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# Review of Inorganic Salt Hydrates with Phase Change Temperature in Range of 5°C to 60°C and Material Cost Comparison with Common Waxes

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## ABSTRACT

Phase change materials (PCMs) with desirable phase change temperatures can be used to provide a constant temperature thermal source or sink for diverse applications. As such, incorporating PCMs into building materials, equipment, or appliances can shift and/or reduce the energy load. The motivation of this work is to identify low-cost inorganic salt hydrate PCMs that can complement current building systems and designs, and compare them with common paraffins.

In this work, we analyzed inorganic salt hydrates with phase change temperatures in the range of 5-60°C, to target both space heating and cooling applications. The properties of the salt hydrates were compared with paraffins over the same temperature range. The results showed that PCMs with a melting temperature above 20°C, salt hydrates have advantages over paraffins including higher thermal energy density (45-120 kWh/m<sup>3</sup> for salt hydrates; 45-60 kWh/m<sup>3</sup> for paraffins) and generally lower material energy cost (1-20 \$/kWh for salt hydrates; 20-30 \$/kWh for comparable paraffins). For PCMs with a melting temperature less than 20°C, the material cost is higher for both salt hydrates and paraffins (30-110 \$/kWh for both classes of materials) and salt hydrates retain their advantage of greater thermal energy density (50-120 kWh/m<sup>3</sup> for salt hydrates; 45-60 kWh/m<sup>3</sup> for paraffins). In all cases, factors including thermal cyclability, stability, congruency, corrosion, and supercooling must be considered when comparing paraffins and salt hydrates for a particular application. Finally, we give an overview of enhancement techniques for salt hydrate PCMs and find that limited efforts have been pursued to tune salt hydrate phase change temperatures, with a wider range of studies investigating stabilization and minimization of supercooling. This analysis shows the potential of developing salt hydrate PCMs for low-cost heating and cooling thermal energy storage systems for a range of applications.

## 1. INTRODUCTION

Phase change materials (PCMs) allow for the capture, storage, and release of thermal energy at a nearly constant temperature. The PCM acts as a thermal source or sink depending on the application. The use of any particular PCM is largely dependent on its phase change temperature where the latent heat can be used in its entirety. Otherwise, the PCM will store heat sensibly which does not offer any advantage over other materials. When properly implemented into a system, PCMs can introduce great energy savings by reducing total energy usage or shifting the energy load.

One use of PCMs is providing thermal mass to dampen temperature extremes for any thermally cyclic system. This is important to thermally sensitive systems where large and sudden temperature swings are undesirable. Examples include incorporation of PCMs into building envelopes and materials (Kenisarin and Mahkamov, 2016), clothing and textiles (Itani *et al.*, 2018), electronics (Mustaffar *et al.*, 2018), batteries (Zou *et al.*, 2018), solar photovoltaics (Su *et al.*, 2018), and HVAC and refrigeration systems (Siddharth *et al.*, 2018).

Another broad use of PCMs is a means to store thermal energy, thereby decoupling heat generation and its use. This reduces the wasted heat of a system by recycling thermal energy that would otherwise be discarded. Such uses include hot water systems (Thantong and Chantawong, 2017), solar thermal energy storage (Fadaei *et al.*, 2018), heat exchangers (Altman *et al.*, 2018), and HVAC systems (Li *et al.*, 2018).

While PCMs have been studied extensively for a number of years, two promising candidates for building applications include paraffins and salt hydrates. These materials both have high melting enthalpies generally on the order of 100-200 kJ/kg and melting temperatures between 0-100°C useful for numerous diverse applications in buildings. The present study examines some inorganic salt hydrate and organic paraffins with melting temperatures 5-60°C for space heating and cooling applications.

## 2. PROPERTIES OF PCMS

### 2.1 Salt Hydrates

Salt hydrates are the result of an anhydrous salt forming a solid crystalline structure in the presence of water in specific molar ratios. Depending on the ionic structure of the salt, there is a finite number of hydrates that can form and often only one or two is thermodynamically stable. Calcium chloride ( $\text{CaCl}_2$ ) forms two hydrates examined in this study: the hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) and tetrahydrate ( $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ). In this example, the two calcium chloride hydrates have different melting temperatures that depend on the water content; the hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) has a melting point of around 30°C whereas the tetrahydrate ( $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ ) has a melting point of around 44°C.

Salt hydrates melt when the solid crystal structure releases its water and forms an aqueous solution. In many cases, the stoichiometric water content present in a hydrate is not sufficient to allow the anhydrous salt to dissolve completely into a homogeneous aqueous solution. The salt's insolubility in the stoichiometric water of its hydrate causes incongruent melting, where anhydrous salt settles out of solution and fails to recombine with water upon freezing.

The salt hydrates in Table 1 are commonly studied materials for thermal energy storage applications. Sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), also known as Glauber's salt, is often considered for space heating applications due to its melting temperature of 32.4°C. However, Glauber's salt is plagued by incongruent melting and inconsistent supercooling. Other materials with comparable melting temperatures, calcium chloride hexahydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), sodium hydrogen phosphate dodecahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), zinc nitrate hexahydrate ( $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ ), and iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), may be viable alternatives for space heating applications.

Common measurement techniques to determine PCM characteristics include differential scanning calorimetry (DSC), the temperature-history method (T-H), and coffee cup calorimetry (CC) which may also be referred to as isobaric calorimetry or the water bath method. These are shown in Tables 1 and 2 where reported. Xie *et al.* (2013) present a detailed analysis of each method.

Lithium chlorate trihydrate ( $\text{LiClO}_3 \cdot 3\text{H}_2\text{O}$ ) is of special interest for its low melting temperature and potential use in cold storage systems. The properties reported by Kauffman and Pan (1973) are the earliest found that include values for the enthalpy of melting. However, it is unclear whether this enthalpy value was measured by the authors or surveyed from literature. The melting temperature of lithium chlorate trihydrate is first reported by Kraus and Burgess (1927) as 8°C and later that same year and independently by Berg (1927) as 8.1°C.

Salt hydrates generally have well-defined discrete melting temperatures from the solid to liquid phase. Sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ), for example, has been used historically in the field of thermometry to calibrate instruments due to its precise and predictable melting temperature (Washburn and Clem, 1938). The transition temperature from liquid to solid is often less defined due to supercooling of the aqueous solution. In an extreme example, sodium acetate trihydrate ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ),  $T_m = 58^\circ\text{C}$ , has been observed to supercool down to  $-12.7^\circ\text{C}$ , nearly  $71^\circ\text{C}$  below its melting temperature, before spontaneous crystallizing into its solid phase (Johansen *et al.*, 2015). Table 1 presents only the melting temperature of the solid to liquid transition.

Table 1. Inorganic Salt Hydrate Thermophysical Properties

Name	Chemical Formula	T <sub>m</sub> (°C)	ΔH (kJ/kg)	Measurement Technique	Source
Lithium Chlorate Trihydrate	LiClO <sub>3</sub> ·3H <sub>2</sub> O	8.1	253.0	–	Gawron and Shröder (1977)
		8.0	253	–	Kauffman and Pan (1973)
Dipotassium Hydrogen Phosphate Hexahydrate	K <sub>2</sub> HPO <sub>4</sub> ·6H <sub>2</sub> O	14	108	–	Lane (1983)
		13.3	109.3	CC	Kauffman and Pan (1973)
Potassium Fluoride Tetrahydrate	KF·4H <sub>2</sub> O	18.7 ± 0.1	231.4 ± 19.3	CC	Counioux and Cohen-Adad (1976)
		18.7 ± 0.1	200.5 ± 26.9	CC	Reznitskii and Filippova (1997)
		18.5 ± 0.2	246 ± 2	DSC	Shamberger and Reid (2013)
Manganese Nitrate Hexahydrate	Mn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	25.0	128.5	DSC	Nagano <i>et al.</i> (2003)
Calcium Chloride Hexahydrate	CaCl <sub>2</sub> ·6H <sub>2</sub> O	29.7	171	–	Abhat (1983)
		24	140	DSC	Tyagi and Buddhi (2008)
		29	170	–	Lorsch <i>et al.</i> (1975)
		29.2	172.5	–	Gawron and Shröder (1977)
		30.0	170	–	Kauffman and Pan (1973)
Sodium Sulfate Decahydrate	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	32.4	251.2	–	Gawron and Shröder (1977)
		32.4	254	–	Abhat (1983)
		32.4	239	DSC	Cantor (1979)
Sodium Hydrogen Phosphate Dodecahydrate	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	36	280	–	Lorsch <i>et al.</i> (1975)
		36.5	279	DSC	Guion <i>et al.</i> (1983)
		35.0	281	–	Abhat (1983)
Zinc Nitrate Hexahydrate	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	36	134	–	Lorsch <i>et al.</i> (1975)
		36.4	147	–	Abhat (1983)
Iron (III) Chloride Hexahydrate	FeCl <sub>3</sub> ·6H <sub>2</sub> O	36.1	226	–	Kauffman and Pan (1973)
		37.0	186.2	DSC	Guion <i>et al.</i> (1983)
Calcium Chloride Tetrahydrate	CaCl <sub>2</sub> ·4H <sub>2</sub> O	44.2	99.6	DSC	Ushak <i>et al.</i> (2016)
Calcium Nitrate Tetrahydrate	Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	43	138	–	Lane (1983)
		47	142	–	Lorsch <i>et al.</i> (1975)
Sodium Thiosulfate Pentahydrate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	48	209	–	Lane (1983)
		48.0	200	DSC	Guion <i>et al.</i> (1983)
		48.0	206	T-H	Zhang <i>et al.</i> (1999)
		48	201	T-H	Zhang <i>et al.</i> (1999)
		48	201	–	Bajnoczy <i>et al.</i> (1995)
		48.0	201	–	Abhat (1983)
Sodium Acetate Trihydrate	C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub> ·3H <sub>2</sub> O	58	289	DSC	Guion <i>et al.</i> (1983)
		58	272	–	Guion <i>et al.</i> (1983)
		58.0	248	T-H	Zhang <i>et al.</i> (1999)
		58	226	T-H	Zhang <i>et al.</i> (1999)
		58	252	–	Bajnoczy <i>et al.</i> (1995)
		58	226	–	Bajnoczy <i>et al.</i> (1995)

## 2.2 Paraffins

Table 2 lists a sample of n-alkanes and paraffin waxes with melting points comparable to the above salt hydrates. Single alkanes contain only one molecule (for example, n-Hexadecane has a carbon distribution denoted C16 and contains only the alkane chain with 16 carbon atoms). Materials labelled generally as ‘paraffin wax’ refer to a semi-refined hydrocarbon blend with many n-alkane chains of varying lengths. The carbon distribution is reported as a range (e.g. C16-C28) and contains alkane chains within these bounds, though the exact distribution of these chains may be unknown in the reported studies or commercially available materials.

The melting temperature of paraffins increases with chain length. For example, n-Octadecane consists of n-alkane chains of 18 carbon atoms and has a melting temperature of around 27°C, while n-Eicosane describes a chain of 20 carbon atoms and has a greater melting temperature of around 35°C. The less refined paraffin waxes containing chains of varying lengths may cause the melting temperature to be broad as the varying n-alkanes melt at different temperatures. The phenomenon is commonly referred to as the temperature glide. The reported melting temperature in Table 2 is considered the temperature recorded at the onset of the melt as determined by the cited source.

Akin to salt hydrates, the freezing temperature may be less defined for paraffin waxes containing many chain lengths. The onset of melt may be reported when the shorter chains begin to melt, but the onset of freeze may be reported when the longer chains begin to solidify. This phenomenon is commonly referred to as the temperature hysteresis. This hysteresis can result in the melting and freezing point to have different values by several degrees. Paraffins rarely supercool, thus the freezing point is unlikely to be lower than the melting point.

**Table 2.** Paraffin Thermophysical Properties

Name	Carbon Distribution	T <sub>m</sub> (°C)	ΔH (kJ/kg)	Measurement Technique	Source
n-Tetradecane	C14	5.5	215	–	Veerakumar and Sreekumar (2016)
n-Hexadecane	C16	17.75 ± 0.006	235.13 ± 0.13	DSC	Vélez <i>et al.</i> (2015)
n-Octadecane	C18	28	244	–	Abhat (1983)
		27.5	243.5	–	Ukrainczyk <i>et al.</i> (2010)
		27.07 ± 0.095	243.68 ± 0.096	DSC	Vélez <i>et al.</i> (2015)
n-Eicosane	C20	35.69 ± 0.15	247.05 ± 0.14	DSC	Vélez <i>et al.</i> (2015)
6106	C16-C28	42	189	–	Abhat (1983)
P116		45	210	–	Abhat (1983)
5838	C20-C33	48	189	–	Abhat (1983)
6035	C22-C45	58	189	–	Abhat (1983)
6403	C23-C45	62	189	–	Abhat (1983)
6499	C21-C50	66	189	–	Abhat (1983)
Paraffin Wax (1)		53	184.48	–	Ukrainczyk <i>et al.</i> (2010)
Paraffin Wax (2)		41.92	207.22	–	Muhammad <i>et al.</i> (2018)

(1) (2) The two materials labeled as “Paraffin Wax” by Ukrainczyk *et al.* (2010) and Muhammad *et al.* (2018) are assumed to be different materials. The exact chemical formula or carbon distribution is not included in the respective studies. The number in parentheses is used to identify the material in subsequent tables and figures.

## 2.3 Energy Storage Density

The PCM density is often excluded from studies of its melting behavior. And in cases where it is included, it may not be clear whether the values were measured or surveyed from literature. Table 3 shows the solid phase density of PCMs and their calculated volumetric energy storage density based on the latent heat of melting. For many materials, the density and enthalpy values were taken from different sources which may result in some error in the calculation of energy storage density. Nevertheless, salt hydrates have generally higher volumetric thermal energy storage density than paraffins which is largely attributed to the greater mass density of salt hydrates.

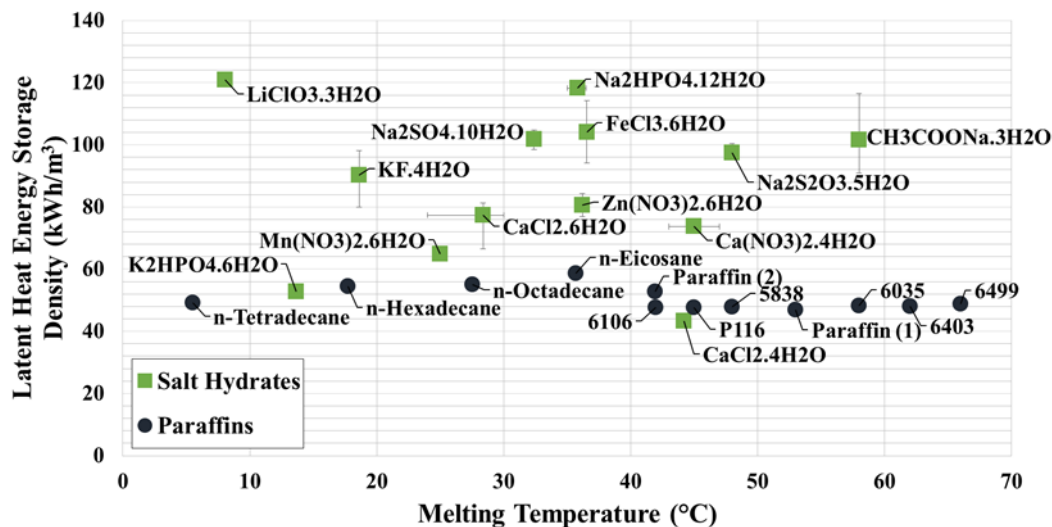
**Table 3.** Solid density of PCMs

Name	Solid Density (g/cm <sup>3</sup> )	Energy Storage Density (kWh/m <sup>3</sup> )	Source
<b>Salt Hydrates</b>			
Lithium Chlorate Trihydrate	1.72	120.88	Gawron and Shröder (1977)
Dipotassium Hydrogen Phosphate Hexahydrate	1.75	52.82 ± 0.32	Kajiwara <i>et al.</i> (2003)
Potassium Fluoride Tetrahydrate	1.437	90.21 ± 10.16	Shamberger and Reid (2013)
Manganese Nitrate Hexahydrate	1.8	64.96	Nagano <i>et al.</i> (2003)
Calcium Chloride Hexahydrate	1.710	77.40 ± 10.90	Abhat (1983)
Sodium Sulfate Decahydrate	1.485	101.75 ± 3.16	Abhat (1983)
Disodium Phosphate Dodecahydrate	1.520	118.22 ± 0.42	Abhat (1983)
Zinc Nitrate Hexahydrate	2.065	80.59 ± 3.73	Abhat (1983)
Iron (III) Chloride Hexahydrate	1.82	104.18 ± 10.04	<i>CRC Handbook of Chemistry and Physics</i> (2005)
Calcium Chloride Tetrahydrate	1.5666	43.34	Ushak <i>et al.</i> (2016)
Calcium Nitrate Tetrahydrate	1.896	73.73 ± 1.05	Yaws and Chen (2009)
Sodium Thiosulfate Pentahydrate	1.73	97.55 ± 2.88	Bajnoćzy <i>et al.</i> (1995)
Sodium Acetate Trihydrate	1.45	101.57 ± 14.84	Bajnoćzy <i>et al.</i> (1995)
<b>Paraffins</b>			
n-Tetradecane	0.825	49.3	Shlosinger and Bentilla (1965)
n-Hexadecane	0.835	54.5 ± 0.03	Shlosinger and Bentilla (1965)
n-Octadecane	0.814	55.0 ± 0.06	Shlosinger and Bentilla (1965)
n-Eicosane	0.856	58.7 ± 0.03	Shlosinger and Bentilla (1965)
6106	0.910	47.3	Abhat (1983)
P116	0.817	47.8	Abhat (1983)
5838	0.912	47.7	Abhat (1983)
6035	0.920	47.9	Abhat (1983)
6403	0.915	48.3	Abhat (1983)
6499	0.930	48.0	Abhat (1983)
Paraffin Wax (1)	0.916	48.8	Ukrainczyk <i>et al.</i> (2010)
Paraffin Wax (2) <sup>A</sup>	0.916	46.9	–

<sup>A</sup> Density not reported. Value from Ukrainczyk *et al.* (2010) used as reference.

The density values reported in Table 3 are the density of the solid phase of the PCM. Both salt hydrates and paraffins change density upon melting, but this is not consistent across the various materials. As such, special considerations will be needed for both classes of materials to handle this volumetric change in any particular system.

Figure 1 shows the volumetric thermal energy storage density of salt hydrates and organic paraffin PCMs plotted against their melting temperature. Salt hydrates have a thermal storage energy density ranging from 40-125 kWh/m<sup>3</sup> whereas paraffins have a fairly narrow range energy storage density from 40-60 kWh/m<sup>3</sup>. Since the energy storage density of paraffins is typically less than salt hydrates, salt hydrates can be a better option than paraffins in systems where volumetric constraints are important.



**Figure 1.** Thermal energy storage density of salt hydrates and paraffins

### 3. PCM MATERIAL COST

The material costs per unit mass of PCMs are shown in Table 4 and Figure 2. Material costs were found from commercial suppliers for bulk quantities, typically 1-10 metric tons. The material costs per unit energy are calculated with the reported enthalpy values from Tables 1 and 2. Many salt hydrates are sold in an anhydrous form and must be hydrated with the stoichiometric amount of water to reach the desired hydrated form. This additional cost is not considered here, but is not expected to greatly increase the cost of the system.

Many salt hydrates with melting points greater than 20°C generally have lower material cost than paraffins (even lower than the least-refined paraffins). This translates to a low material energy cost generally from 1-20 \$/kWh for salt hydrates. Paraffins with comparable melting temperatures have material energy costs from 20-30 \$/kWh.

Most commercially available semi-refined paraffins are sold with melting temperatures greater than 40°C, so a single n-alkane chain length may be required for applications requiring a lower temperature. The single chain length n-alkanes have a higher material cost than the semi-refined paraffins likely caused by the more precise refining procedure required.

For PCMs with a melting temperature less than 20°C, the material cost is higher for both salt hydrates and paraffins. This leads to similar material energy costs for both classes of materials, 30-110 \$/kWh. For these PCMs, the material cost of salt hydrates and n-alkanes is similar despite the increased processing cost of single alkanes. This is likely due to the availability and safety precautions required of these salt hydrates. For example, anhydrous potassium fluoride (KF) is highly corrosive, hygroscopic, and poses a fatal health risk to people. As such, it is recommended to store potassium fluoride under an inert atmosphere and avoid contact with water (LabChem, 2014). Special precautions in handling and processing potassium fluoride would likely lead to increased system-level costs for potassium fluoride tetrahydrate (KF·4H<sub>2</sub>O). Lithium chlorate (LiClO<sub>3</sub>) is not commercially available due to its instability. The price used in the analysis is for lithium perchlorate (LiClO<sub>4</sub>) due to its similar chemical formula. Lithium salts generally have higher material costs due to the competing electric battery industry.

**Table 4.** Phase change material costs

Name	Material Cost (\$/kg)	Vendor	Material Energy Cost (\$/kWh)
<b>Salt Hydrates</b>			
Lithium Chlorate Trihydrate	5.21 <sup>A,B</sup>	Famouschem Technology (Shanghai) Co., Ltd.	74.10
Dipotassium Hydrogen Phosphate Hexahydrate	1.45 <sup>B</sup>	Sinoright International Trade Co., Ltd.	47.76 – 48.33
Potassium Fluoride Tetrahydrate	4.85 <sup>B</sup>	Shanghai Richem International Co., Ltd.	70.98 – 87.07
Manganese Nitrate Hexahydrate	0.29 <sup>B</sup>	Zibo Jiashitai Chemical Technology Co., Limited	8.15
Calcium Chloride Hexahydrate	0.39 <sup>B</sup>	Tianjin TYWH Import & Export Co., Ltd.	2.30 – 2.83
Sodium Sulfate Decahydrate	0.11 <sup>B</sup>	Lianyungang Huaihua International Trade Co., Ltd.	1.53 – 1.63
Disodium Phosphate Dodecahydrate	1.38	Langfang Huinuo Fine Chemical Co., Ltd.	17.66 – 17.78
Zinc Nitrate Hexahydrate	0.60 <sup>B</sup>	Zouping Changshan Town Zefeng Fertilizer Factory	14.69 – 16.12
Iron (III) Chloride Hexahydrate	2.64	Taian Health Chemical Co., Ltd.	41.99 – 50.95
Calcium Chloride Tetrahydrate	0.39 <sup>B</sup>	Tianjin TYWH Import & Export Co., Ltd.	3.98
Calcium Nitrate Tetrahydrate	0.32	Zhenjiang Ginte Materials Company Limited	8.11 – 8.35
Sodium Thiosulfate Pentahydrate	0.19	Lianyungang Huaihua International Trade Co., Ltd.	3.24 – 3.38
Sodium Acetate Trihydrate	0.85	Lianyungang Crown Sue Industrial Co., Ltd.	10.55 – 13.49
<b>Paraffins</b>			
n-Tetradecane	2.48	Shaanxi Dideu Medichem Co., Ltd.	41.48
n-Hexadecane	4.00	Beyond Industries Ltd.	61.24
n-Octadecane	8.17	Shaanxi Dideu Medichem Co., Ltd.	120.47 – 120.71
n-Eicosane	2.05	Hangzhou Fanda Chemical Co., Ltd	29.87
6106	1.31 <sup>C</sup>	–	24.89
P116	1.31 <sup>C</sup>	–	22.40
5838	1.31 <sup>C</sup>	–	24.89
6035	1.31 <sup>C</sup>	Beijing Dongke United Technologies Co., Ltd.	24.89
6403	1.31 <sup>C</sup>	–	24.89
6499	1.31 <sup>C</sup>	–	24.89
Paraffin Wax (1)	1.31 <sup>C</sup>	–	25.50
Paraffin Wax (2)	1.31 <sup>C</sup>	–	22.70

<sup>A</sup> Lithium chlorate (LiClO<sub>3</sub>) is not commercially available. Price estimate is for lithium perchlorate (LiClO<sub>4</sub>)

<sup>B</sup> Quote for anhydrous form

<sup>C</sup> Price quote is for semi-refined paraffin wax with a melting point of 58°C which most closely matches the melting point of material 6035 by Abhat (1983). Price is used as estimate for other semi-refined paraffin waxes.



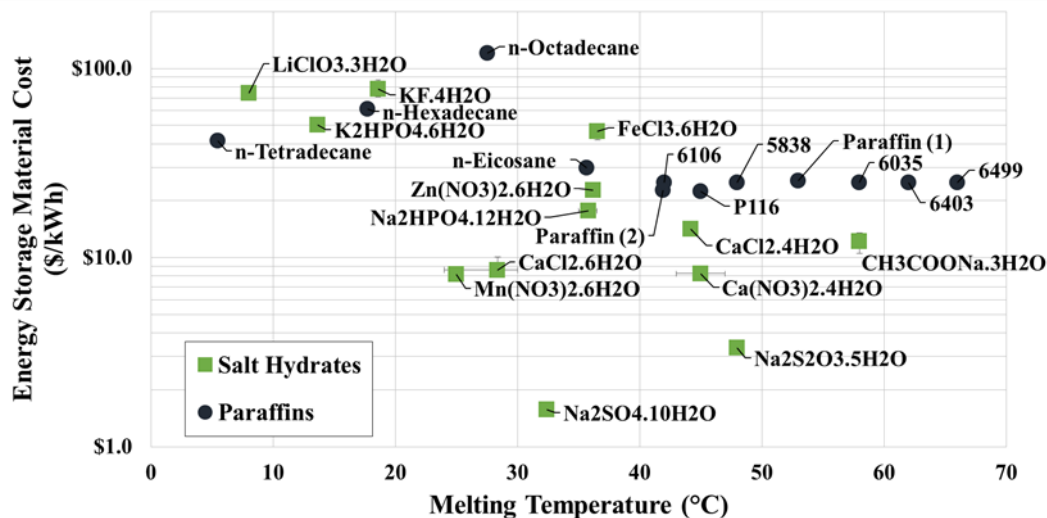


Figure 2. Energy storage material cost of salt hydrates and paraffin compounds

#### 4. ENHANCEMENT TECHNIQUES FOR INORGANIC SALT HYDRATES

Salt hydrates often exhibit incongruent melting and large supercooling which has historically limited their implementation in energy storage systems. The most common method to stabilize incongruently melting salt hydrates is to include a filler material that limits the mobility of the different species upon melting or serves as a form-stable framework around the PCM. Examples of fillers include thixotropic gels (Telkes, 1980), carboxymethyl cellulose (CMC) (Mao *et al.*, 2017), graphite flakes, platelets, and powders (Zhou *et al.*, 2017; Xiao *et al.*, 2018; Song *et al.*, 2018; Johansen *et al.*, 2015). The method of encapsulation also serves to prevent separation (Aftab *et al.*, 2018). Methods involving high thermal conductivity materials (graphite, metallic nanoparticles) are often used in an attempt to increase the thermal conductivity of the resulting composite (Fu *et al.*, 2018). Filler materials comprise a small percentage of the resulting composite, generally less than 20% by mass. Despite additional costs associated with adding these filler materials, salt hydrates are still cost effective compared to paraffins.

Compared with salt hydrates, the melting temperature of paraffins can more readily be tuned by mixing n-alkanes varying length. Some attempts to tune the melting temperature of salt hydrates have been explored by mixing other salts or additives with the salt hydrate of interest (Nagano *et al.*, 2003), but few mixtures have been fully examined.

Attempts to limit or prevent supercooling in salt hydrates include mixing other salts or other additives. Generally, additional salts are those with similar crystal structure to the salt hydrate of interest. One example is the addition of sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) to sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) (Telkes, 1952). These two salts have similar crystal structures (Ruben *et al.*, 1961). When freezing liquid sodium sulfate decahydrate solution, the sodium tetraborate decahydrate can act as a template for sodium sulfate decahydrate recrystallization, thereby limiting the observed supercooling. Adding additional salts reduces the energy storage density by displacing the salt hydrate of interest, but does not increase the system material energy cost significantly.

#### 5. CONCLUSIONS

This study sought to identify low-cost inorganic salt hydrates for space heating and cooling applications. Salt hydrates generally have a greater thermal energy storage density compared to paraffins, though technical challenges of salt hydrates must be resolved, especially congruency, stability, and supercooling. For applications with temperatures above 20°C, salt hydrates are the more cost effective option. As an example, sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) has a reported melting enthalpy as high as 209 kJ/kg at a temperature of 48°C. With a solid density

of  $1.73 \text{ g/cm}^3$ ,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  has an energy storage density of  $97.5 \text{ kWh/m}^3$ . A comparable paraffin wax (melting temperature of  $48^\circ\text{C}$ , enthalpy of  $189 \text{ kJ/kg}$ , and density of  $0.912 \text{ g/cm}^3$ ) has an energy storage density of  $47.9 \text{ kWh/m}^3$ , nearly half of sodium thiosulfate pentahydrate. The energy cost is  $\$3.30/\text{kWh}$  and  $\$24.89/\text{kWh}$  for  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and paraffin wax, respectively.

For applications requiring temperatures less than  $20^\circ\text{C}$ , paraffins and salt hydrates have similar energy material costs. With stringent volumetric constraints, the higher density of salt hydrates can make them a more appealing choice. Potassium fluoride tetrahydrate ( $\text{KF} \cdot 4\text{H}_2\text{O}$ ) has a melting temperature of  $18.5^\circ\text{C}$ , enthalpy around  $230 \text{ kJ/kg}$ , solid density of  $1.437 \text{ g/cm}^3$ , and material energy cost of around  $\$77/\text{kWh}$ . n-Hexadecane has a melting temperature of  $17.8^\circ\text{C}$ , enthalpy of  $235 \text{ kJ/kg}$ , solid density of  $835 \text{ g/cm}^3$ , and a material energy cost of  $\$61/\text{kWh}$ . The energy storage densities of potassium fluoride tetrahydrate and n-hexadecane are  $90 \text{ kWh/m}^3$  and  $54 \text{ kWh/m}^3$ , respectively.

## NOMENCLATURE

CC	coffee cup calorimetry, isobaric calorimetry, water bath method	(–)
DSC	differential scanning calorimetry	(–)
T-H	temperature-history calorimetry	(–)
T	temperature	( $^\circ\text{C}$ )
$\Delta H$	enthalpy of fusion	( $\text{kJ/kg}$ )

### Subscript

m melting

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