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Boosting Innovative Solar Energy Technologies and Applications in Mediterranean Countries Education

ERASMUS+ PROGRAMME – VET

Project number: 101092041

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Course Energy Storage Systems (with PV off grid PV)

Chapter 1 Thermal energy storage (TES) Materials

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Course Content

- **Chapter 1 Thermal Energy Storage (TES) materials**
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- Chapter 3 TES Systems and Applications
- Chapter 4 Mechanical Energy Storage
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Chapter 1 Thermal Energy Storage (TES) materials

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Chapter 1.0 Overview of Thermal Energy Storage

Contents

1.0.1 Significance and role of Thermal Energy Storage

Why Bother Thermal Storage ?

- **Energy demand**

- The increasing global population and industrial development necessitate a surge in energy demand, necessitating the use of thermal energy storage (TES) to store excess energy during low-demand periods.

- **Renewable energy integration**

- Transitioning to renewable energy sources like solar and wind presents challenges due to their intermittent nature.
- TES allows for the storage of excess energy for future use.

1.0.1 Significance and role of Thermal Energy Storage

- **Cost saving**

- Optimizing energy resource usage, reducing electricity bills and expenses by shifting consumption to off-peak periods during lower rates for businesses and households.

- **Grid stability**

- Regulating the electrical grid by reducing fluctuations in energy supply and demand, ensuring grid stability and reliability.

- **Environmental impact**

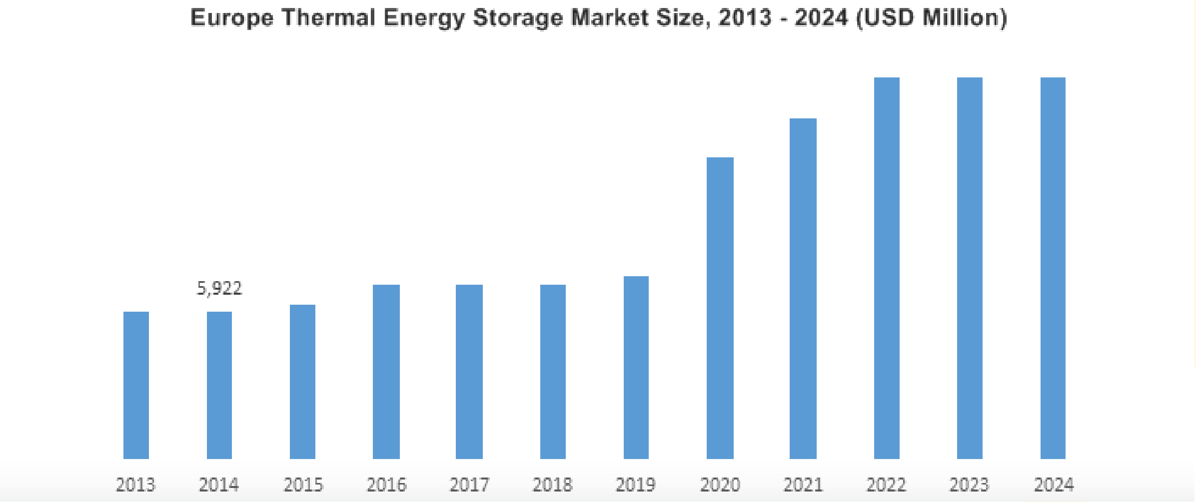
- Reduce our dependency on fossil fuels and decrease greenhouse gas emissions.
- Preventing the need for additional power generation from polluting sources, Combatting climate change.

1.0.1 Significance and role of Thermal Energy Storage

Thermal Energy Storage Market

Europe: Around 1.4 million GWh/year of energy can be saved, and 400 million tons of CO_2 emissions can be avoided, in residential and industrial sectors by extensively using heat and cold storage technologies.

- The heating and cooling sector, which accounts for half of Europe's energy consumption, is generating significant demand for thermal energy storage.



(Source: Ref. [9])

1.0.1 Significance and role of Thermal Energy Storage

- Despite increasing renewable energy awareness, 85% of thermal energy still comes from fossil fuels, indicating potential growth opportunities.
- Europe's regulatory landscape is promoting renewable energy integration for a decarbonized economy, presenting further growth opportunities in the thermal energy storage market.

China Thermal Energy Storage Market

- In the first half of ***2018***, Henan, Qinghai, Jiangsu, and Guangdong provinces announced the construction of 340.5 MW of energy storage projects.

1.0.1 Significance and role of Thermal Energy Storage

United States Thermal Energy Storage Market

- In ***2017***, nearly 41.8MW of energy storage systems were installed across the region ≃ 46% of y-o-y growth.
- 14 U.S. States have deployed around 2GW of energy storage into Integrated Resource Planning (IRP), highlighting the growing popularity of energy storage technology in the region.
- U.S. thermal energy storage market share stood at USD 6 billion in 2017, reported by Global Market Insights.

The worldwide thermal energy storage industry to surpass a revenue of USD 55 billion by ***2024***.

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Chapter 1.0 Overview of Thermal Energy Storage

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1.0.2 Fundamentals of Thermal Energy Storage
Classification of energy storage systems

Energy Storage Systems				
Mechanical: -Hydrostorage - Compressed air storage - Flyweels	**Chemical:** - Electrochemical batteries - Organic molecular storage	**Biological**	**Magnetic**	**Thermal:** - Sensible Heat Storage - Larent Heat Storage - Chemical Heat Storage

- Classification of Energy storage systems

1.0.2 Fundamentals of Thermal Energy Storage

Thermal Energy Storage ?

Definition

- Technology that allows for the storage of thermal energy in a certain medium such as a liquid or solid material.
- This stored energy can then be used later for various applications, such as heating or cooling purposes, without the need for immediate generation or extraction of the.

Significance

- The storage of excess thermal energy enhances energy system efficiency, reliability, and sustainability, enabling optimal utilization during peak periods and reducing energy waste and cost savings.

Role

- Renewable energy sources like solar or wind power are integrated into the grid, allowing for excess energy storage and ensuring a stable and consistent energy supply.

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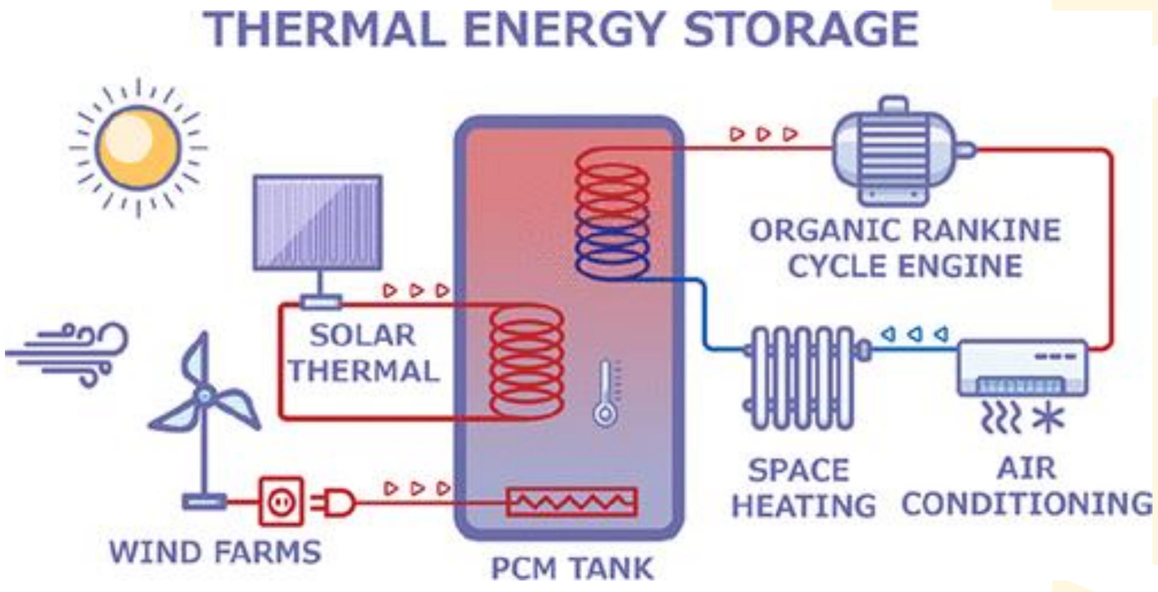
1.0.2 Fundamentals of Thermal Energy Storage

Thermal Energy Storage (TES)

- The storage of Energy in the form of heat or cold for up to several months.
- The energy will be collected whenever it is available and will be used when it is needed.
- TES will help in smoothing out fluctuations in Energy demand during Different time periods of the day.



(Source: Ref. [18])

- **Field of application of thermal storage**

1.0.2 Fundamentals of Thermal Energy Storage

- Working temperature

- Energy storage temperature below 100 °C:

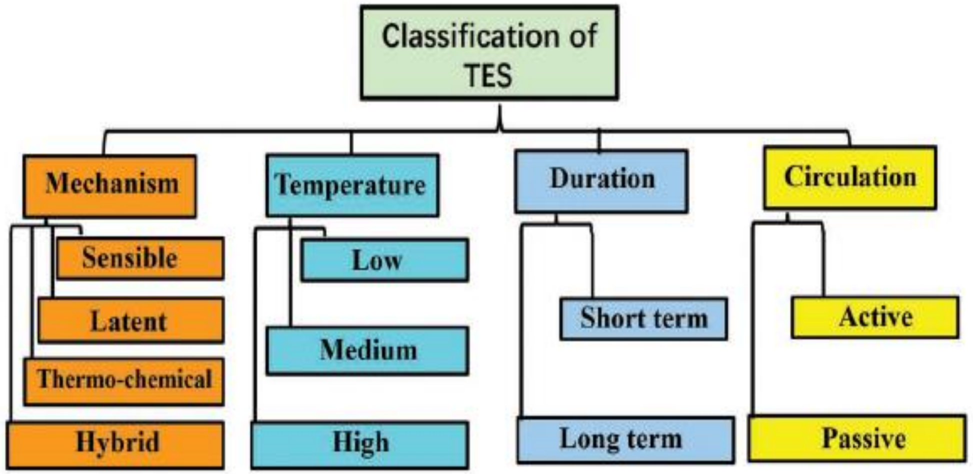
Low Temperature Energy Storage.

- Energy storage temperature between 100°C–200°C:

Medium Temperature Energy storage.

- Energy storage temperature beyond 250°C:

High Temperature Energy storage.



Thermal energy storage (TES) technologies may be classified according to four aspects

1.0.2 Fundamentals of Thermal Energy Storage

- Duration of storage

- Long term storage : Energy storage system is stored for months or seasons.

- Short-term storage: Energy storage system is charged or discharged daily or weekly.

- Circulaton of heat transfer medium

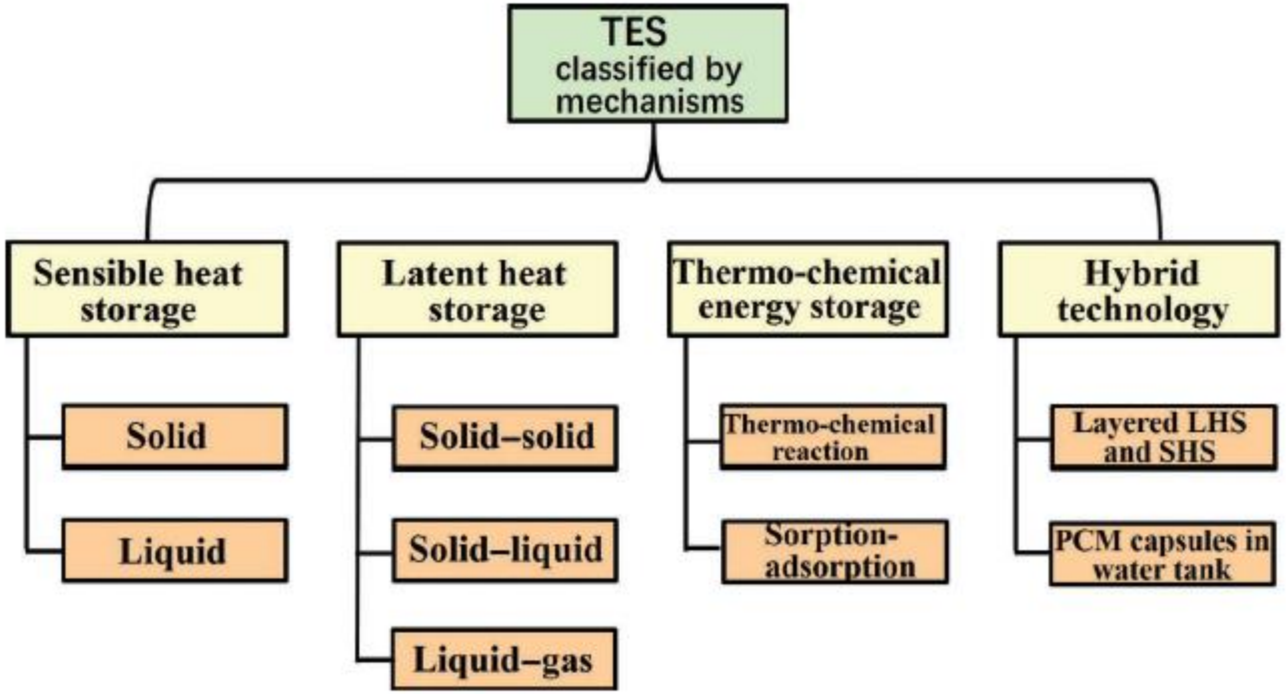
- Passive system: Heat transfer fluid (HTF) circulated by buoyancy effects without external force (such as a fan or a pump).

- Active system: HTF is driven by an external force.

- Energy storage mechanism

1.0.2 Fundamentals of Thermal Energy Storage

- ***Sensible heat storage-***
  - Heat capacity of materials
  - Water, solids (e.g. concrete, rocks).
- ***Latent heat storage-***
  - Phase change
  - Water, organic and inorganic PCMs.
- ***Thermochemical heat storage –***
  - Physical or chemical bonds.
  - Adsorption, absorption, chemical reactions.



Classification of the TES concepts by energy storage mechanism

Chapter 1 Thermal Energy Storage (TES) materials

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Chapter 1.1 Sensible Thermal Energy Storage Materials

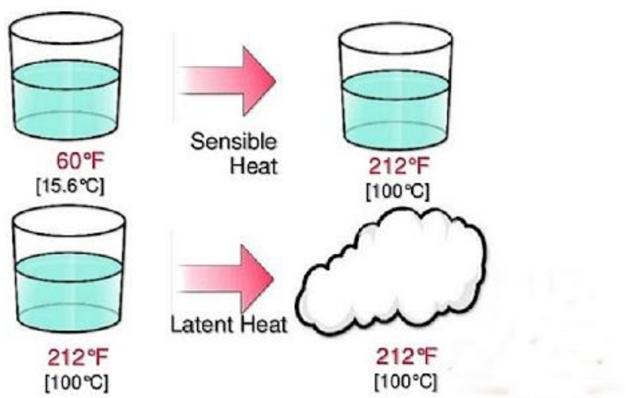
Contents

1.1.1 Properties and selection criteria

1. Definition

Sensible Thermal Energy Storage:

- Type of thermal energy storage system
- The storage of heat by changing the temperature of a storage medium, such as water, air, or rock.
- Without changing its phase.



(Source: Ref. [19])

All materials have a **specific heat capacity Cp** at constant pressure, allowing them to absorb and store heat.

$$Q_{sensible} = m \cdot c_p \cdot (T_2 - T_1) = m \cdot c_p \cdot \Delta T$$

$\Delta T = T_2 - T_1$ Temperature difference
T_2: the material temperature at the end of the heat absorbing (charging) process.
T_1: Temperature at the beginning of the process
M: Mass of the material.

Q sensible: heat is released in the respective discharging process.

1.1.1 Properties and selection criteria

2. The principles of sensible TES

- **Storage medium**
  - Suitable Storage medium
  - Examples: Water, air, rock
  - Absorb and store heat energy by changing its temperature

{ Cost
Availability
Temperature range }

- **Heat transfer**
  - The transfer of heat energy between the storage medium and a heat source or sink.
  - Through direct contact between the storage medium and the heat source or sink or through a heat exchanger.

- **Storage capacity**
  - Depends on the heat capacity of the storage medium.
  - The temperature difference between the storage medium and the heat source or sink.
  - Determines the storage capacity and the duration for which the stored heat energy can be utilized.

1.1.1 Properties and selection criteria

- **Temperature control**

- Effective temperature control mechanisms to ensure efficient storage and retrieval of heat energy.
- Insulation to minimize heat loss, temperature sensors and control systems.
- Maintain the desired storage temperature, and thermal management techniques.

- **Heat extraction**

- The extraction of stored heat energy when needed.
- The stored heat can be used for various applications, such as space heating, water heating, or industrial processes.

- **Energy efficiency**

- The design and operation of STES systems should focus on maximizing energy efficiency.
- Minimizing heat loss during storage and retrieval.
- Optimizing heat transfer processes.
- Considering the overall energy balance of the system.

1.1.1 Properties and selection criteria

3. Thermophysical properties and general material requirements

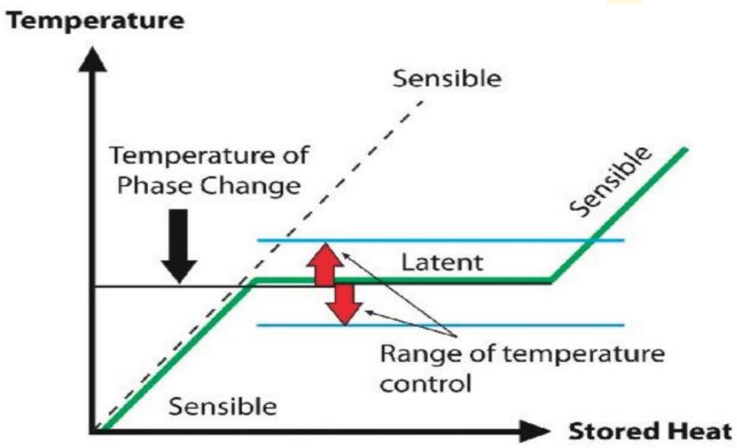
- Large gravimetric storage capacity (high heat capacity, latent heat or heat of reaction).
- Large volumetric storage capacity (high density and gravimetric values listed above).
- Long service life, nontoxic, nonflammable, no explosive phases, simple in handling.
- Non-corrosive with respect to the containment, the heat exchanger and heat transfer enhancement structures; utilization of inexpensive structural materials.
- Ability to undergo charging – discharging cycles without losses in performance and storage capacity over many cycles (high cycling and thermal stability).
- Suitable material costs, high availability.
- High thermal diffusivity and thermal effusivity values (high heat transfer rates).
- Small density change versus temperature to minimize thermo-mechanical stress.

1.1.1 Properties and selection criteria

4. Working Mechanisms of Sensible Thermal Energy Storage:

- STES systems consist of a container or reservoir to store the material, along with inlet and outlet pipes for the flow of energy.

- The working mechanism of STES primarily relies on the principles of heat transfer, where energy flows from areas of higher temperature to areas of lower temperature.



(Source: Ref. [20])

- During the charging phase, excess thermal energy is added to the storage material, increasing its temperature. This can be achieved by using renewable energy sources like solar, geothermal, or waste heat from industrial processes.

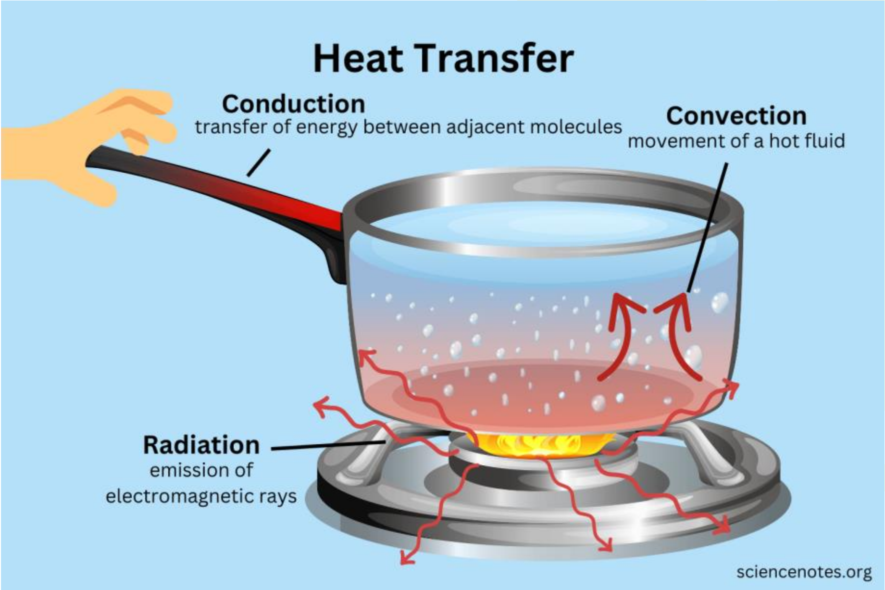
- The stored energy can then be withdrawn during the discharging phase, by extracting heat from the material for various applications such as space heating, water heating, or industrial processes.

1.1.1 Properties and selection criteria

- Conduction:
- Heat transfer occurs within the storage material through molecular or particle interaction.
- Higher temperatures at one end of the material cause increased molecular activity, leading to the propagation of heat along the material.

- Convection:
- The movement of the storage material's particles or molecules, as a result of their changing density due to the variation in temperature, transfers heat.
- Convection enhances the heat transfer rate within the material.

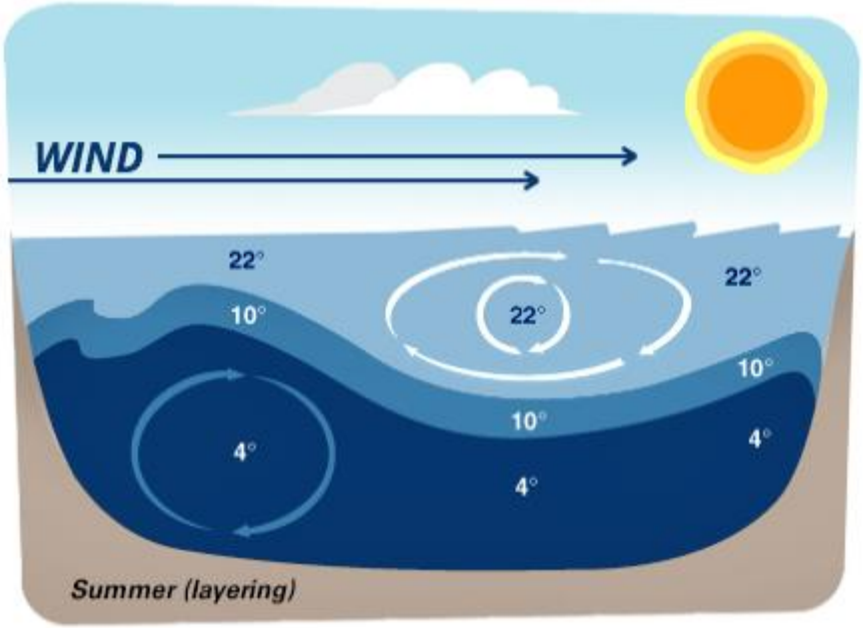
- Radiation:
- Energy transferred through electromagnetic waves from hotter regions of the storage material to cooler regions.
- This mode of heat transfer is applicable when there is a temperature difference between the storage material and its surroundings.



1.1.1 Properties and selection criteria

- Thermal stratification:

- The storage material forms layers of different temperatures due to buoyancy forces.
- This stratification can be desirable or undesirable depending on the application.
- It affects the overall performance and efficiency of the STES system.



(Source: Ref. [21])

Example: Water stratification

1.1.1 Properties and selection criteria

- Heat loss:

- Sensible thermal energy storage systems are subject to heat losses to the surroundings.
- Can reduce the overall energy storage capacity.
- Heat losses include conduction through the storage container, convection through the inlet and outlet pipes, and radiation from the outer surface of the storage unit.
- Minimizing these losses is important to maximize the efficiency of the STES system.

Chapter 1.1 Sensible Thermal Energy Storage Materials

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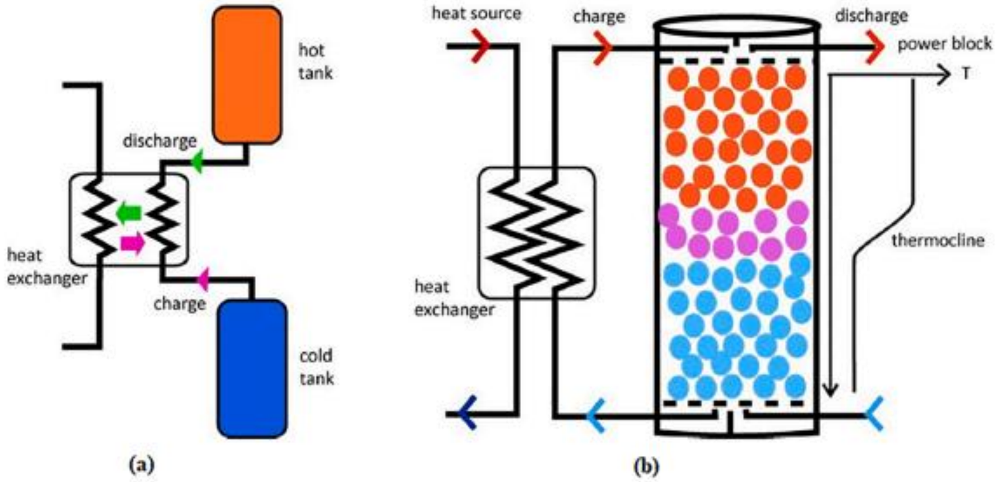
1.1.2 Common Sensible Thermal Energy Storage Materials

1. Sensible heat storage in liquids

- Advantage of a possible use as both storage medium and heat transfer fluid.
- Most widely applied media: water and thermal oil.
- Storage approach using liquids

Single Tank concept
Thermal stratification is desired.
The value of high temperature heat is maintained in one part of the vessel, while low-temperature fluid (as backflow from a heat consumer) can still be stored in another part of the vessel.

Two tank concept:
Two individual tanks at different temperature and fluid level.



(Source: Ref. [22])

Sensible heat storage systems a) Two-tank storage system b) Single-tank thermocline storage system

1.1.2 Common Sensible Thermal Energy Storage Materials

Characteristic liquids and their thermo-physical properties at atmospheric pressure

Material	T, °C	ρ, [kg/m^3]	c_p, [kJ/(kg·K)]	λ, [W/(m·K)]	$10^6 \times a$, [m^2/s]	$10^{-3} \times b$, [J/(m^{2}Ks$^{1/2}$)]
Water	20	998	4.183	0.598	0.142	1.58
Silicone oil (AK250)	25	970	1.465	0.168	0.118	0.49
Transformer oil	60	842	2.09	0.122	0.069	0.46
Molten salt (K-NaNO$_3$)	230	1950	1.57	0.50	0.16	1.24
Paraffin (liquid)	20	900	2.13	0,26	0.14	0.71
Sodium	100	927	1.385	85.84	66.85	10.50

a: Thermal diffusivity; b: Thermal effusivity; T: Temperature; ρ: Density; Cp: Specific heat capacity, λ: Thermal conductivity

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1.1.2 Common Sensible Thermal Energy Storage Materials

Low-temperature water systems (< 100 °C)

WATER

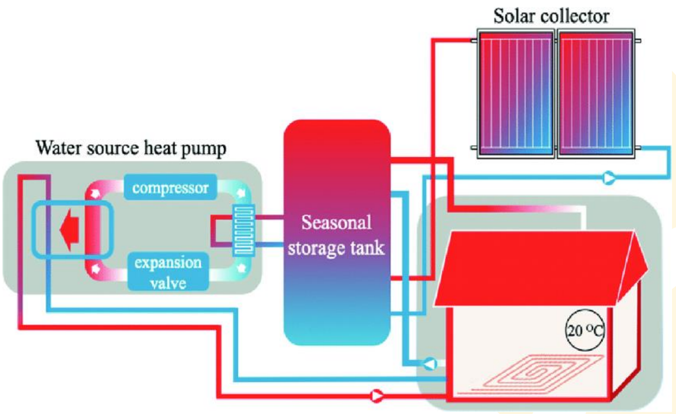
- Abundant and inexpensive.
- High thermal effusivity (b = 1.58 × 10^3 J m^{-2} K^{-1} $s^{-1/2}$).
- A relatively low thermal (temperature) diffusivity (a = 0.142 × 10^{-6} m^2/s); an advantage for thermal stratification within a hot-water storage tank.
- Easily stored in all kinds of containers.
- Highly flexible of the control of water flow systems.
- Used without heat exchangers.
- Easy to handle, nontoxic, noncombustible, experience with water is common.
- Easily mixable with additives (antifreeze, anticorrosive).

- It only provides a limited operation range between 0 ºC (freezing) and 100 ºC (boiling).
- Corrosive.
- High vapor pressures (p > 5 bar) at temperatures > 155 ºC.

1.1.2 Common Sensible Thermal Energy Storage Materials

Large stores (e.g., seasonal stores for solar energy)

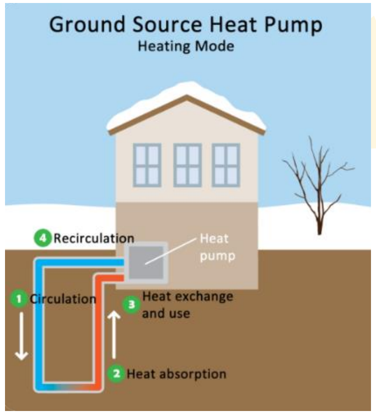
- Water is commonly used in large thermal stores as a storage medium and heat transfer fluid.
- These stores can only be turned over once or three times a year, making stored heat expensive unless the container is inexpensive.
- Steel tanks have a technical/economic boundary of 100,000 m^3, while ground containers have a capacity of 80 kWh/m^3.



(Source: Ref. [23])

Ground stores

- Store low temperature heat in soil or pebbles using a mixture of water and solid particles.
- The thermal conductivity depends on the mixture's composition.
- Heat is exchanged with the ground by tubes containing a circulating carrier fluid, typically water.

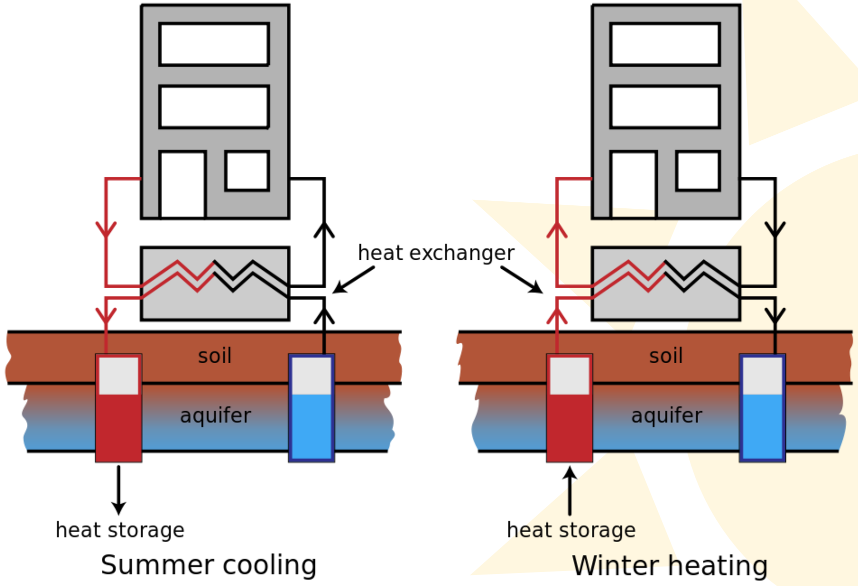


(Source: Ref. [24])

1.1.2 Common Sensible Thermal Energy Storage Materials

Aquifer stores

- Geology allows for aquifer stores
- Permeable layers of soil and impermeable material are enclosed.
- Two fountains can be drilled apart, allowing hot water to be inserted in summer and withdrawn in winter.
- Man-made aquifers are built in 10000 m^3 sizes, filled with pebbles and water, sealed with plastic sheets.



(Source: Ref. [25])

Storage volume of different storage media compared to pure water for 1 m^3 water equivalent and 60 kWh capacity at $\Delta T = 50$ K.

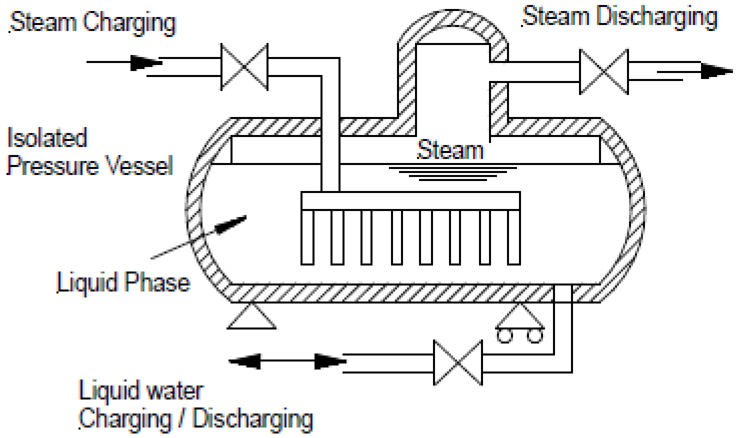
Storage media	Storage volume
Hot water storage	1 m^3
Pebble – water storage	1.3 – 2 m^3
Aquifer storage	2 – 3 m^3
Borehole storage	4 – 5 m^3

1.1.2 Common Sensible Thermal Energy Storage Materials

High-temperature water systems (> 100 °C)

Steam Accumulator

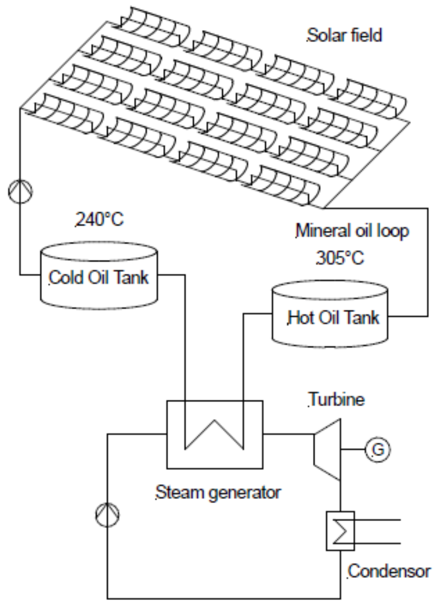
- Steam accumulator technology = the Ruths storage systems.
- Use sensible heat storage in pressurized saturated liquid water.
- Steam is produced by lowering the pressure of the saturated liquid during discharge.
- Water's dual use as storage and working medium allows for high discharge rates.
- Capacity is limited by pressure vessel volume and temperature, with pressure vessel costs dominating.
- The discharge process decreases pressure in a storage vessel, removing saturated steam, affecting storage capacity.
- The change in temperature is linked to the pressure change of saturated steam, as the water in the volume is in the saturation state.



Scheme of a steam accumulator

(Source: Ref. [26])

1.1.2 Common Sensible Thermal Energy Storage Materials



Simplified scheme of SEGS-I (California) parabolic trough plant with direct storage of heat transfer fluid.

(Source: Ref. [26])

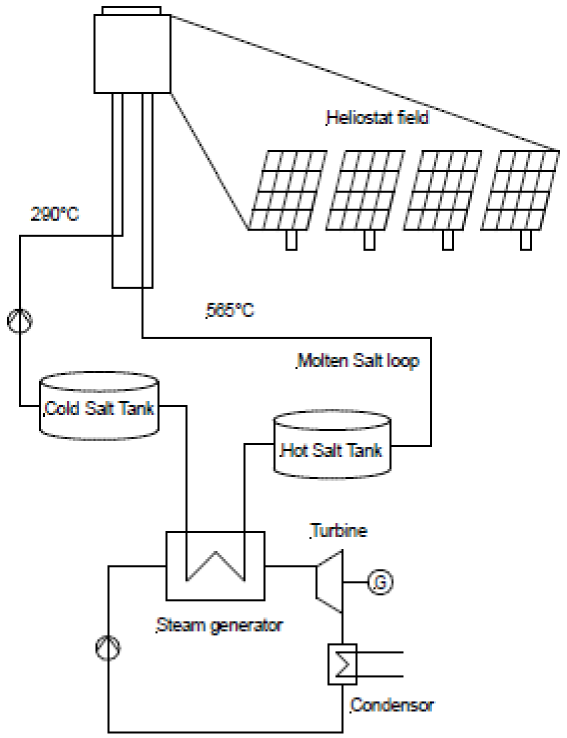
Thermal oil systems

- Oil is a common heat transfer fluid , used as a liquid storage material.
- E.g. mineral oil can be used at ambient pressures up to about 300 °C.
- Synthetic oils are thermally stable up to 400 °C, at higher temperatures they have to be pressurized = uneconomic.
- Filler material= cast iron.
- In SEGS-I about 3260 m^3 mineral oil were stored in the hot tank at a temperature of 307 °C.

(Source: Ref. [10])

1.1.2 Common Sensible Thermal Energy Storage Materials

Molten salt systems



- For T above 100°C, molten salts are attractive candidates for sensible heat storage in liquids.

Advantages:

- Low cost
- High thermal stability
- Low vapor pressure = Storage designs without pressurized vessels.
- Requires the consideration of the lower temperature limit defined by the melting temperature.

Limitation:

- Unwanted freezing during operation
- Freezing must be prevented in the piping, the heat exchanger and in the storage tanks.
- Risk of corrosion and difficult handling of hygroscopic salts.

Simplified scheme of Solar Two power plant with central receiver and direct storage of molten salt used as heat transfer fluid.

E.g. ***solar salt*** : non-eutectic salt mixture of 60 wt% sodium nitrate and 40 wt% potassium nitrate. T melting = 222°C; Thermal stability limit = 550 °C.

(Source: Ref. [26])

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1.1.2 Common Sensible Thermal Energy Storage Materials

2. Sensible heat storage in solids → Wide temperature range and heated up to very high temperature

Materials

e.g. magnesia bricks in Cowper regenerators to 1000 °C

- Chemically inert.
- Low vapor pressure.
- The containment can often be simpler compared to systems based on liquids.

❖ Storage materials can be broadly classified as :

➢ Metals.

➢ Non-metals.

(Source: Ref. [27])

1.1.2 Common Sensible Thermal Energy Storage Materials

Thermophysical properties of solids for sensible heat storage

Material	T, °C	ρ, [kg/m^3]	c_p, [kJ/(kg·K)]	λ, [W/(m·K)]	$10^6 \times a$, [m^2/s]	$10^{-3} \times b$, [J/(m^{2}Ks$^{1/2}$)]
Aluminum 99.99 %	20	2700	0.945	238.4	93.3	24.66
Copper (commercial)	20	8300	0.419	372	107	35.97
Iron	20	7850	0.465	59.3	16.3	14.7
Lead	20	11340	0.131	35.25	23.6	7.24
Brick (dry)	20	1800	0.84	0.50	0.33	0.87
Concrete (aggregates)	20	2200	0.72	1.45	0.94	1.52
Granite	20	2750	0.89	2.9	1.18	2.67
Graphite	20	2200	0.61	155	120	14.41
Limestone	20	2500	0.74	2.2	1.19	2.02
Sandstone	20	2200	0.71	1.8	1.15	1.68
Slag	20	2700	0.84	0.57	0.25	1.13
Sodium chloride	20	2165	0.86	6.5	3.5	3.5
Soil (clay)	20	1450	0.88	1.28	1.0	1.28
Soil (gravelly)	20	2040	1.84	0.59	0.16	1.49

1.1.2 Common Sensible Thermal Energy Storage Materials

Natural materials

- ✓ Form of rocks and pebbles: abundant and cheap.
- ✓ Low temperatures: Rock and soil can be used as ground storage.
- ✓ High temperatures: Thermomechanical stability important , Granite, basalt, quartzite, pebbles.

Manufactured solid materials

- ✓ Ceramics as heat storage materials.
- ✓ Low temperature range : bricks act as a buffer for the climatization of buildings.
- ✓ High temperature : refractory bricks based on oxides (silica, alumina, magnesia and iron oxide - feolite), carbonates (e.g. magnesite) and their mixtures.
- ➢ Application : Cowper regenerators, night-storage heaters and tiled stoves.

1.1.2 Common Sensible Thermal Energy Storage Materials

Graphite

Benefits

High thermal conductivity:

Excellent thermal conductivity for efficient heat transfer and storage.

Lightweight:

Lightweight material, making it easier to handle and manipulate in thermal storage systems.

Low cost:

Relatively inexpensive compared to other materials :cost-effective option for thermal storage.

High melting point:

High melting point, allowing it to withstand high temperatures without degrading or melting.

Ability to store heat for long periods:

Suitable for applications that require continuous or intermittent thermal energy supply.

(Source: Ref. [28])

1.1.2 Common Sensible Thermal Energy Storage Materials

Graphite

Limitations

1. **Chemical reactivity**: Can react with certain chemicals: limit its performance in some applications.
2. **Limited storage capacity**: Although graphite has the ability to store heat for long durations, its storage capacity may be limited compared to other materials, such as metals.
3. **Thermal expansion**: Significant thermal expansion when subjected to high temperatures, can lead to dimensional changes and potential structural damage.
4. **Susceptibility to oxidation**: Can oxidize at high temperatures, leading to degradation of the material and decreased efficiency in thermal storage systems.

1.1.2 Common Sensible Thermal Energy Storage Materials

Metals

E.g. **Aluminum and copper** : used in electronics as a heat sink and for thermal management.
Cast iron : used for high-temperature storage together with oil as heat carrier.

1. **High thermal conductivity:** Many metals, such as copper and aluminum, have excellent thermal conductivity, ensuring efficient heat transfer and storage.
2. **High storage capacity:** higher heat storage capacity compared to graphite, allowing them to store larger amounts of thermal energy.
3. **Durability and strength**: Strong and durable materials, capable of withstanding mechanical stresses and high-temperature environments.
4. **Versatility and availability**: Widely available and have a wide range of applications, allowing for greater versatility in thermal storage systems.

1.1.2 Common Sensible Thermal Energy Storage Materials

- **High costs:** Copper, Titanium, Nickel, Silver, Aluminum:
- **Weight:** Metals are heavier compared to graphite, making them more challenging to handle and manipulate in thermal storage systems.
- **Corrosion and oxidation:** Certain metals can corrode or oxidize when exposed to specific chemicals or environmental conditions, limiting their performance and lifespan.
- **Thermal cycling limitations**: Repeated heating and cooling cycles can cause some metals to experience fatigue or degradation, reducing their long-term performance in thermal storage applications

1.1.2 Common Sensible Thermal Energy Storage Materials

Composite material

made up of a mixture of cement, water, and aggregates such as sand and gravel.

High thermal mass

- Ability to absorb and store heat energy.
- Absorb heat during wcarm periods and release it slowly during cool periods,

High specific heat capacity

- Ranges from 0.70 to 1.25 kJ/kg°C.

Good conductor of heat

- Heat energy to flow easily within its structure.
- Ranges from 0.8 to 1.5 W/m°C

Conclusions – Sensible thermal storage materials

- There is an urgent need to switch from fossil fuel-based energy systems to renewables in industry. Solar energy is the most abundant and promising renewable source, but it is still not widely used in industrial applications.
- STESMs such as rock, sand, or soil are well-known and abundant natural materials used for medium–high-temperature ranges.
- The need for thousands of tonnes of STESMs in industrial applications may not be a sustainable solution due to the extensive depletion of natural sources.
- Waste-based materials such as STESMs are promising for high-temperature TES applications up to 1000 °C. Such STESMs increase the sustainability of solar heat applications in the industry by decreasing greenhouse gas and embodied emissions and reducing costs. They have good thermal properties with high thermal stability, heat capacity and thermal conductivity.

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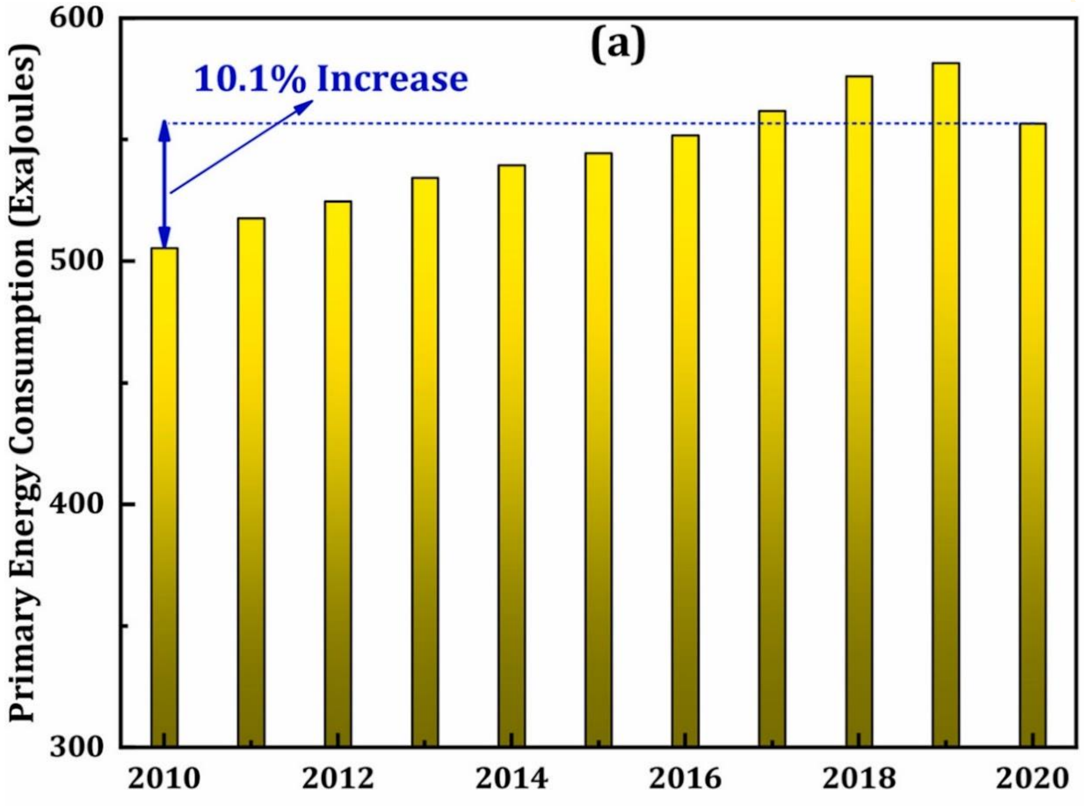
Chapter 1.2 Latent Heat Storage Materials

Contents

1.2.1 Principles of Latent Heat Storage

- World primary energy consumption (EC) has increased by 10.1% from 2010 to 2020 .
- Energy consumption in 2019 compared to 2010: growth of 15%.
- The reason for the decrease: the Covid-19 virus.

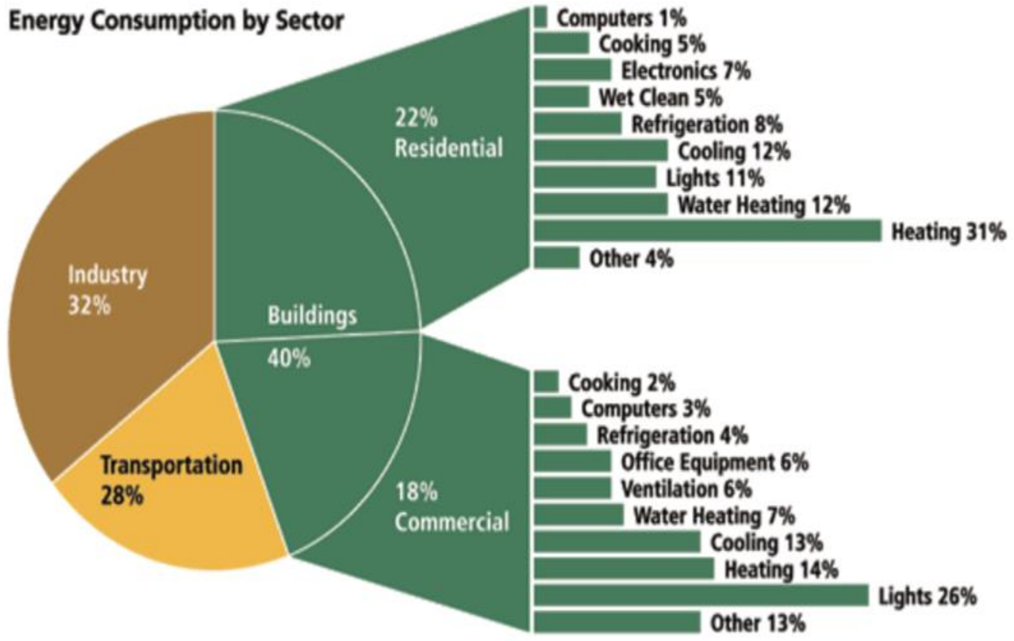
➢ This disease reduced energy consumption worldwide by 4.28% (from 581.51 to 556.63 ExaJoules).



World primary energy consumption:
Source: Statistical Review of World Energy, 2021

1.2.1 Principles of Latent Heat Storage

- Building operations contribute to 30% of global greenhouse gas emissions and 40% of primary energy consumption.
- This sector is expected to grow due to economic growth.
- In the US, building operations account for 40% of total US primary energy consumption, with commercial and residential buildings accounting for 46% and 54% respectively.
- Reducing energy consumption for heating and cooling would significantly improve building energy efficiency.
- **California and the European Union** have set goals to reduce energy consumption in the building sector, with California aiming for zero net energy by 2020 and commercial buildings by 2030.



(Source: Ref. [11])

1.2.1 Principles of Latent Heat Storage

❖ Lot of energy is utilized in HVAC systems and many efforts were conducted to improve it:

- Using heat pumps
- Passive housing block
- Renewable energy
- Hybrid ventilation
- Natural
- Active
- Energy storage
- Phase change material PCM

HVAC = Heating, ventilation, and air conditioning

1.2.1 Principles of Latent Heat Storage

- **Latent heat-** Energy released or absorbed by a body during a constant temperature process (During phase transition of a material).

- Latent heat storage relies on phase changes of medium for instance from Solid to Liquid (one phase to another), that use latent heat to store energy.

- Materials used for Latent Heat Storage are : **Phase Change Materials**

1.2.1 Principles of Latent Heat Storage

Sensible heat

- When an object is heated, its temperature rises.
- The increase in heat is called sensible heat.

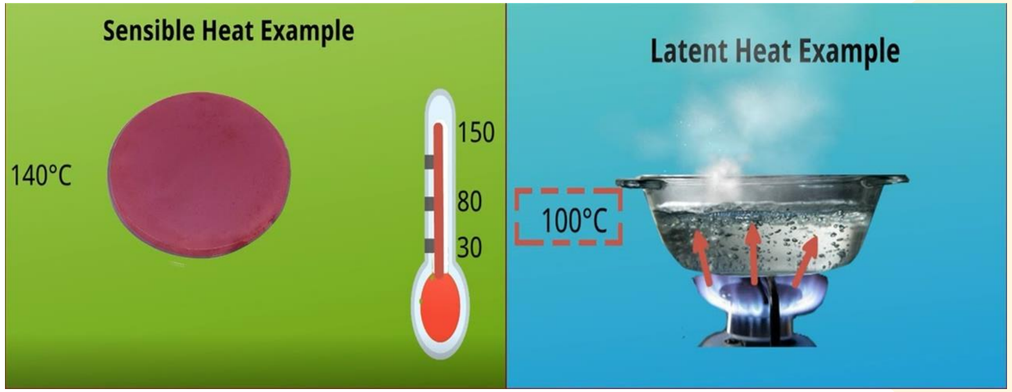
Similarly, when heat is removed from an object and its temperature falls, the heat removed is also called sensible heat.

- **The heat that causes a change in temperature in an object or substance is called sensible heat.**

1.2.1 Principles of Latent Heat Storage

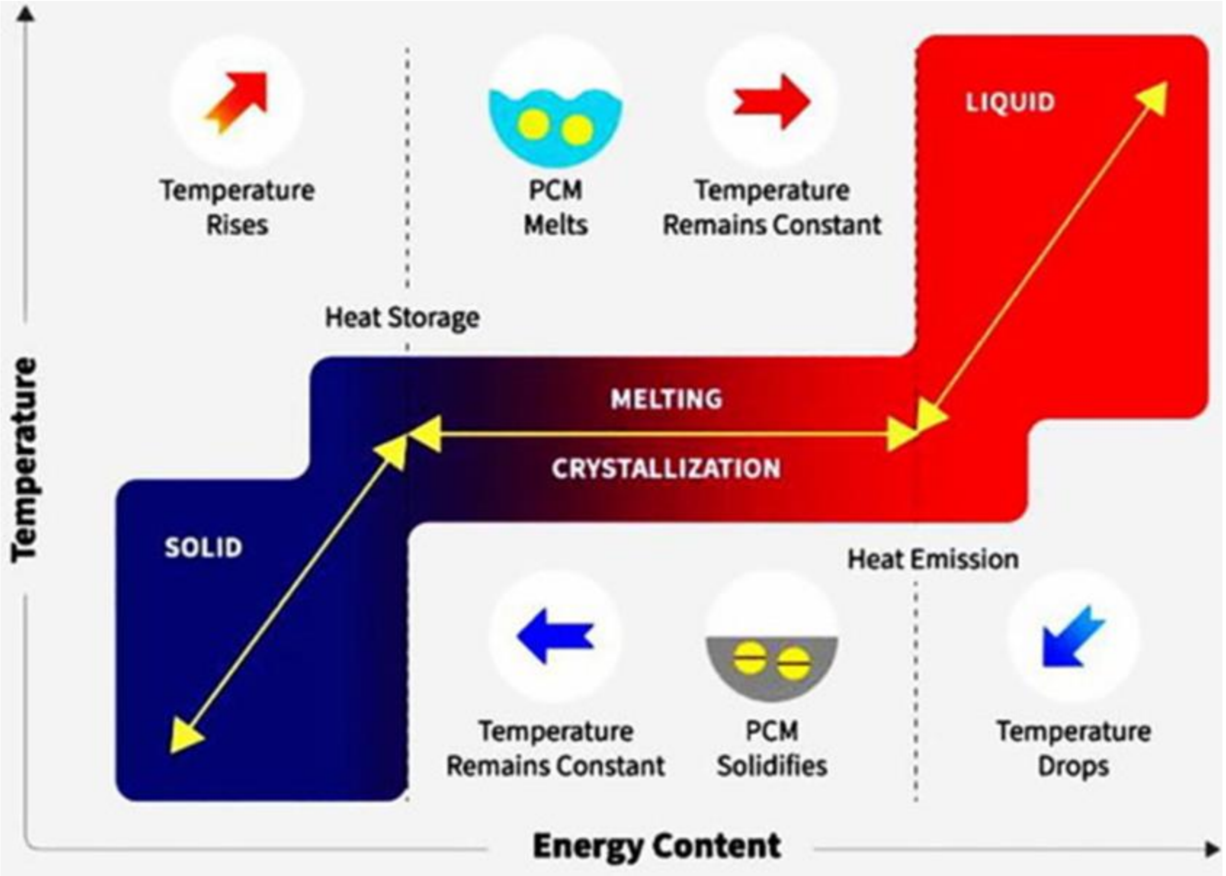
Latent heat

- All pure substances in nature are able to change their states. Solids can become liquid (ice to water) and liquids can become gases (water to vapor) but changes such these require the addition or removal of heat.
- The heat that causes a change in state is called latent heat.
- Latent heat, however, does not affect the temperature of a substance-for example water remains at 100ºC while boiling. The heat added to keep the water boiling is latent heat.
- The heat that causes a change in state with no change in temperature is called latent heat.



1.2.1 Principles of Latent Heat Storage

LATENT HEAT



(Source: Ref. [12])

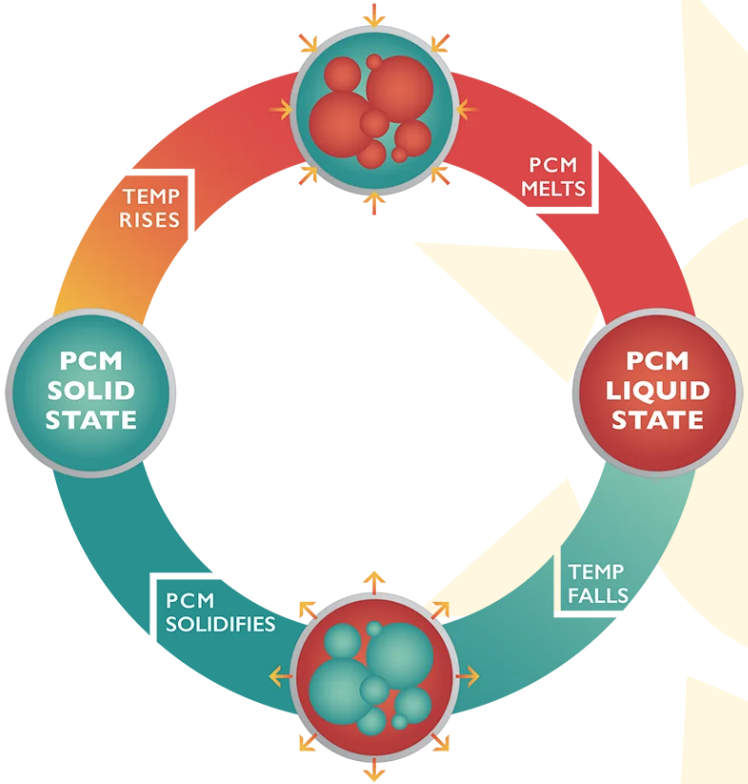
The role:

- Provides a practical and efficient means of storing and releasing energy.
- Refers to the storage and release of thermal energy through the phase change of a material, such as the transition from solid to liquid or liquid to gas.

1.2.1 Principles of Latent Heat Storage

PHASE CHANGE MATERIALS

- Phase change materials (PCM) are substances that can store and release large amounts of thermal energy during phase transitions.
- They undergo a change in their physical state (solid to liquid or liquid to gas) at a specific temperature called the melting or boiling point, respectively.
- They use chemical bond to store and release the heat.
- When the PCM absorbs heat, it undergoes a phase transition and the temperature remains constant until all the material has changed phase.



(Source: Ref. [13])

1.2.1 Principles of Latent Heat Storage
Phase change materials

Specific PCM requirements are the following:

- A suitable phase change temperature
- A large phase-change enthalpy
- A suitable thermal stability with a low vapor pressure at the maximum operation temperature
- A small volume change during the melting process
- Little or no sub-cooling during freezing, little or no supersaturation during melting, neither segregation (e.g., like Glauber's salt)
- A high heat capacity, if sensible heat is additionally utilized

1.2.1 Principles of Latent Heat Storage
Phase change materials

Benefits

High energy storage capacity

Store and release large amounts of heat energy during phase transitions, offering higher storage capacity than sensible heat storage materials.

Constant temperature during phase change

Maintain a nearly constant temperature during the phase transition process, which allows for controlled and stable heat release.

Compact and lightweight : Store a significant amount of energy in a small volume, making them suitable for applications with limited space or weight constraints.

Long-term stability: Undergo numerous heating and cooling cycles without a significant decrease in their thermal properties, ensuring long-term stability and durability.

Energy efficiency.: Reduces the need for large heating or cooling systems, as they can absorb or release heat during off-peak hours when energy costs are lower, leading to energy savings and improved efficiency.

Environmental friendliness: Non-toxic, non-flammable, and environmentally safe, reducing potential health and environmental risks.

1.2.1 Principles of Latent Heat Storage
Phase change materials

Limitations

Limited operating temperature range: Effective only within a certain temperature range. Outside this range, the PCM may not function effectively.

Low thermal conductivity: Lower thermal conductivity compared to traditional heat storage materials like water or concrete= slower heat transfer rates, requiring larger surface areas or longer time periods for effective heat exchange.

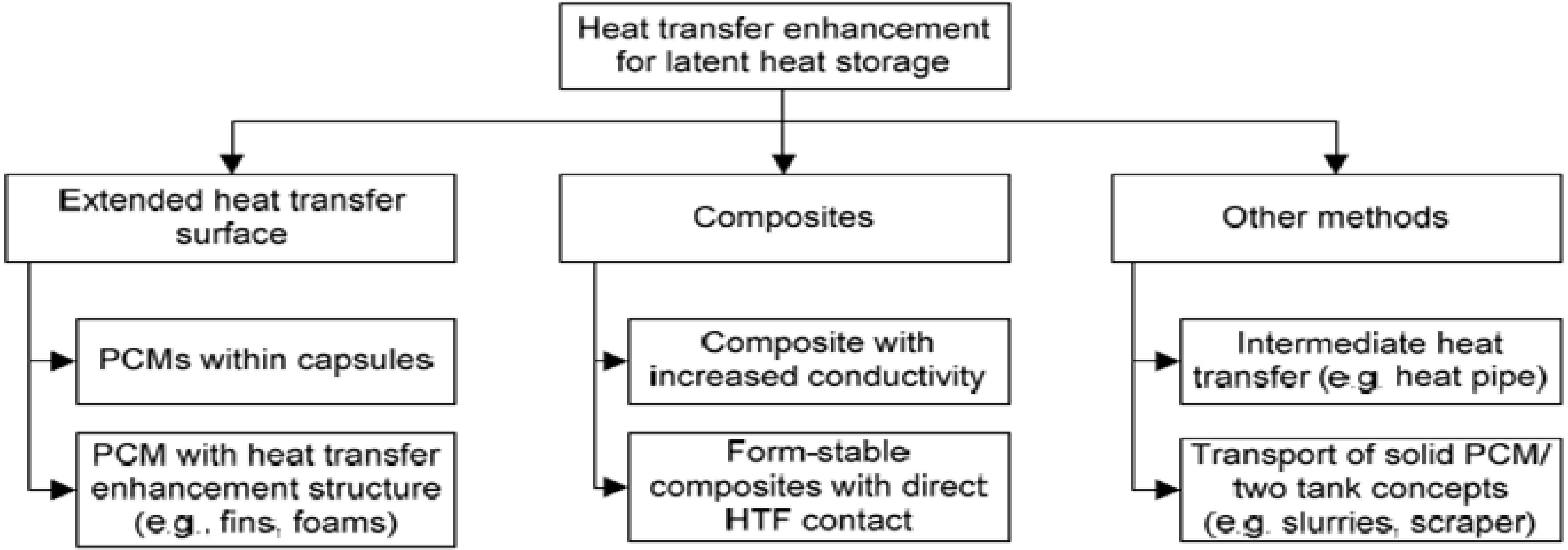
Supercooling and subcooling: Phase transition occurs at a temperature higher or lower than the specified transition temperature. This can impact the accuracy and reliability of the system.

Cost: Some PCMs can be relatively expensive compared to conventional heat storage materials, which can affect the initial investment cost of systems utilizing PCM for latent heat storage.

Volume expansion: Undergo a slight expansion during phase transition, which can pose challenges in design and structural integrity when used in confined spaces or tightly sealed systems.

1.2.1 Principles of Latent Heat Storage
Heat transfer concepts

Heat transfer enhancement concepts for latent heat storage systems



Overview of PCM storage concepts with enhanced heat transfer between the storage material and heat transfer fluid.

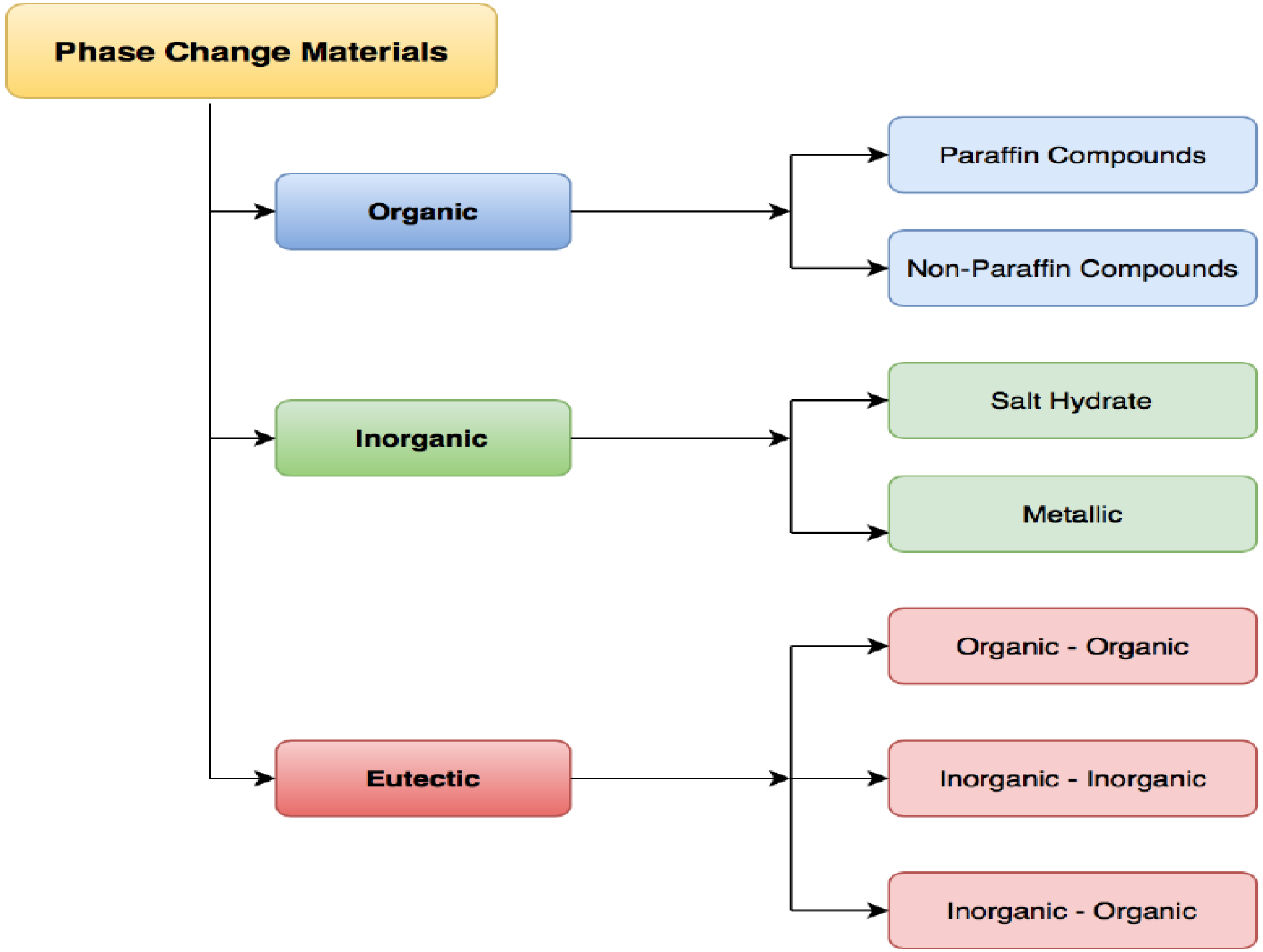
Chapter 1.2 Latent Heat Storage Materials

Contents

1.2.2 Latent Heat Storage Materials Classification

- Organic PCMs
- Inorganic PCMs
- Composite PCMs

1.2.2 Latent Heat Storage Materials Classification



(Source: Ref. [14])

1.2.2 Latent heat storage materials
Organic PCMs

1. Organic PCMs

- Generally categorized into paraffins and non–paraffins.
- This type of material melts and solidifies congruently, i.e. under repeated melting or solidification cycles, there is no phase segregation.
- Organic PCMs present self-nucleation, which is the property of crystallizing with little or no supercooling.
- Not corrosive in nature. Paraffin is further distinguished into paraffin hydrocarbons and paraffin waxes.

1.2.2 Latent heat storage materials
Organic PCMs

Paraffin Hydrocarbons

- Consist of straight chains of n-alkanes $CH_3 - (CH_2) - CH_3$.
- Crystallization of this CH_3 chain releases a large amount of latent heat.
- Melting temperatures of paraffin usually range from **35 to 40** ºC.
- Most widely used for thermal management of electronic devices.
- Melting point of these alkanes increases with increase in carbon atoms.

Common paraffin along with their melting point and heat of fusion

n-alkanes at $20°C$	Melting Point $(°C)$	Heat of fusion $(kJ.kg^{-1})$
Hexadecane	18.1	236
Heptadecane	21.9	214
Octadecane	28.1	244
Nonadecane	32.0	222
Eicosane	36.6	248
Heneicosane	40.2	213
Docosane	44.0	252
Tricosane	47.5	234
Tetracosane	50.6	255
Pentacosane	53.5	238
Hexacosane	56.3	250
Octacosane	61.2	254
Triacontane	65.4	252

Thermal properties of alkanes

1.2.2 Latent heat storage materials
Organic PCMs

Paraffin wax

- Generally a **mixture** of alkanes.
- It is **easie**r to use paraffin waxes also known as *grade paraffin* (the paraffin hydrocarbons are expensive).
- Possess the **same properties** as pure alkanes, but their melting point is an **average** of all the alkanes present in it.
- Able to sustain **over 1500 cycles** while maintaining their properties unchanged.
- Optimal **cost-effective** substitutes.

(Source: Ref. [15])

1.2.2 Latent heat storage materials
Organic PCMs

Non-paraffin compounds

- Flammable in nature.
- Not applicable for high-temperature storage.
- Non-paraffin compounds are further distinguished as **Fatty acids**, **Glycols**, and **Polyalcohols**.

❖ Fatty acids

- ➢ Obtained from animal fats and vegetable oil.
- ➢ Have similar properties to that of paraffin waxes but melt slower.
- ➢ Characterized by the general formula $CH_3(CH_2)2nCOOH$.
- ➢ Have congruent melting, good stability, biodegradability, and non-toxicity.
- ➢ Mildly corrosive and have high sublimation rate, along with a bad odor.

Common name at $20°C$	Melting point ($°C$)	Heat of fusion ($kJ.kg^{-1}$)
Caprylic acid	16.1	144.2
Capric acid	31.5	155.5
Lauric acid	43.6	184.4
Myristic acid	57.7	189.7
Palmitic acid	61.3	197.9
Stearicacid	66.8	259.0

Thermal properties of some fatty acids

1.2.2 Latent heat storage materials
Organic PCMs

❖ **Polyalcohols**

- Characterized by a relatively low enthalpy of fusion.
- Capable of releasing and absorbing a large amount of heat during a solid-solid transition.
- Almost null volume change.
- Long lifespan.
- No segregation

Common name at 20°C	Melting point (°C)	Heat of fusion ($kJ.kg^{-1}$)
Pentaerythritol (PE)	187-188	269-289
Pentaglycerine (PG)	81-89	193-269
Neopentylglycol (NPG)	40–48	110–131
Aminoglycol (AMPL)	78	233.6
Tris-amino$CH_4(TAM)$	134.5	285

Thermal properties of solid-solid phase transition for polyalcohols and amine derivatives

1.2.2 Latent heat storage materials
Organic PCMs

Advantages	Disadvantages
No supercooling while undergoing phase change	Poor thermal conductivity (1-tetradecanol: only 0.32 W/mK for example)
Homogeneous and continuous phase change meaning no phase segregation	High cost
High compatibility with encapsulation materials	High flammability especially for non-paraffin PCMs
Congruent melting	High volatility
Corrosion resistance	Low phase change enthalpy (most below 400 J/g)
Most have no toxicity	Paraffins are less compatible with plastic containers
Low vapour pressure while undergoing phase change	Should not be exposed to oxidizing agents (especially for non-paraffin PCMs)
Adjustable and gradually increasing melting point	Not eco-friendly
Small volume change	
Good reliability after thermal cycling	
Excellent freezing and melting behavior	

1.2.2 Latent heat storage materials

2. Inorganic PCM

- Generally salt hydrates, metallic salts
- Typically, an alloy of inorganic salts and water.
- Forming a crystalline solid of general formula $A.B.nH_2O$.
- Have a longer lifespan compared to some organic PCMs.
- Less prone to degradation over time.
- Can withstand harsh environmental conditions.

1.2.2 Latent heat storage materials
Inorganic PCMs

Salt hydrates

- Their melting temperature ranges from 10 to 900 ºC.
- High latent heat of fusion per unit volume.
- Relatively high thermal conductivity.
- Small volume change on melting and higher density.
- The most representative salt hydrates: sodium sulfate decahydrate, calcium chloride hexahydrate, sodium phosphate, dodecahydrate and magnesium chloride hexahydrate.

The most widely studied PCMs for the latent heat thermal energy storage system.

Material at 20 °C	Melting point (°C)	Heat of fusion ($kJ.g^{-1}$)
$CaCl_2$. $12H_20$	29.8	174
$LiNO_3$ $2H_2O$	30.0	296
$LiNO_3$ $3H_2O$	30.0	189
$KFe(SO_4)_2$ $12H_2O$	33.0	173
$LiBr_2$ $2H_2O$	34.0	124
$FeCl_3$ H_2O	37	223
$CoSO_4$ $7H_2O$	40.7	170
$Ca(NO_3)$ $4H_2O$	47.0	153
$Fe(NO_3)_3$ $9H_2O$	47.0	155
$Ca(NO_3)_2$ $3H_2O$	51.0	104
$FeCl_3$ $2H_2O$	56.0	90
CH_3COONa $3H_2O$	58.0	265
$MgCl_2$ $4H_2O$	58.0	178
$NaAl(SO_4)_2$ $10H_2O$	61.0	181
NaOH H_2O	64.3	273
$Al(NO_3)_2$ $9H_2O$	72	155
$MgCl_2$ $6H_2O$	117.0	167

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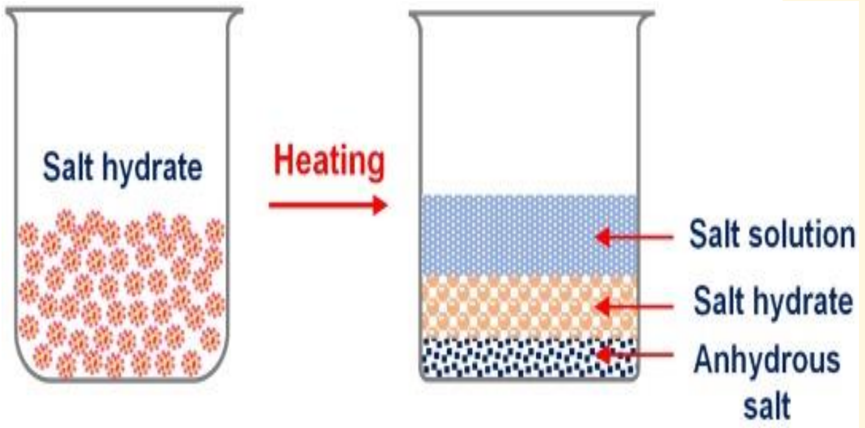
1.2.2 Latent heat storage materials
Inorganic PCMs

Salt hydrates

- **The major issue:**
- They melt incongruently (melting occurs when salt is not entirely soluble in its water), hence the solution is supersaturated at its melting temperature.
- Have a tendency for supercooling, which in turn discharges the energy at much lower temperature instead of discharging at fusion temperature.
- This issue is generally tackled by adding chemicals and stimulating the nucleation to happen



(Source: Ref. [16])

1.2.2 Latent heat storage materials
Inorganic PCMs

Metals

- Basically a combination of low melting point metals and metal eutectics.

- High heat of fusion per unit volume.
- High thermal conductivity.
- Low specific heat.
- Low vapor pressure.

- Have been little studied because of their **very high density.**

Material at 20°C	Melting Point (°C)	Heat of fusion ($kJ.kg^{-1}$)
Gallium	30.0	80.3
Cerrolow eutectic	58.0	90.9
Bi–Cd–In eutectic	61.0	25.0
Cerrobend eutectic	70.0	32.6
Bi–Pb–In eutectic	70.0	29.0
Bi–In eutectic	72	25.0

Thermal properties of metallic compounds

1.2.2 Latent heat storage materials
Inorganic PCMs

Advantages	**Disadvantages**
Large phase change enthalpy	Problematic supercooling
Superior thermal conductivity (usually more than 1 W/mK, up to 180 for Cu)	Less compatible with encapsulation materials compared with organic PCMs
Cheap (metallic excluded)	Phase segregation
Sharp phase change	Low thermal stability
Low flammability	Low reliability, dehydration, after thermal cycling
Compatible with plastic	Corrosion
Recyclable	Incongruent melting
Small volume changes on melting	Poor nucleating behaviour
Small volume changes on melting	Too heavy for metallic PCMs
High latent heat of fusion per unit volume	Decomposition
	Slight toxicity

1.2.2 Latent heat storage materials Eutectic PCM

3. Eutectics

- Eutectic is a material composed of two or more components.
- Solidify congruently and without segregation at a temperature that is normally lower than the one at which single components solidifies, called "**eutectic temperature**".
- Have sharp melting points comparable to pure substances and a higher volumetric storage density than organic compounds

Material at (20°C)	Meting point (°C)	Heat of fusion ($kJ.kg^{-1}$)
Triethylolethane + Water +Urea	13.4	160
$CaCl_2^+ MgCl_2 \ . \ 6H_2O$	25	95
$CH_3CONHH_2^+NH_2CONH_2$	27	163
Triethylolethane^+urea	29.8	218
$CH_3COONa \ \ 3H_2O + NH_2CONH_2$	30	200.5
$NH_2CONH_2^+NH_2NO_3$	46	95
$Mg(NO_3)_3 \ \ 6H_2O + NH_4O_3$	52	125.5
$Mg(NO_3)_3 \ \ 6H_2O + MgCl_2 \ \ 6H_2O$	59	132.2
$Mg(NO_3)_3 \ \ 6H_2O + MgBr_2 \ \ 6H_2O$	66	168
$NH_2CONH_2 + NH_4Br$	76	151

Thermal properties of Eutectics materials.

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1.2.2 Latent heat storage materials
Eutectic PCM

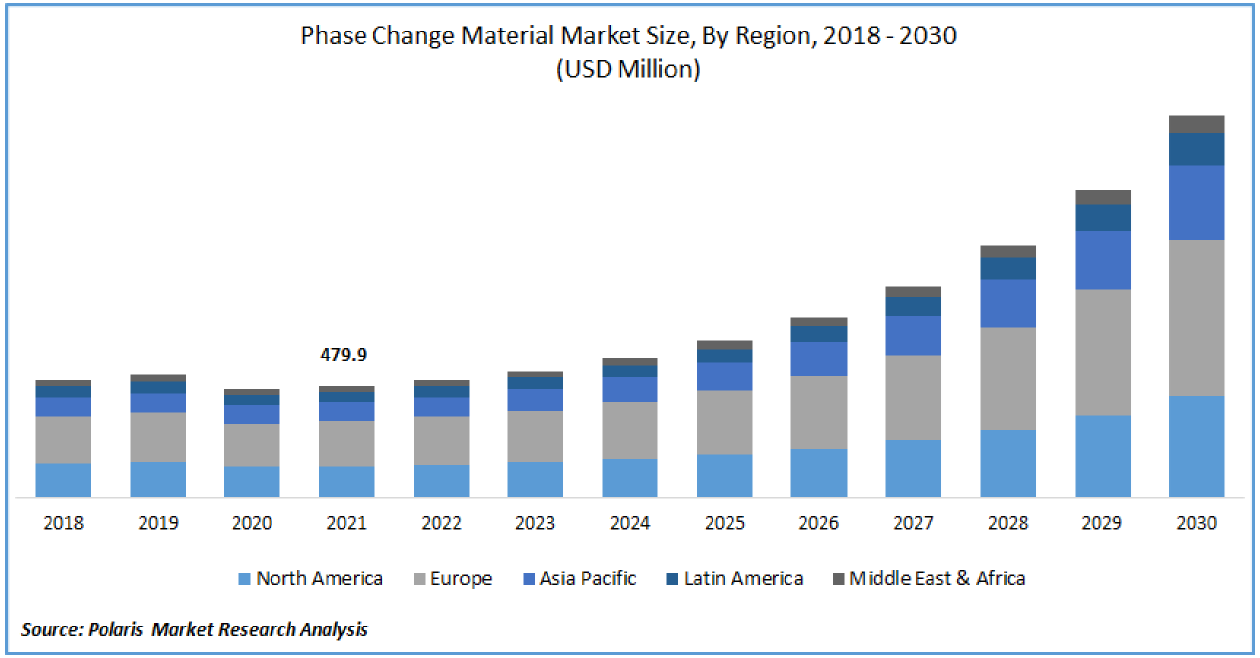
Advantages	Disadvantages
Sharp melting temperature	Supercooling exists
No phase segregation	Unpleasant and strong odors
High volumetric thermal storage density	High cost
Adjustable melting point and latent heat due to different kinds and dosage combination	Insufficient combinations have been studied

1.2.2 Latent heat storage materials Selection criteria

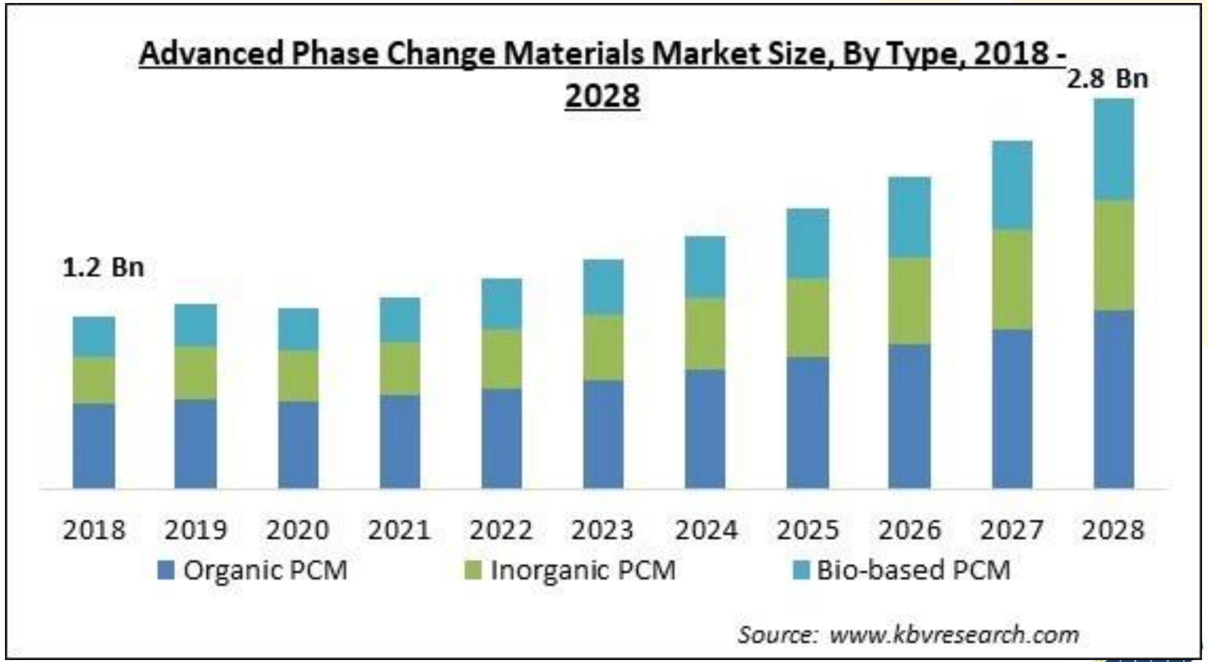
SELECTION CRITERIA FOR PCMs

- Melting temperature
- Latent and sensible heat capacities
- Thermal stability, mechanical stability
- Cyclic property degradation
- Heat transfer characteristics
- Cost
- Corrosiveness
- Ozone depleting potential
- Fire hazard
- Ease of encapsulation

1.2.2 Latent heat storage materials
PCM market size



By Region

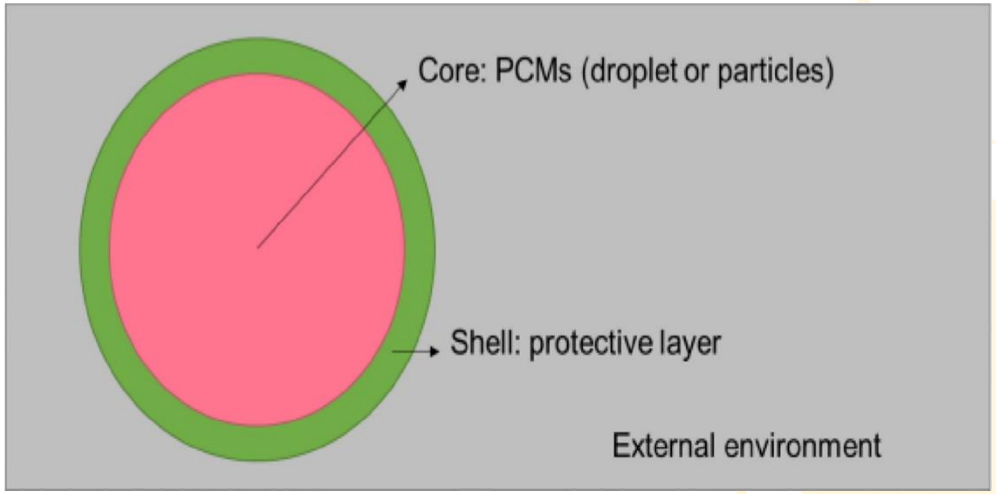


By Type

1.2.2 Latent heat storage materials
PCM encapsulation

PCM ENCAPSULATION

- Encapsulated PCM involves incorporating phase change materials into a protective structure or container
- The shapes formed for encapsulations are usually spherical (irregular shapes are also possible) due to surface tension, and the size varies from nanometer to millimeter.
- The key factors that determine a successful encapsulation are a **completed shell formation**, **no leakage**, and **no incorporation of impurities** that have negative effects on PCMs properties.
- Encapsulation **helps control and enhance** the utilization of PCM in various applications.



(Source: Ref. [17])

The schematic of the structure of a PCM capsule

❖ Commonly used materials:

1. **Core Material** = **Paraffin Wax**: a well-defined melting point and high latent heat storage capacity.
2. **Shell Material**: **Polymer-based Materials**: Polymers, such as polyethylene, polypropylene, or polyurethane. These materials offer good mechanical strength, flexibility, and durability.

Conclusions – Latent thermal storage materials

- It's important to note that ongoing research and development in the field of PCM encapsulation may lead to the exploration of new materials and combinations to optimize performance for specific applications
- The choice of materials may vary based on factors such as the required temperature range, thermal conductivity, and the intended use of the encapsulated PCM.
- The field of latent heat storage materials is dynamic and evolving, with ongoing research focused on enhancing the performance and applicability of Phase Change Materials.

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