Technology of Latent Heat Storage for High Temperature Application: A Review

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To save energy and reduce CO2 emissions, the utilization of solar energy and waste heat using latent heat storage (LHS) has emerged as an attractive solution because of advantages such as large density of heat storage, constant-temperature heat supply, and repeatable utilization without degradation. This review describes research trends in LHS technologies using phase-change materials (PCMs) based on papers published from 2001–2009, and state-of-the-art LHS technologies for high-temperature applications over 100°C, such as solid–solid PCM, encapsulation of PCMs, PCM composites, solar power generation with LHS, and waste heat recovery systems.

KEY WORDS: phase change material; PCM; latent heat thermal storage; solar energy; waste heat.

1. Introduction

The utilization of industrial waste heat is one of the most promising solutions to mitigate the problem of global warming. In fact, in Japan, the amount of waste heat is as much as a half the amount of primary energy.1) For the recovery of waste heat generated locally and periodically, new thermal energy storage (TES) technologies are strongly required, because conventional methods for steam generation from waste heat is not available in long-distance heat transport and long-term heat storage. TES technologies can be classified into six types: (1) sensible heat utilization, (2) latent heat utilization, (3) chemical energy utilization, (4) thermoelectric device, (5) utilization of different concentration, (6) utilization of photochemistry reaction. In this classification, Sensible Heat Storage (SHS) is regarded as the most conventional technology and Latent Heat Storage (LHS), as second one (see Table 1).

In SHS, a temperature difference of a solid or a liquid such as brick, rock, or water is utilized; however, the low density of thermal storage is unsuitable for realizing the efficient use of energy presently. In contrast, LHS using a phase-change material (PCM) such as paraffin, fatty acid, and molten salt affords many advantages such as (1) large density of thermal storage, (2) change from periodically emitted heat to constant-temperature heat source, and (3)

<table>
<thead>
<tr>
<th>Heat storage methods (Difficulty)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Utilization of sensible heat (Most Easy)</td>
<td>Utilization of temperature difference of solid or liquid. As an example, heating a brick by blast furnace gas is well known.</td>
</tr>
<tr>
<td>2. Utilization of latent heat (PCM) (Comparatively Easy)</td>
<td>The production of ice as cold storage at nighttime for a reasonable cost of electric power is practical. The energy can be successfully stored during the melting of the solid. Paraffin, organic materials, etc., can be phase change materials (PCMs).</td>
</tr>
<tr>
<td>3. Utilization of chemical reaction heat (Under Development)</td>
<td>A) Utilization of reversible reaction: Ca(OH)2 + CaO + H2O, reversible storage alloys, composition and decomposition of methanol, etc., has been carried out. B) Irreversible reaction: direct heat storage by endothermic reactions such as C + H2O → CO + H2, CaCO3 → CaO + CO2 is under development from co-production.</td>
</tr>
<tr>
<td>4. Thermoelectric conversion (Under Development)</td>
<td>Thermoelectric couple, BiTe, SiGe, Mg2Si, etc., can be used.</td>
</tr>
<tr>
<td>5. Utilization of different concentrations (Less Easy)</td>
<td>The concentration-dilution of sulphuric acid solution is one example.</td>
</tr>
<tr>
<td>6. Utilization of photochemistry (Least Easy)</td>
<td>The photochemistry of anthracene is promising.</td>
</tr>
</tbody>
</table>
repeatable utilization without degradation. LHS has been widely applied in building materials,1–18) free cooling,19–22) electronics cooling,23–34) solar water heating,35–42) solar power generation,43–49) and waste heat utilization.50–56) However, recent LHS technologies for the recovery of relatively high-temperature waste heat such as combustion off-gas have not been studied in detail despite their large potential. Therefore, this paper outlines the trends in recent technologies for LHS using PCM on the basis of papers published from 2001–2009; in addition, it introduces a state-of-the-art LHS technology for high-temperature (over 100°C) applications, in which a large amount of energy can potentially be saved, as suggested by exergy theory. New technologies such as solid–solid PCM, encapsulation of PCM, composite solar power generation using LHS, and waste heat recovery system are reviewed.

2. Latent Heat Storage

2.1. LHS and SHS

LHS is based on heat storage or release when a PCM undergoes a phase change from solid to liquid or solid to solid or vice-versa. Figure 1 shows a comparison between SHS and LHS from the viewpoint of heat storage capacity, in which the cumulative heat storage capacity of both SHS and LHS was compared in the temperature range from 250–350°C. Here, as one example, KNO3/NaNO2/NaNO3 (53/40/7 wt%),45,57) also called HTS,57) was selected as a typical SHS material, and NaNO3 with two points of phase change at 276°C (transformation)45) and 307°C (fusion) was selected as reference PCM.

The capacity of SHS is given by the following equation:

\[ Q = \int_{T_i}^{T_f} mC_p dT = mC_p(T_f - T_i) \]  \hspace{1cm} (1)

Here, the temperature difference is quite important. The capacity of LHS with a solid–liquid PCM is given by the following equation:

\[ Q = \int_{T_i}^{T_f} mC_p dT + mL + \int_{T_i}^{T_f} mC_v dT \]

\[ = mC_p(T_f - T_i) + L + mC_v(T_f - T_i) \]  \hspace{1cm} (2)

Here, the value of latent heat is much more important as compared to the temperature difference. Figure 1 shows the contribution of latent heat to the capacity of energy storage. In this example, the heat storage capacities of LHS and SHS are 396 and 157 kJ/kg, respectively. In addition, PCM can transform intermittently emitted thermal energy into a constant-temperature heat source, because it can store and release a large amount of thermal energy at a constant temperature at the melting point during phase change (see Fig. 1). Basically, PCM can be used repeatedly semi-permanently without degradation.

2.2. Required Conditions for PCM

According to literature,11,59–64) commercially available...
PCMs should possess the following 23 properties; these properties can be classified into four categories.

2.2.1. Thermal Properties

(1) Suitable phase change temperature, (2) large latent heat, (3) large specific heat, (4) large thermal conductivity in both solid and liquid phases, (5) rapid heat transfer,

2.2.2. Kinetic or Physical Properties

(6) large density, (7) small volume change during phase change, (8) low vapor pressure, (9) no supercooling, (10) sufficient crystallization rate, (11) favorable phase equilibrium,

2.2.3. Chemical Properties

(12) long-term chemical stability, (13) compatibility with construction and container materials, (14) completely reversible freeze/melt cycle, (15) no chemical decomposition, (16) no fire hazard, (17) non-toxic, (18) non-flammable, (19) non-explosive, (20) no chemical decomposition,

2.2.4. Economic Factors

(21) abundant, (22) available, and (23) cost effective.

2.3. Classification of PCM

Figure 2 shows the classification of PCMs into single- and multi-component materials, together with examples of the melting points and applications of the proposed PCMs.47,58,61,65,66) The tree-like classification diagram shows that single-component materials include organic and inorganic materials; organic PCMs include paraffins and non-paraffins such as fatty acid and sugar alcohol, and inorganic PCMs include hydrates, molten salts, and metal.

In general, paraffins (the most popular PCM), fatty acids, and hydrates have a low phase-change point. Many PCMs have been applied in building materials and solar heaters, and their thermophysical properties have been studied in detail.11,59,61,67) In general, sugar alcohols such as erythritol and mannitol have a phase-change point of over 100°C. Recently, erythritol with a melting point of 118–119°C has been reported as a promising new PCM for applications in solar cookers64,68) and for the recovery of waste heat at relatively low temperatures under 200°C.53–56)

Molten salts were the most popular PCMs, and they had a high phase-change point. In addition, several metallic materials have been proposed as PCMs with high phase-change points,52,66) for applications in solar power generation systems and for the recovery of waste heat at relatively high temperatures over 200°C. Table 2 lists the thermophysical properties of the proposed PCM candidates for high-temperature applications over 100°C. Here, sugar alcohols, molten salts, and metallic were selected.46,49,52,56,58,61,66,69)

3. Recent Trend in LHS Technology

Figure 3(a) shows the changes in the number of papers published annually on PCM. We found that LHS using PCM has attracted considerable attention in recent years, especially after 2005. In fact, the number of papers increases considerably at the rate of 40%/year. This corresponds to the increasing recent focus on promoting energy saving and utilizing renewable energy such as solar energy. Figure 3(b) shows the distribution of papers published from 2001–2009 against the phase-change temperature of PCM. The fig. suggests that studies on PCMs with phase-change points of 20–60°C were predominant in all years. However, a careful observation revealed that in 2006 or later, there was a gradual increase in the number of papers reporting on PCMs with phase-change points over 100°C. This implies that some researchers shifted their focus from everyday applications to industrial ones. In fact, waste heat emitted
from steelworks has more enthalpy at lower temperature but more exergy at a higher temperature over 100°C.

Table 3 lists frequently selected keywords from the collected papers. Papers on LHS and PCM frequently used general keywords such as “phase-change material”, “PCM”, “thermal energy storage”, and “latent heat”. Apart from these, interestingly, “solar energy” was also frequently used; these papers dealt with PCMs that can store solar energy through melting for various utilities. Keywords such as “phase-change composites”, “thermal conductivity”, “shape-stabilized” should be noteworthy in that these are related to general problems encountered during the use of PCMs, that is, capsulation and low thermal conductivity.

4. Recent Advancements in LHS Technology

4.1. PCM Capsules

Generally, because LHS mainly utilizes the phase change between solid and liquid, the encapsulation of the PCM is necessary to avoid the leakage of a liquid PCM. In addition, Regin et al. noted the functions and requirements of PCM containment: (i) meeting the requirements of strength, flexibility, corrosion resistance, and thermal stability; (ii) acting as a barrier to protect the PCM from harmful interactions with the environment; (iii) providing a sufficient surface for heat transfer, and (iv) providing structural stability and easy handling. PCM capsules are classified into macro- and microcapsules.

Macrocapsules are the most conventional PCM capsules, and many papers have reported various shell materials such as metal and plastics, and various shapes such as spherical and cylindrical. In contrast, micro-encapsulation of PCM has recently attracted considerable attention because it reduces the reactivity of the PCMs with the outside environment, increases the heat transfer area of the PCMs, and enables the core material to withstand frequent changes in the volume of the storage material during phase change.

Table 4 lists trends in manufacturing methods for PCM capsules. Many papers have reported the production of various microcapsules, and the manufacturing methods, core PCM materials, shell materials, thermophysical properties, and capsule sizes of the same have been studied. Micro-interfacial polymerization, in-situ polycondensation, and complex coacervation are the most popular microen-
capsulation methods. Here, organic PCMs with melting points under 100°C were usually used for microencapsulation, except in the case of No. 8.

In contrast, Maruoka and Akiyama proposed the encapsulation of spherical metal PCMs such as Cu and Pb with an electroplated Ni layer to recover industrial high-temperature waste heat such as combustion offgas. The PCM spherical capsule with Ni coverage provided hybrid functions of both heat storage and catalysis. Nickel worked well as a catalyst of the gas phase reaction $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$ at 1000°C.

In summary, the encapsulation of low-temperature PCMs is a state-of-the-art technology; in particular, the development of micro-encapsulated PCMs is becoming increasingly popular, whereas the encapsulation of high-temperature PCMs is less popular despite its engineering importance. In the near future, it is expected that easily producible, encapsulated, high-temperature PCMs with large thermal density will be developed.

### 4.2. Solid–Solid PCM

Generally, LHS utilizes the latent heat between solid–liquid phases; thus, it requires the PCM to be encapsulated in order to prevent the liquid PCM from leaking. However, the capsule lowers the overall density of heat storage of the LHS medium and increases the production cost. To overcome these problems, solid–solid transformed PCM (SSPCM) has been proposed. Figure 4 shows a comparison between PCM and SSSPCMs. SSSPCMs are quite simple, and it affords advantages such as easy handleability and cost effectiveness because it does not use a liquid PCM; therefore, there is no risk of leakage and in turn, there is no need for encapsulation. Table 5 lists recently published papers on SSSPCMs, together with the proposed structure materials and solid–solid phase-change temperatures and latent heat.

Many papers have reported that organic SSSPCMs based on polyethylene glycol and polyurethane can be easily prepared, and mainly, their thermophysical properties have been examined. Steinert et al. prepared symmetrical dialkyl ammonium salts as SSSPCMs. The phase-change point of the new organic SSSPCMs were all under 100°C. In contrast, Nishioka et al. prepared an iron-based metal alloy as an SSSPCM to recover waste heat at high temperature, and mainly investigated its thermophysical properties and oxidation resistance. They increased the latent heat successfully by controlling the alloy composition and the structural or magnetic transformation alloy.

### Table 4. Research trends in encapsulation methods for PCM.

<table>
<thead>
<tr>
<th>No.</th>
<th>Author/Year</th>
<th>PCM</th>
<th>Capsule material</th>
<th>$T_m$ [°C]</th>
<th>$L$ [kJ/kg]</th>
<th>Classification</th>
<th>Size [µm]</th>
<th>Encapsulation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Y. Fang et al. (2008)</td>
<td>n-octadecane (L: 232.3kJ/kg)</td>
<td>Polystyrene</td>
<td>Close to PCM</td>
<td>124.4</td>
<td>Microcapsule</td>
<td>0.1-0.123</td>
<td>Ultrasonic-assistant miniemulsion in-situ polymerization</td>
</tr>
<tr>
<td>4</td>
<td>X. X. Zhang (2005)</td>
<td>n-octadecane ($T_m$: 36.7°C; L: 232kJ/kg)</td>
<td>Urea/melamine/ formaldehyde polymer</td>
<td>36.5</td>
<td>167</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-nonadecane ($T_m$: 41.3°C; L: 233kJ/kg)</td>
<td>-</td>
<td>29.3-41.6</td>
<td>161</td>
<td>-</td>
<td>-</td>
<td>In situ polymerization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-eicosane ($T_m$: 47.0°C; L: 242kJ/kg)</td>
<td>-</td>
<td>45.3</td>
<td>172</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>L. Xing et al. (2006)</td>
<td>Paraffin ($T_m$: 17.0°C; L: 222.0kJ/kg)</td>
<td>Silica gel polymer</td>
<td>18.55-22.60</td>
<td>24.94-153.46</td>
<td>Microcapsule</td>
<td>-</td>
<td>In situ polymerization</td>
</tr>
<tr>
<td>6</td>
<td>S. Qingwen et al. (2007)</td>
<td>Bromo-hexadecane ($T_m$: 17-18°C) with silver nanoparticle</td>
<td>Aminoplast</td>
<td>-</td>
<td>-</td>
<td>Microcapsule</td>
<td>-</td>
<td>In situ polymerization</td>
</tr>
<tr>
<td>7</td>
<td>H. Zhang, X. Wang (2009)</td>
<td>n-octadecane ($T_m$: 28.41°C; L: 214.6kJ/kg)</td>
<td>Resorcinol-modified melamine/formaldehyde</td>
<td>26.49-27.11</td>
<td>93.71-146.5</td>
<td>Microcapsule</td>
<td>20</td>
<td>In situ polymerization</td>
</tr>
</tbody>
</table>
In summary, many SSPCMs have been proposed thus far; while these offer advantages such as absence of leakage, their latent heat is one order smaller than that of liquid–liquid PCMs. This is a major drawback that should be addressed in the future. Metal alloys of PCMs are also expected to be applied in stationary systems, such as structural materials with heat storage function, because they have a small latent heat based on the weight, but a large latent heat based on the volume. This implies that they are suitable for energy storage at the same location but unsuitable for energy transportation.

4.3. PCM Composites

As mentioned above, PCM capsules have drawbacks with regard to their heat storage capacity. The heat storage density of LHS mediums decreases due to the layer of the capsule; in addition, the encapsulation of the PCM increases the production cost. In contrast, the thermal conductivity of non-metallic PCMs such as paraffin and molten salts is small, and this decreases the heat exchange rate in LHS systems. Recently, PCM composites, a mixture of various materials and PCMs, have been proposed; these have an advantage in that no encapsulation is required. Table 6 lists trends in research on PCM composites, together with the thermophysical properties and production methods of the proposed materials. The reported methods for the production of PCM composites can be classified into four types: (1) impregnation/infiltration (with/without vacuum process), (2) dispersion or kneading, (3) compression, and (4) electro-spinning.

The impregnation of PCM with porous materials is the most popular method for producing PCM composites. By using the composites repeatedly, the leakage of the liquid PCM from a porous structure was successfully prevented due to the capillary and surface tension forces. This method can be used to easily produce LES mediums with large thermal conductivity and large porosity, such as porous graphite materials and various porous metals. For applications in building materials and high-temperature processes, porous ceramics such as expanded perlite and vermiculite have also been reported.

Dispersion and kneading methods are relatively easy as well. Added materials such as graphite powders are mechanically dispersed within the molten PCM or mixed with solid PCM powders at room temperature and then melted. The cold compression method is also very simple. In this method, PCM and added powders are first mixed and then compressed at room temperature. Pincemin et al. prepared composites made of graphite and eutectic mixtures of NaNO3/KNO3 for solar thermal power plants. In this system, infiltration, compounding (dispersion), and cold compression were carried out. They concluded that the cold-compressed composite exhibited highly anisotropic properties and a strong improvement in thermal conductivity.

The electrospinning method is a nano- and micro-fiber manufacturing technique. Chen et al. prepared foam-stable PCMs of ultrafine fibers. This is noteworthy as a new method from the viewpoint of nanostructures.

4.4. Solar Power Generation System

Recently, solar power generation systems, which use solar energy to generate electric power, have attracted attention worldwide. A system called “Sunbelt” that was built in semiarid desert areas has been found to be quite economical. It can now be applied to a large-scale energy system. We have found that the LHS system can be applied to a solar power generation system. Table 7 lists trends in recent research on the LHS system for a solar power generation system. The DISTOR project is partly funded from the EC Sixth Framework Program with 13 partners from five countries. The aim of this project is to develop the PCM-
storage systems for steam generation at pressures between 30 bars and 100 bars corresponding to saturation temperatures between 235°C and 310°C. The storage system should have the extension of charging/discharging cycles over several hours.48) Figure 5(a) shows the basic concept of the integration of thermal energy storage and solar thermal parabolic trough power plants using direct steam generation (DSG) technology. Here, the thermal storage block was filled with PCM. Thermal energy from the sun was collected by a solar field via the melting of PCM and it was then used to produce steam to generate electric power.

Morisson et al.44) practically evaluated the DSG technology with an LHS system for electricity generation. To improve the low thermal conductivity of PCM, Pincemin et al.47,49) studied the possibility of using composites made of graphite and eutectic mixtures of NaNO3/KNO3. These were prepared by three different methods—impregnation, dispersion, and cold compression—using different graphite powders. These researches were carried out as part of the DISTOR project.

On the contrary, Hoshi et al.43) investigated the suitability of a PCM with a high melting point of 200–1000°C. The

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Table 6. Recent research direction of PCM composites together with their thermophysical properties and production methods.95-100)

<table>
<thead>
<tr>
<th>No.</th>
<th>Author/Year</th>
<th>Composite</th>
<th>Tm [°C]</th>
<th>L [kJ/kg]</th>
<th>Thermal conductivity [W/m K]</th>
<th>Production method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Y. Shinya, T. Imaizumi (2005)</td>
<td>H2(C12H22O11NaCl Li2CO3) (Porous metal C8, Al and carbon steel)</td>
<td>0 (H2O) 28 (Oxideanode), 333(H2O) 243 (Oxidetode), 723 Li2CO3, 800 (NaCl) 556 (Li2CO3), 483 (NaCl)</td>
<td>-</td>
<td>-</td>
<td>Impregnation</td>
</tr>
<tr>
<td>2</td>
<td>K. Laflè et al. (2007)</td>
<td>Paraffin was/Al foam</td>
<td>25.5–28.9 (Paraffin) 155–157.5 (Paraffin)</td>
<td>0.15–0.25 (Paraffin) 2.8 (Al foam, e=0.966) -7.5 (e=0.884)</td>
<td>Infiltration</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>A. Kanapiecki, A. Sari (2008)</td>
<td>55%eutectic mixture of capric-myristic acid/45%expanded paraffin</td>
<td>21.7</td>
<td>85.40 (Melting) 89.75 (Freezing)</td>
<td>-</td>
<td>Vacuum impregnation</td>
</tr>
<tr>
<td>4</td>
<td>K. Laflè et al. (2008)</td>
<td>Graphite foam/LLI-CaF2</td>
<td>767 (LLI-CaF2) 816 (LLI-CaF2)</td>
<td>1.7–3.8 (LLI-CaF2)</td>
<td>Infiltration (Numerical simulation study)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>H. Yin et al. (2008)</td>
<td>0.9%expanded graphite/Paraffin</td>
<td>57–61 (Paraffin) 189–0.6 (2.25%expanded graphite)</td>
<td>&lt;4.676 (2.25%expanded graphite)</td>
<td>Impregnation</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>A. Naipaul et al. (2008)</td>
<td>Porous Cu/Ecosane</td>
<td>36.5 (Ecosane)</td>
<td>-</td>
<td>-</td>
<td>Impregnation</td>
</tr>
<tr>
<td>7</td>
<td>A. Kanapiecki, A. Sari (2009)</td>
<td>20%eutectic mixture of capric-myristic acid/80%Vermiculite</td>
<td>19.8</td>
<td>27.0</td>
<td>0.12</td>
<td>Vacuum impregnation method</td>
</tr>
<tr>
<td>8</td>
<td>T. Nomura et al. (2009)</td>
<td>RS5Ethylenol/175%expanded paraffin</td>
<td>118</td>
<td>294.4</td>
<td>-</td>
<td>Vacuum impregnation</td>
</tr>
</tbody>
</table>

* Composition: wt%
results indicated that molten salts such as Na$_2$CO$_3$ and NaNO$_2$ and some metals such as Zn were the most promising.

Guo et al. reported numerical simulations and parametric analysis of DSG with PCM and radially distributed aluminum foils for heat transfer enhancement, and they revealed that the added aluminum foils were effective for efficient heat transfer.

### 4.5. Recovery of Waste Heat

PCM stores or releases thermal energy at a constant temperature during phase change, in which periodically emitted thermal energy such as waste heat can be changed into a constant-temperature heat source. Most PCM systems are usually located in the same place without transport; however, a transportation system for PCM using industrial waste heat over a long distance has been industrialized for everyday use.

#### Table 8: Recent research direction of studies on solar power generation systems with LHS

<table>
<thead>
<tr>
<th>No.</th>
<th>Author/Year</th>
<th>PCM</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A. Hoshi et al.</td>
<td>Various organic metals, single molten salts and metal</td>
<td>To investigate the suitability of PCM with high melting point.</td>
</tr>
<tr>
<td></td>
<td>(2005)</td>
<td>(T$_{m.p.}$: 300–1300K)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>W. D. Steinmann, R. Tamme</td>
<td>KNO$_3$/NaNO$<em>2$ systems (T$</em>{m.p.}$: 230°C)</td>
<td>To investigate the basic concepts of latent heat storage for solar steam systems and to demonstrate a storage system using steam provided by parabolic trough collectors.</td>
</tr>
<tr>
<td>3</td>
<td>R. Tamme et al.</td>
<td>Pure nitrates and nitrite salts. (T$_{m.p.}$: 133–337°C)</td>
<td>To select the suitable PCM and to introduce design concept of latent heat storage system for solar thermal power generation and high temperature process heat.</td>
</tr>
<tr>
<td>4</td>
<td>S. Pinzington et al.</td>
<td>Eutectic mixtures of KNO$_3$/NaNO$<em>2$ (T$</em>{m.p.}$: 220°C)</td>
<td>To develop new composite made of salts or eutectics and graphite flakes.</td>
</tr>
<tr>
<td>5</td>
<td>V. Morisson et al.</td>
<td>Binary eutectic KNO$_3$/NaNO$_2$ system</td>
<td>To develop a detailed mathematical model of heat transfer and fluid flow for design and optimization.</td>
</tr>
<tr>
<td>6</td>
<td>C. Guo et al.</td>
<td>KNO$_3$/NaNO$<em>2$ (T$</em>{m.p.}$: 220°C)</td>
<td>Numerical simulation and parametric analysis to accelerate heat release process on direct steam generator with PCM.</td>
</tr>
</tbody>
</table>

Table 8 summarizes the trends in research on the recovery of waste heat using PCM. A waste heat transportation system using PCM has been proposed recently, in which a mobile latent heat accumulator recovers industrial waste heat and distributes it over wide areas from the heat source. Industrial waste heat was compactly stored in the form of latent heat by melting the PCMs, and it was then transported to office buildings, hospitals, hotels, etc. Kaizawa et al. systematically studied a waste heat transportation system called the Trans-Heat (TH) system. Figure 6 shows schematic diagrams of the TH system and heat transportation container with direct-contact heat exchanger: the direct-contact heat exchanger was suitable for transportation from the viewpoint of light weight, large thermal storage density, and high heat exchange rate. First, they revealed that sodium acetate tri-hydrate (T$_{m.p.}$: 58°C) and erythritol (T$_{m.p.}$: 118°C) can be used as PCMs for the system; in particular, when using erythritol as a PCM, hot water over 90°C was generated to run an adsorption chiller, and finally, cold water was supplied for air-conditioning. Second, they performed experiments of heat storage and release using erythritol to observe the heat and fluid flows within a heat transportation container by bench-scale experiments. Third, they evaluated the proposed system from the viewpoint of energy requirements, exergy loss, and CO$_2$ emissions. Those in the proposed system were less than 20% of the conventional system based on the combustion of fossil fuels.

Takahashi and Higashi studied a waste heat transportation system using a PCM storage cassette, and discussed the use of erythritol as a heat medium in a lab-scale reactor. In their experiments, a storage cassette was charged with 400 kg of erythritol and the heat transportation system using the PCM was investigated. Heat transportation systems have been practically applied in Japan. In contrast, Hauer and Storch and Martin and Setterwall noted that PCM-based transportation systems are too expensive as compared to other heat supplying systems such as heat transportation systems using hot water or zeolite.

Maruoka et al. proposed a system for recovering waste heat at high temperatures over 1 000°C, such as converter offgas (LDG), in which spherical PCM capsules were used.
A copper ball was easily encapsulated by nickel. Figure 7 shows a schematic diagram of this system. In this system, intermittent waste gas was stored by the PCM, and then, the stored heat was supplied to coke oven gas (COG) to induce an endothermic reaction of methane steam reforming to produce methanol. They also proposed that the stored heat was supplied for the reforming reaction from methane to hydrogen.

Although some studies of LHS system using high-temperature PCM were proposed, practical application of LHS for recovery of waste heat were still limited to low temperature range (under 200°C such as TH system). Regarding to 235–310°C in temperature, a power generation system like solar power plant has the potential to be applied to the recovery of industrial waste heat. On the contrary, we have still a large amount of high-temperature waste heat over 300°C with larger exergy, which should be recovered. For doing that, the following technologies should be developed.

First, several promising PCMs for high temperature application has been proposed, however, papers has been rarely reported on the strength of the container, the heat transfer tube, and so on against cyclic use from corrosion. Such information is a must for the practical use.

Second, heat transfer at LHS system for industrial use should be more accelerated because batch-wise operating time is short, in comparison to application using solar energy. Remember that molten salts as PCM for high temperature application have low thermal conductivity in general.

### Table 8. Recent research direction of studies on recovery of waste heat using PCM.

<table>
<thead>
<tr>
<th>No.</th>
<th>Author/Year</th>
<th>PCM</th>
<th>Kinds of heat source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N. Maruoka et al.</td>
<td>Pb (T_m: 328°C)</td>
<td>High temperature gas exhausted from industry (&gt; 727°C)</td>
</tr>
<tr>
<td>2</td>
<td>K. Nagano et al.</td>
<td>Magnesium nitrate hexahydrate/magnesium chloride hexahydrate</td>
<td>Urban waste heat from emerged co-generation systems (60–100°C)</td>
</tr>
<tr>
<td>3</td>
<td>N. Maruoka, T. Akiyama</td>
<td>Copper (T_m: 1083°C)</td>
<td>High temperature gas exhausted from the steelmaking converter (&gt; 1600°C)</td>
</tr>
<tr>
<td>4</td>
<td>A. Kaiwara et al.</td>
<td>Various sugars (T_m: 93–172°C) Sodium acetate trihydrate (T_m: 58°C)</td>
<td>Industrial waste heat at low temperature (&lt; 200°C)</td>
</tr>
<tr>
<td>5</td>
<td>A. Kaiwara et al.</td>
<td>Erythritol (T_m: 118°C)</td>
<td>Industrial waste heat at low temperature (&lt; 200°C)</td>
</tr>
<tr>
<td>6</td>
<td>A. Kaiwara et al.</td>
<td>Erythritol (T_m: 118°C) Sodium acetate trihydrate (T_m: 58°C)</td>
<td>Industrial waste heat at low temperature (&lt; 200°C)</td>
</tr>
<tr>
<td>7</td>
<td>K. Takahashi, Y. Higashi</td>
<td>Erythritol (T_m: 119°C)</td>
<td>Industrial waste heat at low temperature (&lt; 200°C)</td>
</tr>
</tbody>
</table>

Fig. 6. (a) Schematic diagrams of waste heat transportation system and container truck for heat storage or release. (b) Trans-heat container.55)
For enhancing heat exchange rate, cost-effective fabrication of PCM composites and PCM capsules having high thermal conductivity is strongly required. Moreover, micro-encapsulated PCMs with melting point of high-temperature is attractive due to rapid heat exchange as well as heat transportation medium. Although these have already studied for low temperature PCM, we have been rarely reported on high temperature one.

Third, note that high temperature waste heat in one industry can proceed to chemical reactions in other industries. In this case, PCM should be designed as catalyst in addition to heat storage material. This technology which proposed and studied by Maruoka et al.30,52 should be studied more deeply.

Based on the technologies abovementioned, LHS technologies extend from low temperature application to high temperature one, gradually.

5. Conclusions

LHS technologies reported in papers published from 2001–2009 were reviewed. First, a comparative analysis between LHS and SHS, and the required conditions for and classification of PCM were presented. Then, the trend in recent LHS technologies was discussed, and finally, recent advancements in LHS technology were summarized from the viewpoints of PCM capsules, solid–solid PCMs, PCM composites, solar power generation systems, and waste heat recovery. We hope that this review of recent LHS technologies will pave the way for promoting the efficient use of energy in high-temperature industries such as the steelmaking industry.

Nomenclature

\( m \): Mass (g)
\( C_p \): Specific heat (J/g K)
\( C_{p,s} \): Specific heat of solid PCM (J/g K)
\( C_{p,l} \): Specific heat of liquid PCM (J/g K)
\( T \): Temperature (K)
\( T_m \): Melting point (K)
\( T_i \): Initial temperature (K)
\( T_f \): Final temperature (K)
\( L \): Latent heat (J/g)

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