

Thermal energy storage with tunable melting point phase change materials

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ABSTRACT

Thermal energy storage systems that rely on the latent heat of fusion of a phase change material (PCM) for enhanced performance are typically constrained by the fixed melting point of the PCM. This constraint is particularly evident in power plant cooling applications. In this application, the PCM absorbs excess heat from the process steam during the comparatively hot day and then regenerates during the comparatively cold night. The time shifting of the heat transfer provides a colder sink temperature to the steam during the hours of peak demand, which in turn increases the efficiency of the power plant. However, the utilization of PCMs latent heat is highly dependent on the melting point of the selected PCM and the ambient temperature. The selection of a low melting point PCM provides higher efficiency if the night time ambient temperature is sufficiently low to regenerate the PCM; however, it is likely that an aggressively low melting point PCM may not be completely regenerated during warmer seasons where the nighttime temperature fails to fall below the melting point of the PCM. Consequently, the choice of a fixed melting point PCM limits the optimally performance to one season in the power plant cooling application. In this research, Advanced Cooling Technologies, Inc. has developed a technique to control the melting point of a calcium chloride hydrate PCM. A bench scale test facility was designed to tune the hydration level in the PCM and further control the phase transition temperature of the PCM. Testing results show that the lower-melting point $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (29 °C) can be tuned to a higher melting point $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (39 °C) by removing moisture with dry air flow. This process can be reversed by adding liquid water. Properties of the PCMs before and after the tuning processes were characterized to verify that the tuning process is controllable and reversible. Our system level models indicate that the melting point tunability feature can further save up to 1.6% of energy in the power plant cooling application when year-round usage is considered.

KEY WORDS: Thermal storage, Energy efficiency, Thermophysical properties, Phase change material, Melting point, Power plant cooling.

1. INTRODUCTION

The air-cooled condensers (ACCs) market for power generation has increased during the past decades due to the restrictions and regulations on water usage for wet cooling. While ACCs may reduce power plant water withdraw, it may also decrease overall efficiency of the power plant, due to the operation temperature of steam condenser associated with ambient air temperature. [1] On an extremely hot day, for example, the condenser temperature may rise above its design condition, thus the power generation by the steam turbine is decreased. Therefore, the levelized cost of electricity (LCOE) of a power plant with ACCs is generally higher than that of wet-cooled power plant, especially in hot weather.

To supplement the performance of ACC for power plant cooling, Advanced Cooling Technologies, Inc. (ACT) is working on a supplemental thermal storage and cooling system to enable power plants to maintain their high efficiency even in hot seasons, [2] as presented in Fig. 1. This supplemental cooling system relies on the latent heat of fusion of selected PCM, with the melting process removing heat from steam during the comparatively hot day via a steam-to-PCM thermosyphon, and the freezing process releasing heat to cool ambient air at night via a PCM-to-air thermosyphon and air-side fins. Finned thermosyphons passively charge (from steam) and discharge (to ambient air) the PCM, so that the operation cost of the system can be minimized without power

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requirement. In order to utilize the day-night temperature difference, the PCM should be melted during the hot day and frozen during night; i.e., the melting point of the PCM should be in a proper temperature range depending on the geographical location of the power plant applications. This system can either be used in series or parallel with an existing ACC or be sized to replace it.

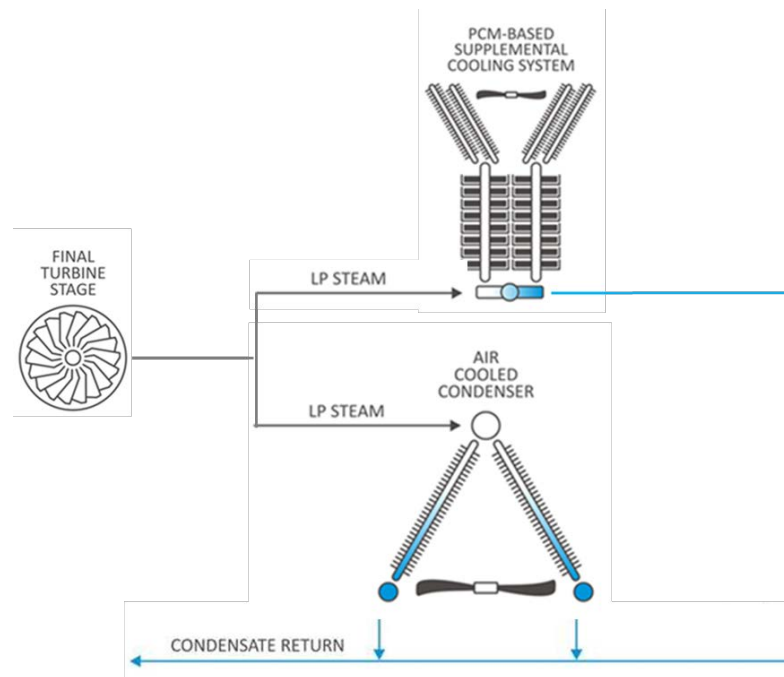


Fig. 1 ACT's supplemental cooling system based on PCM and thermosyphon.

One of the challenges for this supplemental cooling system is that in hot climate when the temperature at night can remain high, if the temperature required for resolidification of the PCM (melt temperature) is lower than the ambient temperature at night, the PCM will not be able to reject the heat to the ambient, thus would not be regenerated. The use of multiple PCMs is a potential solution, [3] where thermal energy storage materials can be chosen to melt or solidify in a wide temperature range. In that case, part of the PCM can be engineered with high melting point so as to be regenerated even if during hot nights. However, this option would decrease the overall storage capacity of the energy storage system and efficiency of the power plant, such that a larger amount of PCMs and a larger storage tank will be required for a mixture of PCMs having different melt temperatures.

In this paper, a flexible thermal storage system in which PCMs are tuned to different melting points to accommodate the different temperature profiles across various weather is investigated. CaCl_2 -based PCM is selected for the thermal storage system. By controlling water content of the salt hydrate, the melting point can be tuned between 29°C and 39°C , in term of fitting the supplemental cooling applications in different weather conditions and climate zones.

2. MATERIALS AND METHODS

Calcium chloride hexahydrate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and strontium chloride hexahydrate, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was purchased from Sigma-Aldrich. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was tested by differential scanning calorimetry (DSC) to determine its thermal performance during melting and freezing before being investigated for tunability, with 3% $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ mixed as the nucleating agent to promote the freezing process and suppress the subcooling. Distilled water was supplied by ACT.

The tunability test was performed in a PCM chamber designed for tuning water content of the PCM using dry or moist gas flow. As shown in Fig. 2, the PCM chamber is built in with PCM temperature measurement, air

temperature and humidity censoring before and after passing PCM chamber, and temperature control of the chamber by water loop from a chiller. In operation, PCM is charged to submerge thermocouples, and gas with controlled humidity is passed through the chamber. The PCM is melted and stirred with a magnetic stirrer in order to maximize the mass transfer of moisture to air flow, so that the water content in the PCM can be tuned, and so the thermophysical properties of the PCM. The thermophysical properties of the PCM before, after, and during the tuning process are tested with DSC.

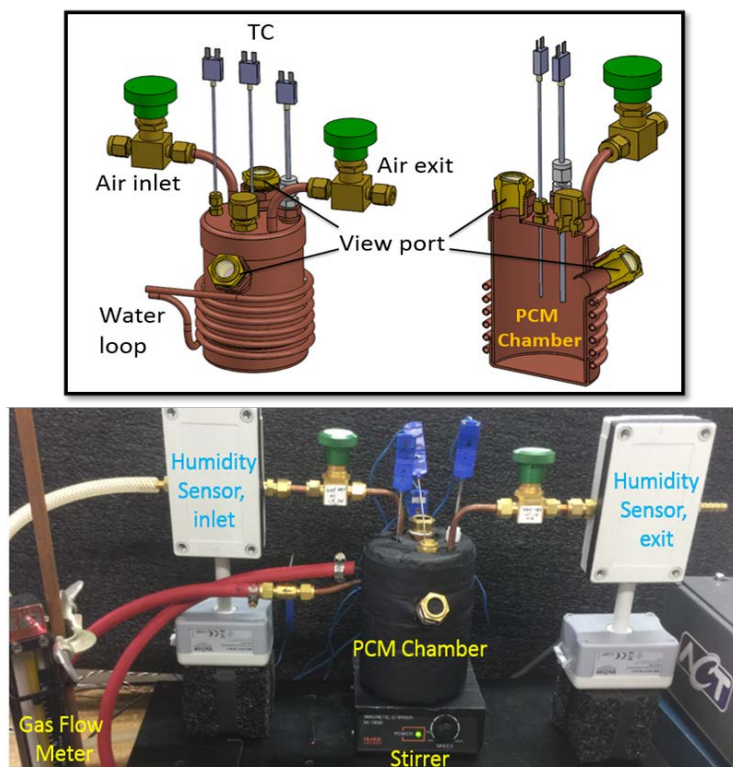


Fig. 2 Schematic (top) and photo (bottom) of the PCM tunability testing facility.

3. RESULTS AND DISCUSSION

PCMs with different phase transition temperatures are required to extend the functional temperature range of the supplemental cooling system. Salt hydrates with tunable melting points in low temperature ranges (20 °C – 45 °C) are excellent candidates to address the need without increasing storage volume and decreasing overall storage capacity. Calcium chloride hydrate is one such promising material and is inexpensive, has a relatively high latent heat, and is environmentally friendly. Calcium chloride hydrate crystallize in different hydrates forms with different hydrate number and possess different melting points. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ melts around 29 °C,[4,5] and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ melts at 39 °C;[6] both of them have relatively high latent heat and thermal conductivity, as listed in Table 1. For a given thermal storage duty within a temperature range swing around the melting point, the size requirements of both storage systems are similar. Therefore, the phase transition temperature of the PCM can be tuned by controlling the hydrate number of the salt hydrate without significant affecting the thermal storage performance.

Table 1 Key thermophysical properties of selected calcium chloride hydrates.

Phase Change Materials	Density	Melting Point	Latent Heat	Specific Heat
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1.71 g/cm ³	29 °C	170-192 kJ/kg	1.42 kJ/kgK
$\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$	1.83 g/cm ³	39 °C	158 kJ/kg	1.34 kJ/kgK
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1.85 g/cm ³	175 °C	n.a.	n.a.

The hydrate number of the salt hydrate is manipulated by gas flow with controlled relative humidity. In a typical melting point tuning experiment, the temperature of the PCM chamber is maintained at 45 – 50 °C to keep the PCM melted and stirred with a magnetic stirrer. Dry air (relative humidity RH \approx 0%) is sent into the PCM chamber and exit after moisture exchange with the PCM under stirring. The relative humidity of the air flow is increased after passing through the PCM chamber due to the mass transfer of moisture from the salt hydrate. To begin with, the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is fully melted, where the water content in the melt is about 49%. The dry gas flow takes moisture away from the melt and decreases the water content of the melt. As a result, the exit flow humidity after passing the dehydrated melt is lowered comparing with that passing salt hydrate melt with higher water content. By integrating the moisture flow rate over time, the water loss from PCM can be calculated, and so the hydrate number of the PCM. The rate of dehydration can be adjusted by the temperature of the PCM chamber and air flow rate. At the end of the tuning process, water content in the melt drops from 49% in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to around 39%, relative humidity of the exit flow drops from around 40% to less than 10%, and the hydrate number of the salt hydrate drops from 6.0 to 4.0, converting $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$.

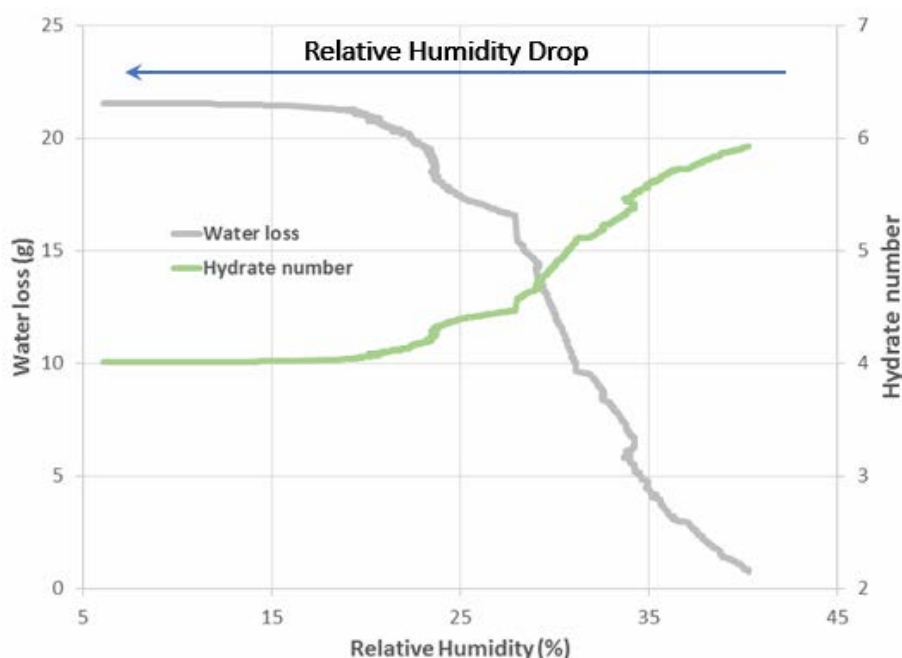


Fig. 3 The water loss and hydrate number as a function of the decrease of relative humidity during the tuning process.

The conversion between hexahydrate and tetrahydrate is also verified by DSC test of the samples taking out of the PCM chamber at different points of the tuning process. As shown in curve a in Fig. 4, the melting curve of pure $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ shows a melting process that onsets at around 29 °C. Dehydration decreases the water content of the salt hydrate melt, which crystallizes partially as $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and partially $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, the ratio depends on the degree of completion of the tuning process. Curve b and c shows the melting curve of the solidified salt hydrate at different points of the tuning process, in which sample b contains more water and therefore forms more $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, while sample c contains less water and forms more $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, the melting process of which onsets around 39 °C. The co-exist of the two hydrates is also found in the freeze-thaw curve measured *in situ* in the PCM chamber, as shown in Fig. 5. At the end of the tuning process, little amount of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is found in the melting curve d in Fig. 4, implying that most of the salt hydrate at lower water content solidifies as $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$.

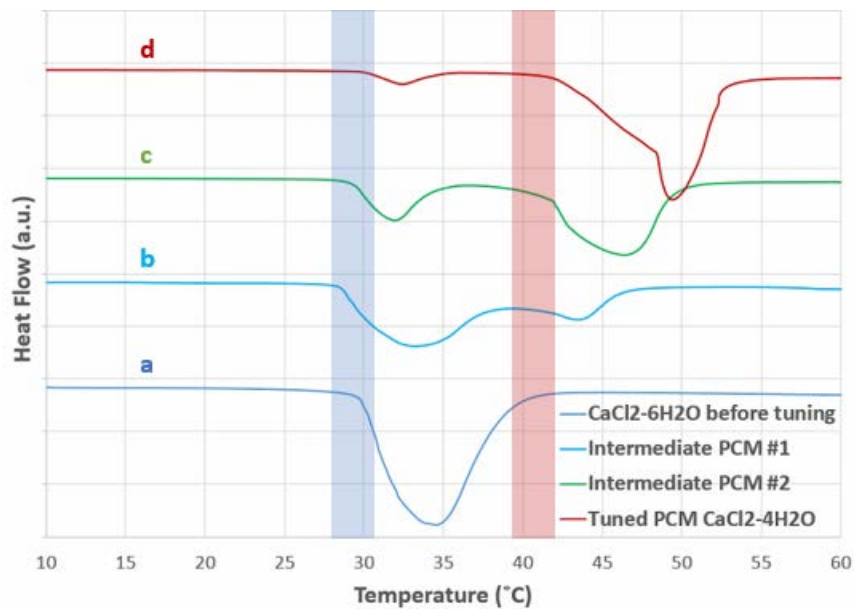


Fig. 4 DSC melting curves of the PCM at different points of the tuning process: a) in the beginning with pure $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, b) and c) with more water removed from the salt hydrate, and d) at the end of the tuning process toward $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. The blue (left) and red (right) slots show the range of expected onset temperatures of the melting process of the two salt hydrates at around 29 °C and above 39 °C, respectively.

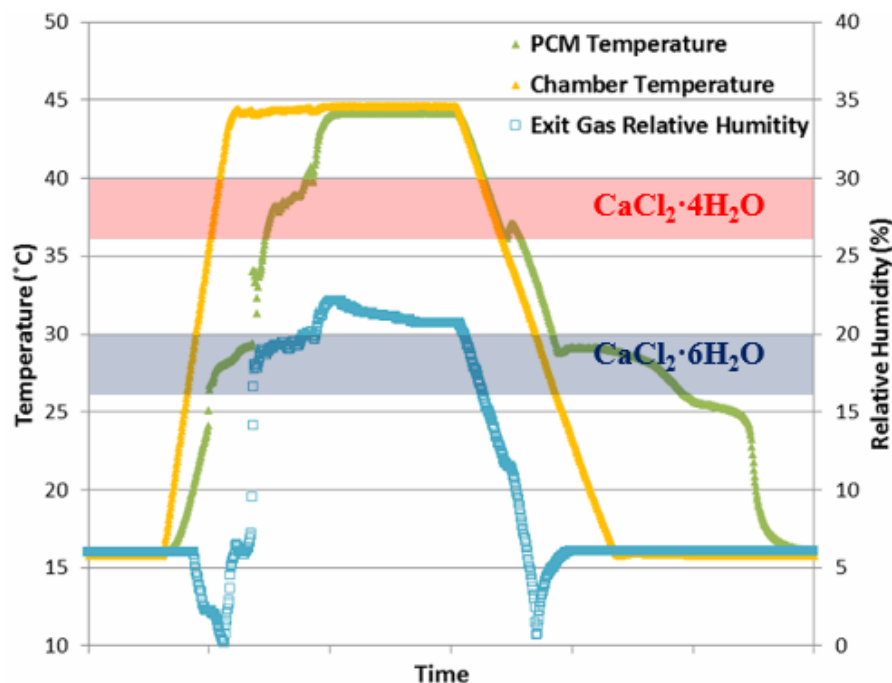


Fig. 5 The freeze-thaw curve of the salt hydrate during the tuning process. The blue (bottom) slot shows the phase transition region of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ around 29 °C, while the red (top) slot shows the phase transition region of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ around 39 °C.

The PCM supplemental cooling system is designed and developed to overcome the dry cooling power plant efficiency drop during the hot weather. [2] Different from wet cooling in which the heat is removed by evaporation of water, performance of dry cooling system for power plant highly depends on the ambient temperature. [7] During a hot summer day, it is not abnormal to find a significant efficiency and performance drop due to the lack of cooling power by hot ambient air, resulting an increased LCOE. With the use of PCM supplemental cooling system, the cooling power can be stored in the PCM during comparatively cold night and used for cooling the

steam from turbine during the comparatively hot day, thus improve the average efficiency of the power plant. Fig. 6 shows the annually average efficiency increase. ACT has developed a system level model to estimate the efficiency and LCOE of a power plant with supplemental cooling [8] modified based on the United States Department of Energy's Office of Fossil Energy National Technology Laboratory (NETL)'s Case 13 in reference [9]. Based on our calculation, using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as the PCM introduces an average efficiency increase of 1.2%, most of which come from the efficiency improvement during hot summer days.

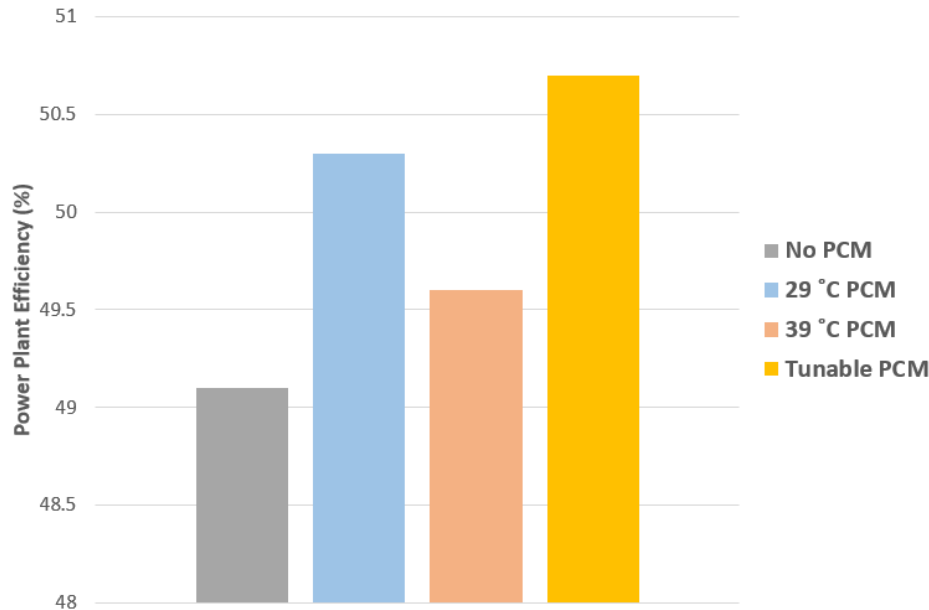


Fig. 6 Power plant annually average efficiency increase with the use of PCM supplemental cooling systems in addition to current dry cooling system.

As discussed above, the PCM supplemental cooling system is limited by the melting point of the PCM. When night temperature is not significantly lower than the melting point of the PCM, the PCM cannot be regenerated by releasing heat to ambient air, and the supplemental cooling system will lose the cooling performance during the day, which may cause significant power plant efficiency decrease and financial loss. Using higher melting point PCM may cover the performance drop during extremely hot days, but the overall efficiency is relatively low comparing with that using lower melting point PCM, due to the less heat transfer driven by smaller temperature difference between the PCM cool storage and the steam from turbine. With the use of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ as the PCM, the annually efficiency elevation (0.5%) of a power plant is estimated.

In contrast, by using the tunable PCM supplemental cooling system based on calcium chloride hydrates, the limit of operation during extremely hot day can be overcome without sacrificing system efficiency at normal weather. When weather turns extremely hot, the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ can be converted to $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ by dehydration to maintain the performance of the PCM supplemental cooling system, while $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ can be converted back to $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ when lower melting point PCM is needed for the PCM to be fully utilized. As a result, the overall efficiency of the power plant can be elevated by 1.6% by using the tunable PCM supplemental cooling system, with a 0.4% increase in addition to a supplemental cooling system without tuning $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for enhanced thermal management.

4. CONCLUSIONS

In summary, a tunable PCM system for maximizing the energy saving of supplemental cooling over a hot weather is described in this research. The tuning process from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ is achieved by dehydration of the melt salt hydrate by dry gas flow, and the reverse process can simply be completed by adding liquid water into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. The tuning process is simple and straightforward, while the saving of energy using the tunable PCM to overcome the extreme weather induced efficiency drop for dry cooled power plant is significant: it is shown that with the use of single PCM in the supplemental cooling system, the efficiency of the

power plant is expected to be increased by 1.2%; while with the tunable PCM, the efficiency can further be increased by 0.4%, giving an overall efficiency elevation of 1.6% above a dry-cooling power plant. The significant energy saving estimated potentially brings future application of the tunable PCM in power plant cooling system. Further optimization of the engineering of the tuning system as well as the PCM supplemental cooling system is under development.

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