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# **Solid State Phase Change Materials for Thermal Energy Storage in Passive Solar Heated Buildings**

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**SOLID STATE PHASE CHANGE MATERIALS FOR THERMAL  
ENERGY STORAGE IN PASSIVE SOLAR HEATED BUILDINGS**

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**ABSTRACT**

A class of hydrocarbon compounds is being evaluated for use in thermal energy storage components for passive solar heated buildings. The most promising compounds are the polyhydric alcohols pentaerythritol ( $C_5H_{12}O_4$ ), trimethylol ethane ( $C_5H_{12}O_3$ ), neopentyl glycol ( $C_5H_{12}O_2$ ), and closely related materials. Solid solution mixtures of these compounds can be tailored so that they exhibit solid-to-solid phase transformations at any desired temperature from well below room temperature up to 188°C (370°F). These crystalline changes reversibly absorb large amounts of thermal energy (80-290 kJ/kg) making the materials suitable for a wide range of energy storage applications. This research has focused upon understanding the molecular mechanisms of the solid state phase transformations in the polyhydric alcohols and upon evaluating their use in thermal storage components for solar buildings. During this last fiscal year, additional research has confirmed that the solid state phase transitions in the polyhydric alcohols depend upon hydrogen resonance bonding within the molecular crystals. Careful density measurements show that mixtures of the polyhydric alcohols, pentaerythritol and trimethylol ethane are probably true solid solutions which undergo crystalline phase changes by the same process as the individual alcohols. Experiments with deuterium isotope substituted pentaerythritol further confirmed the nature of hydrogen bonding in this solid; and x-ray diffraction measurements showed the nature of the crystallographic changes during the solid state transformation. Thermal conductivity measurements showed that this important parameter could be significantly increased by the addition of certain dispersoids such as graphite or aluminum powders in the solid polyhydric alcohols.

Novel building construction materials have been fabricated with large weight fractions of a solid state thermal storage material. These composite materials exhibit much greater thermal storage capacities, but retain most of the characteristics of conventional construction materials which make them practical and easy to use in traditional building practice. Composites based on concrete, gypsum, wood products and others have been fabricated.

Additional systems analyses were conducted in order to define the limits of thermal storage effectiveness in passive solar heated buildings and to guide the laboratory research toward the most promising applications.

**OBJECTIVES**

The objectives of our research are to evaluate the technical feasibility of using solid state phase change materials (SS PCMs) for thermal energy storage in passive solar buildings and to develop a better understanding of the molecular processes involved in solid state transitions.

**EXPERIMENTAL RESULTS**

Earlier work by the authors provided evidence that the SS PCMs of pentaerythritol and homologous compounds exhibited solid state crystalline transitions because of the existence of metastable, resonant hydrogen bonds between molecules in the lattice. At the transition temperature these bonds break, the crystal structure changes and the detached molecules rotate and vibrate more freely, but remain held in their lattice sites by dispersion forces. The more disordered, higher temperature phase stores a large amount of thermal energy. Upon cooling through the transition temperature, the hydrogen bonds reform, the molecules become locked rigidly in place and give up their stored thermal energy. Thermal analyses, infrared spectroscopy, and a quantitative model relating the enthalpy of transition to the number of hydroxyl (hydrogen bonding) sites supported this proposed mechanism.

Within the last year additional evidence has been gathered through infrared spectroscopy and thermal analyses of deuterium-substituted pentaerythritol ( $C-(CH_2-OD)_4$ ). Figure 1 shows infrared absorption spectra of partially substituted pentaerythritol. The strong absorption peak at  $3323\text{ cm}^{-1}$  in the pure material is characteristic of the -OH stretching band in a hydrogen-bonded alcohol. As the deuterium is substituted for hydrogen in the -OH groups, the absorption peak shifts to  $2468\text{ cm}^{-1}$ . Another peak at  $480\text{ cm}^{-1}$  replaces one at  $670\text{ cm}^{-1}$  as the deuterium substitution is increased. If the -OH stretching resonance behaved as a classical oscillator, the doubling of the hydrogen mass would be expected to decrease the resonant frequency by a factor

$$\frac{\nu_0}{\nu_H} = \frac{1}{\sqrt{2}} = 0.707 .$$

The observed frequency shifts are 0.743 and 0.716 for the higher and lower absorption peaks respectively. This is consistent with the expectations.

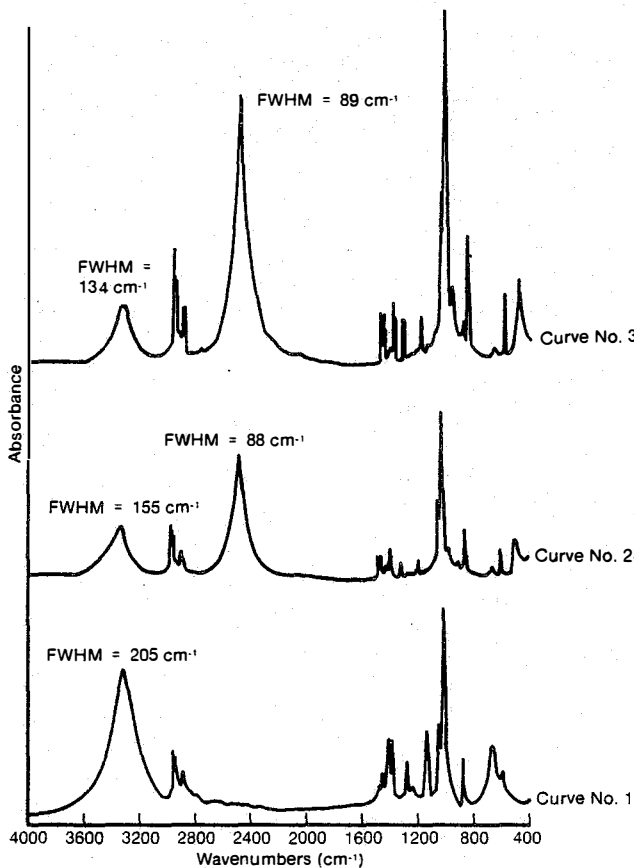
If the controlling hydrogen bonds are affected by deuterium substitution as suggested by the infrared spectroscopy, then the thermal characteristics of the solid transition in the deuterium-substituted pentaerythritol should also be changed. Figure 2 shows differential scanning calorimetric recordings of these same materials. Table 1 summarizes the differences observed. Both the enthalpies and transition temperatures of the partially deuterium-substituted compounds have been decreased. These results support the connection between hydrogen bonding in the solid and the energetics of the storage process.

The mixed SS PCMs have exhibited thermal storage capacities and transition temperatures between those of their constituents. This observation suggested that the binary mixture formed molecular solid solutions in which the minor component substituted molecule for molecule in the lattice of the major component. Careful density measurements were made on one such mixture to test this hypothesis. Figure 3 shows the measured densities of mixtures of pentaerythritol and trimethylol-ethane (pentaglycerine). The solid curve is predicted on the assumption of ideal solid solutions and agrees quite well with the measured

**Table 1. Thermal Properties of Deuterated Pentaerythritol\***

Composition	Peak Temperatures (K)		Enthalpies (kJ/mole)	
	Transition	Melting	Transition	Melting
PE	465	526	39.3	4.48
(63% deuterated) PE	448	505	38.8	4.08
(80% deuterated) PE	446	497	36.8	3.00

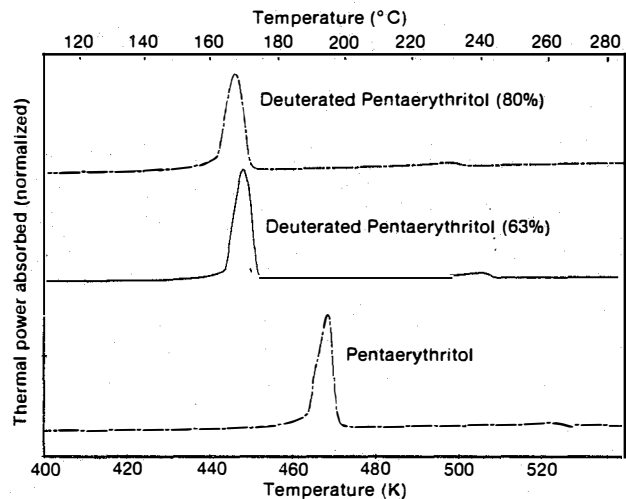
\*See Figure 2.



**Figure 1.**  
Fourier transform infrared absorption spectra  
1. no deuterium substitution, 2. 63% deuterium  
3. 80% deuterium

data. The formation of separate phases would be expected to cause differences in densities which would appear in such a comparison.

Ternary mixtures of the three polyhydric alcohols, pentaerythritol, trimethylol ethane, and neopentyl glycol were examined in an attempt to extend the solid state transition temperatures into the cool storage temperature range. Some low temperature mixtures were discovered, but the enthalpies of transition were small. Other mixtures of SS PCMs and similar compounds were also tested. One promising combination is neopentyl glycol with trimethylol propane (TMP). Table 2 lists some characteristics of these newly discovered SS PCM mixtures.



**Figure 2.**  
Differential scanning calorimetric recordings  
of deuterium substituted pentaerythritol.

X-ray diffraction measurements were made on pentaerythritol as a function of temperature using multiple diffraction pattern recordings on a single sheet of film through a movable slit mask. In this way, small changes in lattice spacings at different temperatures could be measured precisely by microdensitometry. Table 3 lists results between room temperature and 288°C (the solid state transition temperature is 188°C). These results are consistent with the hydrogen bonding model for the SS PCMs.

Stable dispersions of particulates in SS PCMs are readily made by mixing powders with the melted PCM before it is added to its container or composite matrix. The addition of highly conducting powders such as graphite or aluminum significantly increases thermal conductance of solid PCM. Table 4 lists some measured values for representative dispersions. Increased thermal conductance is critical to proper performance of SS PCMs in thick sections.

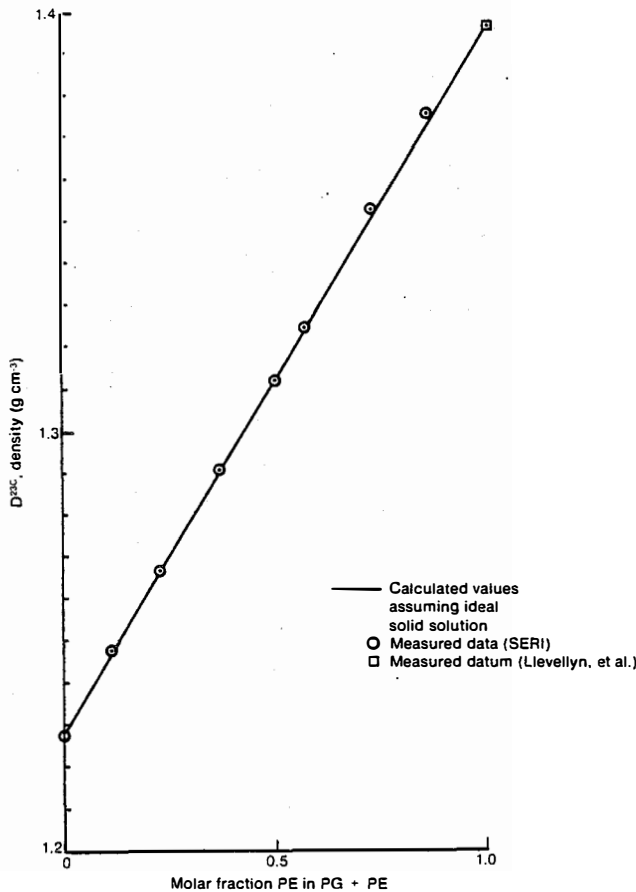


Figure 3.

Densities of pentaerythritol-trimethylol ethane solid mixtures

New composite materials containing SS PCMs were invented during the research. Several different concepts were evaluated. Among the most promising are a set of building material composites which incorporate an SS PCM with a nearly room temperature transition. The details of the fabrication process are the subject of a DOE patent application and will not be described here, but the general characteristics of the composites and their comparison with conventional building materials are presented in Figs. 4 and 5. In Fig. 4 the heat storage capacities of conventional building materials and PCMs are compared. The greater storage possible in PCMs is clearly shown. Figure 5 shows how the heat storage capacities of the composite construction materials may be increased by the addition of a typical SS PCM, neopentyl glycol (NPG). The important point to be made about these composites is that they retain the other characteristics of more conventional building materials--they may be poured on site or precast (concrete); sawed, nailed, etc. (wood); cut, nailed, painted, etc. (gypsum board). Thus there is the possibility with these new experimental composites that traditional construction practices and labor skills could be used; but that the resulting structures would have much greater thermal storage and improved temperature stability.

Thermal energy storage is often assumed to be required in passive solar systems. However, the potential for improvement in storage effectiveness has recently been questioned in some cases, e.g., northern climates where daytime heating loads may exceed solar gains. Systems analysis at SERI includes an investigation of storage effectiveness as a function of building climate and building characteristics. In order to establish upper limits for improvements due to advanced storage materials, ideal PCM storage performance is predicted and compared to performance of conventional sensible storage materials. Preliminary results indicate storage effectiveness to be high in midrange solar fraction passive designs and vanishingly small in other cases.

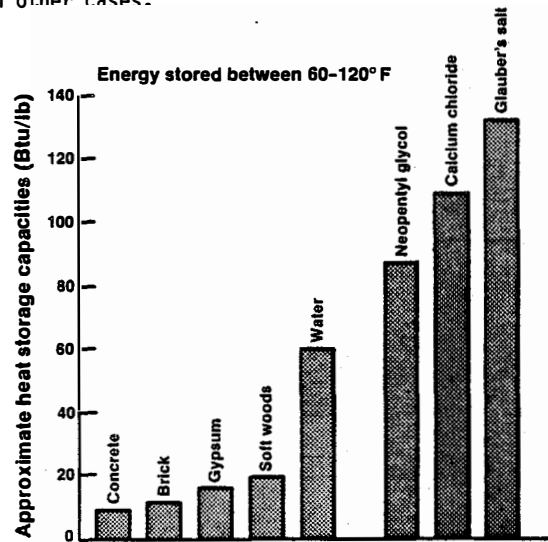


Figure 4.

Comparison of the heat storage capacities

**Table 2. Solid State Transitions In SS PCM Mixtures**

Composition (Molar %)			TMP	Temperature		Enthalpy (kJ/mole)	Entropy (J/Mole K)
PE	TME	NPG		°C	(F)		
10	80	10		79	(174)	15.6	44.4
10	45	45		45	(113)	10.7	33.5
15	70	15		74	(165)	15.5	44.8
15	15	70		17	(63)	6.32	21.8
25	50	25		73	(163)	15.8	43.5
25	25	50		64	(147)	8.08	23.8
30	60	10		94	(201)	18.2	49.4
30	10	60		127	(261)	4.69	11.7
33.3	33.3	33.3		79	(174)	14.2	40.2
45	45	10		109	(228)	21.8	56.9
45	10	45		140	(284)	12.2	29.7
50	25	25		134	(273)	18.1	44.4
70	15	15		158	(316)	25.9	59.8
		100	0	53	(127)	12.7	39.0
		67	33	24	(75)	7.0	23.5
		50	50	15	(59)	4.9	17.0
		33	67	7	(45)	3.4	12.0

\*PE=pentaerythritol, TME=trimethylol ethane, NPG=neopentyl glycol, and TMP=trimethylol propane.

**Table 3. Structure and Lattice Parameter of PE at Various Temperatures**

Film Strip No.	Temp., °C	Tetragonal	Lattice Parameters	Standard Errors
1	26°C (R.T.)	Tetragonal	$a_0 = 6.0756$ $c_0 = 8.7798$	.003 .013
2	72°C	"	$a_0 = 6.0725$ $c_0 = 8.7786$	.001 .003
3	106°C	"	$a_0 = 6.0849$ $c_0 = 8.8430$	.005 .018
4	160°C	"	$a_0 = 6.0928$ $c_0 = 8.9084$	.002 .008
5	180°C	"	$a_0 = 6.10059$ $c_0 = 8.9393$	.003 .01
6	189°C	Cubic	$a_0 = 8.9995$	.00005
7	228°C	"	$a_0 = 9.6549$	.004
8*	228°C	"	$a_0 = 9.6549$	.004

\*Sample was oscillated.

**Table 4. Measured Thermal Conductivities of Solid State Phase Change Materials and Composites**

Material	Temperature (°C)	Density (kg m <sup>-3</sup> )	Thermal Conductivity (w m <sup>-1</sup> K <sup>-1</sup> )
PE	170	1342-1323	.963-1.07
	205	1218	.508
TME	65	1193	.361
	95	1118	.335
NPG	27	1046	.253
	60	984	.209
NPG (60%) + TME (40%)	54	1071	.230
	61	1054	.215
TME + Graphite (3%)	65	1216-1192	.441-.428
	95	1144	.327
TME + Graphite (10%)	65	1257	.638
	95	1196	.427
TME + Aluminum (3%)	66.7	1199	.394
	97.2	1147	.379
TME + Aluminum (10%)	65	1245	.438
	98.3	1200	.716

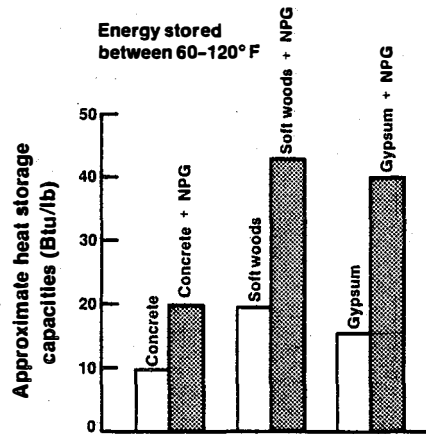


Figure 5. Comparison of heat storage capacities of conventional building construction materials and composites of such materials containing a solid state PCM, neopentyl glycol.

### SUMMARY

This exploratory research has been a continuation of work initiated at SERI in 1980 and carried forward since that time with the support of the Passive and Hybrid Solar Energy Branch of the U.S. Department of Energy under contract Nos. EG-77-C-01-4042 and DE-AC02-83CH10093. Additional support was received during early FY 1984 from the Office of Building Energy Research and Development.\* Limited systems analytic support has been included in the task to provide guidance to the laboratory scientists--for example, by suggesting the most effective applications for thermal storage and the most appropriate characteristics of the ideal storage materials in such applications.

Additional laboratory experiments have improved our understanding of the mechanisms of solid state phase transformations in polyhydric alcohols and their mixtures. Evidence continues to support the hypothesis that the SS PCMs undergo crystallographic phase changes in which hydrogen bonds between adjacent molecules in the molecular crystal are broken (during heating) or reform (during cooling) thereby absorbing or releasing large amounts of thermal energy. Density measurements of mixed SS PCMs indicate that they form solid solutions, one in the other, and undergo crystal transformations by the same mechanism as the pure components. By mixing three different SS PCMs together or by mixing a SS PCM with a solid solution forming compound such as TMP\*\*, lower transition temperatures (as low as 7°C) have been achieved

Composites have been made with the SS PCMs. By adding powders of graphite or aluminum to the molten SS PCMs and then casting them to shape or adding them to composite matrices, components with much higher thermal conductance could be formed. New composites based on concrete, gypsum, wood and other matrices with added SS PCM appear to have desirable properties for building construction as well as much greater heat storage capacities than their conventional counterpart materials.

The results of this research may be useful to the manufacturers of thermal storage components and to manufacturers of building construction materials. Both industries might consider the development of products suggested by this task. The research and marketing staff of companies producing polyhydric alcohols and related compounds should take note of the potential new markets for their chemicals.■

Additional engineering scale testing is needed on prototypical components and composites containing the SS PCMs. Real time testing of full scale components under realistic conditions is recommended. The thermal diffusion and convection processes which are critical to overall performance cannot be reliably modeled nor accurately simulated in small scale or accelerated laboratory tests.

The cost effectiveness of the SS PCM components and composites remains to be determined. Such factors as component/composite design, manufacturing process, scale of production, packaging and marketing methods all contribute to the economics of an application. Such factors are beyond the scope of this exploratory research and could be more accurately assessed by private industry.

Problems which may have to be overcome before an SS PCM product receives market acceptance include flammability, water solubility, and uncertainty about long term toxicity. The incorporation of the SS PCM into a durable package or composite structure should alleviate these concerns.

As the understanding of the basic mechanisms of solid state transitions in these compounds improves, it appears likely that additional research could lead to new SS PCMs with higher heat storage capacities in the range of temperatures suitable for passive solar buildings.

In addition, there is the possibility that such transitions may be designed to be "triggered" to release stored energy from the undercooled SS PCM at the time it is needed rather than when the material happens to reach the transition temperature. Such control over thermal release would greatly increase the utility of the storage and improve thermal control over passive building performance. The authors recommend further research.

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\*This support was intended to explore the feasibility of using solid state thermal energy storage materials for off-peak cooling of energy efficient buildings.

\*\*TMP is the commercial designation for trimethylol propane (C<sub>6</sub>H<sub>14</sub>O<sub>3</sub>).

■One such company, Eastman Chemical Products Co. in Kingsport, TN has already announced its intent to market neopentyl glycol for thermal storage applications.