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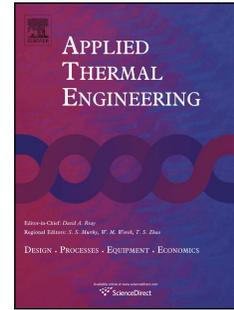
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**NEW METHOD TO EVALUATE THE HEAT STORAGE DENSITY IN LATENT
HEAT STORAGE FOR ARBITRARY TEMPERATURE RANGES**H. Mehling^{1*}, S. Hiebler², E. Günther²

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ABSTRACT

Phase change materials (PCM) are used to store heat or cold in narrow temperature intervals with high storage density. In applications with an exact temperature range, the heat storage density can be calculated straight forward and different PCM can be compared. However, in many applications no exact temperature range is known or the temperature range is not fixed. In such cases, the evaluation of the storage density and the comparison of different PCM is quite difficult and the standard approaches do not give accurate and easy to read results. In this paper we present a new method that is simple, accurate, and allows a visual evaluation of the heat storage density for arbitrary temperature ranges. This is possible by plotting the enthalpy difference in a 2-dimensional contour plot with the upper and lower storage temperatures as the two dimensions. In a second step, the temperature differences used for heat transfer, for example at a heat exchanger, can be included. This way, the new method can be used as an aid in the design of a storage and for its technical and economical optimization.

Key words: latent heat storage, PCM, enthalpy, temperature range, storage density

1. INTRODUCTION

Phase change materials (PCM) are used to store heat or cold in narrow temperature intervals with high storage density. In applications with an exact temperature range (T_{high} , T_{low}), the

heat storage density, that is the enthalpy difference $\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}})$, can be calculated straight forward and different PCM can be compared. To simplify the discussion, PCM with an ideal behaviour, that means melting, nucleation, and solidification at the same temperature, the phase change temperature T_{pc} , will be discussed first (fig. 1). In the ideal case, it is common to determine phase change temperature T_{pc} and the phase change enthalpy $\Delta_{\text{pc}}h$, where $\Delta_{\text{pc}}h$ means that a difference is calculated for the phase change only. Such data are available for many PCM [1, 2, 3]. The calculation of the heat stored between a lower temperature T_{low} and a higher temperature T_{high} , $\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}})$, is by

$$\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}}) = \int_{T_{\text{low}}}^{T_{\text{high}}} c_p(T) \cdot dT \quad (1)$$

which simplifies for the ideal case and with constant heat capacities to

$$\Delta h(T_{\text{high}}, T_{\text{low}}) = c_{p,\text{sol}} \cdot (T_{\text{pc}} - T_{\text{low}}) + \Delta_{\text{pc}}h + c_{p,\text{liq}} \cdot (T_{\text{high}} - T_{\text{pc}}) \quad (2)$$

with $c_{p,\text{sol}}$ and $c_{p,\text{liq}}$ for the heat capacity of the solid and liquid phase. Fig. 1 shows this schematically. The suitability of a PCM for heat storage can be evaluated by $\Delta_{\text{pc}}h$. In most cases however, several different PCM exist and must be compared. In that case, their tabulated values of $\Delta_{\text{pc}}h$ are compared or, when significant amounts of sensible heat are included values of $\Delta h(T_{\text{high}}, T_{\text{low}})$ are calculated. If one of the boundary temperatures, for example T_{low} , is fixed, Δh can be calculated for any T_{high} using eq. 1 and eq. 2, and then visualized in a diagram (fig. 2). This is the standard procedure und used by many authors [4, 5]. However, this procedure has several problems: the result strongly depends on the chosen value of T_{low} (fig.2), in many applications no exact temperature range is known, or the temperature range is not fixed. For example, when PCM are used in buildings to buffer indoor temperatures, there is no general temperature cycle due to variable daily temperature highs

and night lows. Another example are storages for solar heating systems, where the maximum temperature that is reached strongly depends on the solar input. As fig. 2 shows, different temperature ranges result in different PCM with the highest storage density. Further on, even when T_{low} and T_{high} are known as boundary conditions on a latent heat storage, the temperature range applicable at the storage material is reduced by the temperature differences necessary for heat exchange; these are determined by the design of the heat exchanger and thus also not initially known. In such cases, when no exact temperature range is known or when the temperature range is not fixed, the comparison of two different PCM is quite difficult. This is especially true in the case of two PCM with overlapping melting range. The current approaches to evaluate and compare the heat storage capacity, that is a simple comparison of Δ_{pCh} values or of $\Delta h(T_{high}, T_{low})$ for a small number of selected temperature ranges is too simplified to get accurate and general results.

2. OBJECTIVES

The objective of this work was to develop a simple, fast, and accurate method to evaluate and compare the heat storage density for arbitrary temperature ranges. Uncertainties in the result of a comparison should only be due to the uncertainties in the measured data; the evaluation and comparison method should not introduce additional uncertainties. Therefore, it should also be applicable to PCM with a melting range instead a melting temperature. The only restriction used in this paper is that the PCM shows no hysteresis, that means heating and cooling are described by a single $h(T)$ -function (fig.1). The new evaluation and comparison method fulfills all these criteria.

3. NEW EVALUATION AND COMPARISON METHOD

The new method comprises a first step to treat only the storage material and a second step to treat additional temperature restrictions.

In the 1st step, the evaluation of the heat storage density of the storage material alone is performed. Because the temperatures T_{high} and T_{low} are not known or not fixed, the general solution starts with calculating all values of $\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}})$ in fixed temperature steps, e.g. 1 K, for all possible values of T_{high} and T_{low} . For this calculation, $h(T)$ must be given, or it must be calculated by integrating c_p -values using eq.1. In an available standard for quality control [6] it is already required to tabulate c_p -data in fixed temperature steps, with reference to mass and additionally with reference to volume using the lowest density in the temperature range under consideration. Above calculations are easily done with any kind of spread sheet program. For the following examples, an Excel sheet was created that does all the necessary calculations automatically and requires only the $c_p(T)$ or $h(T)$ -function as input. The $\Delta h(T_{\text{high}}, T_{\text{low}})$ values are then displayed in a data table with the two temperatures levels as ordinates, which is an easy to read and accurate way of presentation. For a visual evaluation, the data can be displayed as a 2-dimensional plot, e.g. a contour plot.

In the 2nd step, when additional temperature restrictions apply, e.g. due to heat exchange, these restrictions are incorporated into the data table or into the plot.

Both steps can be done evaluating a single material, or comparing two materials. When comparing materials, the difference or the ratio of the respective $\Delta h(T_{\text{high}}, T_{\text{low}})$ values of the two materials can be used as criterion. In steps 1 and 2, the difference or the ratio then replace the $\Delta h(T_{\text{high}}, T_{\text{low}})$ value of the single material; otherwise step 1 and 2 remain unchanged.

4. EXAMPLES

The following three examples will explain the procedure and highlight the advantages of the new method. The first and second example both treat the 1st step of the new method, that is with the storage material alone without any additional temperature restrictions. They show a comparison “ideal PCM”-water and a comparison of a PCM with melting range and its

“ideal” simplification. Example 3 treats the 2nd step, when additional temperature restrictions due to heat transfer apply. It shows how these restrictions are incorporated into the data table or into the plot and how powerful the new method is.

Example 1: Comparison “ideal PCM”-water

In this example, a PCM with “ideal” behaviour, that means a sharp melting point, is compared to water as storage material. For the ideal PCM, the data used are $c_{p,sol} = 2.0$ kJ/kgK, $c_{p,liq} = 2.0$ kJ/kgK, and $\Delta_{pc}h = 200$ kJ/kg at $T_{pc} = 19.5$ °C. For water $c_{p,liq} = 4.2$ kJ/kgK is used. For the calculations, the data are calculated in steps of 1 K. The integration in eq. 1 is performed using a linear integration model such that $\Delta h(T + 1 \text{ K}, T) = h(T + 1 \text{ K}) - h(T + 0 \text{ K}) = c_p(T + 0.5 \text{ K}) \cdot 1 \text{ K}$. The interval width could of course also be chosen smaller, depending on the accuracy of available $h(T)$ or $c_p(T)$ input data and on the accuracy requirement of the problem that has to be solved. Fig. 3 shows the heat capacity data of the ideal PCM and water. Due to the discretization in 1 K-steps, the c_p -value at 19.5 °C must represent the sensible heat in that interval of 2 kJ/kg plus the melting enthalpy of $\Delta_{pc}h = 200$ kJ/kg, thus resulting in an effective c_p -value of 202 kJ/(kg·K). To evaluate and compare the heat stored in a temperature range (T_{high} , T_{low}), the heat capacity is integrated over the temperature using eq.1. Fig. 4 shows the result of the calculation with common procedure, which is a comparison of h of the ideal PCM (◆) and of water (■) using h -data with reference to a normalization temperature. For both materials, h is normalized to 0 kJ/kg at 25 °C. From these data, the heat stored between any two temperatures can be calculated using the difference between the two temperatures and the values for PCM and water can be compared. As long as T_{high} is equal to the normalization temperature, the enthalpy difference for any T_{low} is read directly from the h -axis. For any $T_{high} \neq 25$ °C the value of $h(T_{high})$ must be determined and the evaluation and comparison is at additional effort. For example, between 19 °C and 27 °C, the reading from the graph indicates

that about 220 J/g are stored. With the new method, this effort in reading the graph can be avoided. Following the new method, at first all $\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}})$ are calculated for the PCM as well as for the water. Tab. 1 shows the result of this calculation for the PCM. Because the lower temperature is by definition lower, one half of the data table is empty. Further on, for $T_{\text{high}} = T_{\text{low}}$ it follows that $\Delta h(T_{\text{high}}, T_{\text{low}}) = 0$ kJ/kg. The data table now readily shows the exact storage density $\Delta h(T_{\text{high}}, T_{\text{low}})$ in any arbitrary temperature range; for example, between 19 °C and 27 °C, exactly 216 J/g are stored. The resulting table for $\Delta h(T_{\text{high}}, T_{\text{low}})$ of water is not shown here; its calculation is straight forward. For the comparison of water and ideal PCM, the ratio of the calculated $\Delta h(T_{\text{high}}, T_{\text{low}})$ of both materials can be used. The result shows tab. 2. The data are complete, accurate, and easy to read. Tab. 2 readily indicates that, for example, between 19 °C and 27 °C, the ideal PCM stores 6.43-times as much heat as water. This results from the 216 kJ/kg for the ideal PCM (tab. 1), and from and $(27 \text{ °C} - 19 \text{ °C}) \cdot 4.2 \text{ kJ/kgK} = 33.6 \text{ kJ/kg}$ for water.

The calculated data can also be visualized, for example as contour plot (fig. 5). The contour plot readily indicates that the ratio is up to a value in the range of 40 to 50, but in a very narrow temperature range. The exact value is found in tab. 2: 48.1 from $T_{\text{low}} = 19 \text{ °C}$ to $T_{\text{high}} = 20 \text{ °C}$. This is not surprising: the phase change temperature is 19.5 °C, and from 19 °C to 20 °C the PCM stores 202 kJ/kg while water stores 4.2 kJ/kg ($202 / 4.2 = 48.1$).

Example 2: Comparison of a PCM with melting range and its ideal simplification

Today, it is possible to determine the stored heat as a function of temperature with an accuracy better than 0.5 K in temperature and better than 5 % in the heat stored [6, 7, 8, 9]. But even for PCM with a broad melting range, the measured data are often simplified: the melting enthalpy is completely attributed to a melting temperature. To discuss this case, c_p -data for a PCM with a melting range are discussed (fig. 6), where the melting enthalpy in the melting range is the

same as for the ideal PCM, as discussed before, and where the onset of melting is equal to the melting temperature of the ideal PCM. Fig. 7 shows the result of the comparison of the PCM with melting range to water using the new method and displaying the result as contour plot. The contour plot readily indicates that the ratio is now only up to a value in the range of 20 to 25. This is a dramatic change to the result close to 50 for the ideal (simplified) PCM in fig. 5. The exact value is 23.8 and therefore less than half of the value for the ideal PCM, even though both PCM data sets have the same melting enthalpy. Further on, the highest value is not reached from $T_{\text{low}}=19\text{ }^{\circ}\text{C}$ to $T_{\text{high}}=20\text{ }^{\circ}\text{C}$, but from about $22\text{ }^{\circ}\text{C}$ to $23\text{ }^{\circ}\text{C}$; this corresponds to the c_p -peak of the PCM with the melting range (fig. 6).

The comparison of both data sets is not a comparison of two real cases but a comparison of a real and an idealized case; the comparison thus shows the error introduced by the simplification. It shows that a simplification of the data with an attribution of the melting enthalpy to a melting point can result in large errors in the evaluation of the performance of the PCM.

Example 3: Treatment of additional temperature restrictions due to heat transfer

Example 3 now treats the 2nd step of the new method, which is the treatment when additional temperature restrictions apply. It shows how these restrictions are incorporated into the data table or into the plot. A very common application with additional temperature restrictions is free cooling, that is the storage of cold from cold night air to use for space cooling in daytime [10, 11]. The maximum temperature of the room is usually well defined, e.g. to $26\text{ }^{\circ}\text{C}$. The minimum temperature reached at night is however highly variable and depends on the weather, climate, as well as the location. These maximum and minimum temperatures are however still not equal to T_{high} and T_{low} of the PCM, because there is always a temperature difference due to heat transfer at the heat exchanger and within the PCM. To discuss this

situation, again the real PCM with a melting range is compared to water; thus the result from the 1st step in example 2 (fig. 7) can be used as the starting point.

T_{high} is now restricted in two ways (fig. 8). The requirement to cool the building to less than 26 °C, that is the maximum room temperature, defines a first limit on the upper temperature in the PCM; all temperatures T_{high} above 26 °C cannot be used. However, this temperature is practically never reached in the PCM itself, because with the absence of a temperature difference for heat transfer the cooling power would become zero. As fig. 8 indicates, for the heat transfer a temperature difference of about 2 K (26 °C to 24 °C) might be used. This includes heat transfer at the heat exchanger (denoted by hex) as well as within the PCM. This restriction is thus determined by the design of the storage, like the heat exchanger area, the wall to air heat transfer coefficient, and whether measures to improve the heat transfer in the PCM like fins or graphite additives are used. Any design error that leads to a slightly larger temperature difference will significantly reduce the advantage of the PCM to water, because the area with the highest advantage (factor 20-25 when $T_{\text{high}} = 23$ °C and $T_{\text{low}} = 21$ °C to 22 °C) might not be available for heat storage anymore. T_{low} is now also restricted in two ways. The cooling of the heat storage by night air has no well defined minimum temperature. Using again 2 K temperature difference for heat transfer, a reasonable assumption when loading and unloading are done at the same heat exchanger surface, the main area where the PCM is significantly better than water can be used as long as the night air temperature drops below 18 °C. The new method now readily shows how critical these temperatures are. If the night air temperature is above 20 °C, the temperature difference at the heat exchanger of 2 K will cause the PCM temperature T_{low} to stay above 22 °C. The temperature range where the PCM is 20 – 25 times better than water is then not accessible for heat storage any more. A slight further increase in temperature by 1 K will even reduce the advantage to a factor of 0 – 5 only! This

example shows the full power of the new method. A simple comparison of c_p or h data (fig. 3, 4, 6) could never allow such a simple and accurate treatment of this problem.

5. SUMMARY AND CONCLUSIONS

In applications with an exact temperature range (T_{high} , T_{low}), the heat storage density can be calculated straight forward and different PCM can be compared. However, in many applications no exact temperature range is known or the temperature range is not fixed. In such cases, the comparison of two different PCM is quite difficult. Current approaches to evaluate and compare the heat storage capacity are too simplified to get accurate results, or too complex to get easy to read results.

In this paper we presented a new method that is simple and at the same time accurate. It is based on the calculation of all values of $\Delta h(T_{\text{high}}, T_{\text{low}}) = h(T_{\text{high}}) - h(T_{\text{low}})$ for all possible values of T_{high} and T_{low} , such that no information is missing any more. In a 1st step, when dealing with the storage material alone without any additional temperature restrictions e.g. due to heat exchange, accurate values of the heat storage capacity $\Delta h(T_{\text{high}}, T_{\text{low}})$ can be read from the calculated data table or a two dimensional plot, e.g. a contour plot, can be used for a better overview. In a 2nd step, when additional temperature restrictions apply, these restrictions can be incorporated into the data table or into the plot. Both steps can be done evaluating a single material, or comparing two materials using the difference or the ratio of the respective $\Delta h(T_{\text{high}}, T_{\text{low}})$ values of the two materials as criterion.

The examples presented show that the new method for evaluation and comparison of the heat storage capacity of PCM is extremely helpful when the upper and lower temperatures of the PCM are not known exactly or not fixed at all. In addition, the new method is also very helpful in understanding the requirements on heat exchangers and heat transfer enhancement within the PCM; it allows an easy and fast identification of the critical temperature related

issues. Besides the uncertainties in the measured input data, the new method does not rely on any simplifications and does not introduce any new uncertainties.

ACCEPTED MANUSCRIPT

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FIGURES

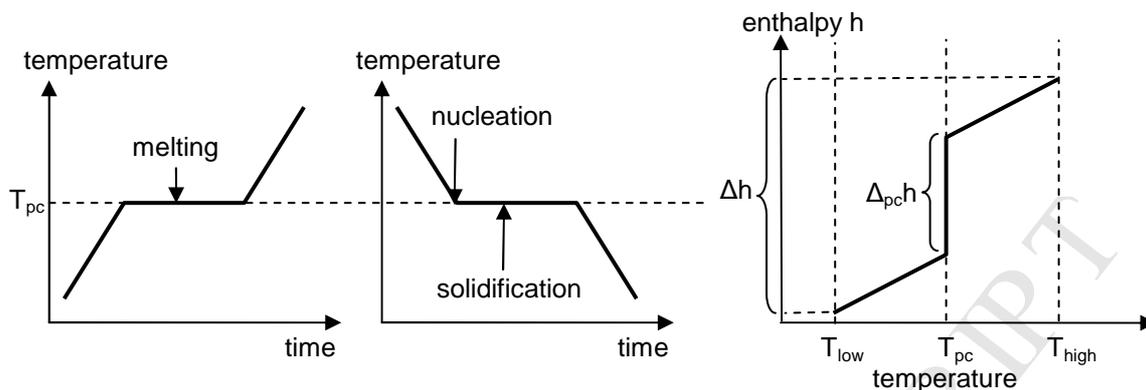


Figure 1: “Ideal” behavior of a PCM: melting, nucleation and solidification (crystallization) happen at the same temperature, the phase change temperature T_{pc} .

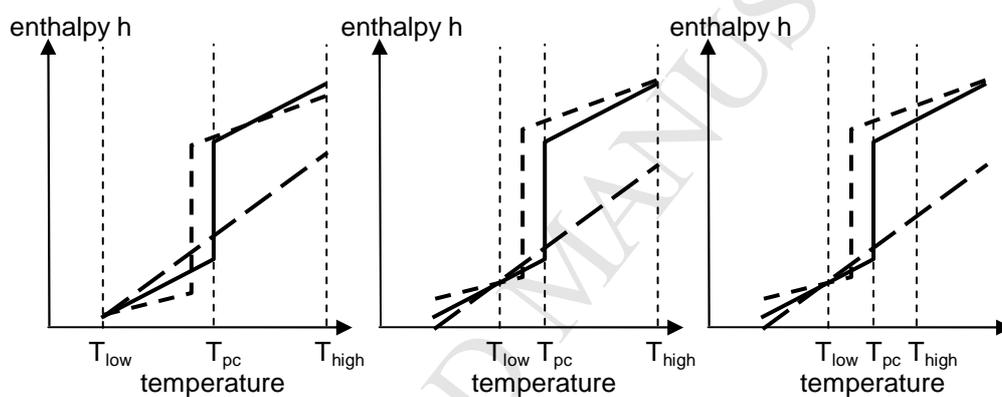


Figure 2: Comparison of the enthalpy difference Δh between T_{high} and T_{low} for two PCM and a material without phase change using different T_{high} and T_{low} . In all cases h is normalized to 0 at T_{low} .

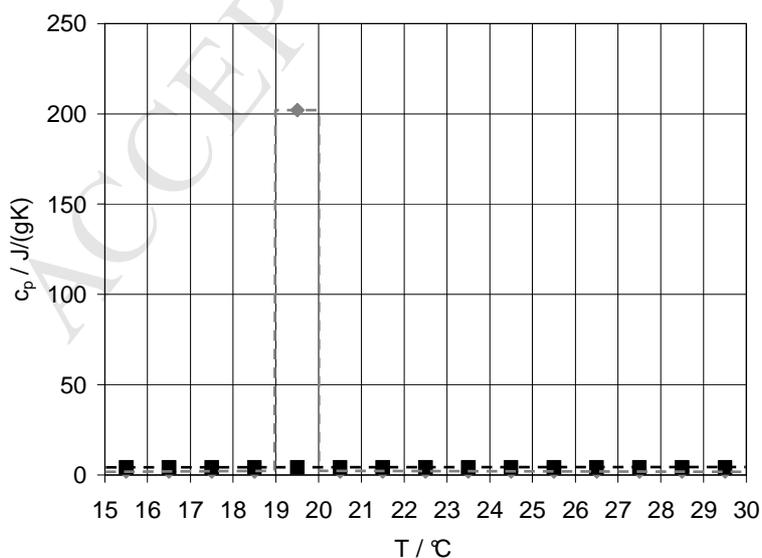


Figure 3: Comparison of the ideal PCM (\diamond) and of water (\blacksquare) using c_p -data.

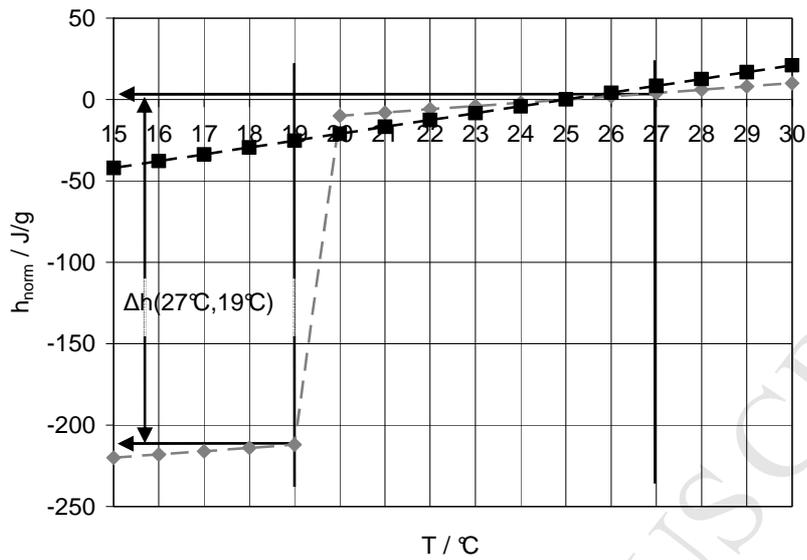


Figure 4: Comparison of the ideal PCM (◆) and of water (■) using h-data. For both materials, h is normalized to 0 kJ/kg at 25 °C.

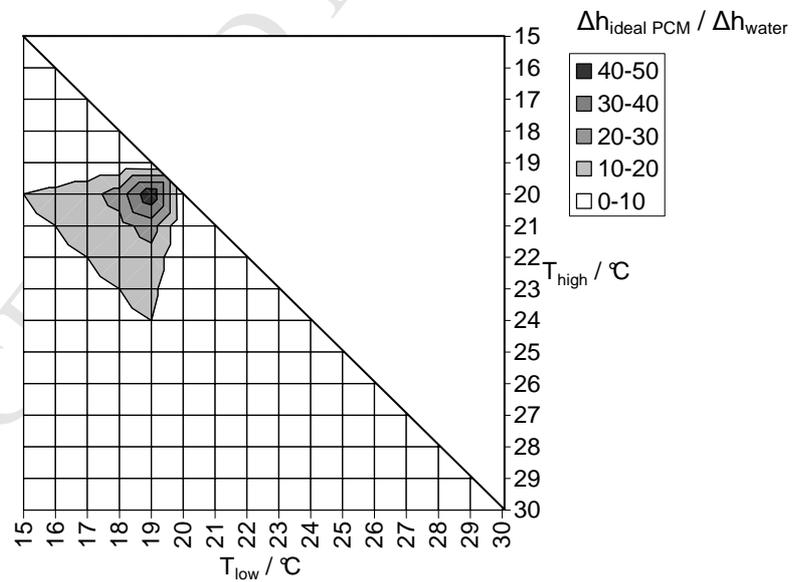


Figure 5: Ratio of the enthalpy difference of the ideal PCM to that of water between different upper and lower temperatures, using the new method.

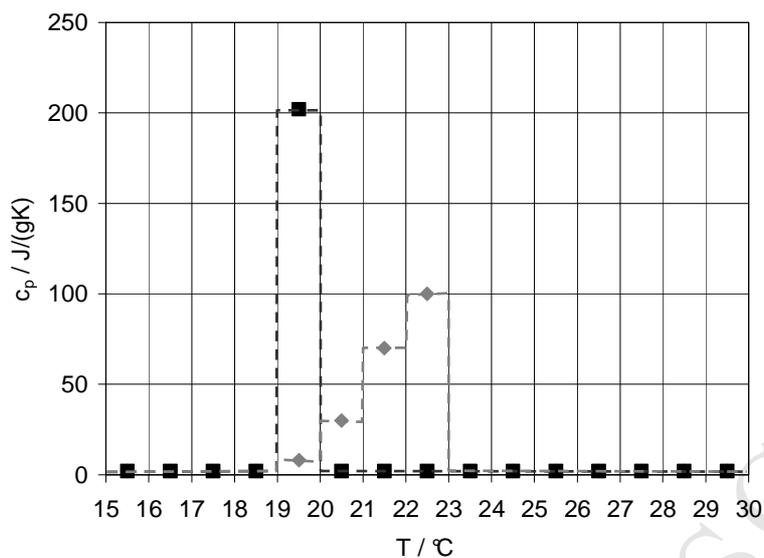


Figure 6: Comparison of c_p -data of a PCM with a melting range, and a PCM with a melting temperature.

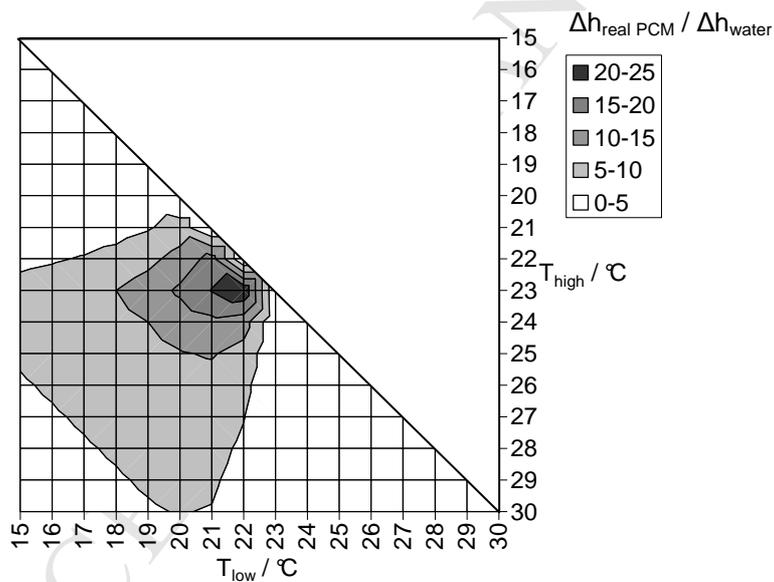


Figure 7: Ratio of the enthalpy difference of the PCM with a melting range to water between different upper and lower temperatures, using the new method.

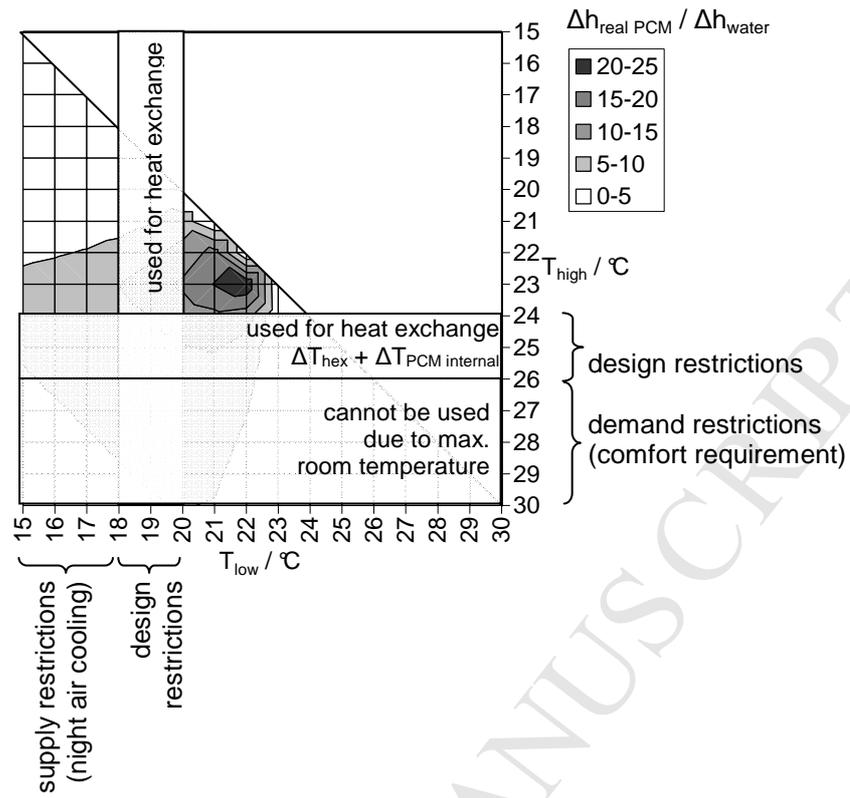


Figure 8: Ratio of the enthalpy difference of the PCM with melting range to that of water when additional temperature restrictions apply.

FIGURE CAPTIONS

Figure 1: “Ideal” behavior of a PCM: melting, nucleation and solidification (crystallization) happen at the same temperature, the phase change temperature T_{pc} .

Figure 2: Comparison of the enthalpy difference Δh between T_{high} and T_{low} for two PCM and a material without phase change using different T_{high} and T_{low} . In all cases h is normalized to 0 at T_{low} .

Figure 3: Comparison of the ideal PCM (\blacklozenge) and of water (\blacksquare) using c_p -data.

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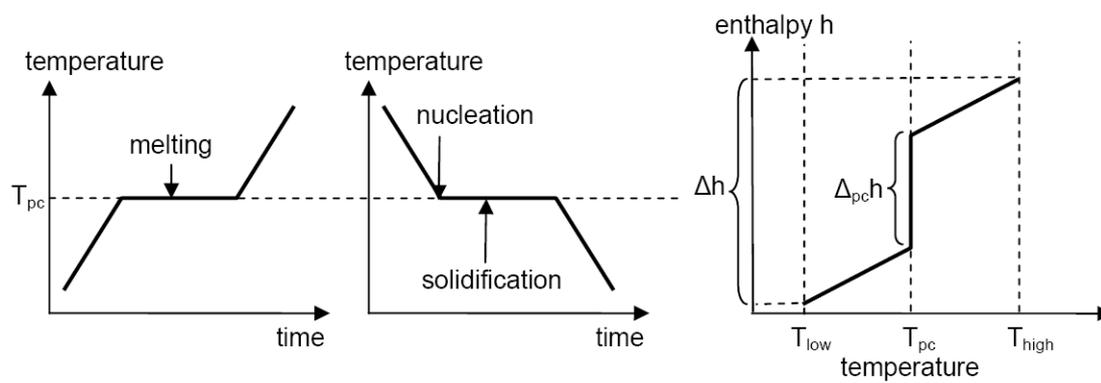
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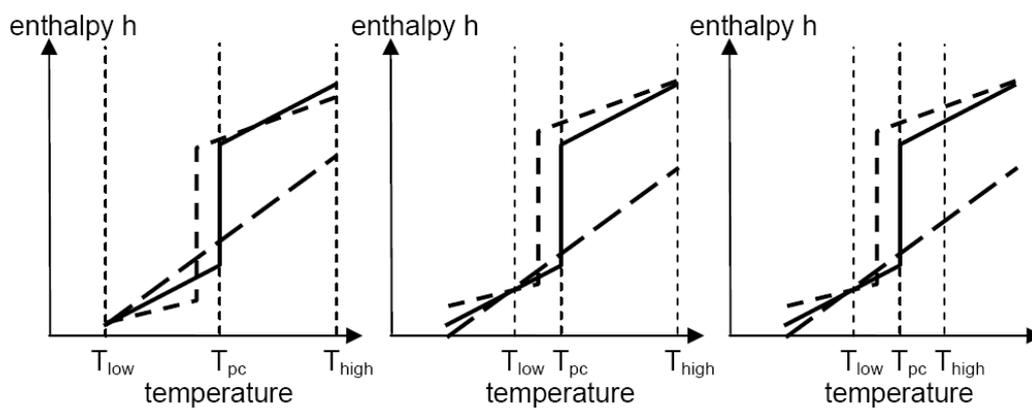
TABLE CAPTIONS

Table 1: Enthalpy difference $\Delta h = h(T_{\text{high}}) - h(T_{\text{low}})$ in kJ/kg between different upper and lower storage temperatures for the PCM with ideal behavior.

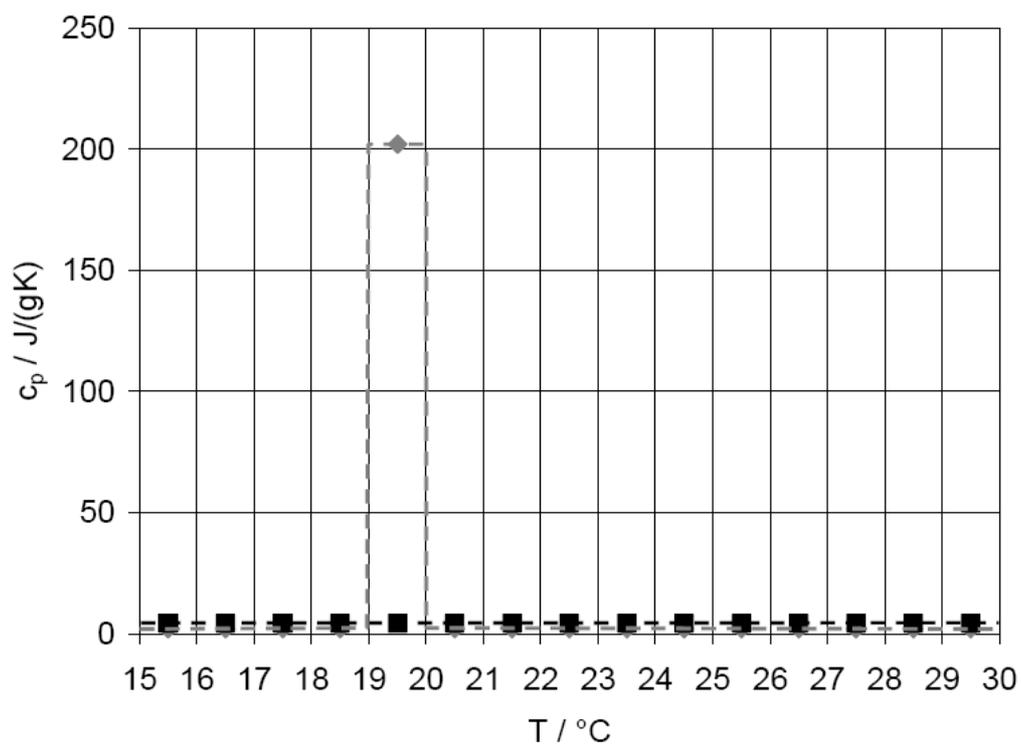
Table 2: Ratio of the enthalpy difference $\Delta h = h(T_{\text{high}}) - h(T_{\text{low}})$ in kJ/kg of the ideal PCM to that of water, between different upper and lower temperatures, using the new method.

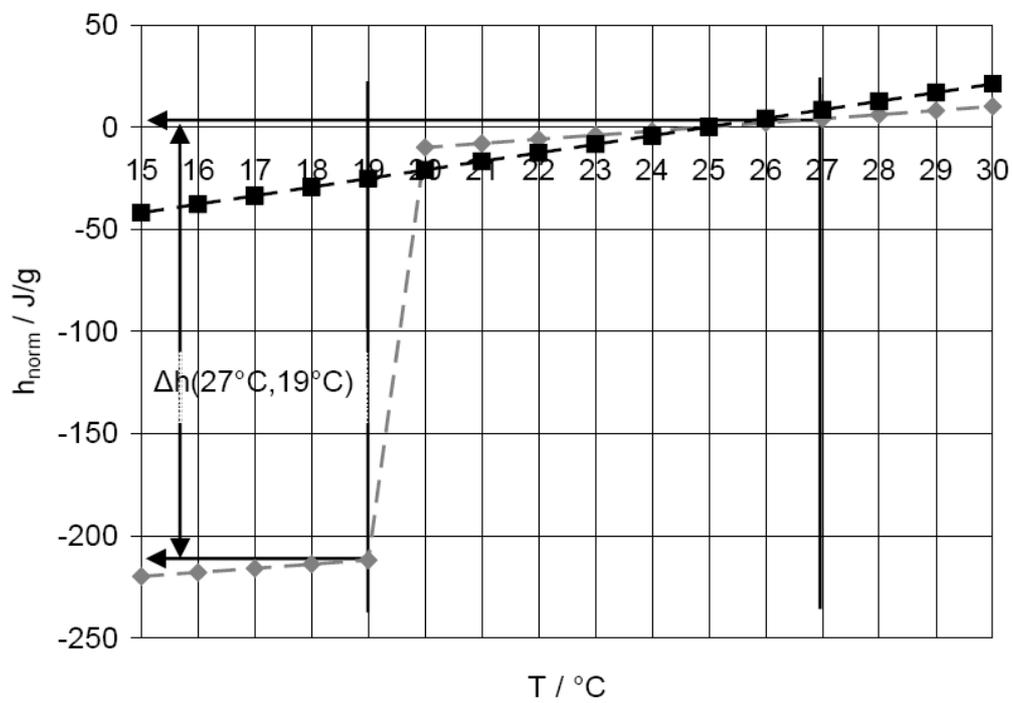
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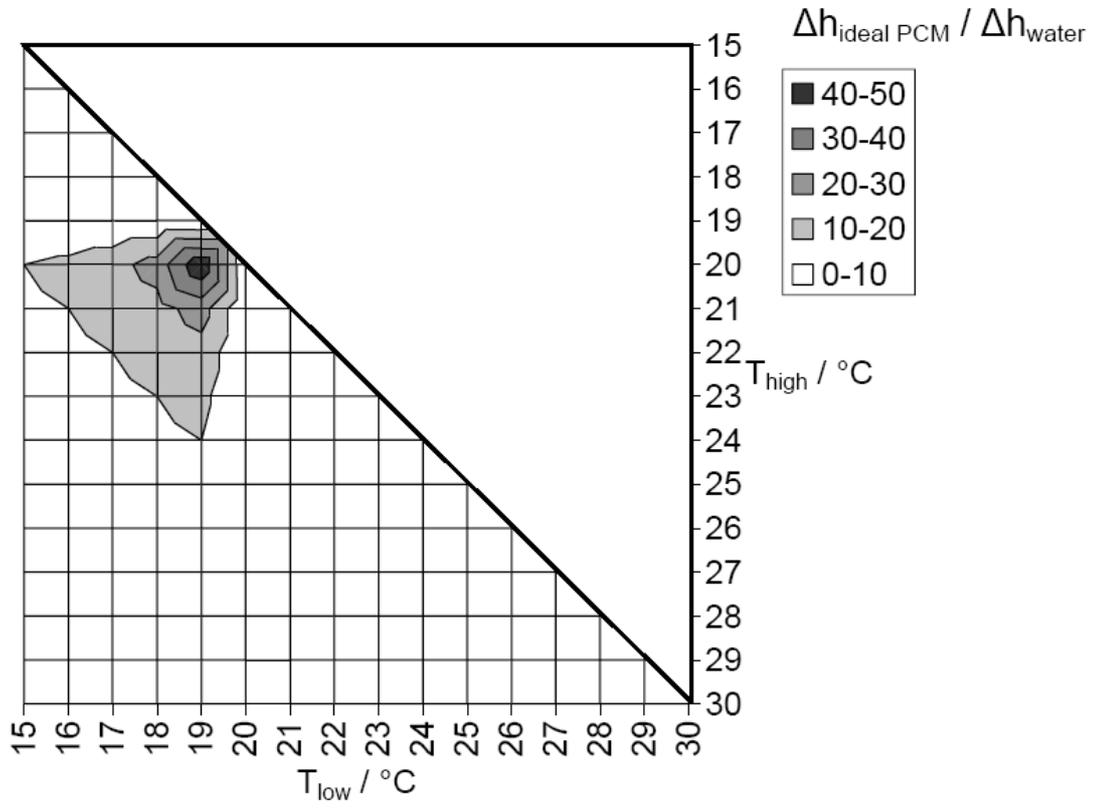


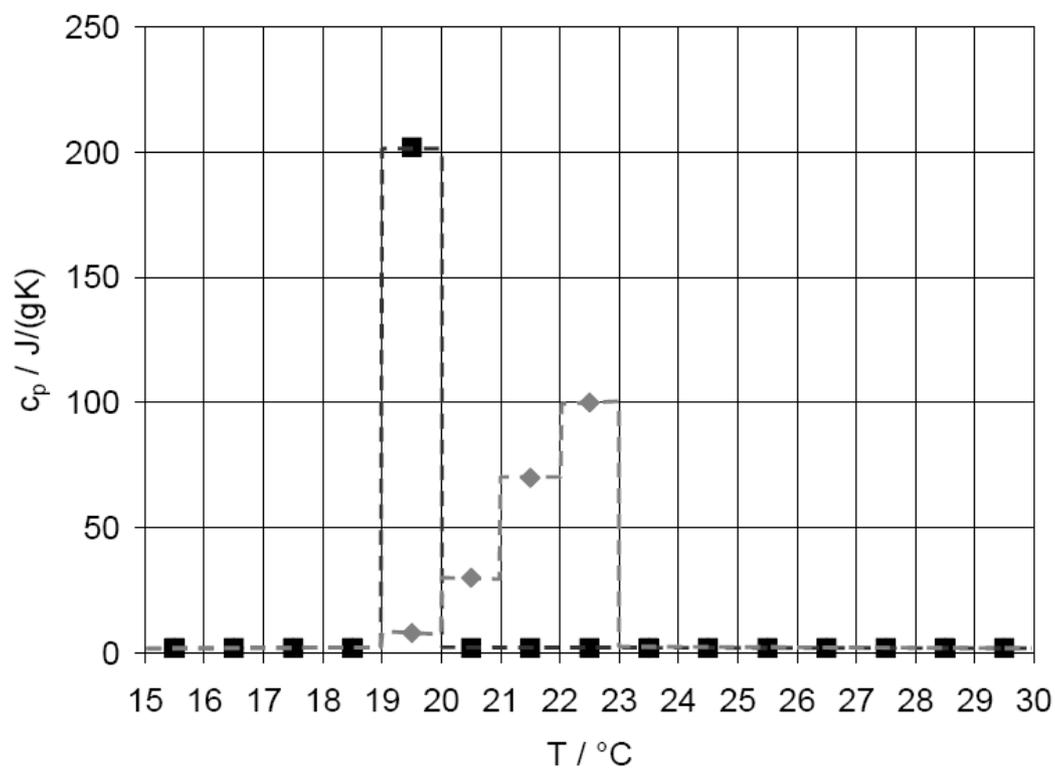


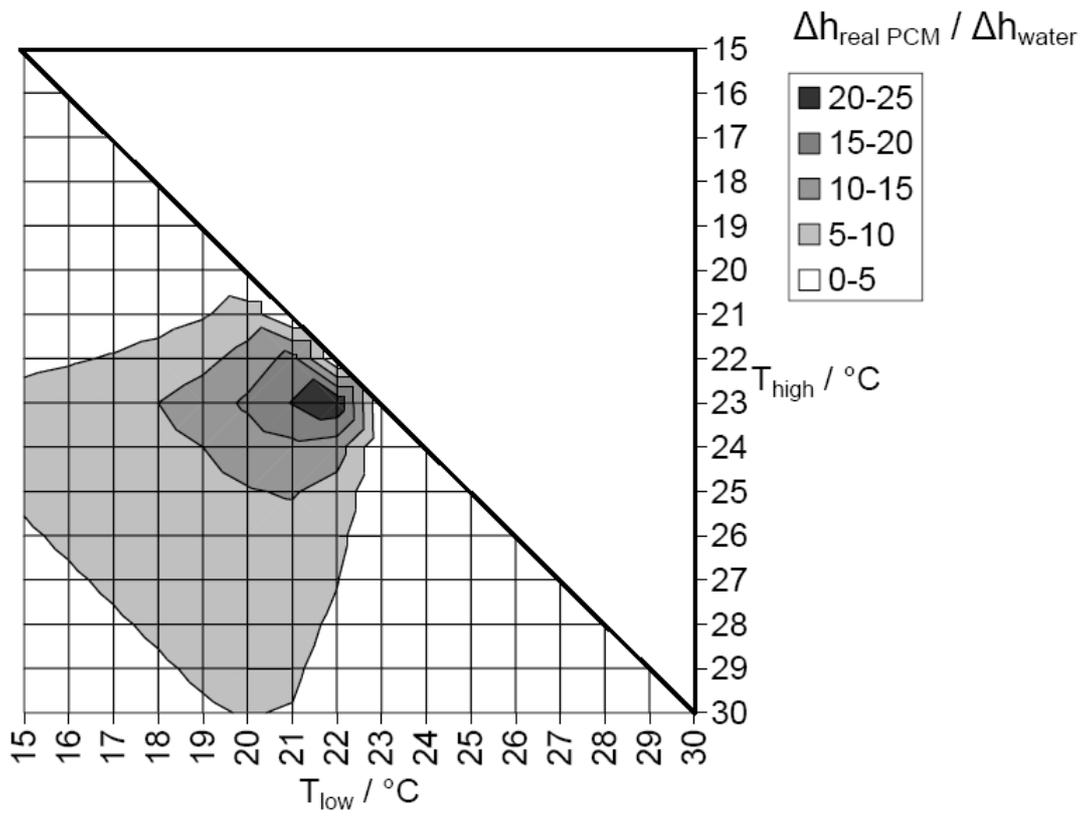
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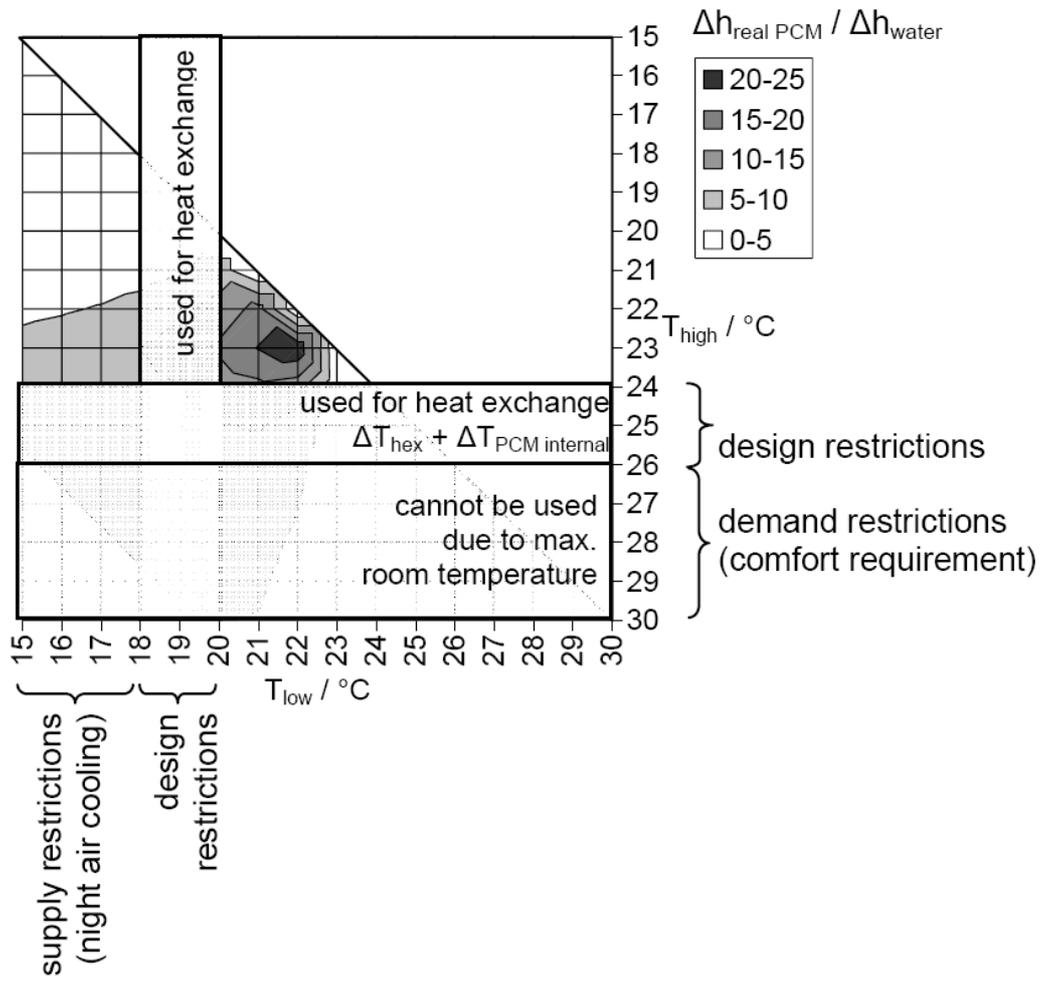












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