material (sand).

	Heating	Cooling	Unit
Dry sand	8.3	8.3	t
Water	2.5	2.5	t
Wet sand UTES (10K)	171.0	171.0	MJ

Table 11
Thermophysical properties of GHX2 backfilling material (PCM granules).

	Heating	Cooling	Unit
Dry sand	6.1	6.1	t
Water	1.8	1.8	t
Wet sand UTES (10K)	126.5	126.5	MJ
PCM type	A8	A27	
Melting point	8	27	°C
Specific heat	2.16	2.22	kJ/(kg·K)
Latent heat	180	250	kJ/kg
PCM mass	174	89	kg
Product mass	348	178	kg
PCM STES	3.8	2.0	MJ
PCM LTES	31.3	22.2	MJ

Table 12
Thermophysical properties of GHX3 backfilling material (macro-encapsulated PCM).

	Heating	Cooling	Unit
Dry sand	7.6	7.6	t
Water	2.3	2.3	t
Wet sand UTES (10K)	156.5	156.5	MJ
PCM type	S8	S27	
Melting point	8	27	°C
Specific heat	1.90	2.20	kJ/(kg·K)
Latent heat	130	185	kJ/kg
PCM mass	241	120	kg
Number of containers	112	56	–
PCM STES	4.6	2.6	MJ
PCM LTES	31.3	22.2	MJ

which can lower the coefficient of performance (COP) of ground source heat pumps (GSHPs). To address this, PCMs were integrated into BHEs for a GSHP system in a small building in Cyprus (Fig. 23). Adding up to 35 % PCM (upper limit to avoid compromising grout integrity) improved thermal energy storage and smoothed out thermal waves through latent heat capacity during phase change.

2.3.5.2. Small-scale prototype of the IDEAS System (Italy). In 2020, UNIFE installed shallow ground heat exchangers (GHEs) with integrated PCMs at the TekneHub Laboratory under the CLIWAX (grant agreement No. F71F18000160009) [97] and IDEAS [90] projects. The system included three geothermal loops (GHX, UNIFE patent EP2418439A2 [98]) using different backfilling materials: sand (GHX1), sand mixed with paraffin-based PCM granules (GHX2), and HDPE containers (TubeICE) filled with hydrated salts (GHX3) [99]. Key properties are listed in Tables 10–12. These were paired with a 5 kW multi-source heat pump, PV/T panels, and a dry-cooler (Fig. 24). PCMs, with melting points of 8 °C (heating) and 27 °C (cooling), moderated temperature extremes effectively in summer but provided limited benefits in winter, where water sufficed. Challenges included high PCM costs, low conductivity, and compatibility issues, with paraffin offering stability at higher costs and hydrated salts showing higher storage potential but phase stability concerns. The HP achieved a winter COP above 5 by using different thermal sources. Ground regeneration via air and sun was effective, though PCM impact was modest due to the short loop's length.

2.3.6. Solar Energy

2.3.6.1. Pilot plant with cascaded PCMs (Spain). At the University of Lleida (Spain), a pilot plant with two cascaded organic PCMs was tested [100]. Two shell-and-tube storage tanks, containing hydroquinone and d-mannitol respectively (melting temperature between 150 and 200 °C), were connected in series. The system was coupled with a 24 kW_e electrical boiler (heat source) and a 20 kW_{th} air HX, simulating user consumption. The operation of the system was compared to two case studies, i.e. single PCM with hydroquinone or d-mannitol, and the cascaded configuration resulted in higher heat transfer rates and improved effectiveness by 19.36 %. The possible applications include both solar refrigeration coupled with CSP and IWH recovery.

2.3.6.2. FIFA 2022 World Cup solar stadium (Qatar). In the FIFA 2022 World Cup stadium, parabolic solar collectors generated hot oil during the day to power absorption chillers, and cooling was stored in PCM-TES tanks [101]. Each day, approximately 5 MWh of cooling energy was stored, sufficient to meet the entire cooling demand for evening football games lasting 2–3 h, when temperatures were cooler. After the game, the TES tanks were fully discharged and ready for recharging the next day. Data from the demonstration stadium showed that solar energy in

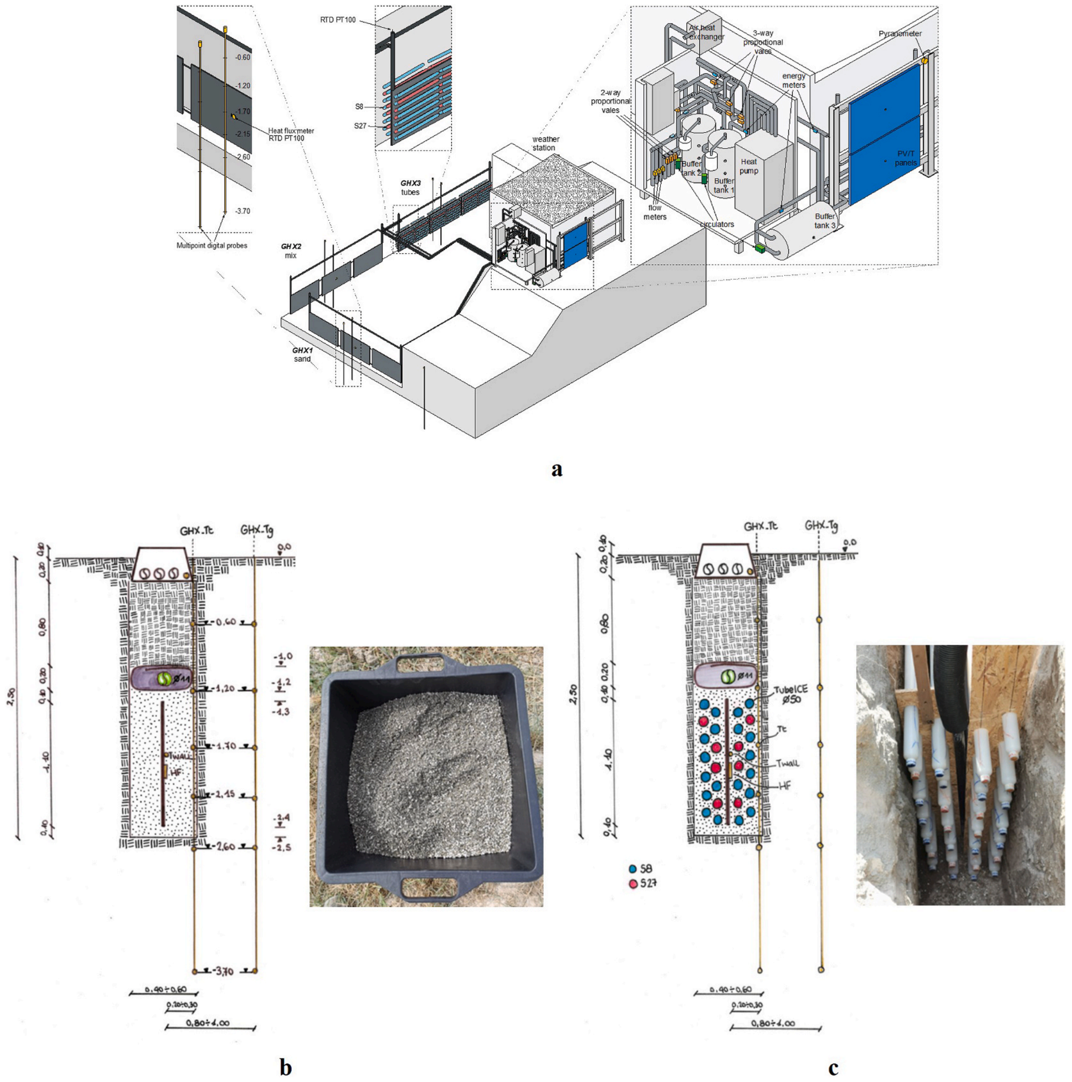

Fig. 24. Axonometric scheme of the system (a); section of GHX1 and GHX2 with detail of sand mixed with PCM granules (b), section of GHX3 with detail of PCM containers (c). Reprinted from Michele Bottarelli, Eleonora Baccega, Silvia Cesari, Giuseppe Emmi, "Role of phase change materials in backfilling of flat-panels ground heat exchanger", Renewable Energy (2022), under the terms of the Creative Commons CC BY license.

Fig. 25. Solar large scale off-grid cooling application in Qatar [101].

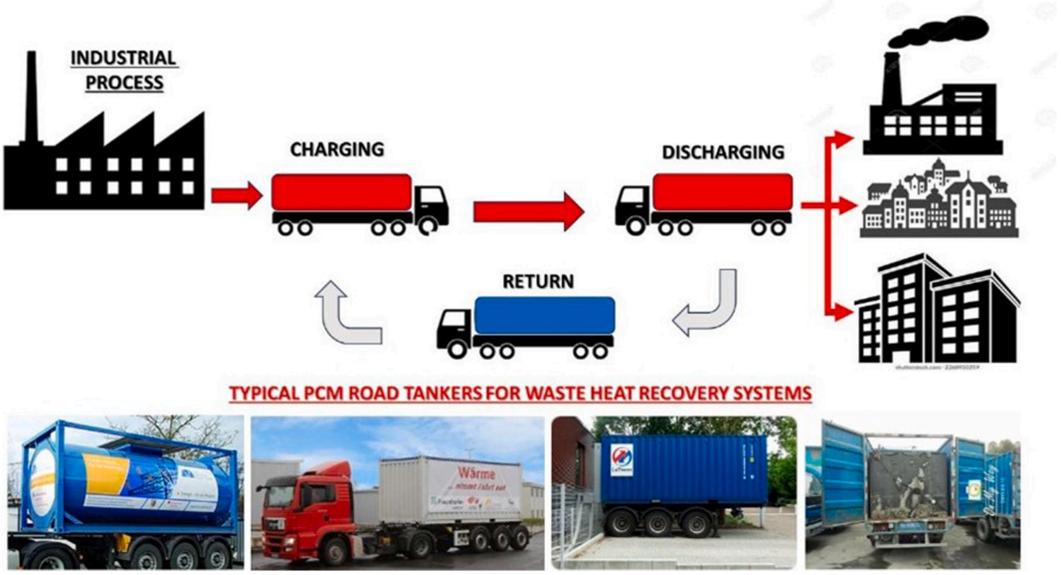

Fig. 26. Waste heat recovery and transfer applications [38].

Table 13
TES density and main features of LTES case studies (A active, P passive, H heating, C cooling).

Application	PCM type	TES density	Energy savings/improvement	Reference
Bergen Airport	PCM Products' S10 (melting temperature of 10 °C)	41.67 kWh/m^3	n.a.	[83]
Dekra HQ	PCM Products (melting temperature of 15 °C)	36.25 kWh/m^3	Up to 14 % reduction of summer operation costs and 22 % of winter operation costs	[84]
National Theatre	PCM Products (melting temperature of 8 °C)	n.a.	n.a	[83]
University of Bergen	PCM Products' FlatICE (melting temperature of 10 °C)	45 kWh/m^3	53 % reduction in chiller capacity needs	[38]
Norwegian University of Life Sciences	PCM Products' FlatICE (melting temperature of 10 °C)	45 kWh/m^3	n.a.	[38]
Lusail Towers	PCM Products' TubeICE (melting temperature of 6.5 °C)	40 kWh/m^3	n.a.	[38]
Sir John Laing Building	PCM Products' TubeICE (melting temperature of 27 °C)	1.7–2.2 kWh/m^2	n.a.	[86]
P, ventilated roof	macroencapsulated inorganic salt	60.0 MJ/m^3	−8 % (whole day) and −15 % (hottest hours) on incoming energy	[87]
P, plasters	n.3 types of paraffin based granules	19.8, 14.0 and 36.4 MJ/m^3	−11 %, −13 % and −35 % on incoming energy	[89]
A, H RF system	macroencapsulated inorganic salt	147.4 MJ/m^3	+75 % heat flux for the under-piping PCM configuration	[91]
A, H/C RF system	macroencapsulated inorganic salt	147.4 MJ/m^3 (H), 175.3 MJ/m^3 (C)	12–18h latent heat release (H)	[92]
A, H/C RF system	macroencapsulated inorganic salt	147.4 MJ/m^3 (H), 122.5 MJ/m^3 (C)	−13 % energy for the AHU integrated with the RF system (rather than the sole AHU)	[93]
A, H RF system	10 wt% paraffin based granules + 0.2 wt% hydrophobic graphene	14.2 MJ/m^3	+9 h latent heat release	[94]
A, TES tank	paraffin +1.5 wt% and 3 wt% of graphene oxide	200.0 MJ/m^3	heat flux: +24 % in melting and +31 % in solidification (for 3 wt%)	[95]
A, TES tank	macroencapsulated inorganic salt	225.2 MJ/m^3 (H), 291.5 MJ/m^3 (C)	UTES recharge when integrated with PV/T	[90]
A, UTES for HP	paraffin-based granules with sand (GHX2), macroencapsulated inorganic salt (GHX3)	9.3 MJ/m^3 (H) and 6.6 MJ/m^3 (C)	GHX2 and GHX3 T_{out} = 1.5 K lower than GHX1 (only sand)	[99]
Pilot plant with cascaded PCMs	QUIMIVITA's hydroquinone and d-mannitol (melting temperature between 150 and 200 °C)	0.09–0.115 kWh/kg	19.36 % improvement in effectiveness compared to single storage tank	[100]
FIFA 2022 World Cup Solar Stadium	PCM Products' S15 FlatICE (melting temperature of 15 °C)	50 kWh/m^3	n.a.	[101]
Scalable medium-temperature pilot plant	HeatMate Technology (Shanghai) Co., Ltd. (melting temperature of 225.35 °C)	45.37 Wh/kg	n.a.	[102]

off-grid operation is an optimal solution for large-scale cooling (Fig. 25).

2.3.7. Industrial applications

2.3.7.1. Scalable medium-temperature pilot plant (China). A pilot system employing a commercial nitrate mixture PCM was tested at Zhejiang University (China), with the purpose of supporting the design of a large-scale system for solar power plants and recovery of waste heat [102]. 270 kg of PCM, with a melting temperature of 225.35 °C, were integrated into a multi-tube LTES configuration and resulted in efficiencies of 71.41 % during the discharging phase and 77.67 % during the charging phase.

2.3.7.2. Heat transport application. The most common industrial application of PCM materials, apart from in-situ waste heat recovery systems, is in heat transport. Waste energy from industrial processes like foundries and steel or ceramic production is used to melt a PCM in a road tanker for storage [103]. Sodium acetate is commonly used [104]: it

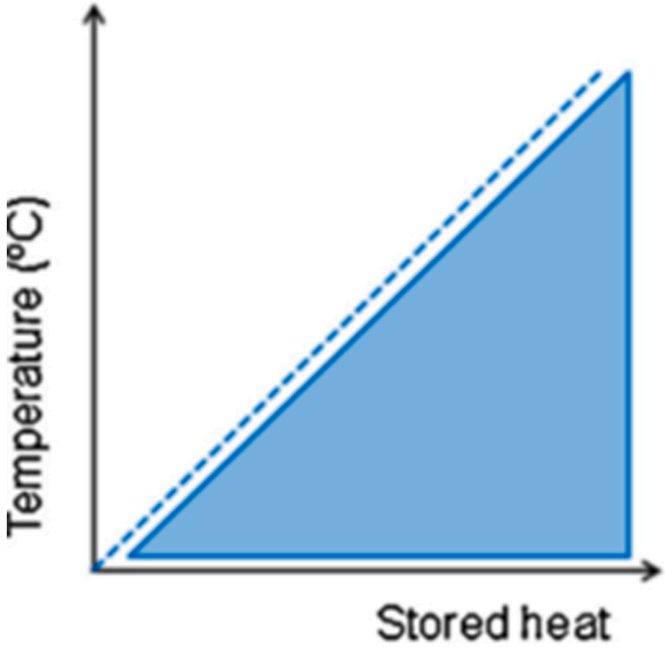

Fig. 27. Graphical representation of the working principle of STES. Reprinted from Alvaro de Gracia, Luisa F. Cabeza, "Phase change materials and thermal energy storage for buildings", Energy and Buildings, Volume 103, Page 6, Copyright (2015), with permission from Elsevier.

melts at 53 °C and sub-cools below ambient temperature without freezing, allowing minimal heat loss during transport even with minimal insulation. At the delivery site, the PCM is activated to freeze at 53 °C, releasing stored heat via a heat exchanger into the delivery process (Fig. 26). Once depleted, the tanker returns to the original heat source, where waste heat remelts the PCM for reuse. This shuttle process between energy source and use sites is economically and environmentally beneficial. Widely applied in the EU and predominantly in China, this system effectively repurposes waste heat for valuable end uses.

2.3.8. Battery thermal management

An emerging application of PCMs is the thermal management of electric batteries, which must be maintained at the optimal temperature range to avoid thermal runaway and battery degradation [105]. Karimi et al. [106] evaluated the performance of a hybrid TMS integrating a PCM (melting point between 25 and 32 °C) with six heat pipes for a lithium-ion capacitor (LiC) cell. Both simulation and experimental tests were considered, showing the benefit of the PCM in terms of temperature profile control. In a later study, Karimi et al. [107] compared active and passive TMSs. A combination of the two methods, consisting of liquid-cooled TMS enhanced with PCM, allowed to decrease the maximum temperature and uniform the LiC cell temperature. Active and passive methods were compared also by Hémery et al. [108], demonstrating the improvement in temperature uniformity and in reducing the weight of the cans given by the PCM, a commercial paraffin wax.

The TES density and main features of the LTES case studies reviewed above are reported in Table 13.

3. Sensible thermal energy storage (STES)

3.1. Functioning of STES

STES is based on sensible heat transfer, which determines an increase or decrease of temperature in the selected medium [109]. The stored sensible heat can be calculated as in Eq. (2).

$$Q = m \cdot C_p \cdot \Delta T \tag{2}$$

where m is the mass of the chosen medium, C_p is the heating capacity and ΔT is the achieved temperature difference in the medium. This concept is represented in Fig. 27. The main disadvantage of these systems is the low energy density [8], especially when compared to LTES and TCES. On the other hand, its main strengths are simplicity, maturity and reliability [30,33].

3.2. STES medium

The simplicity of STES systems is not only attributable to the working principle, but also to the employed materials. Indeed, they are usually available without requiring special manufacturing processes [30]. A large variety of materials, both in solid and liquid form, is available for usage in this type of TES. Therefore, choosing the most suitable material for a certain application is the main challenge when considering these systems [15].

3.2.1. Water

Among the different STES mediums which can be used, water is particularly suitable for domestic and low temperature applications. It is characterized by higher energy density and heat capacity, as well as being favored by its availability, lack of harmfulness and low cost [8, 33]. On the other hand, its main disadvantages are related to the high vapor pressure, requiring expensive insulation and suitable containment when dealing with high temperature applications [111]. Water storage in tanks is the most spread and well known STES application [33]. In the most used technique, thermal stratification is achieved by avoiding mixing, ensuring that the highest temperature is reached at the top of the tank, increasing the efficiency of the system [111]. This stratification, caused by the reduced density at high temperatures, enhances the performance of the system [33]. Design of these systems should focus on minimizing heat losses through insulation and avoiding thermal bridges. Inlet stratifiers improve the design by letting the water enter the tank at the required height, that is at the same temperature as the incoming water [112].

3.2.2. Steam

Steam accumulators are steel tanks containing pressurized saturated liquid water. They are particularly suitable for solar applications, or in general when excess steam is available. The system is discharged by decreasing the pressure of the saturated liquid, which partially flashes into saturated steam [113,114]. During charging, the introduced steam condenses and the level of the water increases [115].

3.2.3. Solid materials

STES can also consist of storing heat in solids such as concrete blocks, rocks, or sand-like particles. They are usually arranged in packed beds, through which a heat transfer fluid flows. A thin layer of thermocline ensures stratification, keeping the hot and cold regions apart [34]. Both concrete and natural materials are cheap, non-toxic and non-flammable, and work as heat transfer surface without the need of heat exchangers. Thanks to its good mechanical properties, concrete does not require a container. It is characterized by moderate thermal conductivity and high specific heat compared to other materials for construction [116]. Rocks and sands are selected considering their availability, density, heat capacity and thermal conductivity. Resistance to abrasion, porosity and mechanical strength are other factors to take into account [7]. Compared to liquids, solid materials can be applied at high temperatures in an easier way, without encountering the leakage issue. However, their low specific heat capacity requires more space [15]. The recent development of new cementitious materials, insulation techniques and system designs allows to reach higher storage capacity and heat transfer [116].

3.2.4. Molten salts

Molten salts are a liquid medium suitable for high temperature

Fig. 28. Warm TES application in a UK hospital [38].

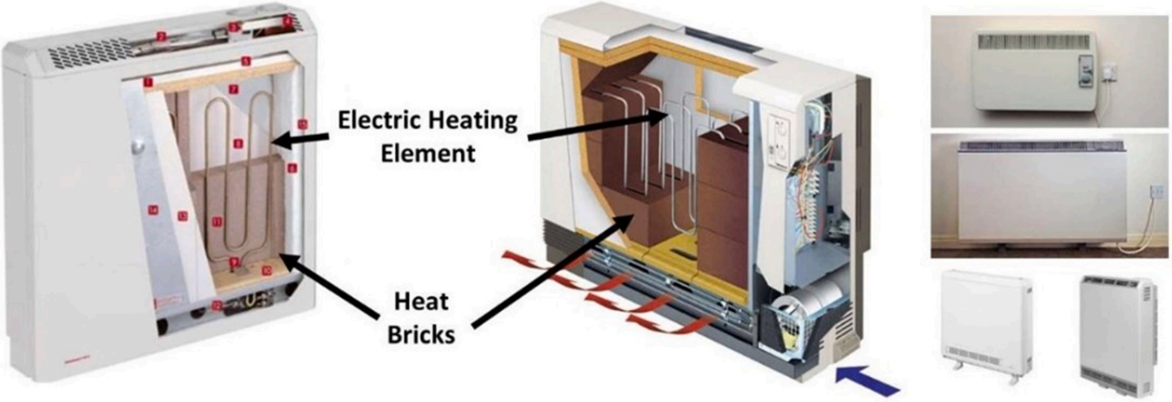

Fig. 29. Storage heater examples [120].

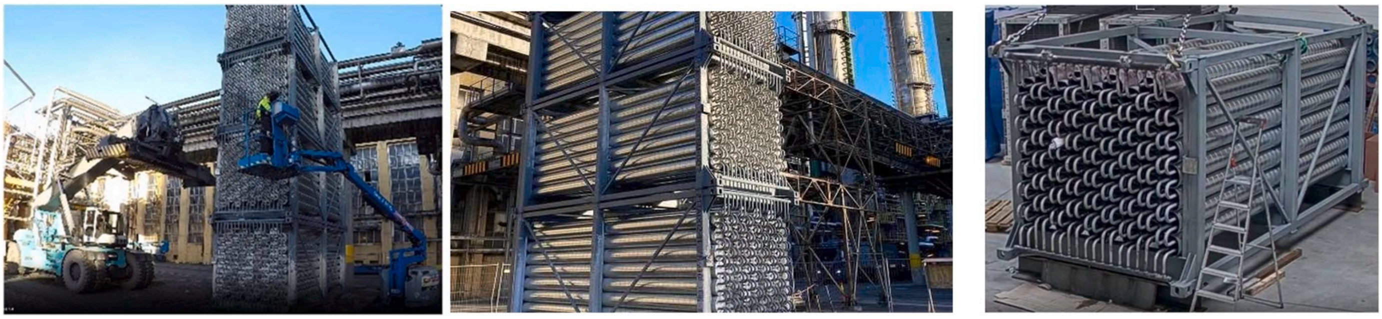

Fig. 30. Concrete STES module installation [122].

applications, especially employed in CSP plants [30]. They usually consist of a mixture of sodium nitrate $NaNO_3$ and potassium nitrate KNO_3. Their main disadvantage is related to the low solidification point, which requires specific piping and insulation to avoid their solidification [15]. Despite this, they are characterized by high volumetric energy density and low cost [117].

3.3. Case studies

3.3.1. HVAC systems

In Heating, Ventilating and Air Conditioning systems (HVAC), STES systems are normally employed and can provide cooling, heating and domestic hot water supply. The storage medium is usually water or a water-glycol mixture.

An example of cooling supply was reported by Muthaiyan et al. [118], who worked on an experimental low temperature sensible heat storage for domestic cooling supply, consisting of a tank filled with brine. The room comfort condition was maintained for 285 min with 29 operation cycles.

3.3.1.1. The Royal Wolverhampton Hospital heating TES (UK). The Royal Wolverhampton Hospital (UK) adopted a STES system which relies on heat recovered from the heat pumps, balancing the heating and cooling load (Fig. 28) [38]. The system consists of both cool PCM tanks and of a 90 m^3 STES tank, providing 930 kWh TES capacity. While the cool PCM tanks are charged, the waste heat is stored in the STES tank.

3.3.1.2. Storage heaters. A particular application of STES with solid materials is represented by storage heaters, which take advantage of the low cost of electricity at night. Heat is stored in bricks thanks to electrical resistance elements and is released during the day when needed [119]. All the components are included in a casing, as shown in Fig. 29.

3.3.2. Solar Energy

A common application example for STES is the conventional hot water production for domestic or commercial applications, where water is heated by thermal solar energy through a direct or indirect loop. However, thermal solar energy has recently been integrated into novel solutions. Graphite energy storage was integrated into heliostat-field

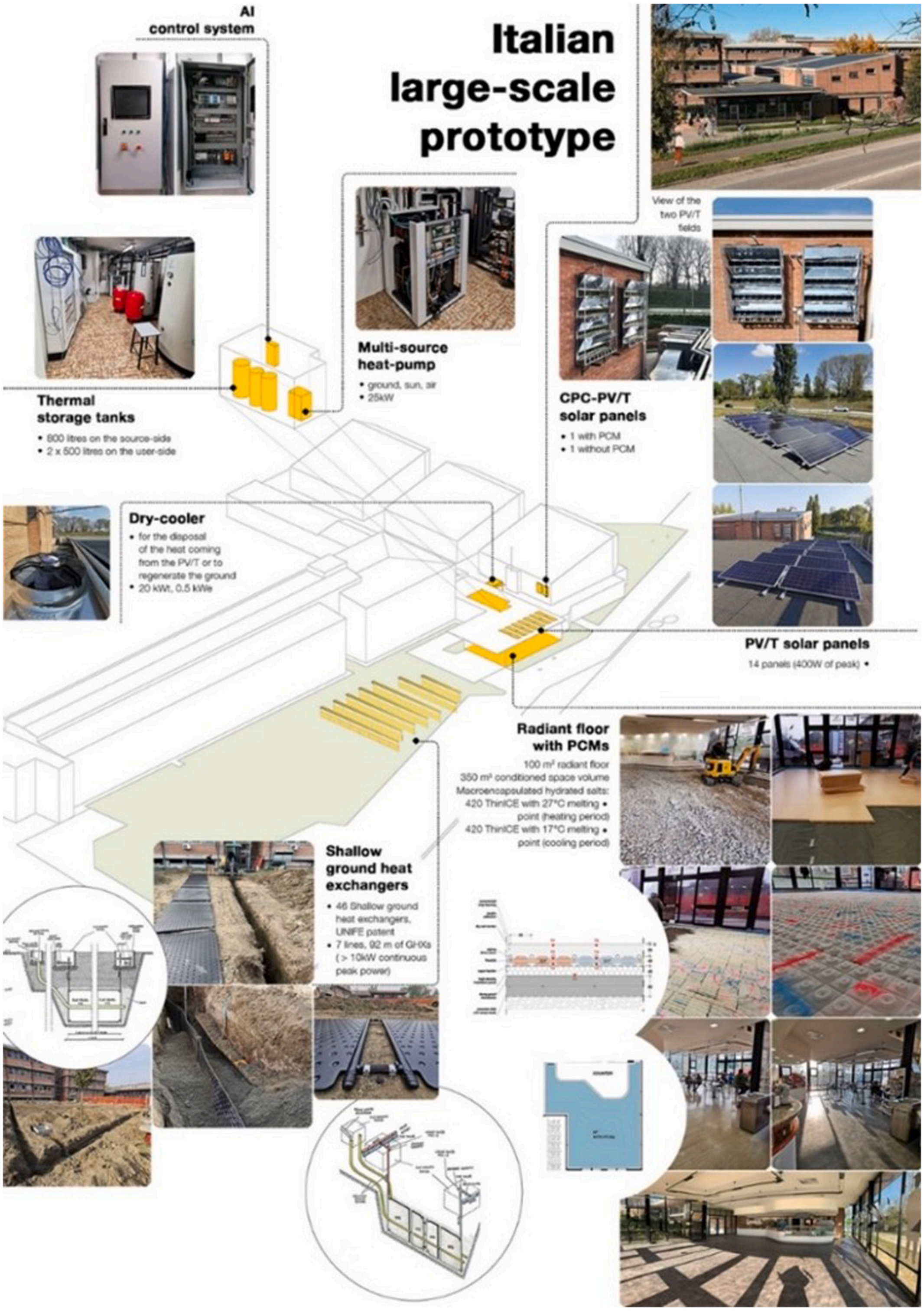

Fig. 31. Axonometric scheme and description of the full-scale installation of the IDEAS system [90].

collectors in a plant in Lake Cargelligo, Australia [121]. EnergyNest developed an innovative modular system consisting of concrete elements connected in parallel and series through steel tubes, where synthetic oil flows (Fig. 30) [122]. Vijayan et al. [123] integrated a porous pebble bed on a solar air heater, which resulted in an increase of energy and exergy efficiencies. The Universy of Lleida (Spain) and Abengoda (Spain) developed a pilot plant consisting of a two-tank molten salts TES up to 400 °C, integrated with a CSP plant [124]. The hot and cold tank (0.57 m^3 each) could be arranged in parallel or counter flow, and both charging and discharging phases were tested.

3.3.2.1. Snack-bar of the Department of Biomedical and Specialties Surgical Sciences, University of Ferrara (Italy). In the framework of the H2020 European project IDEAS (GA 815271) [90], the University of Ferrara installed a building demonstrator in the snack-bar of the Department of Biomedical and Specialties Surgical Sciences (Fig. 31). The core of the system is the 25-kW multi-source water-to-water heat

Fig. 32. Spanish brewery solar TES system [127].

Fig. 33. Sand-based STES installation in Finland [130].

pump, which operates by means of two primary loops between two sensible TES tanks, one on the source-side (800 l), and one on the user-side (2 × 500 l). On the source-side, the system operates between three thermal sources (ground, sun, and air) to optimize the operation, providing the snack bar with space heating/cooling. Innovative horizontal ground heat exchangers (GHXs), called Flat-Panels, were developed and installed (UNIFE patent EP2418439A2 [98]) [125]. In July and August, the cooling activity accounted for 890 kWh_t, whilst the heating for 340 kWh_t. Consequently, the temperature just occasionally achieved values over 60 °C, even with high solar irradiance (>800 W/m^2).

Monitoring data showed that the cooling mode allowed a net increase of 7.6 % in peak power conversion. In terms of efficiency, the cooled panel achieved 14.3 %, whilst the not-cooled one 13.3 %. Furthermore, the cooling of PV/T panels was only functional to increase the peak power (+7.6 %) and not to increase the energy production.

3.3.3. *Industrial applications*

Industries can benefit from STES thanks to its low cost, for example employing it for recovering waste heat [12] or integrating concentrating solar thermal (CST) technologies, in the so-called solar heat for industrial processes (SHIP). Siemens Gamesa developed an electric thermal energy storage (ETES) demonstration plant, consisting of crushed volcanic rocks [126]. Exploiting low price electricity, a heater increases the air temperature, which flows through the solid storage material. The discharged heat produces steam for generating electricity through a 1.4 MW_{el} turbine. A 30 MW CST plant was installed in a brewery in Spain (Fig. 32), covering 55 % of the heat demand, with the remaining 45 % being covered by other energy sources [127]. Mirror configurations were chosen to reflect and concentrate the sun's direct normal irradiance (DNI) into a receiver to heat a high temperature fluid, and solar energy is stored in hot oil storage units for the brewery's needs.

Fig. 34. Chilled water STES in the US [131].

Table 14

TES density and main features of STES case studies (H heating, C cooling).

Application	Medium	TES density	Energy savings/ improvement	Reference
Royal Wolverhampton Hospital (H)	water	46.5 kWh/m^3 (H)	−50 % reduction in equipment size	[38]
EnergyNest	concrete/ molten salts	173.2 kWh/m^3	n.a.	[122]
Two-tank TES	molten salts	1.33 kWh/m^3	n.a.	[124]
Thermal solar energy	water	33.4 MJ/m^3 (H), 83.6 MJ/m^3 (C)	+7.6 % in peak power conversion through panel cooling	[90]
ETES	crushed volcanic rocks	269 kWh/m^3	n.a.	[126]

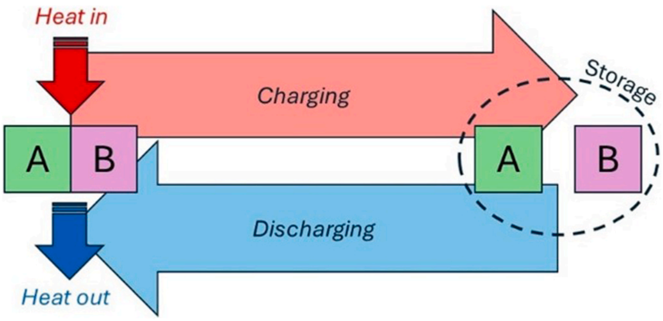

Fig. 35. Representation of TCES processes.

3.3.3.1. Steel production and recovery of waste heat (Netherlands). At the Ijmuiden steel plant in the Netherlands, a project showcased the potential of fully harnessing the waste heat generated as a byproduct of various processes [128]. By implementing a 500 MWh TES system on a large scale, the facility achieved an annual saving of 2.3 million GJ of natural gas (65 million Nm^3), a reduction of 130,000 tons in CO$_2$ emissions, and a return on investment within three years.

3.3.4. District Heating and Cooling

STES is the most widespread technology for storing energy in DHC networks [129]. Although water has been usually employed, innovative solutions have also emerged. A high temperature STES system exploiting sand was installed to provide district heating to the town of Kankaanpää in western Finland (Fig. 33). The system can supply 100 kW of heating power and is characterized by 8 MWh of energy capacity [130].

The storage is embedded in a 4 m × 7 m high steel container and can store electricity in the form of heat for several months, at temperatures ranging between 500 °C and 600 °C. The heat supplied by the storage is used to enhance the temperatures of the waste heat from the servers, before the heat is fed into the district heating network. A stratified chilled water TES tank was built in Raleigh, North Carolina [131]. The system is based on a precast, prestressed, wire-wound concrete tank, and is coupled with a new high efficiency packaged chilled water plant. The system can deliver 96 MWh of cooling capacity, serving 20 buildings (Fig. 34).

3.3.5. Shallow geothermal energy

BTES systems store heat by using soil and/or rocks as medium [19]. An underground BTES system was installed at the University of Ontario Institute of Technology (UOIT) in Oshawa, Canada, for heating and cooling four new campus buildings with a total cooling load of 7000 kW [132]. The system comprised 370 boreholes, each 200 m deep, and included the installation of five temperature monitoring boreholes. The water-filled BHEs were opted for over the grouted BHEs, resulting in enhanced efficiency and ensured borehole longevity. The BHEs, arranged on a 4.5 m grid, covered an area of 7000 m^2, with a total volume of 1.4 million m^3.

The volumetric TES density and main features of the STES case studies reviewed above are reported in Table 14.

4. Thermochemical energy storage (TCES)

4.1. Functioning of TCES

TCES employs materials which release or store heat during reversible exothermic and endothermic chemical reactions, involving dissociation or sorption mechanisms [133]. These thermochemical materials (TCMs) can be distinguished depending on the reaction involved, which can be described in general as in Eq. (3). During the charging process, the reactant AB is dissociated into products A + B by introducing heat, i.e. through an endothermic reaction. The products can be stored separately for a certain amount of time. During the discharging process, products A and B are recombined in an exothermic reaction, which releases the required heat. The storage cycle is schematically represented in Fig. 35. Thanks to the strong chemical bonding forces involved in the process, TCES is characterized by high energy storage density compared to STES and LTES. Moreover, any thermal losses during the storage period can be neglected, because the stored chemical potential energy is not released to the environment or converted into other energy forms [134].

$$AB + \Delta H \leftrightarrow A + B \tag{3}$$

In the case of a sorption process, an example is represented by

Table 15
Some of the most promising TCM options.

TCM	Type	Mechanism	Volumetric energy density [GJ/m^3]	Reference
NH_3	ammonia	reaction	0.000675	[140]
$CaCO_3$	carbonates	reaction	3.26–3.3	[9,140]
$SrCO_3$	carbonates	reaction	1.2–1.5	[140]
CaH_2	hydrides	reaction	7.374	[140]
Mg_2FeH_6	hydrides	reaction	2.344	[140]
Mg_2NiH_4	hydrides	reaction	3.143	[140]
MgH_2	hydrides	reaction	3.995	[140]
$NaMgH_2F$	hydrides	reaction	1.968	[140]
$NaMgH_3$	hydrides	reaction	1.721	[140]
$Ca(OH)_2$	hydroxides	reaction	1.64–2.2	[9,133,140]
$2BaO_2$	redox active oxides	reaction	3.015	[140]
$6Mn_2O_3$	redox active oxides	reaction	0.225	[140]
LiBr	bromides	sorption	1.37–2.01	[141]
$SrBr_2$	bromides	sorption	0.22	[133]
K_2CO_3	carbonates	sorption	0.96–1.3	[141]
$BaCl_2$	chlorides	sorption	0.5–1.5	[141]
$CaCl_2$	chlorides	sorption	1.06–1.54	[141]
LiCl	chlorides	sorption	1.36–2.08	[141]
$MgCl_2$	chlorides	sorption	1.24–1.93	[141]
$SrCl_2$	chlorides	sorption	0.83–1.87	[141]
$Fe(OH)_2$	hydroxides	sorption	2.2	[9,133,137]
$Ca(NO_3)_2$	nitrates	sorption	0.42–1.71	[141]
$LiNO_3$	nitrates	sorption	2.13	[141]
$Zn(NO_3)_2$	nitrates	sorption	0.86–1.61	[141]
$Al_2(SO_4)_3$	sulphates	sorption	3.19	[141]
$CaSO_4$	sulphates	sorption	1.4	[9,133,137]
$CuSO_4$	sulphates	sorption	0.93–2.56	[141]
$MgSO_4$	sulphates	sorption	2.8	[9,133,137]
Na_2S	sulphides	sorption	1.58–2.8	[133,141]

hydrated salts, whose charging phase consists of an endothermic dehydration reaction. On the contrary, the discharge of heat is performed through an exothermic hydration reaction. Eq. (4) describes this kind of process.

$$Salt \bullet yH_2O\ (s) + \Delta H_{reac} \rightarrow Salt(s) + yH_2O\ (g) \tag{4}$$

The forward and the reverse reactions may take place in different steps at different temperature levels, where intermediate hydrate phases occur.

Sorption includes adsorption and absorption processes. Adsorption is the process which enriches or depletes one or more components in an interface. An adsorbent is a material which can adsorb other components, while the adsorbate is the component which is adsorbed. On the other hand, the process in which the adsorbed molecules enter the structure of the bulk solid/liquid, changing the composition of at least one phase, is called absorption [135]. The release of the material is called desorption, which is an endothermic process.

Sorption systems can be open or closed. Open systems work at ambient pressure, exchanging mass and energy with the environment, while closed systems are generally evacuated and exchange only energy. Open systems usually require additional equipment, such as fans and humidifiers, and are characterized by a limited temperature lift. On the other hand, closed systems benefit from a fast transport mechanism, but are affected by formation of incondensable gases and lower energy density [133,136].

The aforementioned advantages make TCES a promising technology for effectively utilizing renewable energy, IWH and off-peak electricity. Furthermore, when integrated with long-term seasonal TES techniques, TCES can result in enhanced thermal performance of the storage system without giving up energy efficiency and environmental sustainability [137]. Nevertheless, TCES is the latest TES technology in recent decades and remains in the laboratory investigation stage, though many potential TCES processes exist.

4.2. TCES medium

At present, many reactions and materials are suitable for TCES applications [133], over an extensive range of temperatures and conditions. The main criteria for selecting TCMs are [135,138].

- Good thermal stability and mechanical strength
- High sorbate uptake
- Large energy storage density
- Low charging temperature
- High thermal conductivity/heat and mass transfer
- Non-toxicity, non-corrosiveness
- Environmental acceptability
- Low cost.

Some of the most common TCMs are shown in Table 15. The volumetric energy storage densities can vary depending on the operating conditions, such as pressure and the morphology of the solid species [139].

More extensive lists of TCMs are found in literature reviews specific to TCES systems. Yu et al. [135] provide a list of typical sorption pairs, including composite materials. Donkers et al. [141] collect the 25 most suitable salt hydrates' reactions, while Sunku Prasad et al. [140] focus on reactions suitable for high temperature applications. Jarimi et al. [142] provide lists of solid adsorption, liquid absorption and composite materials. Composites consisting of salt hydrates are addressed by Lin et al. [134].

Among sulphates, magnesium sulfate is considered the most promising TCM, even if its usage as powder is subject to agglomerates, which limit gas transfer and reversibility. The low temperature lift achieved results in poor performance of the systems [143]. Despite its potential, calcium sulfate is mainly used for industrial processes for chemical heat pumps. Its main advantages include high heat density, negligible expansion in hydration, long-term storage of the absorbent and products, and low heat losses. Copper sulfate relies on low-temperature heat sources of 60–85 °C, making it ideally suited to be driven by solar energy or other renewable energy heat sources. Potassium carbonate (K_2CO_3) was found to be particularly suitable for domestic seasonal TES applications, thanks to a dehydration temperature below 120 °C and low corrosivity. Among bromides, strontium bromide hexahydrate and lithium bromide monohydrate are the most promising TCMs both for closed processes, such as in solar cooling, and for open processes involving the seasonal storage of solar energy. Moreover, LiBr offers the possibility to work between 80 °C and 90 °C, dehydrating to monohydrate without incurring incongruent dissolution of water vapor in the solid phase. Commonly used nitrates are zinc nitrate hexahydrate and calcium nitrate tetrahydrate, while lithium nitrate trihydrate is not being extensively studied due to the limited lithium resources. Due to their hygroscopicity, chlorides such as calcium chloride, magnesium chloride and lithium chloride are affected by the deliquescence issue, which consists in their tendency to form a solution in closed systems. This phenomenon can lead to salt segregation, corrosion and reduction of heat and mass transfer. $CaCl_2$ and $MgCl_2$ are characterized by high energy density, but $CaCl_2$ tends to agglomerate and $MgCl_2$ undergoes thermal decomposition over cycles and formation of hydrochloric acid (HCl). Barium chloride demonstrated the ability to complete fully reversible dehydration–hydration cycles. Further studies and development are required for hydroxides, such as $Fe(OH)_2$, which can be potentially applied to solar seasonal storage. Sodium sulfide is the most promising among its category, although it is highly corrosive and subject to outgassing [31].

Solid sorbents are usually arranged in packed beds. Pure water vapor is applied in closed cycles while water vapor contained in wet air is

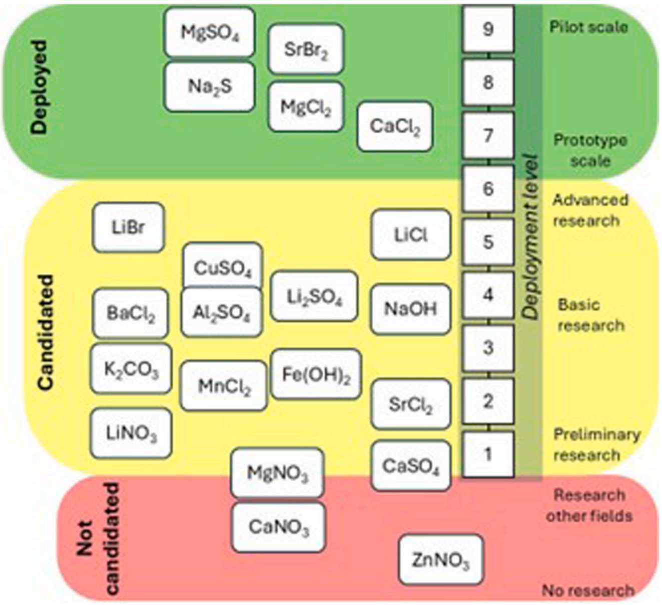

Fig. 36. Potential solution materials for sorption TES (adapted from Ref. [31]).

exploited in open cycles. Adsorption processes employ pairs like zeolite/water or selective-water-sorbents/water. On the other hand, absorption mainly employs water- and ammonia-based working pairs [144]. The working pairs silica gel/water, magnesium sulfate/water, lithium bromide/water, lithium chloride/water, and NaOH/water are the most promising for achieving high values of heat storage capacity [137]. One of the challenges associated with solid adsorption seasonal storage is the need for a high amount of adsorbent material, consequently requiring big and expensive heat exchangers. However, the dispersion in high porous matrixes improves the heat and mass transfer process.

Fig. 36 shows a screening of the most promising candidates and their deployment level according to Palacios et al. [31]. The same study highlighted also the dependence of the technology readiness level (TRL) on the TCM manufacturing strategies, which differ depending on the considered material. They distinguished between conventional procedures, such as shaping and insertion in a binder, and emerging procedures, including nano-alternatives, encapsulation, and extrusion. Since there is still no agreed procedure for manufacturing at laboratory scale (from grams to kilos), large scale TCM manufacturing has had little development. An overview of the current manufacturing routes is shown in Fig. 37.

4.2.1. Composite thermochemical materials

Using pure salt hydrates in TCES systems can be problematic, leading to limited water vapor diffusion, poor heat and mass transfer, slow thermodynamic and kinetic, and deliquescence. Moreover, salt hydrates are characterized by low thermal conductivity and poor stability. Porous host matrixes are being investigated to enhance the performance of salt hydrates, forming a particular type of composite TCM, called salt in matrix (SIM) [25,26,147]. The main advantages of composite adsorbents are their porosity, mechanical strength, increased heat and mass transfer, thermal conductivity, and enhancement of cycle stability [146]. Salt hydrates are generally impregnated in the host matrix through different techniques depending on the material [147]. Among the most common materials suitable as host matrices, silica gel has low regeneration temperature and strongly adsorbs water at low humidity. It has low cost but is characterized by low thermal conductivity. Salt hydrates commonly combined with silica gel are $CaCl_2$, $MgCl_2$, LiCl, $SrBr_2$ and LiBr [145,147]. Thanks to its hydrophilic microporous structure, zeolites are characterized by high water uptake, resulting in high storage capacity. However, they are costly and the high regeneration temperatures decrease the efficiency of the system. The most promising type is zeolite 13X [145,147]. Vermiculite is a lightweight natural mineral characterized by high porosity [148]. Its large pores allow easier salt retention, providing higher stability and making it suitable for salts subject to deliquescence, such as LiCl, $CaCl_2$ and $SrBr_2$ [145].

4.3. Case studies

Although many TCES processes are potentially available, these systems have not been implemented on a commercial scale yet. However, several lab-scale and pilot demonstrations have been reported.

4.3.1. HVAC systems

The heating system of a house in the UK was retrofitted with a low temperature (70–90 °C) seasonal TCES system, in the framework of an Innovate UK project [38]. The system was based on a $CaCl_2$ adsorbed in vermiculite and dehydrated by solar thermal collectors (Fig. 38). The

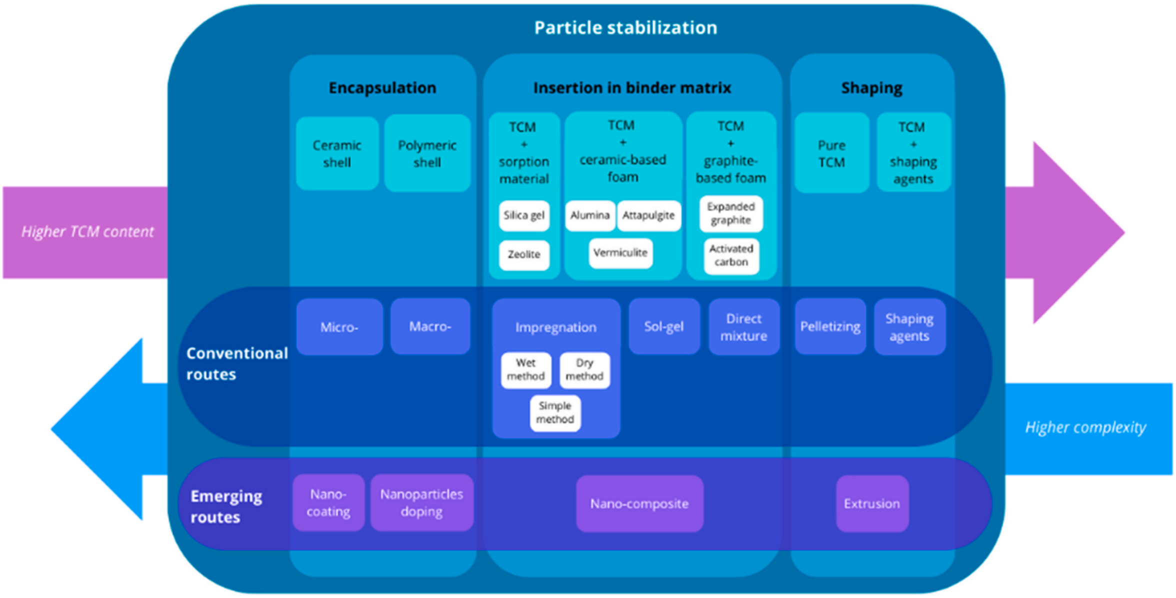

Fig. 37. TCES materials manufacturing routes (adapted from Ref. [31]).

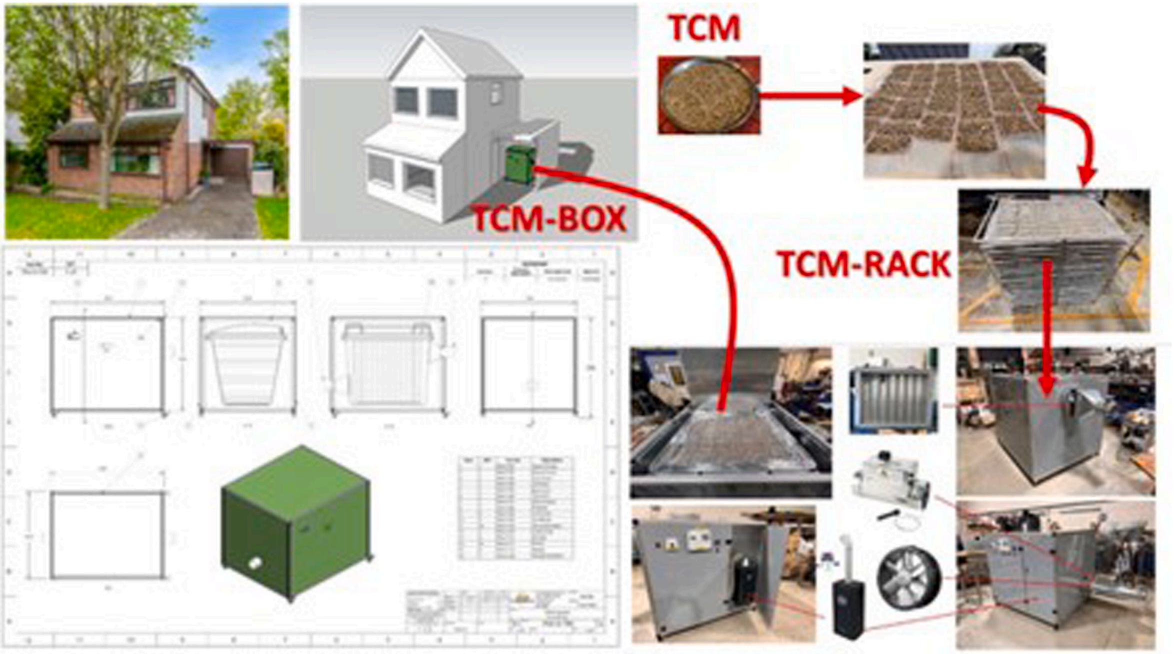

Fig. 38. UK House TCES heating conversion [38].

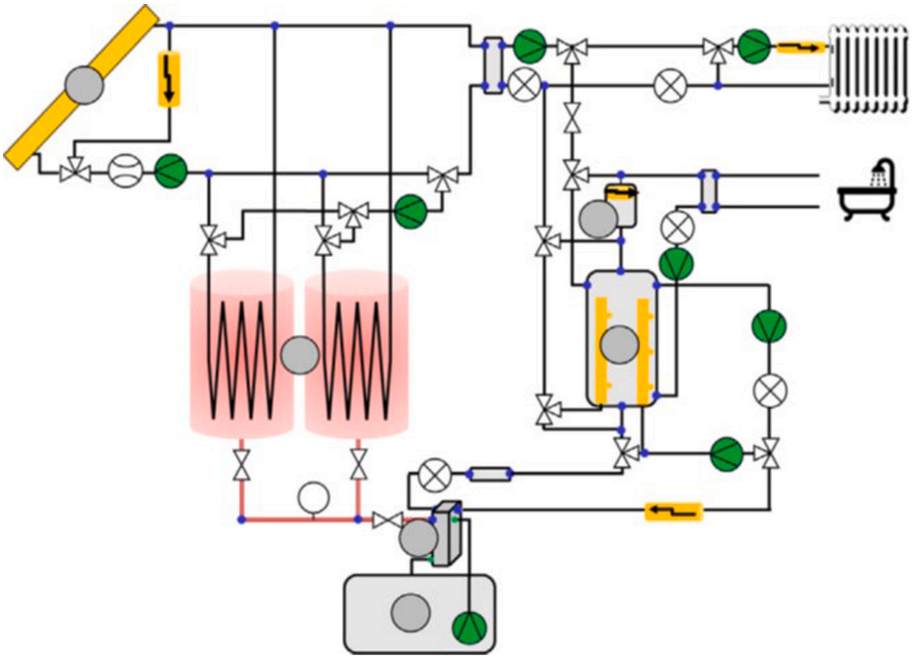

Fig. 39. Scheme of the demonstration system used in Ref. [150]. Reprinted from R. Köll,W. van Helden,G. Engel,W. Wagner,B. Dang,J. Jänchen,H. Kerskes,T. Badenhop,T. Herzog, "An experimental investigation of a realistic-scale seasonal solar adsorption storage system for buildings", Solar Energy, Volume 155, Pages 388–397, Copyright (2017), with permission from Elsevier.

regeneration phase employed a conventional humidifier, and heat was transferred to the building through small fans. The system was exploitable also with a heat pump, taking advantage of off-peak electricity. Due to the cost and the size of the TCM tank, it was possible to use the storage only for weekly operation.

Laboratory scale tests were developed by Johannes et al. [149], where a zeolite thermal storage system using water vapor sorbate has been analyzed. The open reactor reached a supplied power of 27.5 W/kg of material, being able to provide 2250 W in 6 h. Longer tests were performed by Köll et al. [150], where a closed sorption storage system was designed to supply domestic hot water and space heating demand of a single-family house. The system consists of evacuated tube collectors and of cylindrical tanks filled with zeolite 13XBF (Fig. 39). Short term storage for space heating and domestic hot water is addressed respectively by a conventional stratified storage and a hot water tank. Results showed a total energy density of 178 kWh/m^3. A pilot 4-kW system was constructed at the Eindhoven University of Technology, exploiting zeolite 13X and achieving an average reactor energy density of 108 kWh/m^3 [151].

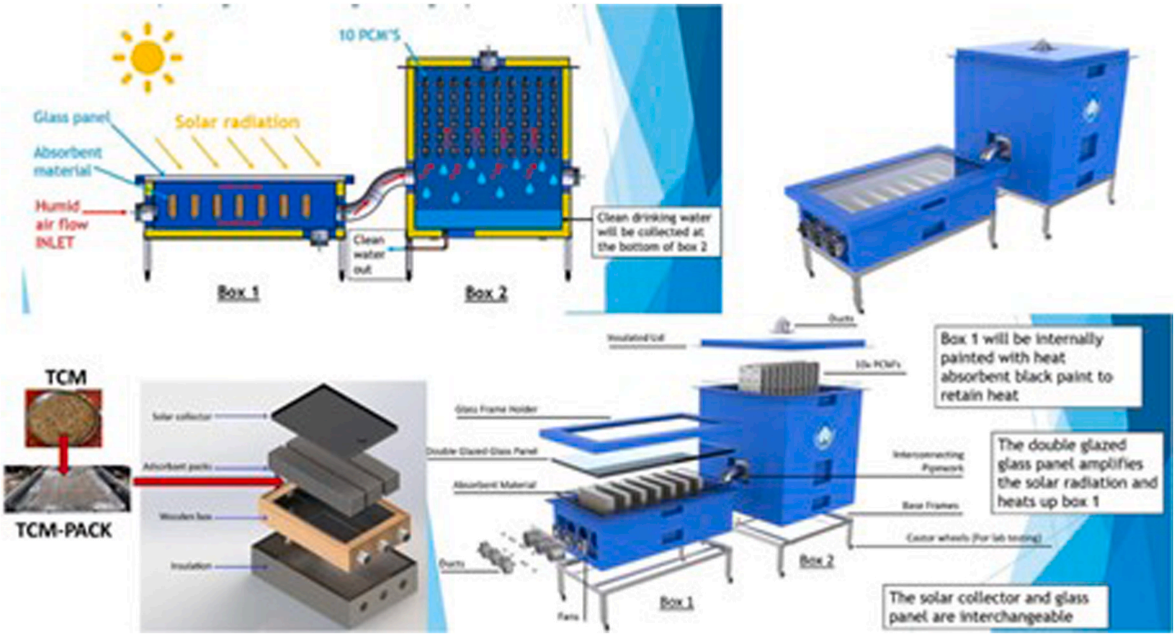

Fig. 40. TCES solar application for water harvesting [38].

Fig. 41. Pilot-scale storage plant combining long-term sorption storage and short-term sensible designed to cover yearly energy demand of a low-energy single family home. Reprinted from B. Fumey,R. Weber,P. Gantenbein,X. Daguenet-Frick,Sascha Stoller, Reto Fricker,V. Dorer, "Operation Results of a Closed Sorption Heat Storage Prototype",Energy Procedia, Volume 73, Page 7, Copyright (2015), with permission from Elsevier.

4.3.2. *Solar Energy*

The integration of solar energy with TES systems has mainly focused on STES and LTES systems [152], but research is moving towards the development of TCES systems. Almasri et al. reviewed case studies of sorption materials applied to solar cooling systems [153]. One of the most-developed TCES systems is the ammonia-based reaction, which was particularly investigated at the Australian National University. A solar driven closed-loop TCES pilot system was demonstrated, including ammonia synthesis heat recovery reactors [154]. Jiang et al. [155] investigated a seasonal resorption system to store solar energy employing $MnCl_2$-$CaCl_2$-NH_3 and a graphite matrix. They obtained a maximum heat storage density equal to 1149 kJ/kg. Dudita et al. [156] studied a 1-kW closed sorption storage system, integrating solar collectors and the working pair water/NaOH. The working principle was based on the falling film, requiring focus on optimization of heat and mass transfer during absorption. TCES has been applied for water harvesting in a combined application funded by Innovate UK, employing both a highly absorbent TCM and PCM plates [38] (Fig. 40). At night, a PCM freezes and stores cold, while the TCM absorbs water from the inlet humid air flow. During the day, solar radiation extracts the stored moisture and heats up the air passing through the plates, condensing water which is collected at the bottom.

A pilot storage plant based on the working pair sodium hydroxide (NaOH)/water was developed in the framework of the COMTES project [157]. The hybrid system exploits both sensible heat for short-term storage and sorption TCES for seasonal operation. The closed sorption system is supplied by solar collectors (Fig. 41). The same research group developed a spiral finned tube heat and mass exchanger for liquid

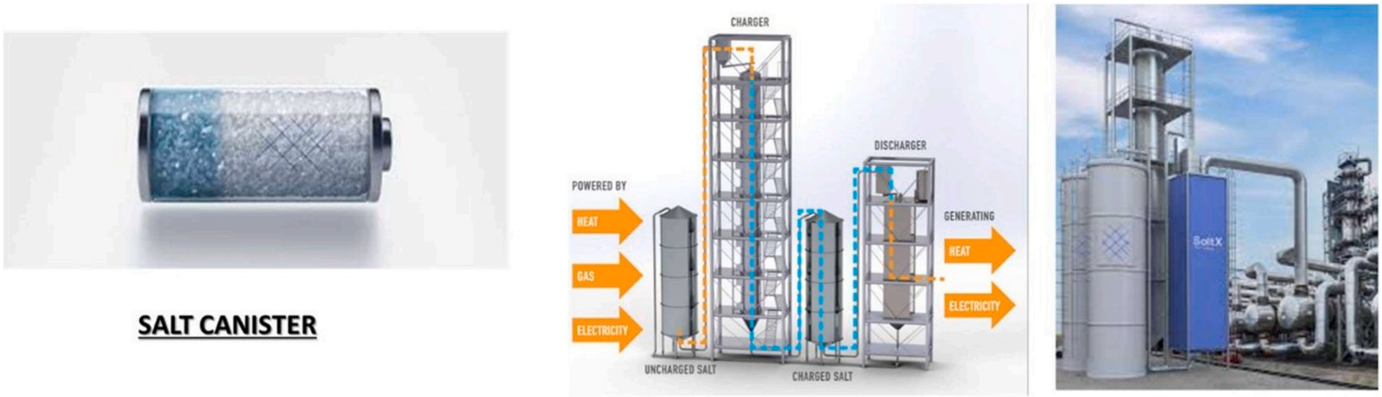

Fig. 42. Salt based TES systems [146].

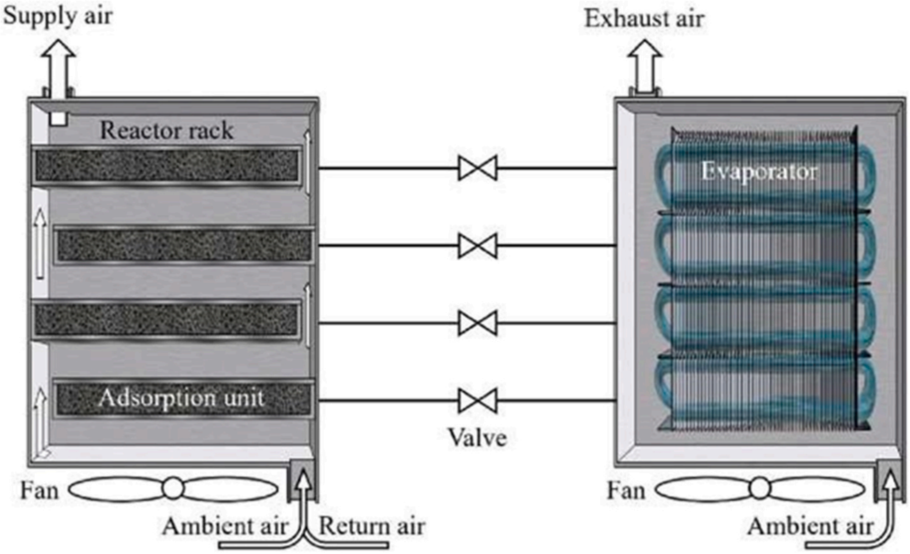

Fig. 43. EV car cabin heating concept. Reprinted from Megan Wilks, Chenjue Wang, Janie Ling-Chin,Xiaolin Wang, Huashan Bao, "Thermochemical energy storage for cabin heating in battery powered electric vehicles", Energy Conversion and Management (2023), under the terms of the Creative Commons CC BY license.

sorption, reaching a theoretical energy density of 435 kWh/m^3 [158].

The German Aerospace Center developed a pilot thermochemical system for CSP application [159]. The system consisted of cordierite honeycomb supports coated with cobalt oxide, and stored an average of 47 kWh at about 700–1000 °C.

4.3.3. *Waste heat recovery*

An application of waste heat recovery was provided by the Swedish company SaltX [160]. A large-scale energy storage technology based on the dried salt calcium oxide aims to store surplus electricity generated by wind and solar power plants (Fig. 42). The energy can be stored in the salt for weeks or months until it is needed without any heat losses, thus offering a cost-effective long-term TES option. Salt is retained in sealed containers and when hydrated turns into calcium hydroxide. This chemical process generates heat, and the temperature rises to approximately 120 °C. By adding hot steam instead of water to the salt, the steam temperature rises up to 500 °C.

4.3.4. *Electrical vehicles*

Wilks et al. [161] proposed an adsorption TCES system for cabin heating of a battery electric vehicle. The reactor stack has different modular units consisting of different layers, each independently controlled by an individual valve (Fig. 43). The sequential use of the units allows to rapidly increase the air supply temperature and to avoid high consumption of sensible heat during discharge.

Nasri et al. [162] developed two waste heat recovery concepts for a fuel cell electric vehicle, exploiting the TCES technology. The waste heat recovered from the fuel cell can be used for heating the cabin of the vehicle. The proposed concepts consist of one or two TCES tanks and the storage material is $LaNi_{4.75}Al_{0.25}$, suitable for the high temperature required by the operation of the fuel cell. In the first concept, preheating of the battery is provided with an electric heater, a commonly used solution. On the contrary, in the other concept the second heat storage tank is partly used to store low temperature heat, required for the preheating of the battery. A different metal hydride ($LmNi_{4.91}Sn_{0.15}$) was chosen for the second tank, to allow an efficient coupling between the reactors.

5. Comparative analysis of TES technologies

5.1. *Technology readiness levels (TRLs)*

The readiness or maturity of TES technologies is assessed based on the TRL, a standardised reference value firstly introduced by NASA in 1974 and then adopted by the U.S. Department of Energy in 2011 [163] for evaluating the commercial readiness of a given technology. The TRL indicator includes nine levels of development.

Table 16

Summary matrix of the TRL for each tecnology.

TES Category	Technology	TRL	TRL justification
Latent Heat Thermal Energy Storage (LTES)	Low-/medium-temperature PCMs (organic & inorganic salts)	7–9	Building applications on market (TRL $\geq$7); economic viability and integration still under optimization [166–169].
	High-temperature PCMs (metallic alloys, salts & eutectics)	4–6	Lab-scale & pilot prototypes exist, but no commercial high-T deployment yet; materials/methods still maturing.
Sensible Heat Thermal Energy Storage (STES)	Water-based Storage	8–9	Mature, widely commercialized in heating/cooling networks, district heating systems, and solar thermal plants.
	Molten Salt Storage	5–9	Proven at large CSP sites (TRL $\geq$7) but some chemistries & high-T designs still at pilot (TRL = 5–6) [165].
	Solid Media Storage (rocks, concrete, sand, ceramics)	5–9	From pilot lab (TRL = 5–6) to mature commercial systems (TRL = 8–9) in various plants; reactor design remains critical [165].
	Thermal oils	7–9	Commercial in industry & CSP; high-T stability and heat-transfer reliability proven.
Thermochemical Energy Storage (TCES)	Chemical reactions (metal oxides, hydrides, carbonates)	4–7	Proof-of-concept and lab demos up to pilot; kinetics and system complexity limit full commercial roll-out.
	Adsorption/ Desorption (e.g., zeolites, silica gels)	4–6	Lab demonstrations and small-scale pilots; sorbent stability & cycle efficiency still under R&D [171, 172].
	Absorption (e.g. LiBr–H$_2$O, NH$_3$–H$_2$O)	5–7	Bench-scale tests in HVAC/DHC contexts; integration and durability under real cycles still improving.

- TRL 1 – basic principles observed.
- TRL 2 – technology concept formulated.
- TRL 3 – experimental proof of concept.
- TRL 4 – technology validated in lab.
- TRL 5 – technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies).
- TRL 6 – technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies).
- TRL 7 – system prototype demonstration in operational environment.
- TRL 8 – system complete and qualified.
- TRL 9 – actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space).

The first three TRL levels refer to the idea of the technology, involving basic research and full development of the concept. The fourth and fifth levels refer to the prototype phase, developed in laboratory or in another appropriate environment. The validation phase is represented by the sixth and seventh levels, considering an operational environment. The final levels (8 and 9) describe the production phase, when the technology is demonstrated and approved [164].

5.1.1. Latent Thermal Energy Storage (LTES)

LTES systems have achieved TRLs ranging from 7 to 9, indicating a high level of maturity and readiness for commercial deployment. This TES technology has undergone extensive laboratory testing and field demonstrations. However, further development is required to face crucial issues and achieve widespread commercial deployment. One of the main challenges in assessing the TRL of LTES is the need to address technical barriers such as PCM leakage, thermal cycling stability, and integration technologies. Moreover, TRL is dependent on the application field [165]. LTES for building applications has reached high TRL levels by entering the market, although the economic feasibility of the integration of PCMs in the envelope has not been fully demonstrated yet [166]. Therefore, optimization of PCMs for low and medium temperature applications is a current research topic [167–169]. On the other hand, technologies for high temperature applications are not yet commercially available. Significant advancements have been made in the field of LTES, particularly in materials science and system design. Researchers have focused on developing PCMs with enhanced thermal properties and improved cycling stability. Moreover, innovative encapsulation techniques have been developed to prevent PCM leakage and ensure long-term durability. These advancements have contributed to the improved performance and reliability of LTES systems, bringing them closer to commercial viability. Despite the progress made, latent TES technologies still face several challenges that hinder their TRL progression. One of the key challenges lies in optimizing PCM properties to achieve higher energy storage density and faster charging/discharging rates. Additionally, ensuring the scalability and cost-effectiveness of LTES systems should be further investigated by researchers, improving the design for pre-commercial applications [170].

5.1.2. Sensible thermal energy storage (STES)

STES is a well-established technology already on the market for several years, with high TRLs in various applications. The TRL of STES typically ranges from 7 to 9, indicating a high level of maturity and readiness for commercial deployment. These systems have undergone extensive testing and validation in real-world applications and in diverse sectors such as district heating, concentrated solar power, and industrial processes, demonstrating their reliability, effectiveness, and commercial viability. Steady research and development efforts focused on improving thermal efficiency, durability, and cost-effectiveness with the aim to further elevate the TRLs of sensible TES technologies. Many activities are focusing on high temperature applications. The best materials for this purpose are rocks and molten salts, which maintain their mechanical and thermo-physical properties. However, the main challenges for these systems are material selection and reactor design [165]. For this reason, the TRLs of solid materials (like stones, ceramic, sand, concrete) and molten salt still range between 5 or 6 and 9. Furthermore, the integration of STES systems with RES such as solar and wind power holds immense potential for positioning them as key components of future energy systems.

5.1.3. Thermochemical energy storage (TCES)

Assessing the TRL of TCES technologies require evaluating factors such as reaction kinetics, material stability, energy density, and system efficiency. The TRL of TCES systems ranges from 4 to 7. At this stage, they have undergone laboratory-scale demonstrations, proof-of-concept studies and preliminary testing in real-world applications. While not yet fully mature for widespread commercial deployment, sorption TES technologies have demonstrated promising performance and potential for various practical applications, including decentralized cooling and heating systems [138]. Among the main challenges hindering TRL progression, the optimization of reaction kinetics is necessary to achieve fast charging and discharging rates, as well as the stability and durability of materials under cyclic operation. Moreover, the complexity and cost of system integration poses challenges to the widespread adoption of TCES technologies. For these reasons, progress focused on developing

Table 17
Cost comparison of various TES technologies. Adapted from Laura Pompei, Fabio Nardecchia, Adio Miliozzi, "Current, Projected Performance and Costs of Thermal Energy Storage", Processes (2023), under the terms of the Creative Commons CC BY license.

Technology	Cost (EUR/kWh)	Investment Cost (EUR/kW)	O&M Cost (EUR/kW/y)
STES	0.1–50	3400–4500	70–250
LTES	8–50	6000–15,000	120–750
TCES	8–100	1000–30,000	20–1500

new reaction systems, optimizing reactor designs, and improving system efficiencies. Researchers have explored a wide range of chemical reactions and materials to identify suitable candidates for energy storage applications. Additionally, innovations in reactor configurations, control strategies and heat transfer processes have contributed to improving the overall efficiency and reliability of TCES systems, especially regarding application in buildings [171,172]. Despite considerable progress, TCES technologies face several challenges that impact their TRL progression towards market readiness. Further research and development are required to address technical challenges and enhance system performance before widespread commercial deployment can be realized.

Table 16 presents a comprehensive summary matrix linking each category of thermal energy storage (TES) technology—latent heat (LTES), sensible heat (STES), and thermochemical (TCES)—to its corresponding Technology Readiness Level (TRL) range. This table synthesizes the detailed discussion in Section 5.1, highlighting that low- and medium-temperature PCMs have reached TRL 7–9, while high-temperature PCM materials remain at TRL 4–6. Sensible heat systems span TRL 5–9 depending on the storage medium, and thermochemical approaches currently lie at TRL 4–7. By juxtaposing technology type, maturity range, and key justifications, the matrix enables rapid assessment of development status and identifies areas requiring further research and scale-up (see Table 17).

5.2. Cost considerations

The market analysis indicates a dominance of STES due to its affordability and versatility [173]. However, advancements in LTES and TCES could shift the market dynamics, offering enhanced storage capacities and efficiencies. While STES currently leads in market penetration and cost-effectiveness, the evolving landscape of LTES and TCES technologies holds significant promise for advancing TES solutions, potentially transforming the energy storage sector with improved performance and cost-efficiency. To provide a more detailed analysis of the costs associated with various TES technologies we examine deeper into each TES type: STES, LTES, and TCES.

5.2.1. Sensible thermal energy storage (STES)

Cost Range (EUR/kWh): 0.1–50. This wide range indicates that STES can be very cost-effective but can also escalate depending on the specific materials and scale of the system.

Investment Cost (EUR/kW): 3400–4500. This investment cost is relatively moderate, making STES a viable option for both small-scale residential and large-scale industrial applications.

Operation and Maintenance (O&M) Cost (EUR/kW/y): 70–250. The ongoing maintenance and operational costs are manageable, which contributes to the popularity of STES in various sectors.

5.2.2. Latent Thermal Energy Storage (LTES)

Cost Range (EUR/kWh): 8–50. While generally more expensive than STES, LTES offers higher energy density, which can justify the higher cost in applications where space is a constraint.

Investment Cost (EUR/kW): 6000–15,000. The higher investment cost reflects the complex technology and materials (e.g., PCMs) used in LTES, which are crucial for its efficient operation.

O&M Cost (EUR/kW/y): 120–750. The maintenance and operational costs are higher, likely due to the need for specialized equipment and potential replacement of PCMs.

5.2.3. Thermochemical energy storage (TCES)

Cost Range (EUR/kWh): 8–100. TCES systems exhibit a broad cost range, reflecting the diversity of materials and processes involved, from simple reactions to more complex systems requiring advanced materials.

Investment Cost (EUR/kW): 1000–30,000. This range is quite wide, indicating that TCES can vary significantly in complexity and scale. The higher end of the range is likely associated with cutting-edge systems employing novel materials and reactions.

O&M Cost (EUR/kW/y): 20–1500. The operational costs for TCES are notably variable, suggesting that some systems are relatively straightforward to maintain, while others may require extensive and costly maintenance protocols.

Cost comparison of various TES technologies is presented in Table 16.

In summary, the choice of TES systems depends heavily on the specific needs and constraints of the application. While STES emerges as the most economically feasible option, particularly when prioritizing affordability over energy density, LTES presents a compelling alternative for scenarios where space constraints or enhanced efficiency are crucial factors. Furthermore, TCES showcases promising advancements in TES technology, offering potential long-term solutions for energy storage challenges. However, its widespread adoption is hindered by substantial costs and intricate maintenance demands. Ultimately, a nuanced understanding of these trade-offs is essential for informed decision-making in implementing TES solutions across various industries and contexts.

5.3. Environmental impact

To correctly understand the environmental impact of TES technologies, a life cycle approach is needed. Life Cycle Assessment (LCA) serves as a leading methodological tool that allows to measure the product sustainability, both quantitatively and qualitatively, by showing the negative environmental impacts and also the benefits, which leads to proper decision making with a sustainable approach [174]. LCA has been applied for a long time in the practical engineering, and has become a standardized by the ISO 14040 series method [175]. LCA takes into account all the life cycle stages of the system under study [176]: from the raw material extraction, their transport, the manufacturing or production, installation, use and maintenance and including the end of life.

To make comparisons in LCA terms, the definition of a common functional unit is needed. In LCA context, a functional unit is a quantified performance of a product system for use as a reference unit. Therefore, the functional unit provides a reference from which input and output data are normalized [177].

In the specific field of TES technologies, the most used functional unit is the storage of 1 kWh. On the other hand, there are studies that define the functional unit as 1 kWh of thermal energy delivered [178]. This reference allows for a comparison of the environmental performance of different types of TES in a specific use scenario, highlighting the technology that generates the least manufacturing impact while offering great performance.

Depending on the system under analysis and in close relationship with the functional unit definition, the scope of the environmental impact assessment must be defined. Within the scope, the system boundaries of the assessment are established, defining what must be included in the analysis and what is out of scope and are described for each of the life cycle stages. For example, a cradle to grave approach implies that all life cycle stages of the TES technology will be considered

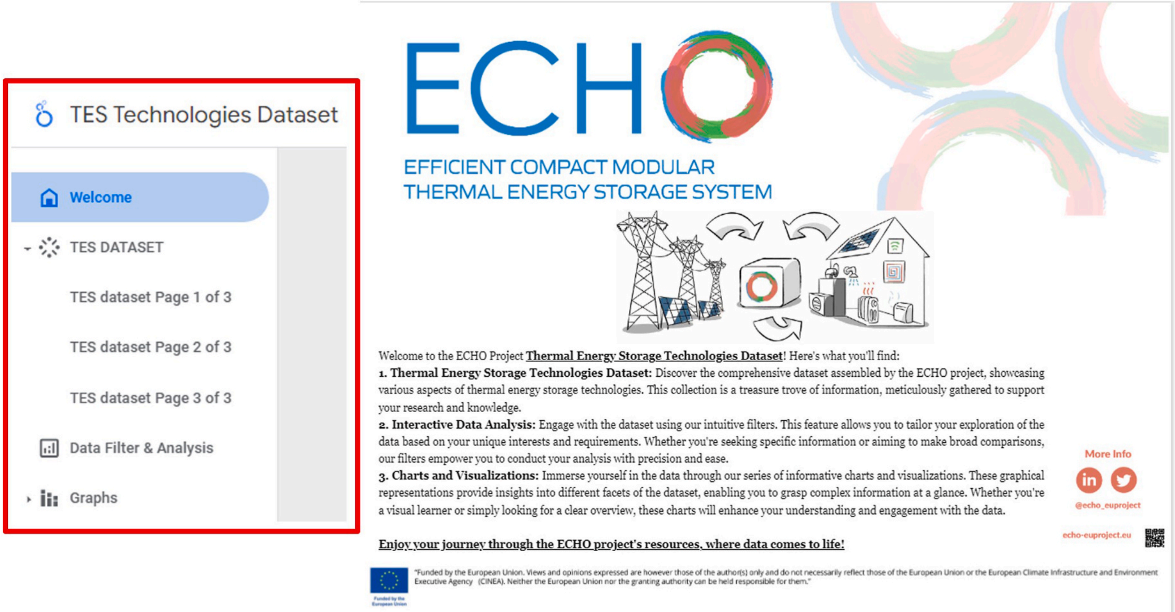

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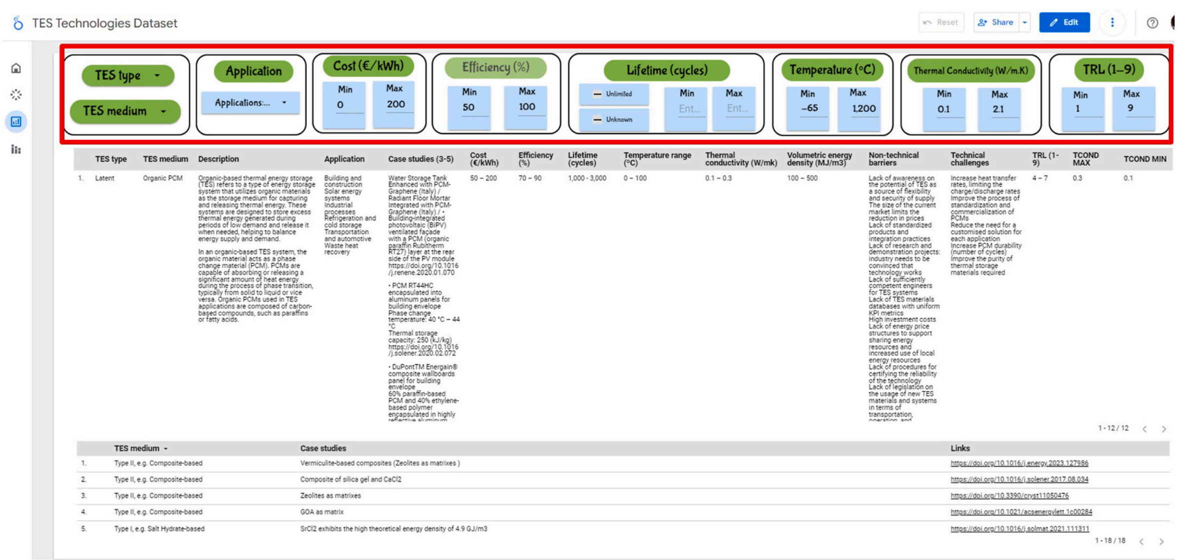
Fig. 44. Home page of the ECHO database.



	TES type	TES medium	Description	Application	Case studies (3-5)	Cost (€/kWh)	Efficiency (%)	Lifetime (cycles)	Temperature range (°C)	Thermal conductivity (W/mk)	Volumetric energy density (MJ/m3)	Non-technical barriers	Technical challenges	TRL (1-9)	TCOND MAX	TCOND MIN
1.	Latent	Organic PCM	Organic-based thermal energy storage (TES) refers to a type of energy storage system that utilizes organic materials as the storage medium for capturing and releasing thermal energy. These systems are designed to store excess thermal energy generated during periods of low demand and release it when needed, helping to balance energy supply and demand. In an organic-based TES system, the organic material acts as a phase change material (PCM). PCMs are capable of absorbing or releasing a significant amount of heat energy during the process of phase transition, typically from solid to liquid or vice versa. Organic PCMs used in TES applications are composed of carbon-based compounds, such as paraffins or fatty acids.	Building and construction Solar energy systems Industrial processes Refrigeration and cold storage Transportation and automotive Waste heat recovery	Water Storage Tank Enhanced with PCM-Graphene (Italy) / Radiant Floor Mortar Integrated with PCM-Graphene (Italy) / • Building-integrated photovoltaic (BiPV) ventilated façade with a PCM (organic paraffin Rubitherm RT27) layer at the rear side of the PV module https://doi.org/10.1016/j.renene.2020.01.070 • PCM RT44HC encapsulated into aluminum panels for building envelope Phase change temperature: 40 °C – 44 °C Thermal storage capacity: 250 (kJ/kg) https://doi.org/10.1016/j.solener.2020.02.072 • DuPontTM Energain® composite wallboards panel for building envelope 60% paraffin-based PCM and 40% ethylene-based polymer encapsulated in highly	50 – 200	70 – 90	1,000 - 3,000	0 – 100	0.1 – 0.3	100 – 500	Lack of awareness on the potential of TES as a source of flexibility and security of supply The size of the current market limits the reduction in prices Lack of standardized products and integration practices Lack of research and demonstration projects: industry needs to be convinced that technology works Lack of sufficiently competent engineers for TES systems Lack of TES materials databases with uniform KPI metrics High investment costs Lack of energy price structures to support sharing energy resources and increased use of local energy resources Lack of procedures for certifying the reliability of the technology Lack of legislation on the usage of new TES materials and systems in terms of transportation,	Increase heat transfer rates, limiting the charge/discharge rates Improve the process of standardization and commercialization of PCMs Reduce the need for a customised solution for each application Increase PCM durability (number of cycles) Improve the purity of thermal storage materials required	4 – 7	0.3	0.1

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	TES medium ▾	Case studies	Links
1.	Type II, e.g. Composite-based	Vermiculite-based composites (Zeolites as matrixes)	https://doi.org/10.1016/j.energy.2023.127986
2.	Type II, e.g. Composite-based	Composite of silica gel and CaCl2	https://doi.org/10.1016/j.solener.2017.08.034
3.	Type II, e.g. Composite-based	Zeolites as matrixes	https://doi.org/10.3390/cryst11050476
4.	Type II, e.g. Composite-based	GOA as matrix	https://doi.org/10.1021/acsenergylett.1c00284
5.	Type I, e.g. Salt Hydrate-based	SrCl2 exhibits the high theoretical energy density of 4.9 GJ/m3	https://doi.org/10.1016/j.solmat.2021.111311

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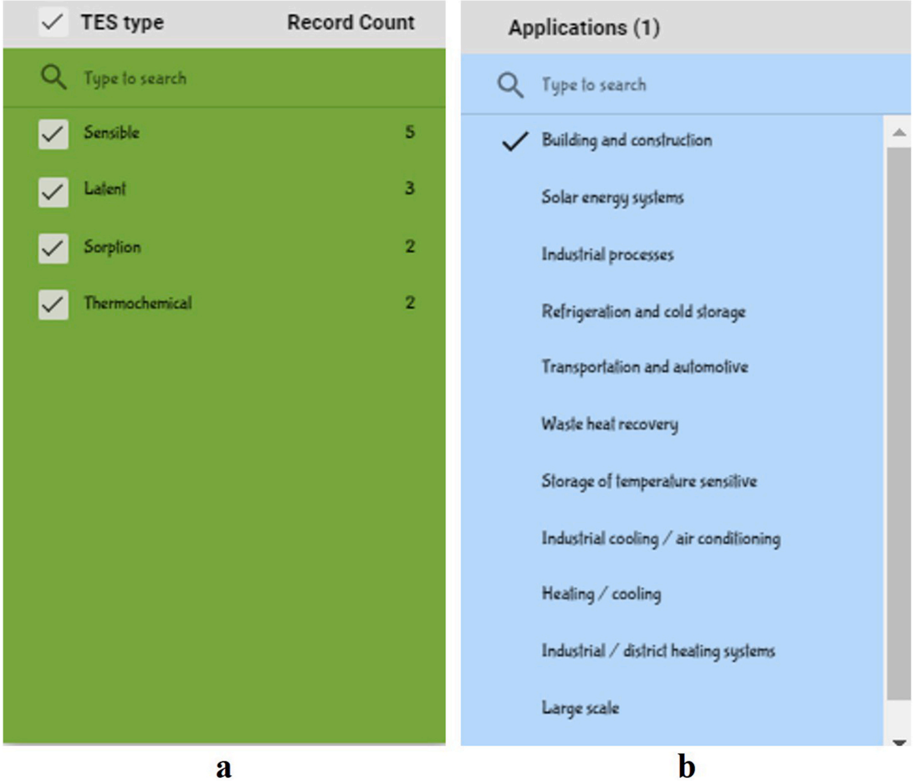
Fig. 45. Data filter & analysis section. The available filters are highlighted in red.

in the assessment.

To report the environmental impact, a set of indicators or environmental impact categories is provided. The most common indicator is the global warming potential (GWP), measured in kilograms of CO_2 equivalent. The standards focused on this category are commonly known as "Carbon Footprint" [179]. In the field of energy technologies, a relevant indicator that must be considered is the primary energy (PE), divided into renewable and non-renewable and measured in MJ. Beyond the GWP and the PE, the impact of the PCMs in LTES can be characterized thanks to indicators like ecotoxicity or environmental scarcity [180]. When comparing, it is important to note that it is difficult to find a TES technology that complies with the lowest impact in all the environmental impact categories studied. This makes the consideration of a complete set of indicators more interesting and needed to provide more detailed conclusions and, thus, to be more accurate in defining environmental impact reduction strategies.

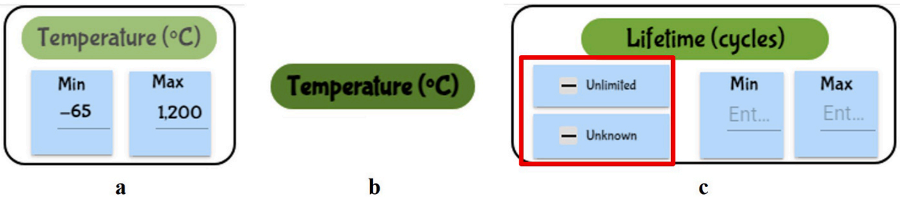
The state of the art regarding LCA methods and studies shows that electrical storage has been deeply studied in LCA terms, while only few articles provide useful information on the LCAs of TES systems [174]. The main insights regarding TES include.

- In general, numerical studies on TES systems focus on solar energy and PCMs. Recently a new trend focusing on thermal systems applied to buildings has emerged.
- Most of the reviewed articles on thermal storage refer to STES and LTES. PCMs related to thermal energy storage show the highest number of research studies, while thermochemical systems are scarce [181].
- In the case of thermochemical systems, the most studied area focuses on the development of new compounds to achieve the required energy density, high temperature applications in concentrated solar power plants and their application to buildings for seasonal storage.
- The research gaps identified in the TCES studies are related to LCA studies on materials and systems, application of sorption



✓ TES type	Record Count
☑ Sensible	5
☑ Latent	3
☑ Sorption	2
☑ Thermochemical	2

Fig. 46. TES type filter (a). Application filter (b).



Temperature (°C)
Min –65
Max 1,200

Fig. 47. Temperature range filter (a). Activation of the filter (b). Lifetime filter with the checkboxes Unlimited and Unknown are highlighted (c).

technologies, optimization techniques and environmental/economic analysis of sorption systems.

- Latest studies show the relevance of considering time-dependent LCA result representation when it comes to designing a sustainable technology [182].

5.4. *Selection criteria for TES systems*

The selection of TES systems is influenced by several criteria, which should all be taken into account in a optimized way [183]. Primary considerations include the intended application environment, distinguished among residential, industrial, or grid-scale contexts. The scale of storage, encompassing both capacity and power output, must align with the dynamic energy demands and supply fluctuations of the system. The thermophysical properties of the storage medium, such as heat capacity, thermal conductivity, and phase change characteristics, significantly impact system efficiency. Economic factors, comprising initial and operational costs, must be carefully balanced to ensure cost-effectiveness over the system's lifecycle. Compatibility with existing or planned energy infrastructures and the environmental impact of the chosen technology are also crucial considerations. A holistic evaluation of these criteria is indispensable for the optimal selection of TES systems, ensuring their alignment with application-specific needs, and contributing to enhanced energy efficiency and sustainability.

5.4.1. *Scale of storage and application environment*

Small-scale TES systems are typically designed for localized applications, such as residential buildings, small commercial establishments, or individual industrial processes. In these cases, the following key factors are attentively considered.

- space availability: in residential contexts, as well as in small commercial ones, space destined for installing TES systems is often limited. Thus, compact and space-efficient designs are preferred.
- cost-effectiveness and affordability: TES systems should offer a reasonable return on investment through energy savings and reduced utility bills.
- ease of installation and maintenance.
- integration and compatibility with existing HVAC systems.
- energy storage capacity, adequate to meet the thermal energy demand of the targeted application, especially during peak periods.
- flexibility in operation, allowing users to adjust energy storage and discharge based on varying demand patterns.

Differently, medium-scale TES systems cater to larger applications such as district heating and cooling networks, medium-sized industrial facilities, or community-based energy projects. The selection criteria for medium-scale TES systems include.

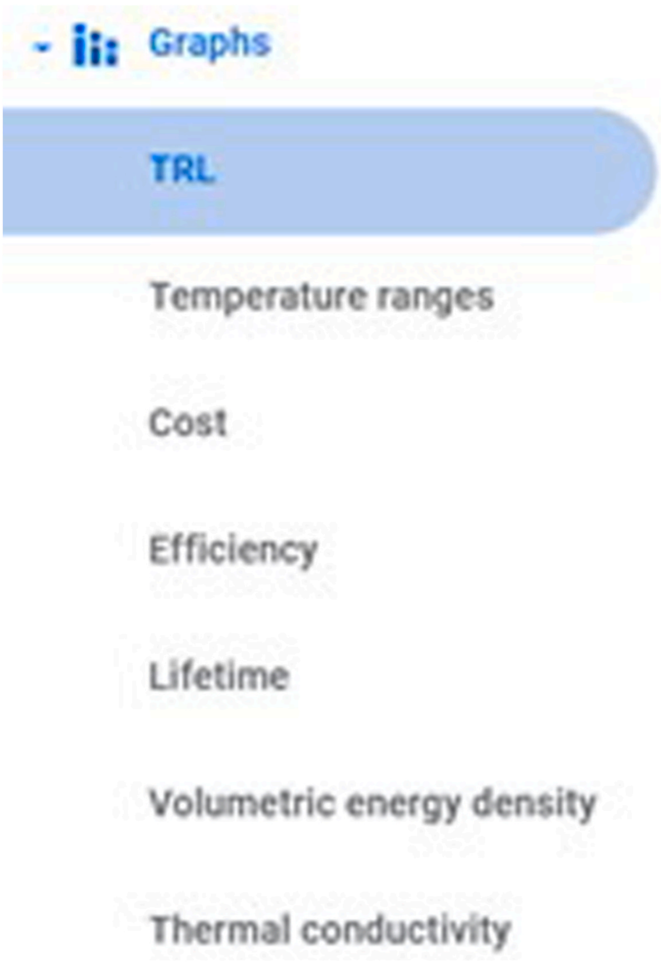


Fig. 48. Pages in the graphs section.

- storage capacity and rate: these systems must find a balance between storage capacity and the rate of energy transfer to meet the diverse energy demands of medium-sized applications effectively.
- scalability: these systems should be scalable to accommodate future expansions or changes in energy demand, ensuring long-term viability and adaptability.
- compatibility with infrastructure: medium-scale TES systems should integrate seamlessly with existing infrastructure, including heat distribution networks or industrial process systems.
- reliability and durability: reliability is paramount for medium-scale applications to minimize downtime and maintenance costs and ensure uninterrupted operation. TES systems must also exhibit durability to withstand operational demands over extended periods.
- lifecycle cost: considerations such as initial investment costs, maintenance expenses, and operational efficiency contribute to assessing the lifecycle cost of medium-scale TES systems.

Large-scale TES systems serve utility-scale applications, grid stabilization initiatives, and centralized industrial processes requiring substantial thermal energy storage capacities. Thus, when selecting large-scale TES systems the following aspects are evaluated.

- high storage capacity: large-scale TES systems must offer significant storage capacities to support utility-scale energy storage requirements, grid stabilization, or industrial processes with high thermal energy demands.
- fast response time: rapid response capabilities are essential for large-scale TES systems to provide grid ancillary services, stabilize renewable energy integration, and meet fluctuating demand patterns.
- grid compatibility: these systems should comply with grid interconnection standards and regulatory requirements to ensure seamless integration with the existing power infrastructure.
- cost-effectiveness: large-scale TES systems must demonstrate competitive capital costs and operational efficiency to justify their deployment on a utility scale.
- sustainability: environmental considerations, such as the use of eco-friendly storage materials and energy-efficient operation, are crucial for large-scale TES systems to align with sustainability objectives.

5.4.2. *Thermophysical attributes of the storage medium*

The selection of an appropriate storage medium is a critical aspect of designing effective TES systems. Thermophysical properties such as heat capacity, thermal conductivity, and phase change characteristics significantly influence the performance and suitability of TES systems for specific applications.

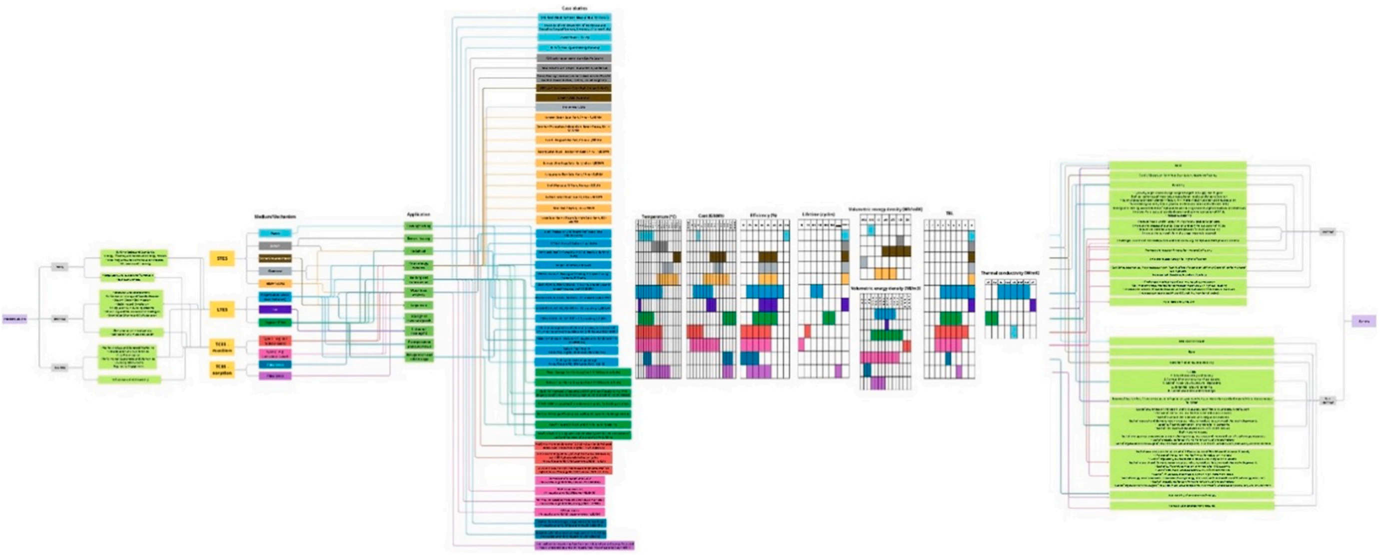


Fig. 49. Taxonomy of the TES technologies.

In TES systems, a high heat capacity is desirable as it allows for the storage of large amounts of thermal energy. Materials with high thermal conductivity facilitate fast charging and discharging cycles, minimizing energy losses and improving system efficiency. The enhancement of thermal conductivity is one of the main challenges for PCMs: possible solutions include the addition of nanoparticles or foams, the creation of composite PCMs or the usage of encapsulation techniques [184]. The selection of PCMs depends on their melting and solidification temperatures, which should align with the temperature requirements of the TES system's operating conditions [10].

Finally, also the stability and compatibility of the storage medium are essential aspects in TES system design [179]. The storage medium must exhibit thermal stability over numerous charging and discharging cycles to ensure long-term performance reliability. Compatibility with other system components, such as containment vessels, piping, and insulation materials, is also essential to prevent material degradation and ensure system integrity. Additionally, the storage medium should be compatible with the operating conditions and environmental factors of the intended application to minimize the risk of corrosion, degradation, or leakage.

5.4.3. *Economic factors*

The economic feasibility of TES systems involves evaluating the initial investment, operational costs, and return on investment (ROI) [185]. Capital costs cover equipment (such as storage tanks, heat exchangers, insulation materials, and control systems), installation, and specific system requirements, and varies depending on the TES system's scale, technology, and application. Operational costs encompass daily expenses for running and maintaining TES systems, including the energy consumption for charging and discharging processes, maintenance activities, system monitoring, and personnel costs. These costs depend on system efficiency, energy losses, frequency of maintenance interventions, and the complexity of control and monitoring systems. Stakeholders must conduct cost-benefit analyses to ensure that the expenses align with the expected returns in terms of energy savings, operational efficiency, and potential revenue. A lifecycle cost analysis is also essential for evaluating the economic feasibility of TES systems, accounting for total ownership cost. This comprehensive approach helps stakeholders make informed decisions about TES systems' economic and sustainable value compared to other energy storage options. Finally, assessing the ROI and payback period is crucial for understanding the financial attractiveness of TES systems. ROI compares the net benefits (e.g., energy savings, revenue generation) against the initial investment. Together, these parameters help stakeholders prioritize TES investments based on expected returns and risk tolerance levels.

5.4.4. *Compatibility with existing or planned energy infrastructures*

Selecting TES systems implies also assessing their compatibility with existing energy infrastructures. Whether in residential, commercial, industrial, or utility-scale applications, TES systems must seamlessly integrate with the prevailing energy systems to ensure efficient operation and minimal disruption. Compatibility encompasses various aspects, including.

- thermal compatibility in terms of temperature requirements, heat transfer mediums, and thermal storage capacity.
- system interconnectivity, featuring compatible interfaces and control mechanisms to integrate seamlessly with existing energy infrastructures. Compatibility in communication protocols, data exchange formats, and control signals enables effective coordination and synchronization between TES systems and other energy components.
- operational synergy should complement the operation of energy generation, distribution, and utilization systems, contributing to overall system reliability, stability, and efficiency. For example, TES systems can help mitigate peak demand periods, optimize renewable energy integration, or enhance grid stability through coordinated operation with existing energy infrastructures.
- Scalability, to accommodate future expansions, changes in energy demand patterns, or the integration of additional RES.
- Flexibility, including configurable storage capacities, charging and discharging profiles, and operating modes to adapt to varying energy demand patterns and system requirements.

5.4.5. *Environmental impact*

The main environmental impacts and aspects to take into account when selecting a TES system are summarized in the following points.

- Resource utilization: TES systems employ various materials for TES, and assessing their impact involves evaluating the availability and sustainability of these resources. Opting for abundant, renewable, or recycled materials can minimize resource depletion and environmental damage.
- Emissions: during the lifecycle of TES systems, emissions may occur from manufacturing, operation, and disposal phases. Evaluating these emissions involves considering factors such as energy consumption during production, GHG emissions, and air pollutants.
- Energy efficiency: higher energy efficiency implies reduced energy consumption and lower environmental burden. TES systems with efficient thermal storage and retrieval processes, as well as minimal energy losses, contribute to overall energy conservation and environmental protection.
- Lifecycle assessment (LCA): conducting an LCA helps evaluating the environmental impact of TES systems throughout their entire lifecycle, from raw material extraction to end-of-life disposal (see 5.3).
- Recyclability and reusability: materials used in TES systems should be recyclable, and systems should be easily disassembled for component reuse or recycling at the end of their lifecycle, promoting circular economy principles and minimizing waste production.
- Ecological footprint: it involves considering their impact on ecosystems and biodiversity. Factors such as land use, habitat disruption, and water consumption should be evaluated to minimize adverse effects on the environment.
- Environmental impact reduction of the energy system due to flexibility improvement: TES systems contribute to improve the reliance of renewable energy sources, in particular solar and wind. They contribute to reduce the impact of inconsistent energy generation and to maintain a proper balance between demand and energy generation [131].

5.5. *Summary of the main barriers for TES*

Research in the field of TES should particularly focus on addressing the limitations which still affect both technologies and materials. Space constraints are still an issue for most TES systems, as well as modularity and scalability. The development of LTES systems is particularly dependent on the performance of PCMs, which suffer from low thermal conductivity, leakage, thermal cycling instability. Salt hydrates can undergo phase segregation and deliquescence and are characterized by limited vapor diffusion and poor heat and mass transfer, as well as subcooling. Organic PCMs are stabler but more expensive, while metal PCMs are penalized by their weight and low latent heat. Despite their maturity, STES systems are limited by their low energy density and, for example, by the need for suitable containment and insulation for high-temperature water applications. Solid STES materials might present non-uniform heat distribution and durability issues. Being the least developed technology, TCES adds further complexity, related to the optimization of the reaction kinetics, on the durability of TCMs and on the integration with other components, which should consider potential deliquescence and corrosion issues. All these aspects limit the scalability of TES systems, including transferability to the commercial scale and development of modular solutions. Other than technical aspects, the high initial cost and consequent payback period of TES systems is a relevant barrier to their implementation. Moreover, the deployment of TES systems is still hindered by many social barriers, including lack of subsidies, unclear and incomplete regulations, lack of awareness and knowledge [186].

6. Database of TES technologies and visualization tool

In alignment with the aim of this comprehensive review article, a visualization tool showcasing available TES technologies was developed within the framework of the ECHO project [187]. The platform chosen for this visualization effort is *Looker Studio* [188], a software specifically suited to managing and displaying complex datasets. This tool enables users to explore the full database, with the flexibility to filter and refine the displayed data based on various criteria, including the type of TES system, intended applications, operational temperature ranges, system efficiency, and more. This interactive approach facilitates tailored data exploration, enhancing user engagement and accessibility to critical information. The tool is available at the link https://lookerstudio.google.com/reporting/1dd662a1-938f-4dd8-91a9-ef70ccdd72ab.

The home page shows a brief description of the tool, as in Fig. 44. On the left-hand side, the user can navigate through different labels: *Instructions* displays the home page, *TES DATASET* contains the raw data, the *Data Filter & Analysis* section allows to filter and refine the data, and the last section consists of different graphs related to each numerical parameter available in the database.

In the *Data Filter & Analysis* section (Fig. 45), the user can apply multiple filters. These can be found in the upper part of the page, and include.

- TES type
- Medium
- Application
- Temperature range [°C]
- Cost [€]
- Lifetime [number of cycles]
- Efficiency [%]
- TRL
- Volumetric energy density [MJ/m^3]
- Thermal conductivity [W/m/K] (applicable to LTES).

The filters *TES type* and *TES medium* work in the same way. The user can select one or more items through the dropdown list, as shown in Fig. 46-a. If all items are selected but the user would like to only select one option, the button *ONLY* can be clicked.

The filter *Application* consists of a dropdown list as well, where only one option can be selected, as shown in Fig. 46-b. To show the results, the filter must be activated by clicking on the green *Application* button. Once activated, the button's color becomes darker.

All the other filters allow the user to insert a range for the chosen parameter, showing then the TES technologies characterized by values included in it.

For example, the steps for setting a temperature range between −65 °C and 1200 °C are as follows.

1. Insert the desired minimum temperature in the entry box *Min.*
2. Insert the desired maximum temperature in the entry box *Max* (Fig. 47-a).
3. Activate the filter by clicking on the green *Temperature* button (Fig. 47-b).
4. The records are now filtered, showing technologies that can operate in the selected temperature range.

To remove all filters, the user can click on *Reset*, in the upper part of the window.

Finally, the *Lifetime* filter can be used by following the procedure described above, and/or by selecting the checkboxes *Unlimited* or *Unknown*, as shown in Fig. 47-c.

In the *Graphs* section, the user can find various pages. Each page corresponds to a TES parameter, including TRL, temperature range of operation, cost, efficiency, lifetime, volumetric energy density, and thermal conductivity (Fig. 48).

For each parameter, a graphical representation in the form of a table is displayed, showing the possible values that can be taken by that parameter for each TES technology. Each row refers to a specific medium or mechanism (e.g. concrete, organic PCMs, absorption, etc.), with the relevant value range shown as one or more contiguous colored cells. The numerical values are listed in the top row of the table. Technologies within the same TES type (sensible, latent, or chemical) share the same color scheme.

These graphs are useful to provide users with a clear overview of the differences among the various technologies regarding these key parameters, thus allowing an easier comparison.

7. Conclusions

TES systems make a significant contribution to the fight against climate change, by integrating RES and balancing energy supply with the increasing demand. This study provides a comprehensive theoretical overview and a multifaceted comparison of different TES technologies and their related mediums, analyzing their TRL, selection criteria, as well as economic and environmental considerations.

STES is the simplest and most mature technology, including many solutions available in the market. Consequently, research in this field primarily focuses on enhancing heat storage capacity through the development of innovative materials and advanced insulation techniques. Particular attention is given to certain solid mediums, which currently have TRLs of around 5–6.

LTES systems are also well-developed, though their commercial deployment depends heavily on the specific application. A significant barrier to their widespread use is their low thermal conductivity, which can be enhanced by incorporating metal foams and particles, or by encapsulation techniques.

Research interest in TCES is growing, as most studies to date have been conducted at the laboratory scale. Key challenges for researchers include improving reaction kinetics, stability and durability of TCMs, while also addressing costs and system complexity.

Examples of applications for each TES type have been collected, with a particular focus on real-world case studies. Additionally, this work has introduced an innovative visualization and filtering tool for a comprehensive database created by the authors. The tool offers up-to-date access to detailed information about the analyzed TES technologies and their applications, allowing users to query the database according to specific research or professional needs.

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Declaration of competing interest

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

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Appendix

Prior to the creation of the database, a taxonomy of the available TES technologies has been developed, with the aim of selecting the different parameters to be analyzed and possible interdependence between them. Fig. 49 shows the developed scheme, which especially highlights the ranges of the values corresponding to different variables. The online version with high resolution is available at the link: https://www.canva.com/design/DAF1k5REGxA/MtW8y4j79bHDFjKYtaZNbw/edit?utm_content=DAF1k5REGxA&utm_campaign=designshare&utm_medium=link2&utm_source=sharebutton.

Data availability

Data will be made available on request.

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