

# PCM Price challenge

## 1.1 PCM cost components

The price of PCM is driven by market demand and supply relationships. Presently, the U.S. market for PCMs is not yet fully developed, resulting in a limited demand that is largely responsible for their relatively higher prices. However, there is a huge market potential for PCMs in a wide ranging applications including building energy improvements. Since manufacturers base their prices on the future market expectations, in all likelihood, prices will drop in future. It is expected that the current energy performance studies conducted for PCMs by the U.S. research community will play a crucial role in shaping their prospects for building applications. Encouraging field energy performance data developed during the last decade by different labs and universities will help fuel market demand for PCMs, most likely enabling a reduction in the cost of these products.

PCM product cost is primarily governed by the cost of the raw PCM material and the cost of encapsulation. Encapsulation is required to prevent contamination of the PCM with the external environment by enclosing the material with an inert coating. At the same time, encapsulation allows easy handling of the PCM for most building related applications. There are mainly two approaches to encapsulate PCM: 1) macroencapsulation or packaging, where PCMs are encapsulated in large pouches, tubes, rectangular panels, spherical capsule, etc., and 2) microencapsulation, where microscopic amounts of PCMs are coated with a protective shell material. Microencapsulation provides improved heat transfer between the PCM and the surroundings due to the increased surface area but usually adds more cost to the product since it involves several chemical synthesis steps. The final PCM product cost varies greatly depending on the approach adopted to encapsulate the PCM.

## 1.2 Material Cost

PCMs considered for building applications rely on a solid-liquid transition and may be classified into the following two categories:

### 1.2.1 Organic PCMs

Organic PCMs are most often composed of organic materials such as paraffins, fatty acids and sugar alcohols. For building applications, paraffinic PCMs are the most commonly used ones due to several reasons described below. Paraffinic PCMs are straight chain n-alkane hydrocarbon compounds such as n-heptadecane, n-Eicosane, etc. Their melting temperature and phase change enthalpy increase with the length of the carbon chain. When the number of carbon atoms in the paraffin molecule is between 13 to 28, the melting temperature falls within a range of approximately 5 to 60°C [Mehling and Cabeza - 2008], a temperature range that covers building applications in most of the global climates. In addition, paraffinic PCMs are chemically inert, non-toxic, reliable, biocompatible, and show negligible subcooling effect [Boh and Sumiga - 2008]. Fatty acids are represented by the chemical formula  $\text{CH}_3(\text{CH}_2)_n\text{COOH}$ , for example capric acid, lauric acid, palmitic acid, etc. Fatty acids have storage densities very similar to paraffins, and like paraffins their melting temperatures increase with the length of the molecule. Although chemically stable upon cycling, they tend to react with the environment due to their acidic nature.

Sugar alcohols are a hydrogenated form of a carbohydrate such as D-sorbitol, xylitol, etc. They generally have higher latent heat and density than paraffins and fatty acids. However, they melt at temperatures between 90 and 200°C, making them unsuitable for building applications.

### 1.2.2 Inorganic PCMs

Inorganic PCMs cover a wide range of temperature. Although inorganic PCMs have similar latent heat per unit mass as organic PCMs, their latent heat per unit volume is generally higher due to their higher density. Salt hydrates are one type of inorganic salts containing one or multiple water molecules such that the resulting crystalline solid has a chemical formula of AB.nH<sub>2</sub>O. Some of the examples are CaCl<sub>2</sub>.6H<sub>2</sub>O, LiNO<sub>3</sub>.3H<sub>2</sub>O and KF.3H<sub>2</sub>O. Salt hydrates are non-toxic, non-flammable and less corrosive, and possess higher thermal conductivity compared to organic PCMs. Salt hydrates have melting temperatures in the range of 5 to 130°C, a suitable range for building applications.

### 1.2.3 Material Cost of PCMs

The material cost depends significantly on the classification of the PCM i.e. whether organic, inorganic, biomaterial etc. Commercial paraffinic PCMs are byproducts from the oil refineries; therefore, they are available in abundant supply at a relatively cheaper price. The price of paraffins increases with the purity. Pure paraffin wax (>99%) is more expensive compared to the technical grade p-wax (90–95%) [Mulligan and Gould - 2002]. Current cost of paraffin wax is \$0.85–0.91/lb (\$1.88–2/kg).<sup>[1]</sup> As a reference, pure laboratory grade eicosane is \$24.50/lb (\$53.9/kg), while the technical grade is \$3.20/lb (\$7.04/kg). The estimated cost of microencapsulation for a similar paraffin octacosane is ~45% of the total cost of the paraffin PCM.<sup>[2]</sup> Another low-cost paraffin alternative available is Baker Petrolite's POLYWAX™ that costs \$2/gal (\$0.53/liter).

The cost of fatty acid PCMs such as stearic acid, palmitic acid and oleic acid—\$0.71–\$0.65 (\$1.43–1.56/kg), \$0.73–0.78/lb (\$1.61–1.72/kg) and \$0.76–0.80/lb (\$1.67–1.76/kg), respectively. Biodiesel crude glycerine (bio-crude) is \$0.10–0.13/lb (\$0.22–0.29/kg) CIF China Mainland.

Entropy Solutions Inc. quotes \$0.75–2.50/lb (\$1.65–5.5/kg) for their commercial volume organic PCM products. Chemical components for their products are derived from agricultural sources and the melting temperature ranges between –40 and 150°C. Phase Change Energy Solutions sells bio-based PCMs with melting temperatures of 25, 27 and 29°C. The cost of their products varies with M-values. For example, M-27, M-51, M-91 and M-182 products have wholesale prices in \$/m<sup>2</sup> of 20.88, 30.46, 49.40 and 94.61 (\$1.94, 2.83, 4.59 and 8.79/ft<sup>2</sup>), respectively. The prices in terms of \$/lb (\$/kg) for M-27, M-51, M-91 and M-182 products are 6.47, 5.05, 4.59 and 4.40 (14.26, 11.13, 10.12, and 9.70), respectively.

In 2010, Syntroleum Corporation received the DOE ARRA award (DE-EE0003924) for development of low cost, bio-based phase change material for building envelope applications.<sup>[3]</sup> Syntroleum plant was built to compete with a commodity product—diesel fuel—it can manufacture the octadecane-rich paraffin intermediate at the price of biodiesel (which sells in the \$4.50–5.50/gal (\$1.19–1.45/liter) or \$0.69–0.85/lb (\$1.52–1.87/kg) range. The cost of converting the paraffin into form-stable composites is

<sup>[1]</sup> ICIS pricing: <http://www.icispricing.com/>

<sup>[2]</sup> Private communication with Tim Riazzi – Microtek Labs

<sup>[3]</sup> Low Cost Phase Change Material (PCM) for Building Envelopes.

<http://www.recovery.gov/Transparency/RecipientReportedData/pages/RecipientProjectSummary508.aspx?AwardIdSur=117469>

not well defined yet. But since it uses a low priced commodity plastic (HDPE) in a continuous process using "workhorse" polymers industry equipment (extruder/pelletizer), the cost is expected to be significantly lower than micro-encapsulation. It is expected that the price range for these new PCM pellets having 60 to 70% paraffin in HDPE will be in the range between \$6.6/kg and \$8.8/kg (\$3/lb and \$4/lb) with target enthalpy of approximately 43 Btu/lb (100 kJ/kg).

The average cost of inorganic PCM calcium chloride is \$.059-0.091/lb (\$0.13-0.20 /kg), while the cost of a small quantity of 1lb (1kg) is 0.35 (\$0.77).<sup>[4]</sup> Calcium chloride is a salt of calcium and chloride, and is a colorless, odorless and a nontoxic solution. PCMEnergy India produces salt hydrate PCMs with melting temperature range of 18-48°C. The PCM material is prepared in-house and contains no impurities. The cost of the raw material used is \$0.90-1.80/lb (\$1.98-3.96/kg). The PCM products are in the packaged form rather than being microencapsulated. The price of the final product is \$1.40-2.25/lb (\$3.08-4.95/kg) with the packaging step contributing ~20-35% of the total cost.

Alderman Research produces inorganic PCMs composed of CaCl<sub>2</sub>·6H<sub>2</sub>O as the main compound with viscosity modifiers, nucleating agents, other stabilizers make up less than 20% of the total weight. The PCM material used is prepared in-house and the melting temperature is kept around 30°F. The product cost break-up includes \$0.21/lb (\$0.46/kg) for formula and \$0.18/ft<sup>2</sup> (\$1.94/m<sup>2</sup>) for packaging the film (raw materials only, no labor, overhead, or profit). An ordinary food-packaging machine, similar to the ones that package condiments for national fast food chains, is used to package the PCM. The packaging procedure involves cutting the individual packets at a desired length rather than slitting them. The final cost of the product is \$10.76-21.52/m<sup>2</sup> with the packaging process accounting for 9-18% of the total cost. This product is available in one-pallet size quantities.

### 1.3 Alternatives to paraffin

Cost and volumetric latent heat are two key parameters that will decide the market adoption of PCMs as a building energy efficiency material. Today, paraffins are the most widely used PCMs in building applications for some apparent reasons: they are non-toxic, abundant in supply and easy to microencapsulate. Other attractive features include small subcooling, chemical inertness and good recyclability. Although the technology is ready for the incorporation of paraffinic PCMs in the building materials, the high cost of paraffin chemicals along with low phase-change enthalpies (150-200 MJ/m<sup>3</sup> or 4027-5369 Btu/ft<sup>3</sup>) and high fire loads are proving to be a major barrier to their widespread acceptance. Since paraffins are derived from crude oil, their prices are very sensitive to the season and geopolitical scenario. In fact, crude oil prices have been on the rise in recent years. All these factors underline the need to shift the focus away from paraffinic PCM to some other class of PCM. Following two alternative materials have a great potential to substitute paraffin in the future, and compete with the existing energy efficient building materials and technology:

#### 1.3.1 Salt Hydrates

Inorganic salt hydrates with low chemical cost, higher enthalpies (250-350 MJ/m<sup>3</sup> or 6711-9397 Btu/ft<sup>3</sup>) and thermal conductivity (0.5 W/m/K or 0.29 Btu/hr/ft<sup>2</sup>/°F), and suitable melting temperature (5-120°C) show great promise to become a primary PCM material for building applications. In fact, inorganic salts such as Glauber's salt were the first PCM to be ever applied in building applications.<sup>[5]</sup> So far inorganic

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<sup>[4]</sup> <http://www.kaycircle.com/What-Is-the-Average-Cost-of-Calcium-Chloride-per-ton-lb-Average-Calcium-Chloride-Price>

<sup>[5]</sup> <http://www.eoearth.org/article/Telkes>, Maria – 2009

PCMs have found very limited application in buildings due to their undesirable properties such as poor nucleating properties i.e. subcooling effect, corrosive nature, incongruent melting and phase segregation during transition. However, with the advances made over the last few decades in the fields of salt hydrates, it is now possible to control these adverse properties to a large extent.

### *1.3.1.1 Approaches to improve phase-change properties*

It has been shown that adding a nucleating agent with a crystal structure similar to the energy storage material reduces the amount of subcooling [Garg et al. - 1985]. In addition, uniformly distributing the nucleating seed agent throughout the phase-change media helps increase the rate of crystallization since most salt hydrates suffer from a low rate of crystallization.

Inorganic salts experience incongruent melting. This happens when the solubility of the salt is not high enough to dissolve all the anhydrous salt in the water of crystallization that is released. This effect reduces the efficiency of PCM product since undissolved salt settles down at the bottom of the container and does not contribute to heat storage process. Extra water principle is used to avoid incongruent melting. The method involves using extra water to dissolve the entire anhydrous salt during melting—thickening of the material to gel form as suggested by [Telkes - 1952].

Thickening materials are used to minimize the phase separation in solid and liquid phases and also to prevent nucleating agents from settling down due to the density. Super-absorbent polymer (SAP) synthesized from an acrylic acid copolymer has been used as an effective thickener to prevent phase separation of the high hydrate inorganic salts ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) [Woo et al. -1992]. Inclusion of 3 to 5 wt% SAP was found to be an effective thickener for most of these salt hydrates. For the low hydrate inorganic salts ( $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ ), adding small amounts of 2–4 wt% of carboxymethyl cellulose (CMC) stabilized the salt hydrate. Three different powders of carbon (1.5–6.7  $\mu\text{m}$ ), copper (1.5–2.5  $\mu\text{m}$ ) and titanium oxide (2–200  $\mu\text{m}$ ) are found to reduce the subcooling of thickened  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . Also, the subcooling of thickened  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  is reduced from 20 to 2–3°C by adding 2 wt% potassium sulfate. Thixotropic thickening agents are another low-cost option.

To improve thermal/mechanical properties, foreign materials such as graphite fiber or metal may be embedded into the PCM to form a composite. Alternatively, PCM may be incorporated into matrix of other materials such graphite, metallic or polymer matrix. Matrix network holds the PCM inside the pores even when it has melted. Li et al. developed novel microencapsulation method where organic PCM were coated with HDPE/wood floor compound [Li - 2009]. They introduced micro mist graphite during the microencapsulation of organic PCM to increase thermal conductivity. Shell and matrix prevented the leakage when PCM was melted thus forming a shape-stabilized PCM. Thermal conductivity was enhanced by 17.7% by adding 8% weight of graphite. The inclusion of graphite was shown to have no adverse effect on the mechanical and thermal stability of the composite PCM.

### *1.3.1.2 Glauber's Salt*

It is worthwhile to describe here the significant technological progress that has been made to improve the adverse properties of Glauber salt such as subcooling, incongruent melting, phase segregation etc. Glauber salt is one of the most inexpensive heat storage materials that can be used in building applications. It is composed of 44%  $\text{Na}_2\text{SO}_4$  and 56%  $\text{H}_2\text{O}$  by weight and has a high latent heat of 254 kJ/kg (377 MJ/m<sup>3</sup>) with a melting temperature of about 32°C, which is well-suited to building

applications. Glauber salt shows a very large subcooling of  $\sim 15^{\circ}\text{C}$ . Borax as a nucleating agent has been successfully used to reduce subcooling of this salt to  $\sim 4^{\circ}\text{C}$ . Addition of borax to the salt improves thermal cycling of the mixture as well. The extra water principle has been employed to prevent incongruent melting and to improve thermal cycling [Farid et al. - 2004]. To avoid phase segregation, thickening agents, such as Bentonite clay, have been used. Bentonite salt provides an additional advantage that its application reduces the heat transfer to the salt due to the lower thermal conductivity of the mixture, a desirable feature for peak hour load shifting in building applications.

### 1.3.1.3 Calcium Chloride Hydrate

Calcium chloride hydrate ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ) is another popular salt hydrate that has received a lot of attention in the scientific community due to its high latent heat and ability to melt congruently.  $\text{SrCl}_2$ ,  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaF}_2$  have been proposed as nucleating agents to reduce subcooling and incongruent melting of  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ . These were chosen for testing based on either their similar crystal structure or using intuition. For example,  $\text{SrCl}_2$  and  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  both have hexagonal structures.  $\text{SrCl}_2$  acts as a site for crystals to grow, allowing  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  to solidify without as much subcooling.  $\text{BaCO}_3$  was also found to be an effective nucleating agent, but it is currently unclear why. In certain quantities, both of these additives can eliminate subcooling [Lane - 1992]. These nucleating agents also help prevent phase segregation of high hydrate  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  into low hydrate  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ .

### 1.3.1.4 Microencapsulation of salt hydrates

Heterogeneous polymerization techniques such as emulsion polymerization, dispersion polymerization, microemulsion polymerization, miniemulsion polymerization, etc., have typically been used to encapsulate inorganic materials [Jing et al. - 2011]. The resulting encapsulated product suffers from low solid content inside capsule and poor encapsulation yield. Microencapsulation of salt hydrates becomes even more challenging due to the fact that salt hydrates are hydrophilic in nature and contain well defined water fraction. To be able to be used in building applications, shell material needs to act as a water/vapor barrier and be made of hydrophobic materials to prevent the salt hydrate from evaporating. Organic polymers are typically used as shell material in encapsulation process; however, they are chemically incompatible with salt hydrates.

Recently, there have been successful efforts to microencapsulate salt hydrates.<sup>[6],[7]</sup> Fraunhofer ISC has developed a method where a salt hydrate melt is encapsulated by an inorganic-organic hybrid polymer known as ORMOCER<sup>®</sup>. The process involves injecting salt hydrate melt drops into the ORMOCER<sup>®</sup> solution that solidifies locally as it comes in contact with the surface of the drop, thus forming a hard encapsulating layer around the salt hydrate drop. The encapsulated drops are removed from the coating solution via mechanical means and washed thoroughly before allowing them to dry in air under ambient condition. Salt hydrate drops subsequently crystallize as they cool down. Capsules produced in such manner have diameters ranging from a few  $\mu\text{m}$  to a few mm. Although the final product has water permeability and stability issues, nonetheless it is an encouraging step.

Hessbrugge and Vaidya developed a novel technique for the encapsulation of water soluble salts [Hessbrugge - 1997]. The method employs a simple process where additives such as emulsifiers and acid

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<sup>[6]</sup> [http://www.messib.eu/about\\_project/messib\\_innovative\\_elements/phase\\_change\\_materials/microencapsulation\\_of\\_salt\\_hydrates.php](http://www.messib.eu/about_project/messib_innovative_elements/phase_change_materials/microencapsulation_of_salt_hydrates.php)

<sup>[7]</sup> <http://www.freepatentsonline.com/y2011/0017944.html>

acceptors that are needed to stabilize the aqueous-organic interface and to remove the excess acid formed due to hydrolysis are not required. This results in a cheaper microencapsulation process since the post-treatment required to remove additives and their byproducts is no longer required. In addition, there is less likelihood of contamination of encapsulated product due to the absence of trace amounts of the reaction components and their byproducts.

Brandt et al. encapsulated powdered  $\text{Na}_2\text{CO}_3$  hydrate particles with an inorganic  $\text{SiO}_x$  layer via a sol-gel process in a TMOS solution [Brandt et al. - 2006, Rößner].

### **1.3.2 Biobased PCMs**

Biobased PCMs are a renewable and green alternative to paraffinic PCMs. Bio PCMs are obtained from animal fat and vegetation such as beef tallow, lard, palm, coconut, soybean etc. They are non-toxic and can be recycled thousands of cycles without experiencing any material degradation. They are hydrogenated hydrocarbons with a saturated electronic configuration; therefore, are chemically stable and can last for decades. In addition, fat and oil based PCMs offer similar or improved performance and a greater degree of fire resistance, and are less expensive.

#### **1.3.2.1 Fatty Acids**

Among all PCMs including biobased PCMs, fatty acids have superior advantages, such as congruent melting and cooling, high latent heat of fusion, low-cost, fire resistance, nontoxicity, very small subcooling and volume change, and good chemical and thermal stability after a large number of thermal cycles [Sari et al. - 2003, Sari et al. - 2009].<sup>[8],[9]</sup> Another attractive feature is that the melting temperatures can be adjusted to match the requirement by selecting a right combination of eutectic binary mixtures of fatty acids. The eutectic mixtures of fatty acids as PCMs also retain their good thermal stabilities as a single fatty acid after repeated thermal cycling [Sari et al. - 2004, Sari - 2005].

In fact, economic studies have shown that fat and oil based PCM chemicals can be only half as much expensive as paraffin PCM products currently produced from crude oil.<sup>[10]</sup> These biobased PCMs have the potential to replace petroleum based PCMs and help reduce  $\text{CO}_2$  green house emission. Since major key properties of fat and oil derivatives are similar to that of paraffin, fat and oil derivatives can be used for similar applications. For example, wax products such as candles, pencils, coatings etc that have been largely dominated by paraffins are now alternatively being manufactured using bio-based and renewable such as hydrogenated soybean oil.

#### **1.3.2.2 Coconut Oil**

Coconut is a staple diet for millions of people living in tropical regions of the world. Coconut oil (Oil extracted from coconut fats) is a type of saturated fatty acid containing about ~~51~~ 44% of lauric acid ( $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ ). For building applications, it is critical that fatty acids are encapsulated well otherwise they tend to flow everywhere when experiencing phase-change. Microcapsules of lauric acid (LA) as the core and melamineformaldehyde (MF) resin as the shell have been successfully prepared as phase change material for latent heat thermal storage by in situ polymerization [Su et al. - 2006, Yan Hua - 2011]. Özonur et al. successfully prepared microcapsules of natural coco fatty acid mixture as core

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<sup>[8]</sup> <http://www.renewablealternatives.com/pcm.htm>

<sup>[9]</sup> <http://www.reeis.usda.gov/web/crisprojectpages/197095.html>

<sup>[10]</sup> <http://www.uiweb.uidaho.edu/bioenergy/Bioenergy2002conference/pdffiles/papers/173.pdf>

and gelatungum Arabic as shell material by a complex coacervation technique [Özonur et al. - 2006]. Chai et al. microencapsulated stearic acid and palmitic with SiO<sub>2</sub> using a one-step, low heating temperature solid-state chemical reaction [Chai et al. - 2007].

### **1.3.3 Shape-stabilized PCM**

Recently, a novel PCM material known as shape-stabilized (ss) PCM have been developed that can retain the shape of the solid structure during phase-transition. ss-PCM is a composite of PCM with another material, such as a ss-paraffin composite consisting of paraffin incorporated on a microscopic level into a porous supporting structure such as HDPE. ss-PCM offer several benefits: high apparent heat capacity, suitable thermal conductivity and no need for a container as PCM does not tend to flow out of the porous structure during melting. Inaba and Hu observed no leakage of paraffin through HDPE network for paraffin loading levels as high as 75% by weight [Inaba and Tu - 1997]. Yinping prepared ss-paraffin with 80% by weight loading of paraffin and found that no containment was required i.e. samples can be cut into pieces without any drainage [Yinping et al. - 2006]. It is to be kept in mind that even with all the benefits mentioned here, HDPE adds to the cost of the final PCM product.

## **1.4 Expected future cost reductions**

The price of the raw material and the encapsulation process determine the cost of PCM products. The cost to macroencapsulate a PCM is ~20% of the total cost, while the microencapsulation process is even more expensive, i.e. ~50% of the final product cost. At present, paraffins are the most popular choice as a PCM since they offer several attractive features, i.e. they are chemically inert, non-toxic and easy to encapsulate.

For building applications, latent enthalpy per unit volume and flammability are the two main performance criteria to decide the type of PCM and paraffins do not fare well on either of these criteria. Salt hydrates due to their higher latent heat per unit volume and non-flammability have the potential not only to replace paraffins as a PCM of choice for building applications, but also to outperform other competing technologies such as thermal insulations. However, there are some technological challenges that need to be addressed before salt hydrates can become a commonplace PCM in building applications: the subcooling effect and the difficulty in microencapsulating the salt hydrates, as they contain water. As a matter of fact, recently there have been successful efforts to microencapsulate salt hydrates. Although these microencapsulated salt hydrate product have water permeability and stability issues, nonetheless it is an encouraging step. The prices have fallen for salt hydrates in recent times, but the real solution lies in developing a low-cost, easy, and chemically, physically, and thermally stable salt hydrate PCMs that will work for building applications.

Biobased PCMs are another renewable, cheap and eco-friendly option to paraffins. With more advanced knowledge to control the transition properties and improvements in the process technology, it is possible that biobased PCMs will become commonplace in near future.