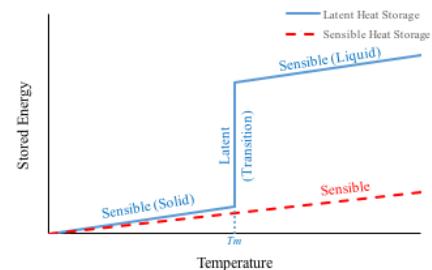


Phase Change Materials

The report provides a review of Phase Change Materials (PCMs) for Thermal Energy Storage applications. Thermal Energy Storage (TES) provides an elegant and realistic solution for more efficient energy use in many areas where there is a mismatch between the energy supply and demand. There are three common ways to store thermal energy: sensible heat, latent heat and thermo-chemical energy. Regardless of the method used to store thermal energy, materials are always the key issue.

In sensible heat storage, thermal energy is stored or released by charging or discharging the material over a range of temperature without changing the phase during this process. Charging occurs by raising the temperature of a solid or liquid, while heat is released when temperature decreases. The amount of stored energy depends on the amount of storage material, the specific heat capacity, and the temperature change.

Unlike sensible heat storage, energy storage by latent heat is very attractive due to its high storage density at constant temperature corresponding to the phase transition temperature. Moreover, latent heat storage offers a higher storage capacity and can absorb and release heat at a constant temperature while it undergoes a phase change. This is illustrated in Figure 1. When heat is applied, the material stores heat as latent heat of fusion and its phase changes from solid to liquid. When the temperature drops, the heat is released and the material changes its phase from liquid to solid.



For energy management and thermal energy storage in buildings room temperature PCMs are ideal candidates; they are solid at room temperature, as the temperature becomes warmer they liquefy or become a gel, absorb and store heat and when the temperature drops they solidify and give off heat. *Simply, PCMs operate like a thermal sponge to help maintain Temperature at the designed set point (i.e. 70 or 73 or 77°F or any desired temperature).*

PCMs have a higher heat storage capacity than conventional thermal mass, and provides excellent heat transfer. It demands no extra structural support and any added installation cost is minimal. Because the exposed surface in building products is so large and the PCMs absorb heat over a narrow temperature range, the building products need not receive direct sunlight.

Classification of Phase Change Materials:

Phase change materials in general are the most efficient method for latent heat thermal energy storage (TES). Energy per unit mass is stored during melting, and released during freezing at constant or narrow temperature range. PCMs have proven ability to improve the performance and reliability of thermal energy storage applications. Recently PCMs have received great interest because of their high energy storage density

and their ability to maintain a constant temperature while absorbing heat during melting and releasing heat when solidifying.

Any PCM that is used in a thermal energy storage system should meet several criteria related to their thermal, physical, kinetic, and chemical properties:

1. Have a melting point which matches the application,
2. Have a high value of heat of fusion and specific heat per unit volume and weight,
3. Have a low vapor pressure at the operational temperature,
4. Have a chemical stability and non-corrosiveness,
5. Not be hazardous, highly inflammable or poisonous,
6. Have a reproducible crystallization without degradation,
7. Have a small super-cooling degree and high rate of crystal growth,
8. Have a small volume variation during solidification,
9. Have a tunable thermal conductivity,
10. Be of abundant supply and at a low cost.

Many PCMs do not fully meet all of these requirements for an ideal TES system. However, a wide range of technical and novel solutions have been developed. For instance, nucleating agents can help suppressing the supercooling effect, fire retardants can help reduce or eliminate flammability concerns and nanomaterial additives can be used to modulate or tune thermal conductivity and specific heat of PCMs. A wide range of PCMs are currently available with varying or tunable thermal properties and wide range of working temperatures.

PCMs can be classified as Organic, Inorganic, and Eutectic. Organic and inorganic PCMs are the main groups of PCMs. Organic materials can be further classified into paraffins, glycols, sugar alcohols and fatty acids and their derivatives. Inorganic materials are subdivided into salt hydrates and metallic. This report will discuss PCMs that are classified as paraffins, plant or bio-based and Salt Hydrates.

Paraffins:

Paraffins consist of saturated hydrocarbon chains of C_nH_{2n+2} . The length of the chain is directly proportional to the latent heat of fusion. Paraffins are known to be non-corrosive, non-toxic, have good stability upon cycling, and able to crystallize with little or no subcooling. However, they also have low thermal conductivity, and high volume change for phase transition, flammable, and are non-compatible with plastic containers due to the chemical similarity which can lead to softening of some polymers.

Plant and Bio-Based PCMS (BioPCMs):

BioPCMs derived from fatty acids and their derivatives (alcohols, amines and esters) have received gained huge interest in thermal energy storage and energy management applications because of their desirable thermal, physical and kinetic properties. Fatty acids consist of hydrocarbon chains of $CH_3(CH_2)_{2n}COOH$. BioPCMs have high latent heat, small volume change for phase transition, sharp well-defined

melting temperature, and reproducible behavior for melting and freezing, which helps to attain an ideal stability upon cycling.

BioPCMs are usually non-toxic, exhibit little or no supercooling and are available in large quantities for many commercial applications such as food, cosmetics, detergents, pharmaceuticals, thermal energy storage among many others. Plant or bio-based PCMs in general have low thermal conductivity and some formulations have some flammability issues at very high temperatures. However, gelled BioPCMs because of the nonflammable natural ingredients used in its formulations, the gelling technology and the environmentally friendly food grade minerals that are used for fire and smoke redundancy are not flammable and they meet the ASTM-E84 plenum, class A and class C fire ratings.

BioPCMs transition from solid to solid or solid to gel eliminating leakage issues. The combination of the gelling technology, the mineral additives for fire redundancy and additives of smart materials allow for tunable thermal properties. Here is a summary of BioPCMs properties:

1. Solid to Gel or Solid to Solid transitions
2. Tunable thermal Conductivity from 0.1-2 W/m.K
3. Melting temperature varies from -50 to 150°C
4. Latent heat of fusion varies from 150-275kJ/kg
5. Long term Stability \rightarrow 85 years of thermal cycling with no thermal degradation, the same transition temperature and the same heat storage capacity.
6. Non-Toxic and Readily Biodegradable
7. Readily available and cost effective.
8. Renewable: they come from vegetable oils and their by-products.
9. Widely used in food, medicine, cosmetics, shipping and others.

Salt Hydrates

Salt hydrates are inorganic PCMs that consist of salt and water in a crystal matrix when they solidify. The material comprises $M \cdot (\text{H}_2\text{O})_x$, where M is an inorganic compound. Depending on the mixture they can have wide range of latent heat and phase change temperatures. Molten salts have a melting temperature range from 250 to 1680°C . There are few salts that melt between 1 and 150°C . Many of the analytical salt hydrates fit in the temperature above 25°C , however from 0°C to 25°C , promising materials are limited. Limited temperature ranges available to salts in meeting specific temperature needs at the desired temperature.

Another common problem for salt hydrates their rate of nucleation is generally very low because of their poor nucleating properties resulting into supercooling of the liquid salt hydrate prior to freezing. To achieve a reasonable rate of nucleation, the solution has to be supercooled and hence energy instead of being discharged at fusion temperature is discharged at much lower temperature. This must be overcome by the

addition of a suitable nucleating agents that has a crystal structure similar to that of the parent substance. These techniques minimize the problem but don't eliminate them.

Compared to other PCMs, they are characterized by a high thermal conductivity in the range of 0.4 to 1 W/m.K but they have major drawbacks of instability upon cycling due the separation of water and salt. The incongruent melting, or phase separation to a saturated aqueous phase and a solid phase different hydrates of the same salt can occur. Due to density differences, the salt phase settles out and collects at the bottom of the container, a phenomenon called decomposition which can cause a loss in enthalpy of solidification as reported by Cantor [S. Cantor. *DSC study of melting and solidification of salt hydrates. Thermochimica Acta, Vol. 26, 1978, pp. 39-47*]. Although thickening agents have been added to prevent phase separation, thermal cycling may still lead to storage capacity drop. As explanation, it has been found that the cause of capacity drop is due to PCM crystal boundary behavior, which leads to parting of thickeners and nucleating agents upon solidification. For example, a 48% drop in stored capacity for Glauber's salt was noted after 200 cycles [S. Marks. *An investigation of the thermal energy storage capacity of Glauber's salt with respect to thermal cycling. Sol. Energy, Vol.25, 1980, pp. 255-258*].

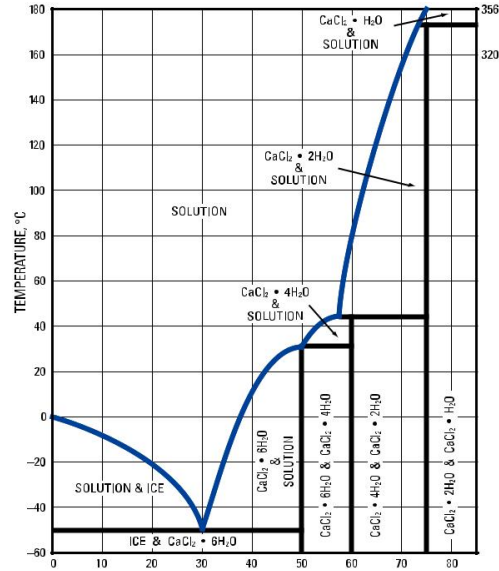
In order for salt hydrates to be fully competitive as PCM materials, technical design, phase separation and cyclic stability must be mastered, along with the subcooling minimization. To avoid these issues researchers around the world studying salt hydrates as PCMs suggested and tried adding thickening and nucleating agents to avoid these problems resulting into minimizing or delaying the decomposition and supercooling problems but not totally eliminating them giving salt hydrates a shelf life of few thousand cycles at best or 3-5 years.

For instance, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (MP: $\sim 30^\circ\text{C}$) is an example of salt hydrates that is widely available at a very low cost. However; it is commonly encountered in one of various hydrated solids with the generic formula $\text{CaCl}_2 \cdot (\text{H}_2\text{O})_x$, where $x = 1, 2, 4,$ and 6 . These hydrated solids have different melting temperatures ranging from 29.9 to 187°C , different densities ranging from 1.71 to 2.24 gm/mL, and different heat of fusion rates ranging from 38 to 73 BTU/lb.

		$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	$\text{CaCl}_2 \cdot \text{H}_2\text{O}$
Composition (% CaCl_2)		50.66	60.63	75.49	86.03
Molecular Weight		219	183	147.	129
Melting Point	($^\circ\text{C}$)	29.9	45.3	176	187
	($^\circ\text{F}$)	85.8	113.5	349	369
Density at 25°C (77°F),	(g/cm^3)	1.71	1.83	1.85	2.24
Heat of Fusion	(BTU/lb)	73	70	38	58

Pure water freezes to ice at 0°C. If CaCl₂ is added to water, the freezing point of the solution will be lower than 0°C. This phenomenon is called a freezing point depression. It can be explained from changes in chemical potentials.

1. A solution containing 31 mass % CaCl₂ has the lowest freezing point of any CaCl₂ solution (~-50°C). This solution is called a eutectic solution. At the freezing point of a eutectic CaCl₂ solution, the solution is in equilibrium with two solid phases: ice and CaCl₂·6H₂O.
2. Between -50°C and 30°C compositions consisting of solutions that are saturated with the hexahydrate, CaCl₂·6H₂O exist.
3. Between 30°C and 45.3°C compositions consisting of solutions that are saturated with the tetrahydrate, CaCl₂·4H₂O.
4. If CaCl₂·4H₂O is heated to 45.3°C or higher it will decompose into a liquid in equilibrium with CaCl₂·2H₂O.



For the CaCl₂·6H₂O – Numerous published articles reports that its latent heat ranges between 150-200J/g; most of them reports a latent heat of 170J/g or lower. To stabilize the compound nucleating agents (1-10%) such as SrCl₂·6H₂O and CaCl₂·2H₂O have to be added. In addition to avoid decomposition (salt-water) separation thickening and gelling agents such as clay, silica, oils, diatomaceous earth, perlites, zeolites and others in the range of 20-30% have to be added.

BioPCMs versus Salt Hydrates.

BioPCMs exhibit more favorable characteristics than salt hydrates; BioPCMs are made from renewable plant based products, have equal or higher latent heats associated with them, typically 200 J/g, able to target more temperature ranges with more product varieties, biodegradable, can be recycled and non-toxic.

Incongruent melting, subcooling, non-stability upon cycling, and segregation are major drawbacks of salt hydrates that must be mastered to become technical and economical sound storage solution. In general salt hydrates have limited temperature ranges available to meet specific temperature needs. Salt hydrates also have poor nucleating properties that result in what is termed supercooling of the liquid salt hydrate prior to freezing. Other drawbacks of salt hydrates involve volume change, corrosively and toxicity.

References

<p><i>Abhat, A., Low temperature latent heat thermal energy storage: heat storage materials. Solar energy, 1983. 30(4): p. 313-332.</i></p>	<p>One major drawback of salt hydrates is their instability upon cycling due the separation of water and salt, which causes a decrease in latent heat with time.</p>
<p><i>Chiu, J.N., Martin, V. and Setterwall, F., 2009. A review of thermal energy storage systems with salt hydrate phase change materials for comfort cooling. In EFFSTOCK 2009.</i></p>	<p>Many of the analytical salt hydrates fit in the temperature above 25°C, however from 0°C to 25°C, promising materials are limited</p>
<p><i>S. Marks. An investigation of the thermal energy storage capacity of Glauber's salt with respect to thermal cycling. Sol. Energy, Vol.25, 1980, pp. 255-258.</i></p>	<p>Reported that a 48% drop in stored capacity for Glauber's salt was noted after 200 cycles</p>
<p><i>S. Cantor. DSC study of melting and solidification of salt hydrates. Thermochimica Acta, Vol. 26, 1978, pp. 39-47.</i></p>	<p>Incongruent melting, or phase separation, can cause a loss in enthalpy of solidification as reported</p>
<p><i>Pasupathy, R. Velraj, R.V. Seeniraj. Phase change material-based building architecture for thermal management in residential and commercial establishments. Renew. Sust. Energy Rev. 12, 2008, pp. 39–64.</i></p>	<p>Major drawbacks of salt hydrates that must be mastered to become technical and economical sound storage solution are incongruent melting, subcooling, non-stability upon cycling, and segregation.</p>
<p><i>Sharma, Someshower Dutt, Kitano Hiroaki, and Sagara Kazunobu, "Phase Change Materials for Low Temperature Solar Thermal Applications", Res. Rep. Fac. Eng. Mie Univ., Vol. 29, pp. 31-64, 2004.</i></p>	<p>Salt hydrates cause corrosion in metal containers.</p>
<p><i>P. Shih, 2013, Thesis: Latent Heat Thermal Energy Storage Device for Automobile Applications, Department of Chemical Engineering and Applied Chemistry University of Toronto.</i></p>	<p>Due the higher density of salt hydrates, the solid salt precipitates at the bottom of the container and is not available for reaction with water for further melting-freezing cycle.</p>
<p><i>A. Sharma, V. Tyagi, C. Chen and D. Buddhi, "Review on thermal energy storage with phase change materials and applications," Renewable and Sustainable Energy Reviews, pp. 318-345, February 2009.</i></p>	<p>The severe problem of using salt hydrates as PCMs is the formation of salt hydrates with a lower number of water molecules in the discharge process.</p> <p>As the mole number of water decreases, there is insufficient water to dissolve salt, so the resulting solution becomes supersaturated at the melting temperature. Therefore, the overall energy storage</p>

	density declines with each charge-discharge cycle.
<p><i>Solé, A., Miró, L., Barreneche, C., Martorell, I. and Cabeza, L.F.. Corrosion of metals and salt hydrates used for thermochemical energy storage. Renewable Energy, (2015) 75, pp.519-523.</i></p>	<p>Five salt hydrates TCM were selected among the most used ones in research to carry out corrosion test: CaCl₂, Na₂S, CaO, MgCl₂, and MgSO₄.</p> <p>Corrosion experiments were carried out between common vessel metals and the five salt hydrates.</p> <p>A coating will be needed to protect the metal corrosion from the salt hydrates. Carbon steel was found to be slightly corroded with CaCl₂ and Na₂S, forming a brittle corrosion layer on the surface.</p> <p>Neither copper nor aluminum can be used as a vessel material to contain Na₂S since the specimens were completely destroyed within days.</p> <p>The most corrosion-resistant metal to all the hydrated salts under the corrosion test conditions was stainless steel.</p> <p>The aforementioned salts with carbon steel are not recommended for service longer than a year and a month.</p>