

SERI/TP-255-2727
UC Category: 62
DE85016861

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October 1985

Prepared for the
ENERSTOCK 85, III International Conference on
Energy Storage for Building Heating and Cooling
Toronto, Canada
22 - 26 September 1985

Solar Energy Research Institute

A Division of Midwest Research Institute

1617 Cole Boulevard
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Prepared for the

U.S. Department of Energy

Contract No. DE-AC02-83CH10093

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Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A02

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NEW PHASE-CHANGE THERMAL ENERGY STORAGE MATERIALS FOR BUILDINGS

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ABSTRACT

A new class of phase-change thermal energy storage materials is under development at SERI. These materials are unusual in two ways. They reversibly absorb large amounts of heat during a solid-state, crystal transformation more than 70°C below their melting temperatures, and their solid-state transformation temperatures may be adjusted over a range from 7°C to 188°C by varying the ratios of binary mixtures of the components.

Because these storage materials remain solid throughout the range of their service temperatures, unique opportunities exist for incorporating them into building materials. Composites have been made with ordinary, porous construction materials such as wood, gypsum board, and lightweight concrete as the matrix and with the solid-state phase change materials (SS PCM) filling the void space. The thermal storage capacities of such composites are thereby increased by more than 100% (see Figure 1) without changing the basic nature and workability of the matrix, construction material.

Parametric analyses have been conducted to determine what combination of properties would be optimum for certain solar and energy conserving building applications including Trombe wall, direct gain, and distributed cool storage (combined with night ventilation).

1. INTRODUCTION

Solid-state phase-change materials (SS PCMs) are crystalline solids that undergo changes in their structure at temperatures well below their melting points. Some SS PCMs with simple, nearly spherical molecules exhibit very large latent heats of transformation per unit weight. Such compounds have potential for providing a practical method to incorporate latent heat storage into building components. Table 1 lists characteristics of representative SS PCMs. Some conventional building materials and solid-liquid, salt-hydrate phase-change materials are also listed for comparison.

The SS PCMs listed in Table 1 are chemicals that are mass-produced in very large quantities for use in resin paints, synthetic lubricants, polymers, etc.

Computer simulations of building energy performances suggest that composite SS PCMs, once perfected, could reduce energy use and costs of operation in both heating load dominated and cooling load dominated buildings.

Table 1. Typical Properties of Thermal Storage Materials

Name/Formula	Transition		Melting Temperature (°C)	Specific Heat ^a (kJ/kg K)	Density ^c (kg/m ⁻³)	Thermal Conductivity ^c (Wm ⁻¹ K ⁻¹)
	Temperature (°C)	Enthalpy (kJ/kg)				
Solid State PCMs						
Pentaerythritol PE (CH ₂ OH) ₄ C	188	323	260	2.84	1333 1218	1.0 0.51
Trimethylolmethane TME (CH ₂ OH) ₃ CCH ₃	81	193	198	2.75	1193 1118	0.36 0.34
Neopentyl glycol NPG (CH ₂ OH) ₂ C(CH ₃) ₂	43	131	126	2.76	1046 984	0.25 0.21
Tris (hydroxymethyl) ² acetic acid (CH ₂ OH) ₃ CCOOH	126	204	219	*	*	*
Composite SS PCMs						
NPG (60%) + TME (40%) (molar basis)	26	76	140	2.64	1071	0.23
NPG (67%) + TMP ^b (33%) (molar basis)	24	61	102	*	*	*
TME + graphite (10%) (weight basis)	81	174	198	*	1257 1196	0.64 0.43
Solid/Liquid PCMs						
Calcium chloride CaCl ₂ 6H ₂ O	--	191	27	2.10	1802 1562	1.09 0.54
Paraffin wax mixed commercial	--	128	47	2.4	770	0.12 0.19
Conventional Materials						
Concrete	--	--	--	0.92	2450	1.82
Gypsum board	--	--	--	1.085	755	0.11

(a) Specific heat of the high temperature polymorph; (b) TMP = Trimethylolpropane, (CH₂OH)₃CCH₂CH₃; (c) low temperature polymorph and high temperature polymorph; * = data not available.

2. MECHANISMS

The SS PCMs listed in Table 1 derive their unusual behavior from their tetrahedral molecular shape and the hydrogen resonant bonding that occurs between neighboring molecules in the crystalline solid. At low temperatures, the intermolecular hydrogen bonding restricts molecular movement. At the solid-state transformation temperature, the intermolecular hydrogen bonds break, allowing the molecules to rotate and vibrate more freely in their lattice sites (1). It is the energy absorbed by this increased molecular motion that imparts the heat storage capacity to these materials. When the material is cooled, the reverse transformation occurs at the same temperature.

The prevalence of intermolecular hydrogen bonds largely controls the amount of energy absorbed at the solid-state transition. By selecting the molecular structure or by mixing molecules of different structure in the same crystal-

line solid, the number of hydrogen bonds per molecule can be altered. Thus, the transition temperatures and heat storage capacities can be "tailored" within limits. Table 1 includes examples of mixed SS PCMs that illustrate this ability.

3. BUILDING COMPONENTS

The SS PCMs may be more readily incorporated into structures and components than can solid-liquid PCMs. The SS PCMs may be melted and then cast into the component or composite structure. Since the heat absorbing transition occurs at a temperature much lower than the melting temperature, the SS PCM will remain solid and in place throughout its service life. Several component and composite designs have been fabricated on a laboratory scale (2). For example, a multichannel, polymer extrusion can be filled with an SS PCM. Transparent polymer panels filled with the translucent SS PCM may be used as a Trombe wall, which not only stores solar heat but also admits diffuse daylight. An SS PCM panel can have metal facing, which strengthens the brittle PCM, provides a decorative durable surface, and may be coated, for example, with a selective solar absorber to enhance the solar energy collection efficiency in a Trombe wall application.

The melted SS PCM is quite fluid and is readily absorbed into porous materials such as wood, gypsum board, fiberglass, and concrete aggregates such as vermiculite, perlite, scoria, etc. The resulting composites have substantially increased heat storage capacities (Figure 1).

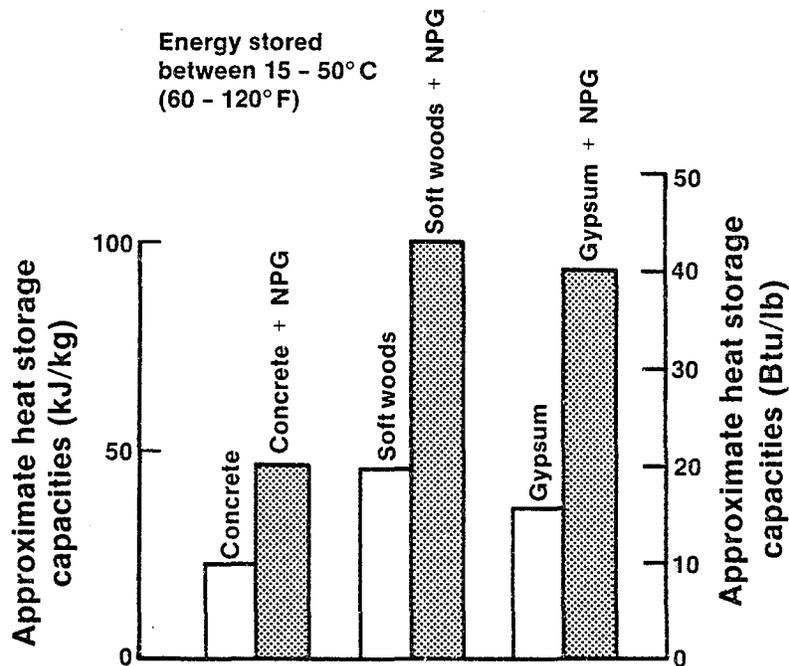


Figure 1. A Comparison of the Heat Storage Capacity of Conventional Building Materials and Similar Materials in which Pore Volume has been Filled with the SS PCM Neopentyl Glycol

4. APPLICATIONS ANALYSES

The heat flow into and out of a building is cyclic with a large diurnal component driven by changing temperature and solar insulation. Thermal energy storage materials are effective when they shift the phase of heat flow to better match the needs of the occupants--delaying delivery of midday solar heat into the evening and night or absorbing unwanted heat during the day so that it may be rejected more efficiently and economically at night. Computer models were used to estimate the energy conservation and economic benefits of using phase-change thermal energy storage materials in a Trombe wall, a direct gain space, and a "cool" storage application. For this reason, the models have been exercised parametrically with, for example, the PCM transition temperature, thermal conductivity, latent heat, surface area, etc. as systematically varied input parameters.

Trombe Wall

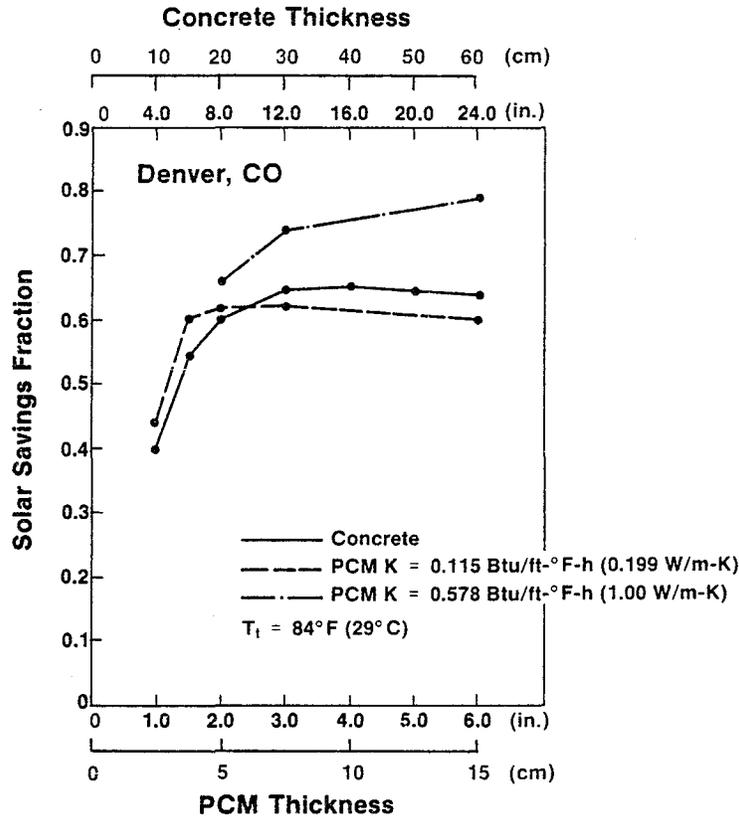
A thermal network model was developed for the Trombe wall and was incorporated into a thermal simulation code for residential buildings. The simulation was performed using forward finite differencing with time steps of one hour or less for entire years (typical meteorological year for Denver, Colorado).

Thermal storage was modeled with multiple thermal nodes to account for the effect of thermal conductivity and the resulting temperature gradients in the wall. For the phase-change materials, this multinode modeling used the SERIRES code with multiple single-node phase-change material layers, each with a specific thermal conductivity. Annual solar savings fractions* were based on annual simulations with and without the Trombe wall.

Simulations were performed for a PCM with a latent heat of 121 kJ/kg (52 Btu/lb), with a solid-state phase-change temperature as a parameter. Assuming no supercooling, the optimum phase-change temperature is about 29°C (84°F). Other simulations showed an incremental benefit from increasing the thermal conductivity of the phase-change material when the transition temperature is near optimum or decreasing the thermal conductivity when the transition temperature is higher than 29°C. An increase in thermal conductivity may be achieved by adding a material with a high thermal conductivity to the phase-change materials.

Figure 2 shows a comparison of a hypothetical solid-state phase-change material wall to a more conventional, concrete Trombe wall. Such a phase-change material wall might perform as well or better than a much thicker and ten times heavier concrete wall.

*The solar savings fraction (SSF) is that part of the annual heating energy requirement which is displaced by the incorporation of the solar component.



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Figure 2. Solar Saving Fraction as a Function of Trombe Wall Thickness for SS PCMs and Concrete

Direct Gain

Buildings designed for direct gain passive solar heating usually include massive components made of concrete, brick, adobe, etc. to absorb the solar heat. A well designed phase-change thermal energy storage material can store the same amount of heat in a much less massive component.

Figure 3 shows the annual energy savings for various types of thermal storage based on simulation results from references 3 and 4 assuming high latent heat capacity (521 Btu per square foot of storage area). More recent analysis (5) indicates that similar performance can be obtained with approximately 1500 Btu of latent heat capacity per square foot of window area. At low values of solar saving fraction, the energy saving per unit window area is great because the solar gains are small compared to heating loads for most of the heating season and are therefore well-utilized. If PCMs are used, then the delivery of absorbed solar heat is delayed and prolonged so that the heat is well utilized even at high solar savings fraction when the solar gains are a large fraction of the total heating load.

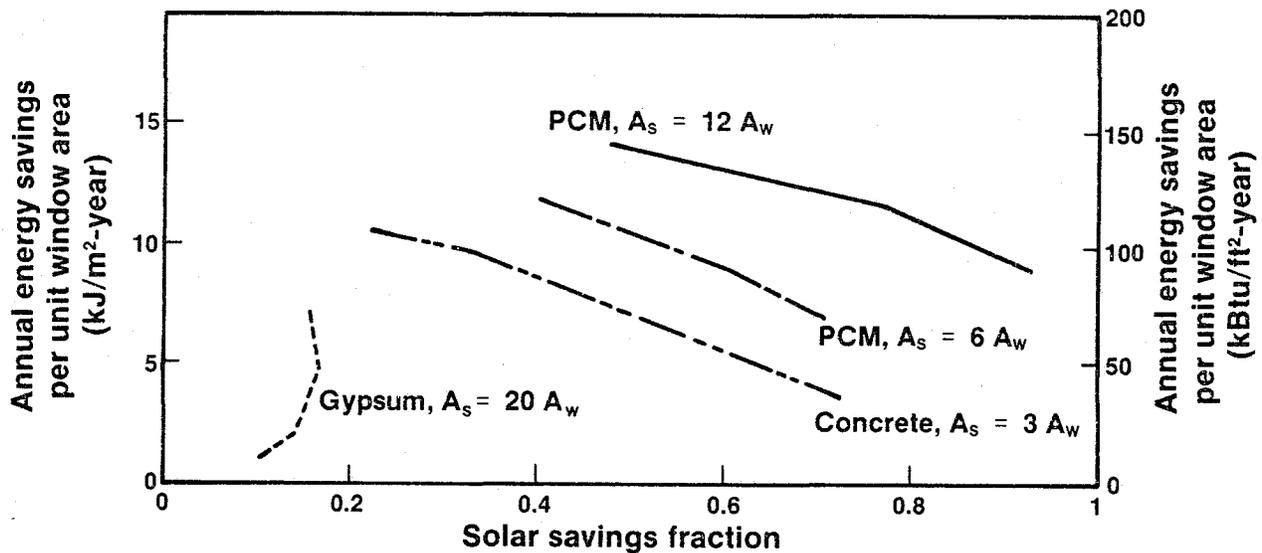


Figure 3. The Net Energy Savings per Unit Window Area for Different Heat Storage Materials in a Direct Gain, Passive Solar Heated Building

The allowable costs of a direct gain solar system are difficult to estimate because they depend on the costs of the storage materials, of the windows required to provide the solar gain, and of heating energy which vary widely with type of fuel used and region of the world in which it is bought. However, the relative value of different kinds of direct gain designs can be calculated independent of energy costs.

For two types of storage in direct gain systems which are equally cost effective:

$$\frac{\text{Cost}_w + \text{Cost}_{s1}}{\text{SAV}_{s1}} = \frac{\text{Cost}_w + \text{Cost}_{s2}}{\text{SAV}_{s2}}$$

and

$$\text{Cost}_{s2} = \frac{\text{SAV}_{s2}}{\text{SAV}_{s1}} \text{Cost}_{s1} + \left(\frac{\text{SAV}_{s2}}{\text{SAV}_{s1}} - 1 \right) \text{Cost}_w$$

where costs and savings are expressed per unit area of window. The relative allowable costs can be expressed in terms of the single parameter $\text{SAV}_{s2}/\text{SAV}_{s1}$ where the denominator describes some reference base case. Figure 4 shows the dependence of allowable costs on SSF for a particular base case with concrete storage at $\$54/\text{m}^2$ ($\$5/\text{ft}^2$ of window area) and window costs at $\$54/\text{m}^2$ ($\$5/\text{ft}^2$). The data are the same as shown in Figure 3. Allowable PCM costs are partially due to the reduced window area required to achieve the same energy savings. If a high value of solar savings fraction is desired, then the allowable PCM cost may be as great as five times the cost of the concrete in the base case.

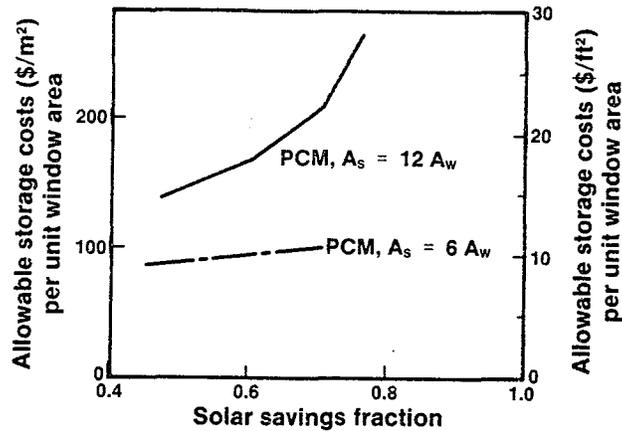


Figure 4. The Allowable Costs of PCM Storage Components in a Direct Gain System

Cool Storage

Using low-temperature PCM distributed throughout the core of a cooling load dominated building can permit overnight cooling and obviate the need for chiller use during the day when utility rates are high. Computer simulations of building energy performance suggest that such an application may be cost effective (6). Annual simulations were performed using the SERIRES code and Denver TMY weather data. To reduce the simulations to only the performance of the SS PCM in the building core, a number of simplifying assumptions were made. First, it was assumed that the building core is isolated from outside weather conditions by the building perimeter areas and by other floors above and below. Latent cooling loads were not included in this simulation. The PCM was placed in the ceiling tiles with a single thermal node midway through the thickness of the PCM representing its temperature.

In the base case, the PCM was sized so that all the daytime chilling load would be shifted to the night. Thus, in the base case, the peak demand level is reduced by an amount equal to the entire cooling load of 43 W/m^2 (4 W/ft^2). The control strategy attempts to use night ventilation cooling as much as possible. Chiller operation is delayed until the latest possible moment while still ensuring that the PCM will be fully discharged during the night so that it will be unnecessary to operate the chiller during the following day. However, with the assumptions used in this study, the simulations show that reduced chiller energy is offset by increased fan energy requirements.

Depending on the local utility rate structure, the savings in demand charges could be substantial. For example, in Denver, Colorado, at the time of this analysis, the rates for commercial customers were \$0.02/kWh and \$11.75/kW demand with an 85% ratchet. This rate structure results in demand charges

that are 2.67 times greater than the energy charges (assuming 220 hours of uniform cooling loads per month). Nearly 3/4 of the air conditioning energy costs could therefore be saved in the base case analyzed above.

5. CONCLUSIONS AND RECOMMENDATIONS

Solid-state phase-change materials have been shown to be potentially useful as constituents in heat storing building components. The crystalline transformation temperature at which most of the heat is absorbed can be selected anywhere over a wide range of values that includes temperatures suitable for cooling as well as heating.

Parametric analyses of building energy performance suggest that the use of phase-change thermal energy storage materials can improve energy efficiency and/or reduce the costs of heating or cooling. More systematic analyses are needed to identify cost optimized designs for PCM thermal storage use in various types of buildings. More research and development are required to perfect the thermal storage components which now exist only as laboratory scale test specimens.

6. ACKNOWLEDGEMENTS

This work was funded by the United States Department of Energy, Office of Solar Heat Technologies under contract No. DE-AC02-83CH10093, as part of the Apertures Research Element of the Solar Buildings Technology Program.

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