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MACRO-ENCAPSULATION OF HEAT STORAGE PHASE-CHANGE
MATERIALS FOR USE IN RESIDENTIAL BUILDINGS

Final Report for September 29, 1976—September 6, 1978

By
George A. Lane
Alan C. Kott
Greg L. Warner
Philip B. Hartwick
Harold E. Rossow

November 1978

Work Performed Under Contract No. EY-76-C-05-5217

The Dow Chemical Company
Midland, Michigan

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	1
I. PHASE CHANGE MATERIALS	2
A. Hydronic Heating	2
B. Water Heating	3
C. Air Heating	4
D. Heat Pump Applications	5
E. Properties of PCM's	5
II. CONTAINER MATERIALS	6
A. Films	6
B. Cans	10
C. Bottles	10
D. Container Costs	11
III. ENCAPSULATION OF PCM'S	14
A. Materials Compatibility	14
1. Film Evaluation	14
2. Plastic Bottle Evaluation	15
3. Steel Can Evaluation	16
4. Compatibility Summary	17
B. Encapsulated PCM Evaluation	17
1. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	19
2. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic	21
3. Stearic Acid - Palmitic Acid	22
4. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	23
5. $\text{NH}_4\text{Br} / \text{Urea}$ Eutectic	23
IV. CONTAINER CONFIGURATION	24
A. Model Heat Exchangers	24
B. Computer Model	25
C. Computer Results	27
D. Sensitivity Analysis	37
V. HEAT STORAGE TEST DEVICE	43
VI. HEAT STORAGE TEST PROCEDURE	46

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
VII. HEAT STORAGE TEST RESULTS	53
A. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	53
B. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	68
C. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic	82
D. $\text{NH}_4\text{Br} / \text{Urea}$ Eutectic	93
E. Double Zone, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} /$ NH_4NO_3	100
F. Discussion of Heat Storage Test Results	111
G. Modelling Refinements: Calcium Chloride Hexahydrate Storage	117
VIII. SYSTEM CONCEPTS AND ECONOMICS	126
A. Passive Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	126
B. Forced Air Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	129
C. Hybrid Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	131
D. Forced Air Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Coupled in Parallel with an Air-to-Air Heat Pump	133
E. Forced Air Solar System Using Encapsulated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic for Thermal Energy Storage	133
F. Double Zone Storage in a Forced Air Solar System	136
G. Economic Analysis and Performance Comparison	139
IX. SYSTEM DESIGN	142
A. Storage Sub-System	143
B. House Plans	145
X. UTILIZATION ACTIVITY	152

TABLE OF TABLES

<u>Table</u>		<u>Page</u>
I	Most Promising Materials for Hydronic Heating Application	2
II	Most Promising Materials for Water Heating Application	3
III	Most Promising Materials for Air Heating Application	4
IV	Most Promising Materials for Heat Pump Application	5
V	Phase Change Materials Selected for Study	6
VI	Physical Properties of R-2 Film	9
VII	Film Container Costs	12
VIII	Bottle and Can Container Costs	13
IX	Evaluation of Plastic Films with PCM's	14
X	Evaluation of HDPE Plastic Bottles with PCM's	15
XI	Evaluation of Sulfonated Plastic Bottles with PCM's	16
XII	Evaluation of Steel Cans with PCM's	17
XIII	Summary of Material Compatibility with PCM's	18
XIV	Selection of PCM-Encapsulant Pairs	19
XV	Encapsulant Lifetime Study	20
XVI	Design Parameters of Model Heat Exchangers	25
XVII	Predicted Efficiencies of Model Systems	28
XVIII	Upper and Lower Air Temperatures for the Five Thermal Batteries Tested	49
XIX	Test Results on Calcium Chloride Hexahydrate Encapsulated in Polyethylene Bottles	62

TABLE OF TABLES (Cont'd)

<u>Table</u>		<u>Page</u>
XX	Theoretical Charge and Discharge Capacities CaCl ₂ ·6H ₂ O in HDPE Bottles	64
XXI	Test Results on Magnesium Nitrate Hexahydrate Encapsulated in Steel Aerosol Cans	75
XXII	Theoretical Charge and Discharge Capacities Mg(NO ₃) ₂ ·6H ₂ O in Steel Cans	80
XXIII	Test Results on Magnesium Nitrate Hexahydrate/ Ammonium Nitrate Eutectic Encapsulated in R-2 Retort Film Pouches	88
XXIV	Theoretical Charge and Discharge Capacities Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ in Plastic Pouches	91
XXV	Theoretical Charge and Discharge Capacities: Urea/Ammonium Bromide Eutectic in Polypropylene Bottles	97
XXVI	Test Results Urea/Ammonium Bromide Eutectic Encapsulated in Polypropylene Bottles	98
XXVII	Theoretical Storage Capacity, Two-Zone Unit	109
XXVIII	Test Results, Double Zone Storage Unit; CaCl ₂ ·6H ₂ O in Aerosol Cans and Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ Eutectic in R-2 Retort Pouches	110
XXIX	Data Used to Calculate NTU Values	114
XXX	Number of Transfer Units and Storage Mass per Unit Area of Collector	115
XXXI	Physical Properties of Storage Media	118
XXXII	Solar Home Specifications	126
XXXIII	Cost Analysis for Solar Collection in Conservatory	128
XXXIV	Cost Analysis for Passive Solar System; CaCl ₂ ·6H ₂ O in HDPE Pipes	129
XXXV	Cost Analysis of Forced Air and Hybrid Solar Systems: CaCl ₂ ·6H ₂ O in HDPE Pipes	131

TABLE OF TABLES (Cont'd)

<u>Table</u>		<u>Page</u>
XXXVI	Cost Analysis for Forced Air Solar System, Using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic	136
XXXVII	Cost Analysis for a Double Zone Solar Heating System	138
XXXVIII	Economic Basis	140
XXXIX	Economics of Various Home Heating systems	141
XL	Solar Home Specifications, Forced Air Solar Heating System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Heat Storage	144
XLI	Storage Unit Cost, Forced Air System, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in High Density Polyethylene Pipe	145
XLII	Thermal Battery Designs for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Pipe	146

TABLE OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Heat Capacity of PCM's	7
2	Thermal Conductivity of PCM's	8
3	Example of Conceptual Designs, Stearic-Palmitic Acid, 3 Day Storage	26
4	Simulated Discharge Cycle Tall #3 Cans, Stearic- Palmitic Acid, 3 Day Storage, 840,000 BTU	30
5	Simulated Discharge Profile Tall #3 Cans, Stearic- Palmitic Acid, 3 Day Storage in Bed, 840,000 BTU	30
6	Simulated Discharge cycle, 300,000 BTU Stearic- Palmitic Acid System	31
7	Simulated Discharge Cycle, Effects of Container Size and Melting Temperature, 300,000 BTU	32
8	Simulated Discharge Cycle, 2.5 in. Cylinders $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ -Heat Pump System	33
9	Simulated Discharge Cycle, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 300,000 BTU Hydronic Heating System, 2.5 in. Cylinders, Water Heat Transfer Fluid	35
10	Simulated Discharge Cycle, Effects of Melt Temperature and Film Coefficients on Pillow Discharge Curves	36
11	Simulated Discharge Cycle, 300,000 BTU-4"x4" Tetrahedra	38
12	Thermal Energy Storage Unit, Calcium Chloride Hexahydrate in HDPE Bottles, Air Heat Transfer Fluid	39
13	Sensitivity Analysis: 2.4 in. Cylinders of Calcium Chloride Hexahydrate in Thermal Battery, Effect of Crystal Conductivity	40
14	Sensitivity Analysis: 2.4 in. Cylinders of Calcium Chloride Hexahydrate in Thermal Battery, Effect of Air Flow Rate	40

TABLE OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
15	Sensitivity Analysis: 2.4 in. Cylinders of Calcium Chloride Hexahydrate in Thermal Battery, Effect of Supercooling	41
16	Sensitivity Analysis: 2.4 in. Cylinders of Calcium Chloride Hexahydrate in Thermal Battery, Effect of Number of Rows of Cylinders in Direction of Air Flow	42
17	Sensitivity Analysis: 2.4 in. Cylinders of Calcium Chloride Hexahydrate in Thermal Battery, Effect of Air Heat Transfer Constant	42
18	Testing Configuration for the Thermal Storage System When the Transfer Fluid is Air	44
19	Latent Heat Storage Unit Test Procedure	47
20	Comparison of ASHRAE 94-77 Approach to Testing Sensible and Latent Storage Devices	51
21	Computer Prediction of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ Test Unit Response, Discharge Mode	52
22	Thermal Energy Storage Unit, Calcium Chloride Hexahydrate Storage Medium, Air Heat Transfer Fluid	54
23	Charge Cycle: Calcium Chloride Hexahydrate in HDPE Bottles	55
24	Discharge Cycle: Calcium Chloride Hexahydrate in HDPE Bottles	56
25	Degrees of Supercooling vs. Bottle Position in Storage Unit $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Bottles	58
26	Outlet Air Temperature vs. Time, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Bottles, Charge Cycles	59
27	Outlet Air Temperature vs. Time, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Bottles, Discharge cycles	60
28	Charge (Discharge) Time vs. Air Flow Rate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Bottles	63
29	Storage Unit Pressure Drop vs. Air Flow Rate, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Bottles	63

TABLE OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
30	Capacity (Energy) vs. Air Flow Rate, CaCl ₂ ·6H ₂ O in HDPE Bottles	65
31	% Capacity (Energy) vs. Air Flow Rate, CaCl ₂ ·6H ₂ O in HDPE Bottles	65
32	Heat Rate vs. Air Flow Rate, CaCl ₂ ·6H ₂ O in HDPE Bottles	67
33	Capacity (Time) vs. Air Flow Rate, CaCl ₂ ·6H ₂ O in HDPE Bottles	67
34	Thermal Energy Storage Unit, Magnesium Nitrate Hexahydrate Storage Medium, Air Heat Transfer Fluid	69
35	Charge Cycle: Magnesium Nitrate Hexahydrate in Steel Aerosol Cans	70
36	Discharge Cycle: Magnesium Nitrate Hexahydrate in Steel Aerosol Cans	71
37	Outlet Air Temperature vs. Time, Mg(NO ₃) ₂ ·6H ₂ O in Steel Cans, Charge Cycles	72
38	Outlet Air Temperature vs. Time, Mg(NO ₃) ₂ ·6H ₂ O in Steel Cans, Discharge Cycles	73
39	Charge (Discharge) Time vs. Air Flow Rate, Mg(NO ₃) ₂ ·6H ₂ O in Steel Aerosol Cans	76
40	Storage Unit Pressure Drop vs. Air Flow Rate, Mg(NO ₃) ₂ ·6H ₂ O in Steel Aerosol Cans	76
41	Transfer of Energy vs. Air Flow Rate	78
42	Transfer of Energy vs. Air Flow Rate	78
43	Capacity (Energy) vs. Air Flow Rate, Mg(NO ₃) ₂ ·6H ₂ O in Steel Cans	81
44	% Capacity (Energy) vs. Air Flow Rate, Mg(NO ₃) ₂ ·6H ₂ O in Steel Cans	81

TABLE OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
45	Heat Rate vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in Steel Aerosol Cans	83
46	Capacity (Time) vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in Steel Aerosol Cans	83
47	Thermal Energy Storage Unit, Magnesium Nitrate Hexahydrate/Ammonium Nitrate Eutectic Storage Medium, Air-Heat Transfer Fluid	84
48	Outlet Air Temperature vs. Time, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ in Plastic Pouches, Charge Cycles	86
49	Outlet Air Temperature vs. Time, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ in Plastic Pouches, Discharge Cycles	87
50	Charge (Discharge) Time vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ in Plastic Pouches	89
51	Storage Unit Pressure Unit vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ in Plastic Pouches	89
52	Capacity (Energy) vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/$ NH_4NO_3 in Plastic Pouches	92
53	% Capacity (Energy) vs. Air Flow Rate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/$ NH_4NO_3 in Plastic Pouches	92
54	Thermal Energy Storage Unit: Ammonium Bromide/Urea Eutectic Storage Medium, Air Heat Transfer Fluid	94
55	Charge Cycle: Ammonium Bromide/Urea Eutectic in Polypropylene Bottles	95
56	Discharge Cycle: Ammonium Bromide/Urea Eutectic in Polypropylene Bottles	96
57	Charge Cycles, Ammonium Bromide/Urea Eutectic in Polypropylene Bottles	99
58	Discharge Cycles, Ammonium Bromide/Urea Eutectic in Polypropylene Bottles	101
59	Test Time vs. Air Flow Rate for Urea/Ammonium Bromide Eutectic in Polypropylene Bottles	102
60	Pressure Drop vs. Air Flow Rate for Urea/Ammonium Bromide Eutectic in Polypropylene Bottles	102

TABLE OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
61	Two-Zone Thermal Energy Storage Unit: Calcium Chloride Hexahydrate and Magnesium Nitrate Hexahydrate/Ammonium Nitrate Eutectic Storage Media, Air Heat Transfer Fluid	103
62	Charge Cycle: Two-Zone Thermal Battery, Charging Configuration	105
63	Discharge Cycle: Two-Zone Thermal Battery, Discharge Configuration	106
64	Two-Zone Thermal Battery, Charge Cycles	107
65	Two-Zone Thermal Battery, Discharge Cycles	108
66	The Average Fraction of Theoretical Charge and Discharge Capacity Achieved in Thermal Battery Testing vs. the Average Number of Transfer Units . .	116
67	Computer Model for Discharging Subscale $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ Thermal Energy Storage Unit, Superimposed on Test Results	120
68	Computer Model for Charging Subscale $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ Thermal Storage Unit, Superimposed on Test Results	121
69	Full-Scale Storage Unit, Calcium Chloride Hexahydrate Encapsulated in HDPE Cylinders	123
70	Simulated Discharge of Full Scale Thermal Energy Storage Units: Calcium Chloride Hexahydrate in High Density Polyethylene Pipes, for Various Pipe Sizes, Air flow 1200 CFM	124
71	Simulated Discharge of a Full Scale Thermal Energy Storage Unit: Calcium Chloride Hexahydrate in 5.25 in. O.D. High Density Polyethylene Pipes, for Various Inlet Temperatures or Thermostat Settings	125
72	Passive Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	127
73	Forced Air Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	130

TABLE OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
74	Hybrid Passive/Active System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage	132
75	Heat Pump-Coupled System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage, Parallel Operation	134
76	Forced Air Solar System Using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/$ NH_4NO_3 Eutectic for Thermal Energy Storage	135
77	Two-Zone Forced Air System Using Magnesium Nitrate Hexahydrate/Ammonium Nitrate Eutectic and Calcium Chloride Hexahydrate for Thermal Energy Storage	137
78	Solar Home Design - Lower Floor Plan	148
79	Solar Home Design - Upper Floor Plan	149
80	Solar Home Design - Section	150
81	Solar Home Design - Exterior View	151

NOMENCLATURE

A	Air heat transfer constant, dimensionless, equation (1)
A	Surface area for heat transfer, M^2 , equation (11)
C	Storage capacity of thermal battery, KJ, equation (7)
CFM	Air flow rate, ft^3/min
C_L	Specific heat of liquid, KJ/Kg $^{\circ}C$
C_S	Specific heat of solid, KJ/Kg $^{\circ}C$
CSM	Minimum cross section area for air flow, M^2 , equation (12)
C_{tf}	Specific heat of transfer fluid, KJ/Kg $^{\circ}C$
CC	Charge capacity of thermal battery, KJ, equation (2)
DC	Discharge capacity of thermal battery, KJ, equation (3)
D	Cylinder diameter, M, eq (12)
f	Friction factor
gc	Acceleration due to gravity
h_o	Air film heat transfer coefficient, KJ/hr $^{\circ}C M^2$, equation (12)
K	Correction factor for non-ideal air flow, dimensionless, equation (13)
K_L	Thermal conductivity of liquid, KJ/hr $^{\circ}C M^2$
K_S	Thermal conductivity of solid, KJ/hr $^{\circ}C M^2$
L	Heat loss factor, dimensionless, equation (14)
$\dot{m}$	Mass flow rate of transfer fluid, Kg/hr
N_{Re}	Reynolds number, dimensionless measure of turbulence
NTU	Number of transfer units, equation (11)
ΔP	Pressure drop across storage unit, in H_2O
q	Heat rate, KJ/hr
q_D	Design rate, KJ/hr, equation (6)

NOMENCLATURE (Cont'd)

Q_{in}	Total heat delivered to storage unit through transfer fluid, KJ
Q_{out}	Total heat recovered from storage unit through transfer fluid, KJ
SCM	Mass based heat storage capacity, KJ/Kg
SCV	Volumetric heat storage capacity, KJ/Kg
T_{in}	Temperature of transfer fluid entering storage unit, °C
T_{out}	Temperature of transfer fluid leaving storage unit, °C
T_M	Melting temperature, °C
ΔT	Temperature difference of inlet and outlet, °C
ΔT_{IN}	Initial ΔT , °C
TC	Time capacity, hours, equation (8)
TCC	Theoretical charge capacity, KJ
TDC	Theoretical discharge capacity, KJ
TSC	Theoretical storage capacity, KJ
U	Overall heat transfer coefficient, KJ/hr °C M ² , equation (11)
V_{max}	Maximum velocity of transfer fluid through CSM, ft/sec
ΔH_m	Latent heat of fusion, KJ/Kg
ρ	Density, Kg/M ³
τ_c	Charging test time, hours
τ_D	Discharging test time, hours

FOREWORD

The work described in this report is an extension of a basic effort already performed under contract NSF-C906. The general objectives are: 1) to assess the technical and economic feasibility of encapsulated phase change materials (PCM's) for storing heat in residential solar energy systems, and 2) to develop and evaluate such encapsulated phase change materials.

The project involves three tasks:

Task 1 - Materials selection, including a limited literature search, selection of candidate phase change materials, and selection and characterization of encapsulating materials.

Task 2 - Procurement of phase-change and encapsulating materials, encapsulation studies, and testing of the encapsulated materials.

Task 3 - Preliminary design and economic evaluation of a residence-sized heat storage sub-system.

All tasks have been completed.

I. PHASE CHANGE MATERIALS

No single phase change heat storage material will satisfy the requirements of all residential solar systems. Substances with various different melting points are needed, for example, for hydronic heating, hot faucet water, forced air heating, or heat pump systems. We selected for this program several different storage media with melting points ranging from 27° to 89°C, which should satisfy the requirements of the heating systems.

A. Hydronic Heating, 70-90°C.

Current practice is to circulate water at 60-80°C through baseboard heaters. Storage at 70-90°C is needed to allow an adequate heat transfer rate from the storage media to the working fluid. Systems could be designed to operate at considerably lower temperatures, but much larger room heaters would be required.

The suitable materials identified under Contract NSF-C906 for this application were subjected to further tests, and using criteria of heat of fusion, freezing behavior, and cost, the selection was narrowed to the substances shown in Table I.

TABLE I

Most Promising Materials for Hydronic
Heating Application

<u>Material</u>	<u>M.P., °C</u>	<u>ΔH_m, Cal/g</u>	<u>Cost, ¢/Lb</u>
Mg(NO ₃) ₂ ·6H ₂ O	89	38	15
Naphthalene	80	35	10
Ba(OH) ₂ ·8H ₂ O	78	64	30

1. Barium Hydroxide Octahydrate (Ba(OH)₂·8H₂O) - This material has a very high heat of fusion, a high density (2.2 g/cc), good freezing behavior, and no supercooling. Its disadvantages are that barium compounds are more expensive than more common salts, barium hydroxide is toxic upon ingestion, and that Ba(OH)₂·8H₂O reacts with atmospheric carbon dioxide to form barium carbonate, which is unsuitable for heat storage.

2. Naphthalene - This is an inexpensive, widely available organic compound. It has excellent freezing behavior with no supercooling. The "moth ball" smell would be objectionable if it escaped into a residence. A major disadvantage is its open cup flash point, 88°C, only a few degrees above the melting point. This could represent a fire hazard.

3. Magnesium Nitrate Hexahydrate ($\text{Mg}\{\text{NO}_3\}_2 \cdot 6\text{H}_2\text{O}$) - This compound exhibits good freezing behavior, except that it super-cools as much as 15°C . Recent Dow-funded research has discovered several practical nucleating agents which will eliminate this problem. Safety tests so far have shown no fire or deflagration hazard, even when mixed with fuels such as grease, glycol, cellulose, cardboard, or iron powder.

This material seemed the best candidate for this application, so it was chosen for encapsulation studies and storage tests.

B. Water Heating, $60\text{--}80^\circ\text{C}$.

Since water below about 55°C will not remove grease in a dishwasher, 60°C is the lower feasible limit for heat storage for this application. The storage materials discussed in the previous section could also be used. However, it is usually desirable to store heat near the lowest practical temperature for an application -- to minimize heat loss, and to maximize solar collector efficiency.

On the basis of laboratory tests of freezing behavior, heat of fusion, and cost, the suitable materials identified under Contract NSF-C906 were reduced to the four materials listed in Table II.

TABLE II

Most Promising Materials for
Water Heating Application

<u>Material</u>	<u>M.P., $^\circ\text{C}$</u>	<u>ΔH_m, Cal/g</u>	<u>Cost, $\text{\\$/Lb}$</u>
Urea + NH_4Br	76	36	30
Naphthalene + Benzoic Acid	67	29	15
Paraffin Wax	64	42	10
Stearic Acid + Palmitic Acid	60	48	25

1. Paraffin Wax - Many different inexpensive paraffin waxes with different melting points can be obtained. These are under study by several groups at present. These materials typically melt over a temperature range of $5\text{--}10^\circ\text{C}$, rather than isothermally. These waxes have a lower density than most other heat storage candidates.

2. Urea-Ammonium Bromide Eutectic ($\text{Urea} + \text{NH}_4\text{Br}$) - This material exhibits excellent freezing behavior with no super-cooling, and good density (about 1.8 g/cc). The fire retardant properties of the bromide are a favorable factor. Bromides are more expensive than the more common salts, but wider use could allow lower prices. This eutectic was selected for encapsulation studies and heat storage tests.

3. Stearic Acid + Palmitic Acid - The fatty acids can be obtained in a variety of mixtures with different melting points. They have excellent freezing properties and no supercooling. The cost is higher than for other candidate materials. We elected to pursue encapsulation studies with the stearic acid mixture melting at 60°C (Emery 421).

4. Naphthalene + Benzoic Acid Eutectic - This organic substance has good freezing behavior, except for supercooling of about 2°C. The flash point (open cup) was determined to be 95°C, providing a margin of safety of 28°C above the melting point. The "moth ball" odor would be objectionable, but would be a ready indicator of a leaking capsule. Encapsulant compatibility studies were done on this material.

C. Air Heating, 40-60°C.

Most forced-air heating systems are designed to discharge air above 30°C. To provide a heat exchange gradient, the storage temperature should be about 40°C, or more. The list of potentially suitable materials discovered under Contract NSF-C906 was narrowed to the candidates shown in Table III through laboratory freezing tests, and consideration of heat of fusion, cost, stability, and hazard.

TABLE III

Most Promising Materials for
Air Heating Application

<u>Material</u>	<u>M.P., °C</u>	<u>ΔH_m, Cal/g</u>	<u>Cost, ¢/Lb</u>
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃	52	30	10
Pinacol·6H ₂ O	45	70	--
Urea + NH ₄ NO ₃	44	--	5

1. Urea-Ammonium Nitrate Eutectic (Urea + NH₄NO₃) - This material is quite inexpensive and has acceptable freezing behavior. It was rejected because some NH₄NO₃ - urea mixtures are explosive. While there is no evidence that this eutectic is hazardous, we feel it best not to take the risk.

2. Pinacol Hexahydrate - This organic hydrate has a very good heat of fusion. It supercools excessively, however, and is not commercially available.

3. Magnesium Nitrate Hexahydrate - Ammonium Nitrate Eutectic (Mg(NO₃)₂·6H₂O + NH₄NO₃) - This substance is inexpensive and has good freezing behavior, except for supercooling 6-8 degrees. Recent Dow-funded research has uncovered a few nucleating agents which minimize supercooling.

The oxidizing nature of nitrates might represent a safety problem. Initial tests, DTA and impact, have not uncovered a hazard.

This material was selected for encapsulation studies and heat storage tests for the air heating application.

D. Heat Pump Applications, 20-40°C.

Phase change materials can be used to store low level solar energy as a source for a heat pump. The isothermal storage property is very beneficial to the COP (coefficient of performance) of the heat pump. The materials identified during Contract NSF-C906, through consideration of freezing behavior, cost, hazards, commercial availability, and heat of fusion, were reduced to those shown in Table IV.

TABLE IV

Most Promising Materials for
Heat Pump Application

<u>Material</u>	<u>M.P., °C</u>	<u>ΔH_m, Cal/g</u>	<u>Cost, ¢/Lb</u>
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	35	67	20
Methylnaphthalene	24	35 (est.)	15 (est.)
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	27	46	5

1. Disodium Phosphate Dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) - This inorganic hydrate salt has a very high heat of fusion. Potentially, the cost could be much lower than at present. Its principal drawback is the freezing behavior. In addition to severe supercooling, there are a multiplicity of hydrates and phases. Several researchers have attacked this problem, with no adequate solution.

2. Methylnaphthalene - This organic compound has excellent freezing behavior. It is not available in bulk, but should be plentiful as new naphtha-cracking plants are built.

3. Calcium Chloride Hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) - This material has good freezing behavior if nucleators, discovered under Contract NSF-C906 and recent Dow-funded work, are used. This substance is inexpensive and readily available commercially. It was chosen for encapsulation work and for heat storage testing.

E. Properties of Phase Change Materials.

The PCM's selected for study are listed in Table V. The heats of fusion listed were determined at The Dow Chemical Company. The value for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is the sum of the melting

endotherm at 89°C (33.3 cal/g) and a crystal transformation at 73°C (2.6 cal/g). The right hand column is an indication of the economy of each PCM, i.e., the number of Kcal that can be stored in a penny's-worth of PCM.

TABLE V
Phase Change Materials
Selected for Study

<u>Materials</u>	<u>M.P., °C</u>	<u>ΔH_m Cal/g</u>	<u>Cost, ¢/Lb</u>	<u>ΔH_m/Cost, Kcal/¢</u>
Mg(NO ₃) ₂ ·6H ₂ O	89	36	15 (est.)	1.09
Urea + NH ₄ Br	76	36	30	0.54
Naphthalene + Benzoic Acid	67	29	15	0.88
Stearic Acid Mix	60	48	25	0.87
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃	52	30	10	1.36
CaCl ₂ ·6H ₂ O	27	46	5	4.17

The heat capacities of both liquid and solid PCM's were measured. Data are shown in Figure 1. The thermal conductivities of the crystalline PCM's were also determined, as displayed in Figure 2.

II. CONTAINER MATERIALS

A variety of containers was examined under this program. They include aluminum and steel cans, plastic bottles, flexible plastic film packages, and plastic tubes.

A. Films.

Film packages potentially are the lowest cost packaging material for an encapsulated HOF heat exchanger. They are not as rugged as cans or bottles and need external support.

The major criteria used in selecting films were:

- i) cost of the finished package
- ii) permeability
- iii) mechanical strength at elevated temperature
- iv) chemical resistance
- v) ease of reliable manufacture using state-of-the-art techniques.

Fifteen commercial types of packaging film were considered as candidates for HOF storage devices. None is wholly suitable. Multi-layer laminations are needed to supply the necessary combination of strength, permeability, and inertness.

Figure 1
HEAT CAPACITY OF PCM'S

Figure 2

THERMAL CONDUCTIVITY OF PCM'S

An economical and universally applicable film is the high density polyethylene/aluminum/polyester combination. It possesses maximum barrier properties, and is an item of commerce, useful in commercial markets other than HOF storage. The raw material costs are lower than those of other combinations. Long production run lamination economics apply.

Two commercial types of high density polyethylene/aluminum/polyester film have been identified. Reynolds Metals Company and Continental Can Company produce R-2 Retort Film. The film is a laminate of 3 mil polyethylene, 3.5 mil foil and .5 mil Dupont Mylar brand polyester. The product, tested at Natick Laboratory for over 14 years, is designed for long term storage followed by boil-in-the-bag preparation of military rations. The film is used commercially overseas for the storage and cooking of foodstuffs. Physical property data are given in Table VI.

R-2 Retort Film was chosen for evaluation as a PCM encapsulant, and for heat storage tests with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic PCM.

TABLE VI

Physical Properties of R-2 Film

<u>Property</u>	<u>Room Temp.</u>	<u>160°F</u>	<u>Test</u>
Tensile Strength, psi			ASTM D882-67
Machine Direction	7320	4550	
Transverse Direction	6785	4575	
Elongation, %			ASTM D882-67
Machine Direction	85	120	
Transverse Direction	80	215	
Tensile Modulus, psi (2% Secant)			ASTM D882-67
Machine Direction	163500	114500	
Transverse Direction	151700	105400	
Water Vapor Transmission g Loss/24 hr/100 sq in/ mil at 100°F, 90% RH		<0.01	

St. Regis Paper Company manufactures the Alure series of aluminized Mylar brand polyester film and polyethylene laminations. Grade CX contains 0.5 mil aluminized polyester laminated to 2 mil high density polyethylene. Although not as effective a barrier as the three part R-2 film, barrier properties are reported as acceptable.

The American Can Company produces Glaminate film, a laminate of polyethylene, aluminum foil, paper, and polyethylene, for use in consumer containers such as toothpaste tubes. The major advantage of Glaminate film over Retort film is that the low density polyethylene on both sides allows a strong lap seam rather than a weak pouch seam. Tubes are presently made up to 1 15/16" diameter and 8" long. The cost of these containers approaches that of bottles and cans, however.

B. Cans.

Aluminum cans were originally proposed as the material of choice for metal containers. Consultation with can manufacturers¹ and packaging specialists² indicates that steel cans will be superior. When compared with steel cans, aluminum cans are:

- i) more susceptible to internal corrosion
- ii) weaker
- iii) subject to size restrictions
- iv) expected to be more expensive.

Aerosol cans are stronger than regular steel cans, and manufactured to stricter tolerances. Standard aerosol sizes more nearly fit needs for the narrow, tall can desired for more efficient heat transfer. Therefore, aerosol cans were chosen for our study, and for heat storage testing with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

C. Bottles.

Four types of plastic were considered as candidates for plastic bottles, high density polyethylene, high density polyethylene-saran laminates, polypropylene, and high barrier styrene-acrylonitrile.

The high density polyethylene and polyethylene-saran laminates have good resistance to water vapor transmission. Calculations based on the equilibrium vapor pressure of water over calcium chloride hexahydrate indicate that after 20 years storage in a standard 25 mil wall thickness, 16 ounce polyethylene or polyethylene-saran laminate bottle, 0.4% of the water of hydration would be lost. This assumes an average

¹Personal Communication, R. J. O'Brian, Aluminum Company of America, Pittsburgh, Pennsylvania.

²Personal Communication, G. Brockman, Continental Can Corporation, Chicago, Illinois.

relative humidity of 25% in the heated space. This water loss should cause a decrease of about 4% in the heat storage capacity of the PCM over the 20 year period. High density polyethylene bottles were selected for evaluation in this program, and for heat storage testing with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Carbon dioxide diffuses through a polyethylene bottle rapidly, and it could not protect a carbon dioxide absorbent HOF material such as barium hydroxide octahydrate. Saran-high density polyethylene laminate bottles exhibit carbon dioxide permeabilities reduced by a factor of 300 when compared to polyethylene. A 16 ounce, 25 mil wall thickness laminate bottle could allow about 7 grams of carbon dioxide to enter during a 20 year exposure.

Aromatic hydrocarbons attack polyethylene at elevated temperatures. The rate through a standard 25 mil wall thickness bottle could approach 0.8 grams per day.

Surface sulfonation of high density polyethylene greatly reduces hydrocarbon permeance. Published data³ state that sulfonation protects the resin from attack by gasoline and can reduce diffusion to 0.002 grams per day or 4% of the net contents of a 16 ounce bottle after 20 years. Sulfonated polyethylene bottles were chosen for evaluation as encapsulants for organic PCM's.

Polypropylene is much more permeable to water vapor than high density polyethylene. However, it will withstand somewhat higher temperatures, and is more resistant to cracking. Polypropylene bottles were selected for evaluation with non-hydrated PCM's, and were used for heat storage tests on NH_4Br /urea phase change material.

D. Container Costs.

Costs for a variety of filled containers are presented in Tables VII and VIII. The costs are based on distributor prices and estimates of filling expense. Mark-ups and cost of HOF materials are not included. The costs of a cubic foot of containment are rounded to the nearest \$0.05. Values shown for containment of 300,000 BTU latent heat are rounded to the nearest \$5.

³ Ziemba, G.P., Thomas, L. S., Parsons, C. P., Hallo, R. A., "Surface Sulfonation-A Practical Solution to Eliminating The Hydrocarbon Permeation Problem with HDPE Fuel Tanks". Society of Plastics Engineers National Technical Conference, "Plastics. . .Serving Man in Motion", Nov. 12-14, 1974, Detroit, Michigan.

As expected, film container estimated costs are lower than those of other containers. The cost of packing a given amount of material increases as the container size decreases.

Although the data presented are tentative, a limited comparison with conventional systems indicates that containment costs are reasonable. At \$0.75 a gallon the containment cost for a 300,000 BTU sensible heat water system with a 40°F swing would be about \$675. The most expensive macroencapsulation estimate is considerably lower.

TABLE VII

Film Container Costs

Film Containers

Material	Polyester/Aluminum Foil/Polyethylene			
Container	Tube	Tube	Pillow	Tetrahedron
Dimensions, in	48 X 4	24 X 2	8 X 5.5 X 1.25	4 X 4
Area, in ²	600	164	124	28
Film Cost, \$	0.265	0.065	0.05	0.011
Fill Cost, \$	0.100	0.03	0.01	0.005
Mesh Bag ² , \$	0.05	0.025	--	--
Total, \$	0.415	0.12	0.06	0.016
Volume-Ft ³	.347	.043	.033	0.0043
Cost/Ft ³ , \$	1.20	2.80	1.80	3.70
Cost for 300,000 BTU CaCl ₂ ·6H ₂ O, \$	40 ¹	95	60	125

¹4-inch diameter not suitable for 300,000 BTU unit.

²Mesh bag used as exterior support for tube.

TABLE VIII

Bottle and Can Container Costs

Bottles

Material	Glass	Glass	Plastic	Plastic
Size - oz.	48	16	48	16
Capacity - in ³	87	29	87	30
Cost, \$	.23	.10	.18	.08
Cost/Ft ³ , \$	4.60	6.00	3.60	4.60
Cost for 300,000 BTU CaCl ₂ ·6H ₂ O, \$	155 ¹	205	120 ¹	160
Stearic Acid	320 ¹	390	230 ¹	300

Cans

Type	Sanitary	Sanitary	Aerosol
Style	No. 3 Tall	No. 300	202 X 708
Dimensions, in	4.25 X 7	3 X 4.43	2.125 X 7.5
Capacity - in ³	83	25	22.5
Cost, \$	.18	.07	.10
Cost/Ft ³ , \$	3.75	4.85	7.70
Cost for 300,000 BTU CaCl ₂ ·6H ₂ O	130 ¹	165	265

¹ 4 inch diameter not suitable for 300,000 BTU unit.

III. ENCAPSULATION OF PHASE CHANGE MATERIALS

To develop suitable encapsulated PCM's, the compatibility of individual PCM's with samples of the candidate encapsulant materials was studied. Selected PCM-encapsulant packages were then prepared and subjected to cyclic freeze-thaw tests.

A. Materials Compatibility.

1. Film Evaluation - The compatibility of PCM's with laminated plastic films was tested by fabricating 3 1/4" x 5 3/4" pillows or 1 11/16" x 6 1/2" cylinders filled with the molten PCM's, and storing them at a temperature 5-15°C above the melting point of the PCM. As shown in Table IX, the lower-melting inorganic materials proved compatible, while the higher-melting materials tended to attack the heat sealed areas at the seams.

TABLE IX

Evaluation of Plastic Films with PCM's

<u>Materials</u>	<u>R-2 Retort Film</u>	<u>Glaminate® Film</u>	<u>Alure Film</u>
Mg(NO ₃) ₂ ·6H ₂ O, 100°C	Seams Leak in 7 Days	Embrittles	Seam Failed, 1-3 Days
NH ₄ Br + Urea, 90°C	-	Film Splits	-
Naphthalene + Benzoic Acid, 90°C	PCM Migrates Thru Seam, 1 Day	Film Delaminates	-
Stearic Acid Mix, 75°C	Leaked Out, 13 Days	-	Seam Rupture, 1 Day
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃ , 70°C	OK, 32 Days	OK, 28 Days	OK, 32 Days
CaCl ₂ ·6H ₂ O, 45°C	OK, 32 Days	OK, 28 Days	OK, 32 Days

R-2 Retort Film was selected for further work with Mg(NO₃)₂·6H₂O/NH₄NO₃ eutectic. It is more rugged than Alure Film and considerably less costly than Glaminate® Film.

2. Plastic Bottle Evaluation - The compatibility of PCM's with high density polyethylene (HDPE) was studied by cutting 4" long "dog bone" test bars 1/8" wide in the test area. These specimens were formed from the sides of the plastic bottles and selected to be similar in thickness. Tensile strength was measured before exposure, after dry exposure to the test temperature, and after immersion 4 weeks at the test temperature in the liquid PCM. Test temperatures were the same as used for the plastic films. As outlined in Table X, only the two lower-melting PCM's are compatible with the bottle material.

TABLE X

Evaluation of HDPE Plastic Bottles with PCM'S

<u>PCM Materials</u>	<u>Storage Temp., °C</u>	<u>Tensile Strength, Psi</u>
None	20	2660
None	100	Failed; brittle
Mg(NO ₃) ₂ ·6H ₂ O	100	3200; brittle
None	90	2860
Naphthalene + Benzoic Acid	90	2200; 8-13% wt. gain
None	75	2820
Stearic Acid Mix	75	2800; 5% wt. gain
None	70	2860
Mg(NO ₃) ₂ ·6H ₂ O + NH ₄ NO ₃	70	2940
CaCl ₂ ·6H ₂ O	45	2870

The two next higher-melting materials will not weaken the bottles, but dissolve into the plastic. No conclusion can be drawn about the highest-melting PCM, since the bottle itself fails at this temperature.

Sulfonated polyethylene bottles were tested, as the surface layer of sulfonated plastic resists chemical migration. Results are outlined in Table XI.

TABLE XI

Evaluation of Sulfonated
Plastic Bottles with PCM's

<u>PCM Materials</u>	<u>Storage Temp., °C</u>	<u>Tensile Strength Psi</u>	<u>Wt. Change, %</u>
None	20	2610	0.00
None	85	2720	-0.09
Naphthalene + Benzoic Acid	85	2750	+0.09
Stearic Acid Mix	85	2750	+0.09

The sulfonated bottles showed negligible uptake of naphthalene-benzoic acid eutectic or stearic acid mixture, in contrast to weight gains of 5-13% observed for the unsulfonated bottles. In spite of the low uptake of PCM, a few tiny crystals of naphthalene were found on the outside of the bottle in an area where sulfonation apparently was spotty.

HDPE plastic bottles were chosen for further studies with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Sulfonated polyethylene bottles were chosen for tests with the stearic acid mixture. Polypropylene bottles were selected for development with the NH_4Br /urea eutectic. At this point in the program it was decided to delete further work on the naphthalene/benzoic acid eutectic, substituting NH_4Br /urea eutectic. This was done because of difficult containment problems, poor heat conductivity, flammability, low heat of fusion, and odor.

3. Steel Can Evaluation - To determine the compatibility of PCM's with metal cans, 1" x 3" coupons were cut from the sides of seamed and drawn aerosol cans. No surface treatment, other than washing with acetone, was used. The coupons were immersed in molten PCM's for 1 month and the corrosion rate determined by weight loss. Table XII shows the results.

Either type of can should be suitable for encapsulating calcium chloride hexahydrate, if air is excluded during filling. The corrosion rates for magnesium nitrate hexahydrate and its eutectic with ammonium nitrate are higher, but could be acceptable for either type of can. Stearic acid mixture is marginal, and further tests should be run, if encapsulation in steel cans is to be recommended. The corrosion rate for the eutectics of naphthalene with benzoic acid and ammonium bromide with urea are too high for these PCM's to be used in steel cans.

TABLE XII

Evaluation of Steel Cans with PCM's

<u>Materials</u>	<u>Temp. °C</u>	<u>Corrosion Rate, lbs/ft²/day</u>	
		<u>Seamed Cans</u>	<u>Drawn Cans</u>
CaCl ₂ ·6H ₂ O*	50	1.1 x 10 ⁻⁶	0.8 x 10 ⁻⁶
CaCl ₂ ·6H ₂ O	50	1.2 "	1.0 "
Mg(NO ₃) ₂ ·6H ₂ O	100	3.1 "	9.6 "
Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃	70	9.1 "	6.6 "
Stearic Acid	75	21.3 "	14.3 "
Naphthalene/Benzoic Acid	90	123. "	113. "
NH ₄ Br/Urea	90	-	400 "

*0.2% Corrosion inhibitor added.

A corrosion rate of 15×10^{-6} lbs/ft²/day is equal to about 0.1 mil/yr, or 2 mils in 20 years. The seamed aerosol can is 10 mil thick, and the drawn can 7.5 to 8.5 mil thick. In actual use, corrosion will be non-uniform.

We elected to pursue studies with drawn steel aerosol cans with Mg(NO₃)₂·6H₂O and CaCl₂·6H₂O.

4. Compatibility Summary - Table XIII summarizes the compatibility data discussed above. For CaCl₂·6H₂O and the Mg(NO₃)₂·6H₂O/NH₄NO₃ eutectic, all the encapsulating materials appear usable. For naphthalene/benzoic acid and stearic acid, the sulfonated polyethylene bottle is the only possible satisfactory encapsulant. For magnesium nitrate hexahydrate, steel cans are the only potentially feasible encapsulating material. For NH₄Br/urea, films and cans are inadequate, but plastic bottles (though not tested) are apt to be acceptable. Polypropylene bottles should withstand a higher temperature than polyethylene, and the superior vapor barrier properties of HDPE may not be needed, since this PCM is not hydrated.

B. Encapsulated PCM Evaluation.

Based on the PCM-container compatibility tests, various PCM's were encapsulated, and the packaged materials subjected to multiple freeze-thaw cycles. The PCM-encapsulant pairs shown in Table XIV were chosen for these tests. In addition, a wider selection of bottles and cans was studied for CaCl₂·6H₂O.

TABLE XIII

Summary of Material Compatibility with PCM's

Encapsulant Material	PCM Material					
	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + NH_4NO_3	Stearic Acid	Naphthalene + Benzoic Acid	NH_4Br + Urea	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Polyethylene Bottle	OK	OK	Weight Gain	Weight Gain	-	Embrittles
Sulfonated Polyethylene Bottle	-	-	OK	OK	-	-
R-2 Retort Film	OK	OK	Seam Leaks	Seam Migration	-	Seam Leaks
Alure Film	OK	OK	Seam Rupture	-	-	Seam Leaks
Glamate Film	OK	OK	-	NG	NG	Embrittles
Drawn Steel Can	OK	OK	Marginal	NG	NG	OK
Seamed Steel Can	OK	OK	Marginal	NG	-	OK

TABLE XIV

Selection of PCM-Encapsulant Pairs

<u>Phase Change Material</u>	<u>Fusion Temp. (°C)</u>	<u>Encapsulant</u>
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	27	High Density Polyethylene (HDPE) Bottle
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ Eutectic	50	R-2 Retort Film
Stearic Acid + Palmitic Acid	60	Sulfonated HDPE Bottle
$\text{NH}_4\text{Br}/\text{Urea}$	76	Polypropylene Bottle
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	89	Drawn Steel Aerosol Can

Table XV summarizes the results of the cycling tests. The heating/cooling modes were performed using forced air when cycled in the storage test unit and free convection when cycled in an oven.

1. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - Two sizes of sealed HDPE bottles (0.47 and 1.00 liter) filled about 90% with liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ were cycled 150 times in an oven. Also, 129 HDPE bottles (0.47 liter) were cycled nearly 70 times in the thermal energy storage unit. The results were similar in both cases with visible signs of stress cracks developing along the top edge shoulder of the bottles. Over half of the bottles in the storage unit developed stress cracks. The most severe cases occurred near the air inlet of the storage unit where the temperature changes are the most rapid. Even though all the bottles in the oven developed cracks by 150 cycles, there were no air or liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ leaks detected in the tests using the oven or storage unit. Stress cracks are due to the contraction/expansion of the bottle with a 10% volume variation upon changing phase.

To overcome the problem of stress crack formation, we investigated the possibility of using a flexible, low density polyethylene (LDPE) bottle, or a polyethylene (50/50 blend of high/low density) "concentina" bottle with bellows (3/8" deep). These bellows are located about 1/2" apart along the full 7" length of the bottle. However, during phase change only the top 2-3 bellows are involved in the expansion/contraction of the bottle. This is especially appealing, since a bottle

TABLE XV

Encapsulant Lifetime Study

Phase Change Material	Encapsulant		Testing Device	No. Of Cycles (Approx.)	No. of Containers		
	Type	Size (Liters)			Tested	Partial Failure	Leaks
<u>CaCl₂ • 6H₂O</u>							
	HDPE Pipe (Phillips)	1.41	Oven	114	4	0	0
	HDPE Bottle (Monsanto)	0.47	Storage Unit	70	129	71	0
	" " "	0.47	Oven	150	6	6	0
	" " (Dow)	1.00	"	150	6	6	0
	"Concertina" Bottle (with Bellows)	0.95	"	130	1	0	0
	LDPE Bottle	1.00	"	130	1	0	0
	Polypropylene Bottle	0.39	"	40	3	0	0
	Steel Aerosol Can						
	Seamless (Drawn)	0.58	"	130	1	0	0
	Seamed (Soldered)	0.58	"	130	1	0	0
	Steel Paint Can	3.79	"	20	2	0	0
<u>Mg(NO₃)₂ • 6H₂O/NH₄NO₃ Eutectic</u>							
	R-2 Retort Film (3.85 mils)						
	Vertical Pouch (3-Seam)	0.24	"	50	3	0	3
	Horizontal " "	0.24	"	100	3	0	0
	R-2 Retort Film (4.15 mils)						
	Horizontal Pouch						
	4 Seams	0.66	"	80	3	0	3
	3 Seams	0.75	"	180	3	1	0
	3 Seams	0.75	Storage Unit	16	75	15	22
<u>Stearic Acid + Palmitic Acid</u>							
	Sulfonated HDPE	0.36	Oven	50	8	8	4
<u>Mg(NO₃)₂ • 6H₂O</u>							
	Steel Aerosol Can						
	Seamless (Drawn)	0.53	Storage Unit	20	128	0	51
	"	0.53	Oven	150	3	0	3
	Seamed (Welded)	0.56	"	10	1	0	1
	Seamed (Soldered)	0.56	"	10	1	0	1
<u>NH₄Br/Urea Eutectic</u>							
	Polypropylene Bottle	0.39	"	110	4	0	0
	" "	0.47	Storage Unit	18	150	0	0

design with only a few bellows near the top would not significantly increase the container cost, while greatly increasing container life. After 130 cycles, both bottle types show no signs of stress cracks. However, compared with HDPE, the moisture loss rate is five times as great for LDPE and probably over twice as fast for the "concertina" bottle.

Polypropylene bottles have also given good results, but this plastic is much more permeable to water vapor than HDPE (about the same as LDPE).

Various types of steel cans have also given promising results with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. If air is excluded from the can, acceptably low corrosion rates can be obtained.

2. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic - R-2 retort film, commercially used for storing and cooking foodstuffs, was used to encapsulate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ eutectic. This film, available from Continental Can Company, is a laminate of 3 mils polyethylene, .35 mils aluminum foil, and .5 mils Dupont Mylar brand polyester. Six 3-seam pouches (.24 liter, about $1 \frac{3}{4}$ " x 11" x $\frac{3}{4}$ ") were made using a Vertrod impulse heat sealer (Model 20P - $\frac{1}{8}$ " wide seal). The film was folded lengthwise and sealed on three sides, leaving a small filling section. After the pouch was filled with liquid eutectic, excess air was squeezed out of the pouch and the fill-hole was heat-sealed closed.

Three pouches were suspended vertically and three were laid horizontally on a metal support. After 50 cycles all three suspended pouches had ruptured at the seam intersection at the lower corner of the pouch. It is believed that the weight of the PCM along with some isolated expansion of the PCM during initial melting created excessive stress on the seam. However, the horizontally laid pouches lasted over 100 cycles. The volume reduction of the material causes the pouch to suck in at the top surface along its entire length. This widely distributed depression of the film was not symmetric in that different size dimples form along the length of the pouch. Fortunately, these dimples appear in different sizes and locations at the top surface with each freezing cycle, thus helping to extend the life of the film.

A second R-2 retort film (3.3 mils polyethylene, .35 mils foil and .5 mils polyester) was used to fabricate larger pouches (about $2 \frac{3}{4}$ " x $17 \frac{3}{4}$ " x 1"). Three 4-seam (.66 liter of PCM) and three 3-seam (.75 liter of PCM) pouches were prepared, filled 87% full, and laid horizontally on a metal support. After 80 cycles the 4-seam pouches had ruptured at the center of one lengthwise seam. However, the 3-seam pouches were still intact after 180 cycles, with one pouch just starting to show

signs of stress at the center of its lengthwise seam. Both pouch types form dimples as observed previously, and even though there was less PCM contained in the 4-seam pouch (both pouches filled to the same % capacity), it is not known why the lifetimes differed so greatly. It is believed that these pouch lifetimes will depend primarily on the size of the pouch, the % filled with PCM, and the quality and width of the seal.

3-Seam pouches were evaluated in the thermal storage test unit. Metal racks were used to support the pouches horizontally, with air blown past them in a vertical flow pattern. Several pouches developed split seams, leaking a portion of their contents. Several more showed signs of delamination of the heat seal in the mid-region of the long seam. Of the 75 pouches in the test unit, 22 split and 15 showed signs of delamination after sixteen cycles. These pouches, exposed in the storage test unit, were 3/4" shorter than the units previously oven tested, and were filled to roughly 88% (compared with roughly 87%) capacity. The higher failure rate is most likely the result of more severe conditions - high air flow and high heat transfer - in the storage test unit. Larger pouches or a lower % fill may be successful.

We conclude that, unless a more reliable sealing technique can be demonstrated, the PCM heat storage environment is too severe for these film packages.

3. Stearic Acid - Palmitic Acid - The inside surfaces of eight round-shouldered HDPE bottles (.36 liter) were sulfonated in an effort to provide extra chemical resistance to the PCM mixture of stearic and palmitic acid. By 50 freeze-thaw cycles in the oven, all of the bottles developed stress cracks, with half of them actually leaking liquid PCM. It is suspected that leaks result much faster once the initial stress crack forms and the unsulfonated material under the sulfonated surface is exposed.

This PCM upon cooling freezes differently from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, in that it doesn't form a pocket in the top center of the solid PCM. Rather, the entire mixture shrinks uniformly, pulling itself away from the inside wall of the container. Unless a container is used which will shrink or collapse with this material, poor heat transfer will result from this dead air space.

This encapsulant is deemed unsatisfactory for this PCM.

4. Mg(NO₃)₂·6H₂O - Various types of steel aerosol cans were cycled both in the storage unit and oven. In nearly all cases, the can developed hair-line stress cracks at various locations. The type of can used (drawn, welded, or soldered) often determined the location of the stress cracks. Cracks developed: (1) on the top edge shoulder just below the dome for drawn seamless cans, (2) on the seam for welded seamed cans and (3) on the dome for soldered seamed cans. It is suspected that in all cases the cracks develop where the steel can had been worked or heat treated the most. Also, there may be variations in stress crack location with procedural changes in can fabrication or different batches of the same type can.

The problem has been identified as intergranular cracking caused by nitrate stress corrosion. Tin plating on the can is corroded away before nitrate attack on the steel. Stress corrosion cracking is difficult to inhibit. However, several means should be tried - cathodic protection, stress annealing, galvanic protection, and chemical inhibition.

5. NH₄Br/Urea Eutectic - Compatibility tests of this PCM with plastics had not been conducted, but we felt confident to proceed with cycling tests in plastic bottles. Experience at Dow has shown NH₄Br compatible with olefin-based plastics. The hydrophillic urea should not attack nor dissolve in hydrophobic plastics such as polyethylene or polypropylene. Due to the cracking experienced with high density polyethylene bottles, we decided to use polypropylene bottles, which are more resistant to cracking and to high temperature, for this PCM. Polypropylene bottles filled with NH₄Br/urea composition were subjected to 110 freeze-thaw cycles in an oven, without any apparent degradation of PCM or encapsulant.

In 18 cycles in the storage test unit, no failure of the polypropylene bottles was observed. However, in every case, separation of the PCM into three layers in the horizontally-oriented bottles was observed. DTA studies showed the middle layer to be little-changed, the top layer to be enriched in urea, and the bottom layer enriched in NH₄Br with a small amount of unidentified new material melting at 150°C.

Infrared analyses were run at liquid nitrogen temperature of KBr discs of the material in the three layers. Essentially the same results were obtained - urea enrichment in the top layer, NH₄Br enrichment in the bottom layer, little change in the middle layer. No new absorption bands were found, giving no information about the 150°C m.p. material. X-ray diffraction analysis showed a new crystal pattern in both the freshly prepared eutectic and in the bottom layer of cycled material. The new pattern did not correspond to those in standard X-ray tables.

IV. CONTAINER CONFIGURATION

The containers considered in this program have been restricted to materials, shapes, and sizes which are commercially available from manufacturers' stock or based on standard tooling and stock materials.

Although the thermal storage test unit constructed during this project is not full-sized, the container sizes, internal geometry, flow rates and heat transfer rates are as close to those of a practical, commercial unit as possible. The container and heat exchanger parameters have been chosen on the basis of computer studies, based on a simple mathematical model of a thermal energy storage unit suitable for a small commercial building or a medium-sized residence.

Three basic container shapes were considered: cylinders, tetrahedra, and pillows. Cylindrical containers include metal cans, glass and plastic bottles, and chub-type flexible film packages. Tetrahedra and pillows must be fabricated from plastic film.

The sizes and shapes for each container candidate were based on trade-offs between calculated heat transfer effectiveness, the magnitude of pressure drops in air heat transfer systems, costs, and the volumetric efficiency of the total heat transfer unit. In general, the container costs, pumping losses, and the floor space associated with a specific mass of heat of fusion (HOF) material are improved as container size increases but the heat transfer rates and efficiency are degraded.

A. Model Heat Exchangers.

The trade-offs used to specify containers were based on a simple computer simulation of a hypothetical heat of fusion thermal energy storage heat exchanger. Three types of exchangers were designed and modeled. They included conventional hot air and hot water systems, and a heat pump system. The hot air and hot water systems passed air or water over encapsulated HOF materials, heated the fluid, then pumped the fluid directly to the load space. The heat pump was assumed to pass HOF-warmed air past the evaporator coils and load space air past the condenser coils. Table XVI lists the flows, pressure drop, and cut-off temperatures used in the models.

Two capacities were simulated. A one-day storage system was assigned a capacity of 300,000 BTU of latent heat, a three day system required 900,000 BTU. These values correspond with approximately 60% of the heating system demand in a 1500 square foot (medium-sized) northern home during the coldest months and 100% of the demand at the beginning and end of the heating season.

The dimensions and capacities of standard sized commercial containers were used to design model heat exchangers for each HOF material and package type. A representative design is illustrated in Figure 3.

TABLE XVI

	Design Parameters of Model Heat Exchangers		
	Hot Air	Hot Water	Heat Pump
Flow	1200 CFM	7.5 GPM	1200 CFM
Pressure Drop	1" H ₂ O	-	1" H ₂ O
Discharge Temperature at Termination	95°F	150°F	35°F
Load Air Temperature	65°F	65°F	65°F
Minimum Permissible Output BTU/HR	38,880	30,000	30,000

Container	Container Dimensions Inches
Cylinder	
Tall No. 3 Can	4.25 x 7
No. 300 Can	3 x 4.4375
16 oz. Plastic Bottle	2.5 x 7
Pillow	8 x 5.5 x 1.25
Tetrahedron	4 x 4

The effects of sizes, shapes, and spacing of the containers on the heat transfer rates, pressure drops, and theoretical efficiencies of the exchanger were calculated.

B. Computer Model.

A simple computer model was used to simulate performance. The model simulated the extreme nonsteady state behavior of an HOF storage unit by following slugs of heat transfer fluid

Figure 3

EXAMPLE OF CONCEPTUAL DESIGNS, STEARIC –
PALMITIC ACID, 3 DAY STORAGE

FACE, 3 REQ'D

STAGGERED GRID

Cans Total	3600
Mass Total	11016 Lb
Heat Transfer Area	2332.5 Sq Ft
Air Flow	1200 Cu Ft/Min.
Velocity (Interstitial)	8 Feet/Sec.
h_f (Air Film Coeff)	3.9 Btu/Hr.-Sq Ft - °F
ΔP (Pressure Drop)	0.7 – 0.8 In. Hg

through the heat exchanger and assuming that groups of HOF material-filled containers experienced steady state heat transfer as the slugs flowed past. Temperatures, heat transfer coefficients and frozen-molten HOF material ratio were recalculated as each slug passed each group of containers in order to approximate the time dependent, location dependent heat transfer behavior of an actual HOF heat storage device.

The model follows an 18 to 27 second slug of heat transfer fluid through the heat exchanger. The exchanger is mathematically divided into 12 to 15 sections. Heat transfer rates, and temperatures are calculated for each section on the assumption that each container in the section behaves identically, and each is momentarily experiencing steady state heat transfer. Coefficients are determined from classical steady state equations based on the assumption that the frozen or molten core retains the original shape of the container. Heat transfer fluid flows continuously. The discharge mode is assumed to be controlling.

C. Computer Results.

Simulation of model heat exchanger behavior indicates that the concept of encapsulating HOF materials in commercial containers is viable. Although restricted by the assumptions of the model, the calculations predict that:

1. Heat transfer rates are acceptable. Most designs could deliver considerably more than the 20,000 to 30,000 BTU/hr estimated residence load. Delivery curves tended to be flat until near exhaustion.
2. Efficiencies appear acceptable. Convenient designs delivered approximately 90% of the stored heat before output temperatures fell below 95°F.
3. Standard commercial containers, with minor axis less than 2.5-3.0 inches and capacities of 7 to 90 in³ per container were acceptable.
4. It was possible to manipulate designs so that pressure drops in air systems were limited to 1 inch of water or less. Blowers of 1 HP or less would be required. Although larger than those of most home heating systems, the size would be reasonable.
5. Macroencapsulated HOF heat exchangers display behavior similar to stratification in sensible heat systems. Containers near the entrance deplete rapidly. Containers near the exhaust retain capacity. Therefore, large capacity units are more efficient than small units.
6. As expected, container material has little effect on heat transfer. Film coefficients and crystal conductivities dominate heat transfer coefficients.

Table XVII lists the HOF materials, container sizes, and calculated fractions of latent heat discharged.

TABLE XVII

Predicted Efficiencies of Model Systems

<u>Material</u>	<u>Melt- ing Temp. °F</u>	<u>Exchanger Capacity 10⁵ BTU</u>	<u>Container</u>	<u>Percent Discharged</u>
Mg(NO ₃) ₂ ·6H ₂ O	192	3	Cylinder 2.5 in. dia.	87 ¹
Naphthalene- Benzoic Acid Eutectic	152	3	Cylinder 3 in. dia.	95
			Pillow 8 X 5.5 X 1.25 in.	95
Stearic Acid- Palmitic Acid	146	8.4	Cylinder 4.25 in. dia.	96
		3	Cylinder 4.25 in. dia.	87
		3	Cylinder 3 in. dia.	93
		3	Tetrahedron 4 X 4 in.	95
		3	Tetrahedron 4 X 4 in.	93 ²
Mg(NO ₃) ₂ ·6H ₂ O- NH ₄ NO ₃ Eutectic	125	3	Cylinder 3 in. dia.	75
		3	Cylinder 2.5 in. dia.	85
		3	Tetrahedron 4 X 4 in.	91
		3	Pillow 8 X 5.5 X 12.5 in.	82
CaCl ₂ ·6H ₂ O	81	3	Cylinder 2.5 in. dia.	97 ³

¹Water as heat transfer fluid

²Air film heat transfer coefficient arbitrarily reduced 45%

³Exhaust air at 35°F, heat pump output 3000 BTU/hr

1. Cylinders - The dimensions of "Tall No. 3" sanitary cans, "No. 300" sanitary cans, and a standard 16 oz. plastic bottle were used to model units based on cylinders. The curves are applicable to chub-type film packages since the diameter and length of film packages are essentially unrestricted.

Output curves for representative air systems are presented in Figures 4 through 8. Figure 4 illustrates the behavior of a "Tall No. 3" can storing 840,000 BTU at the 147°F (64°C) fusion temperature characteristic of a stearic acid-palmitic acid mixture. Over 95% of the stored heat was discharged before the output temperature fell to 95°F. The degree of stratification is illustrated in Figure 5.

The 300,000 BTU unit required smaller cans to improve heat transfer. Figure 6 illustrates the behavior of two 300,000 BTU, 147°F (64°C) units containing "Tall No. 3" and "No. 300" cans. "No. 300" cans appear adequate for service in this temperature range.

When the pronounced effect of capacity on output curves illustrated by Figures 4 and 6 was observed, designs were restricted to 300,000 BTU units as a worst case.

As expected the temperature of fusion has a pronounced effect on the behavior of HOF storage systems. A different sized container may be desirable for each temperature range. As Figure 7 illustrates, the 153°F (67°C) naphthalene-benzoic acid eutectic performs well in 3" diameter cans. The lower temperature magnesium nitrate hexahydrate-ammonium nitrate eutectic requires a smaller container, 2 inches in diameter, perhaps.

A 2.5 inch diameter container appears suitable for use in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - heat pump systems. Figure 8 illustrates calculated discharge temperatures and Coefficients of Performance (COP) of such a system. The simulation was based on the performance curves of a Westinghouse Model HP030D heat pump. Heat of fusion warmed air was passed over the evaporator coils of the heat pump, then returned to the storage unit.

The simple model used to predict air system performance is not well suited to water systems. The assumption of steady discharge in an air system is feasible because of the negligible heat capacity of the stationary air held in a real exchanger experiencing intermittent demand.

The presence of a significant mass of water in an exchanger requires a model capable of predicting non-steady state heat transfer. When coupled with the time dependent, position dependent treatments needed for HOF exchangers, this computation is beyond the scope of this program.

Figure 4

SIMULATED DISCHARGE CYCLE
TALL #3 CANS, STEARIC - PALMITIC ACID,
3 DAY STORAGE, 840,000 BTU

Figure 5

SIMULATED DISCHARGE PROFILE
TALL #3 CANS, STEARIC - PALMITIC ACID,
3 DAY STORAGE IN BED, 840,000 BTU

Figure 6

SIMULATED DISCHARGE CYCLE
300,000 BTU STEARIC - PALMITIC ACID SYSTEM

Figure 7

SIMULATED DISCHARGE CYCLE
EFFECTS OF CONTAINER SIZE AND MELTING
TEMPERATURE, 300,000 BTU

Figure 8

SIMULATED DISCHARGE CYCLE
2.5 IN. CYLINDERS $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ - HEAT PUMP SYSTEM

The simple model was used to generate a curve for a magnesium nitrate hexahydrate-water system. The performance curve is illustrated in Figure 9. The calculated 87% efficiency is acceptable, but the data are interpreted to indicate that the storage system can supply the load with greater efficiency.

The 300,000 BTU exchanger design corresponding to Figure 9 contains over 400 gallons of water in the 0.75 inch spaces between containers. The water could supply a 30,000 BTU load with a 9°F temperature swing. Conduction between the containers and the water during the stagnant portions of the discharge cycle of a real world installation probably would supply a significant fraction of the load demand. The 87% efficiency predicted by the constant discharge, forced convection model probably represents a minimum value.

2. Film Pillows - Simple flat pouches formed by heat sealing the ends of a cylindrical tube of packaging film would appear as pillows if laid flat on a support. Package costs could be among the lowest of any design.

Unfortunately, heat transfer in this configuration is believed poor. The pillows would approximate flat plates. Heat transfer rates between plates and air flowing parallel to the plates suffer from the formation of laminar boundary layers at the surfaces. Film coefficients are about half those of air flowing normal to surfaces or banks of tubes.

Film coefficients of 1.47 BTU/hr-ft²-°F are reported for the flat pan system used in the University of Delaware "Solar One" house.⁴ Heat transfer surfaces in a pillow-filled exchanger exhibit hills and valleys corresponding to the bulges at the centers of the pillows, improving heat transfer coefficients.

Figure 10 illustrates the simulated discharge curves of two heat exchangers based on differing HOF candidates. Two film coefficients, 1.47 and 1.9 BTU/hr-ft²-°F were used in the model.

Heat exchangers containing higher temperature HOF materials are not affected by variations in film coefficients. The short heat transfer path in a pillow exchanger dominates efficiency. Both naphthalene-benzoic acid eutectic (152°F, 67°C) simulations produced efficiencies of 95%.

Pillow designs containing lower temperature HOF materials are sensitive to film coefficients. A design based on magnesium nitrate hexahydrate-ammonium nitrate eutectic would exhibit

⁴Telkes, Maria "Thermal Energy Storage", IECEC '75 Record, p. 111-115.

Figure 9

SIMULATED DISCHARGE CYCLE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 300,000 BTU HYDRONIC HEATING SYSTEM,
2.5 IN. CYLINDERS, WATER HEAT TRANSFER FLUID

Figure 10

SIMULATED DISCHARGE CYCLE
EFFECTS OF MELT TEMPERATURE AND FILM
COEFFICIENTS ON PILLOW DISCHARGE CURVES

an unsuitable 73% efficiency if the 1.47 coefficient prevailed. The higher 1.9 coefficient would increase efficiencies to 82%, a marginally acceptable value.

3. Film Tetrahedra - If the two ends of a short tube of flexible packaging material are heat sealed so that the axes of the seals are at right angles, the package approximates the shape of a tetrahedron. Commercial machinery capable of filling and sealing tetrahedra is available. Standard equipment can process tubes of up to 4 inch diameter and 7 inch length.

The tetrahedral concept produces superior heat transfer. Figure 11 illustrates the simulated performance of exchangers based on differing fusion temperature HOF candidates. The geometry of the package is so conducive to heat transfer that efficiencies are not significantly reduced if the air film coefficients are arbitrarily reduced. This results from the high ratio of surface area to volume.

D. Sensitivity Analysis.

In order to develop a design procedure for thermal batteries, a computer simulation program was used to evaluate the sensitivity of the storage capacity to variation of several parameters: 1) thermal conductivity of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ crystals, 2) air flow rate through the thermal battery, 3) supercooling, 4) the number of rows of cylinders in the direction of air flow, and 5) the air heat transfer coefficient. The purpose of the sensitivity analysis is to help develop design criteria for thermal batteries. Most of the calculations were made for a storage unit with 34 rows of bottles. This would be equivalent to a two-pass thermal battery as diagrammed in Figure 12. Heat loss through the insulation and the sensible heat of the steel in the storage cabinet were neglected. Most of the simulations assumed 4°C of supercooling. The results of the sensitivity analysis are illustrated in Figures 13 through 17. For comparison, the scale of the storage capacity axis is constant in all the figures.

The storage capacity is more sensitive to some parameters than to others, but there is a wide range of design conditions that will give a storage capacity greater than 80% of the theoretical storage capacity (TSC). Storage capacity is relatively insensitive to the thermal conductivity of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ crystals, but increases with decreasing air flow rate, due to increased residence time in the thermal battery. Storage capacity decreases with increasing supercooling, and plunges when the calcium chloride hexahydrate in the bottles near the outlet supercool below the minimum useful outlet air temperature.

Figure 11

SIMULATED DISCHARGE CYCLE
300,000 BTU - 4" X 4" TETRAHEDRA

Figure 12

THERMAL ENERGY STORAGE UNIT
CALCIUM CHLORIDE HEXAHYDRATE IN HDPE BOTTLES,
AIR HEAT TRANSFER FLUID

Top View

Layout 0.024M Spacing Triangular Pitch
Minimum Possible Void Fraction .52
Sixteen Ounce Bottles

Figure 13: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Crystal Conductivity.

Figure 14: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Air Flow Rate.

Figure 15: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Supercooling.

Figure 16: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Number Of Rows Of Cylinders In Direction Of Air Flow.

Figure 17: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Air Heat Transfer Constant.

Storage capacity increases as the number of rows in the direction of air flow increases, but pressure drop across the thermal battery increases faster. Since electrical energy consumed for circulating air is directly proportional to pressure drop, a slight penalty in storage capacity may result in a large savings in pumping costs.

Storage capacity is a strong function of the air film heat transfer coefficient. For this design, the equation describing the air film heat transfer coefficient becomes:

$$h_o = A(CFM)^{.6}, \text{ in KJ/hr. M}^2 \text{ } ^\circ\text{C} \quad (1)$$

where: CFM = air flow rate

A = Air heat transfer constant

The calculated value for A is 8, assuming no short-circuiting. Figure 17 shows a strong decrease in storage capacity with a drop in the air heat transfer constant. This could be caused by short-circuiting of air flow through the thermal battery.

This sensitivity analysis did not address further the parameter of cylinder diameter. Changes in cylinder diameter will effect the storage capacity by changing the surface area for heat transfer and the heat transfer coefficient.

V. HEAT STORAGE TEST DEVICE

A subscale thermal battery was built for evaluating the performance of encapsulated PCM's in thermal energy storage devices. ASHRAE standard 94-77, Methods of Testing Thermal Storage Devices Based on Thermal Performance, was used as a guide in the design. Since containers filled with phase change material offer a relatively large surface area for heat transfer, a relatively poor heat transfer fluid, such as air, can be used, and was chosen for use in the thermal battery. A closed circuit configuration was chosen to avoid transients in humidity and temperature that might be expected when using room air for make-up. The layout and components of the tester are illustrated in Figure 18. When testing a thermal battery it becomes necessary to measure mass flow rate and specific heat of the heat transfer fluid, inlet and outlet temperatures of the heat transfer fluid, room temperature, and pressure drop across the thermal battery. It is also important to know the rate at which the heat transfer fluid leaks from the system.

Figure 18 Testing Configuration For The Thermal Storage System When The Transfer Fluid Is Air

To seek a theoretical understanding of the thermal battery being tested, it is useful to measure temperature periodically at various points in the thermal battery: in the heat transfer fluid, in the energy storage medium, and at the boundary between the two. In the case of phase change materials in rigid containers, it might be possible to monitor the fraction molten by monitoring the volume change associated with phase change. In this study only the phase change material temperature was monitored.

To determine the mass flow rate of the air around the test circuit, an American Air Filter air flow measuring nozzle was incorporated in the thermal battery. Pressure drop was measured across this nozzle, as well as absolute pressure, wet bulb temperature, and dry bulb temperature near the nozzle. For the storage device, the inlet and outlet air temperatures were measured with nickel resistance thermometers, and ΔT was monitored by a 12-junction copper constantan thermopile. Room temperature and the temperature in nine containers of PCM were monitored with iron constantan thermocouples. Pressure drop across the thermal battery and other pressure differences were measured with 4" slant gage manometers. Outlet air temperature was also monitored as input for automatic cycling of the thermal battery.

Thermal battery testing, after aging, involved monitoring the response in the outlet air temperature to a step change in the inlet air temperature. The step change was normally 35°C, bracketing the fusion temperature of the PCM. Inlet air temperatures below the fusion temperature were maintained by first chilling the make-up or outlet air in the air reconditioner and then reheating it to the set point. Inlet air temperatures above the fusion temperature were maintained by heating the make-up air to the set point. Various air flow rates were achieved using a damper on the pressure blower.

Thermal data were recorded on two strip chart recorders, one for the iron constantan thermocouples and the other for 0-10 volt signals from an analog computer that processed data from the thermopile, resistance thermometers, wet bulbs thermocouples, and the thermocouple in the outlet of the thermal battery. Automatic cycling was achieved by switching between two controllers on the air reconditioner when the outlet temperature moved out of the set temperature range. Maximum resolution in the inlet and outlet temperatures was achieved by tuning the input to the 0 to 10 volt recorder to a temperature range of 50°C including the 35°C temperature range of the step change.

VI. HEAT STORAGE TEST PROCEDURE

ASHRAE⁵ Standard 94-77 was followed in the test procedure for our thermal storage test unit, with two exceptions: the definition of test time was modified, and the manner of handling heat loss was altered to be more accurate. This standard requires that the inlet and outlet temperatures, prior to the start of the test, be at steady state with a constant flow of air through the thermal battery. The test period begins with a step change of 35°C in the inlet air stream. For a PCM thermal battery the 35°C step change symmetrically brackets the fusion temperature, causing the storage medium to undergo a change of phase.

Figure 19 shows a temperature-time profile for the inlet and outlet during the test of a near-ideal thermal battery using the latent heat of a PCM for thermal energy storage. In the charging mode the test ends when the outlet temperature reaches a temperature midway between the freezing point of the eutectic and the inlet temperature, defined as the "maximum charge temperature". The charge rate at this temperature is termed the "minimum useful charge rate".

Once steady state conditions are achieved, the inlet air temperature is step changed from the high set point back to the low set point, where it is held constant to generate a discharge profile of the outlet temperature. As in the charging cycle, the test ends when the outlet temperature reaches the "minimum discharge temperature", midway between the inlet and freezing temperatures.

The areas between the inlet and outlet temperature profiles over the test times of charging (τ_c) and discharging (τ_d) are used to determine the charge and discharge capacities, CC and DC respectively, using the following equations:

$$CC = \dot{m} C_{tf} \left(\int_0^{\tau_c} (T_{in} - T_{out}) dt - L \int_0^{\tau_c} \left(\frac{T_{in} + T_{out}}{2} - T_a \right) dt \right) \quad (2)$$

$$DC = \dot{m} C_{tf} \left(\int_0^{\tau_d} (T_{out} - T_{in}) dt + L \int_0^{\tau_d} \left(\frac{T_{in} + T_{out}}{2} - T_a \right) dt \right) \quad (3)$$

The second part of equation (2) is the heat loss from the storage unit during the charging cycle. This heat loss calculation, a modified form of the equation given in ASHRAE (94-77), is more accurate since it does not assume a constant temperature driving force between the storage unit and ambient

⁵American Society of Heating, Refrigeration and Air Conditioning Engineers, Inc., 345 E. 47 St., New York, NY 10017, "Methods of Testing Thermal Storage Devices Based on Thermal Performance".

Figure 19

LATENT HEAT STORAGE UNIT TEST PROCEDURE

air temperatures ($\bar{T}_{\text{unit}} - \bar{T}_a$). The heat loss factor is determined according to the following equation:

$$L = \frac{(T_{\text{in}} - T_{\text{out}})}{[(T_{\text{in}} + T_{\text{out}})0.5 - T_a]} \quad (4)$$

The temperatures are measured after the unit has achieved uniform steady state temperatures.

Table XVIII shows the upper and lower set point for the inlet air, and the maximum and minimum outlet air temperatures used in the various tests. All of them conform to the criteria set down above with the exception of the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ unit and the double zone stratified storage unit. In the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ test the heat loss was so great during charging that it was difficult, impossible in the case of the lowest air flow rate, for the outlet air temperature to reach the midpoint between the inlet air temperature and PCM melting point. Therefore, the "maximum charge temperature" was set at 94.83°C , one third the interval from the melting point to the maximum inlet temperature. The "minimum discharge temperature" was set at 77.33°C , one third the interval from the minimum inlet temperature to the melting point, to maintain a temperature difference between maximum and minimum charge temperatures of 17.5°C , the same as for the other PCM's.

In the double zone stratified storage unit the step change had to be broadened to bracket the fusion temperatures of the two PCM's. The storage unit was designed for a specific application rather than for testing by the ASHRAE standard, so the maximum charge and minimum discharge temperatures were chosen to fit the application.

As mentioned previously, the test time recommended in ASHRAE 94-77 was modified to be based more realistically on design rate. For latent heat storage devices this is essential to avoid misleading results. For sensible heat storage devices it should lead to improved results. An analogy may be made between an electric battery and a thermal battery:

electromotive force (volts) vs. ΔT ($^\circ\text{C}$)

current under load (amps) vs. design rate (KJ/hr)

capacity (watt hrs) vs. capacity (KJ)

TABLE XVIII

Upper and Lower Air Temperatures
for the Five Thermal Batteries Tested

<u>Thermal Battery</u>	<u>Melting Point °C</u>	<u>High Inlet Air Temp. °C</u>	<u>Maximum Charge Temp. °C</u>	<u>Low Inlet Air Temp. °C</u>	<u>Minimum Discharge Temp. °C</u>
CaCl ₂ ·6H ₂ O in High Density Polyethylene Bottles	27	44.5	35.75	9.5	18.25
Mg(NO ₃) ₂ ·6H ₂ O in Aerosol Cans	89	106.5	94.83	71.5	77.33
Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ Eutectic in Plastic Film Pouches	50	67.5	58.75	32.5	41.25
Urea/NH ₄ Br Eutectic in Polypropylene Bottles	76	95.0	85.5	60.0	68.0
Double Zone Stratified Unit	27/50	61.0	49.75	16.0	21.6

Test time is defined in ASHRAE 94-77 as $\tau_D = \frac{TSC}{C_p \dot{m} \Delta T_{IN}}$ (5)

This is the time for an ideal plug flow sensible heat TES unit to discharge. It is illustrative to compare an ideal plug flow sensible heat device with an ideal latent heat device (all stored heat is latent and delivered at the freezing point). In evaluating a latent heat TES unit the high and low set points are chosen to bracket the freezing point of the storage material so the unit would discharge at one-half the initial step temperature change. As shown in Figure 20, for units with the same theoretical storage capacity (TSC), an ideal latent TES would take twice as long to discharge. Since no practical storage unit will behave in an ideal manner, it is even more essential to modify this definition of test time (τ_D).

The ASHRAE 94-77 definition of test time was altered to give consideration to design rate (KJ/hr). At a constant flow rate, the design rate can be used to determine a minimum useful temperature out of storage. This minimum useful temperature was used as the criterion for terminating a test, and τ_D was taken as the time to discharge the TES to the minimum useful temperature. Figure 21 shows a graphical presentation of a TES test in which the temperature axis is normalized by dividing $(T_{OUT} - T_{IN})$ by ΔT_{IN} , and the time axis is also made non-dimensional by dividing by the test time τ_D . This shows the result of a computer simulation of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ TES unit discharge tests at three air flow rates. For the sake of convenience, the minimum discharge temperature was defined as $(T_{IN} + .25\Delta T_{IN})$. For the 75 scfm (153 kg/hr) simulation, the design rate can be calculated from the equation:

$$q_D = C_p \dot{m} \Delta T_{MIN} = 1350 \text{ KJ/hr} \quad (6)$$

Capacity can be calculated from the integration:

$$C = \tau_D C_p \dot{m} \Delta T_{IN} \int_0^{\tau_D} \frac{(T_{OUT} - T_{IN})}{\Delta T_{IN}} dt = 21,350 \text{ KJ} \quad (7)$$

Storage capacity in hours discharge at the design rate is then:

$$TC = C/q_D = 16 \text{ hours} \quad (8)$$

Figure 20

COMPARISON OF ASHRAE 94-77
APPROACH TO TESTING SENSIBLE AND LATENT STORAGE DEVICES

Figure 21

COMPUTER PREDICTION OF $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ TEST UNIT RESPONSE,
DISCHARGE MODE

VII. HEAT STORAGE TEST RESULTS

A series of five sub-scale thermal batteries was tested including: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE bottles, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in aerosol cans, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic in plastic film pouches, urea/ NH_4Br eutectic in polypropylene bottles, and a double-zone stratified unit with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in aerosol cans and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic in plastic film pouches.

A. Heat Storage Test Results: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

The thermal energy storage unit used is shown in Figure 22. Sixteen-ounce high density polyethylene bottles (129) were filled with melted $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to 95% of capacity and sealed before freezing. The bottles were placed in the storage unit in an equilateral triangular pitch arrangement. Thermocouples were placed in nine bottles located at various positions (1-9) in the storage unit, so that temperature-time profiles for individual bottles of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ could be observed. The storage unit was sealed and cycled for 58 complete freeze/thaw cycles before any data were taken.

For a typical charge cycle (Figure 23), the bottle located nearest the inlet (1) has the shortest response time, quickly melting and achieving steady-state. The remaining bottles all melt similarly, each achieving complete melting and steady-state in succession, with the bottle furthest from the inlet (9) finishing last. One exception is that for the bottles at positions 6 and 7 the order of melting is reversed. The presence of the bend in the air flow path of the storage unit causes either short-circuiting or a difference in air heat transfer coefficients. The end of the test time (14.3 hours) is indicated when the outlet air temperature reaches the "maximum charge temperature". At this time, all of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ has melted except for a small portion of a few bottles at position 9. Since the thermocouples are located at the center of the bottle, they measure the temperature of the last portion of material to melt. Thus, the bottles are nearly all charged, and the small amount still frozen shouldn't significantly decrease the charge capacity.

A typical discharge cycle (Figure 24) shows similar successive trend curves for each bottle position, this time for cooling, with curves for positions 3 and 4 reversed as well as for 6 and 7. At the end of this test time (11.5 hours), when the outlet temperature reaches the "minimum discharge temperature", several of the bottles aren't completely discharged (frozen), decreasing the discharge capacity. However, as in the charging cycle, the magnitude of the amount of material failing to discharge is exaggerated, since the temperatures are of the material which is the last to freeze. Still, the unit appears not to have discharged to the extent that it had charged.

Figure 22

**THERMAL ENERGY STORAGE UNIT
CALCIUM CHLORIDE HEXAHYDRATE STORAGE MEDIUM,
AIR HEAT TRANSFER FLUID**

Containers .061M Dia .180 HT Bottles
Walls .74 mm HDPE

Layout .024M Spacing Equilateral Triangular Pitch
Minimum Possible Void Fraction .52
Bottle positions with thermocouples ① → ⑨

Figure 23. CHARGE CYCLE: Calcium Chloride Hexahydrate In HDPE Bottles

Figure 24: DISCHARGE CYCLE: Calcium Chloride Hexahydrate In HDPE Bottles

The temperature profiles for the discharge cycle indicate that some supercooling of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is taking place. A plot of the extent of supercooling vs. the bottle position in the storage unit for four air flow rates is shown by Figure 25. Supercooling ranges from about 7.5°C for bottle positions nearest the inlet (1) to about 2.0°C for bottle positions nearest the outlet (9). Each successive bottle position from the inlet shows a decrease in the amount of supercooling, except for anomalous positions 3, 4, 6, and 7. This increase in supercooling may be attributed to heat transfer variations caused by the presence of the bend in the storage unit as seen for the case of reversed cooling curves during discharging. Similarly, the slightly increased supercooling at position 9 may be attributed to the sudden contraction of the $1\frac{1}{2}$ " x 10" rectangular conduit to a 4" diameter circular conduit. These variations in geometry throughout the unit may result in different rates of cooling, resulting in supercooling variations.

Since laboratory experiments on the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ formulation used in these tests showed much less supercooling, less than 2°C , we believe a kinetic effect is being observed. Evidently, the rate of cooling is greater than the rate of heating produced by crystal growth. When the area of crystals in the medium becomes great enough, the temperature rises to the true freezing point.

Of several functions tested, the following relation gives the best fit of the observed data:

$$\text{Supercooling, } ^\circ\text{C} = 1.0 + 2.0 (\text{cooling rate, } ^\circ\text{C/hr})^{0.4} \quad (9)$$

It was used in the modelling work described in a later section.

A total of eight pairs of charge/discharge cycles (Runs 59-66) were done at four air flow rates (46-75 CFM). Profiles of the outlet air temperature vs. time were generated according to the test procedures stated earlier, and are shown in Figures 26 and 27, for the charge and discharge cycles, respectively.

Even though each successive cycle was allowed to achieve steady-state before initiating the step change for the following cycle, the curves only show the profile generated for the time period of each test. As illustrated for the charging curve at 75 CFM (74 CFM for discharge), the shaded area between the inlet and outlet temperature profiles was manually integrated. As expected, the time necessary for charging (discharging) the unit increases as the air flow rate decreases. Note that the temperature profile obtained for the lowest air flow

Figure 27

rate is most similar to that expected for the case of the nearly ideal latent heat type storage unit. This may be attributed to better equilibrium attainment of heat transfer through the PCM and heat transfer between the air and bottle surface. Also note that the net effect of supercooling and reheating is an increase of about $1/2^{\circ}\text{C}$ observed during discharging.

The reduced data with energy balance results for runs 59-66 are shown by Table XIX. The runs of similar air flow rates have been grouped and arranged in decreasing order. Each group has runs representing the charge and discharge cycles.

The results of the charge (discharge) times and the pressure drops across the storage unit are shown graphically as a function of the air flow rates in Figures 28 and 29. The test times varied from 13 to 22 hours for charging and 10 to 15 for discharging. The longer times for charging reflect the dominating effect of heat loss working against charging, but working for discharging in attaining the final test temperatures. The discharge times are somewhat increased due to solid crystal build-up of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ on the inside walls of the bottles, impeding heat transfer from the molten cores to the air. It is believed that this heat transfer limitation becomes a dominant factor for larger diameter bottles, resulting in a decreased storage capacity. Lower density and specific heat of the heat transfer fluid in the charging mode also contribute to longer test times.

Theoretical pressure drop curves, derived from a relationship for air flow through a staggered arrangement of tube banks,⁶ are shown in Figure 29. There are two curves because of the difference in density of the warm and cool air streams used during charging and discharging. There is good agreement between measured and predicted pressure drops for the range 0.2 to 0.5 inches of water. Decreasing the air flow rate yields a desirable low pressure drop, but increases the time needed to completely charge (discharge) to a given capacity (KJ).

The heat loss during charging increases from about 3,900 KJ at 75 CFM to about 6,800 KJ at 46 CFM. The larger heat loss at lower air flow rates is due to the longer charge time. For the discharge cycle, heat loss shows a similar trend, but is minimal since the average temperature of the storage unit quickly drops below the ambient air temperature. For the energy balance, the loss during discharge is added to the discharge capacity and compared to the charge capacity.

⁶Perry's Engineering Handbook, 4th Ed., 5-47, 48 (1969).

TABLE XIX

Test Results on Calcium Chloride Hexahydrate
Encapsulated in Polyethylene Bottles

Run ^a	Air Flow Rate		Press. Drop ΔP (In. H ₂ O)	Air Heat Capacity C _{tf} (KJ/Kg °C)	Capacity Q _{in} , Q _{out} (MJ)	Energy Loss (MJ)	Corrected Capacity ^b CC, DC (MJ)	Percent of ^c Theoretical Capacity (%)	Design Rate DR (MJ/hr)	Test Time τ _c , τ _d (hr)	Time ^d Capacity (hr)
	CFM (Ft ³ /min)	m ³ (Kg/hr)									
1-62-C	74	133	.42	1.012	26.5	3.7	22.8	94	1.18	12.7	19.3
1-63-C	75	135	.43	1.016	26.9	4.1	22.8	94	1.20	12.8	19.0
1-62-D	74	153	.51	1.002	22.5	0.1	22.6	91	1.34	9.9	16.9
1-63-D	73	152	.50	1.003	22.8	0.2	23.0	93	1.33	10.2	17.3
1-59-C	64	115	.32	1.014	27.2	4.3	22.9	95	1.02	14.6	22.4
1-60-C	65	117	.33	1.012	28.4	5.2	23.2	96	1.04	15.4	22.3
1-61-C	63	114	.32	1.013	27.6	4.0	22.6	93	1.01	14.3	22.4
1-59-D	65	134	.40	1.002	23.0	0.5	23.5	95	1.17	11.0	20.1
1-60-D	63	130	.38	1.002	24.4	0.2	24.6	99	1.14	11.5	21.6
1-61-D	62	129	.38	1.002	23.3	0.1	23.4	94	1.13	12.0	20.7
1-64-C	55	99	.24	1.012	28.6	5.6	23.0	95	0.88	18.2	26.1
1-64-D	55	113	.29	1.002	22.5	0.4	22.9	92	0.99	13.1	23.1
1-65-C	46	82	.17	1.013	29.7	6.7	23.0	95	0.73	21.0	31.5
1-66-C	46	83	.18	1.009	31.4	7.0	24.4	101	0.73	22.3	33.4
1-65-D	45	94	.21	1.001	21.9	1.0	22.9	92	0.82	14.7	27.9
1-66-D	46	96	.22	1.003	22.5	0.2	22.7	91	0.84	14.6	27.0

^aC-Charge, D-Discharge

^bCC = Q_{in} - loss, DC = Q_{out} + loss

^c% = CC/TCC or DC/TDC

^dTime capacity = CC/DR or DC/DR

Theoretical charge and discharge capacities (TCC and TDC) were calculated for the storage unit with pertinent information and results listed in Table XX. The temperature range of the

TABLE XX

Theoretical Charge and Discharge Capacities
CaCl₂·6H₂O in HDPE Bottles

CaCl ₂ ·6H ₂ O		
Fusion Temp., °C		27
Heat of Fusion, Cal/g		46
Specific Heat, Cal/g°C	0.52	(liquid)
	0.33	(solid)
Total Weight, kg		97
Steel (Storage Unit Structure)		
Specific Heat, Cal/g°C		0.10
Total Weight, kg		125
	Charging	Discharging
Temperature Range, °C		
High	35.75	44.50
Low	9.50	18.25
Theoretical Capacity, KJ ¹	24,190 (TCC)	24,860 (TDC)

¹Not including specific heat of polyethylene bottle encapsulant.

storage unit during the test is estimated using the minimum and maximum outlet air temperatures.

The theoretical and measured capacities were plotted against the air flow rate (Figure 30). The measured charge capacity increases slightly with decreasing air flow rate as more time is available for bottle contents and air temperatures to equilibrate. The measured discharge capacity oscillates for an unknown reason. Each measured capacity was divided by its respective theoretical capacity and plotted as a percent capacity vs. the air flow rate (Figure 31). For the flow rates used, the storage unit was able to charge and discharge an average of 95.4% and 91.5%, respectively, of its theoretical capacities. The difference between the percent capacity for

Figure 30

CAPACITY (ENERGY) VS.
AIR FLOW RATE
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ IN HDPE BOTTLES

Figure 31

% CAPACITY (ENERGY) VS.
AIR FLOW RATE
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ IN HDPE BOTTLES

charge and discharge is consistent with the observations of the temperature-time profiles for individual bottles in the storage unit. The charging cycle showed nearly all bottles of material completely charged (thawed) while the discharge cycle showed several bottles not completely discharged (frozen) by the end of the respective test times.

An important design criterion for a thermal storage unit is the charging (discharging) heat rate. A simple heat rate equation for the transfer fluid may be expressed as follows:

$$q = \dot{m} C_{tf} \Delta T \quad (10)$$

The charge (discharge) rate will be a maximum at the beginning, immediately following the step change of the inlet temperature, since the difference of the inlet and outlet temperatures (ΔT) is the greatest. Similarly, the minimum useful charge (discharge) rate corresponds to the smallest temperature difference of the air streams observed at the end of the test time.

These maximum and minimum heat rates are tabulated for each run and plotted against the air flow rate in Figure 32. As expected, the heat rates decrease with decreasing air flow rate. The higher density of the cool air stream used for discharging results in a higher mass flow rate and hence, slightly higher heat rate curves for the discharging cycles.

For a given air flow rate, a nearly ideal latent heat storage unit would quickly decrease from its maximum heat rate to a constant heat rate for most of the test period, while the storage medium absorbed (evolved) its latent heat of fusion. Near the end of the test time the heat rate would again decrease quickly to finish at its minimum value. In actual practice a storage unit might operate between 10 and 90 percent of its storage capacity. This would maintain the heat rate at a fairly constant level, since charging (discharging) would operate almost exclusively on the latent heat of fusion. Note that the design rate for this particular size storage unit is set equal to the value corresponding to the minimum heat rate for a given air flow rate.

A storage capacity expressed in hours can be determined for charging (discharging) the storage unit at a constant heat rate. Such capacities were calculated and plotted against the air flow rate (Figure 33). These curves show the storage lifetime of the unit if total charging (discharging) occurred at the minimum or maximum heat rate. The actual charge (discharge) times, as shown earlier in Figure 28, fall between these hypothetical curves, since the actual heat rate varies from the maximum to the minimum values.

Figure 32

Figure 33

B. Heat Storage Test Results - $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

The thermal energy storage unit is shown in Figure 34. One inch of extra insulation (four inches total) was added to the sides and bottom of the storage unit. Two more inches (five inches) were added to the top of the unit and also on the nine foot long outlet air duct from the storage unit to the temperature sensors. Steel aerosol cans (128 cans, volume .53 liter/can) were filled with liquid $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to 95% of their capacity. The cans were sealed after the PCM froze and were placed in the storage unit in an equilateral triangular pitch arrangement. Thermocouples were placed in nine cans located at various positions (1-9) in the storage unit so that temperature-time profiles for individual cans of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ could be observed. The storage unit was sealed and cycled for 9 complete freeze/thaw cycles before any data were taken.

For a typical charge cycle (Figure 35), the temperature time profiles are nearly identical to those observed for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, except that the test times are longer for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for equivalent air flow rates. This is primarily due to larger heat loss rates through the walls of the storage unit, thereby decreasing the energy available for storage as well as decreasing the energy currently stored in the PCM. All of the PCM melted, except for a small portion of a few cans at position 9. Since these temperatures are for the material which is last to freeze (thermocouple location is at the center of the bottle), the charge capacity isn't significantly decreased. For the discharge profiles (Figure 36), however, there are a number of cans which aren't completely discharged (frozen), thereby decreasing the discharge capacity somewhat. Although the apparent decrease is exaggerated by thermocouple location, the unit appears not to have discharged to the extent that it had charged. Note that the order of melting is reversed for the cans at positions 6 and 7. This is due to the presence of the bend in the air flow path of the storage unit, causing either short-circuiting or a difference in the air heat transfer coefficients. Also note that there is very little supercooling of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1-2°C) due to the presence of additives which provide adequate nucleation.

A total of eight pairs of charge/discharge cycles (Runs 10-15, 19, 20) were done at four air flow rates (52-86 CFM). Profiles of the outlet air temperature vs. time were generated, according to the test procedures stated earlier, for the charge (Figure 37) and discharge (Figure 38) cycles.

The charging (discharging) profiles for the outlet temperature are shown only for the duration of the test, even though steady-state was achieved before initiating a step

Figure 34

THERMAL ENERGY STORAGE UNIT
MAGNESIUM NITRATE HEXAHYDRATE STORAGE MEDIUM,
AIR HEAT TRANSFER FLUID

Containers .066M Dia .157 HT Bottles
Walls .20 mm Tin Plated Steel

Layout .019M Spacing Equilateral Triangular Pitch
Minimum Possible Void Fraction .45
Bottle positions with thermocouples ① → ⑨

CHARGE CYCLE: MAGNESIUM NITRATE HEXAHYDRATE
IN STEEL AEROSOL CANS

DISCHARGE CYCLE: MAGNESIUM NITRATE HEXAHYDRATE
IN STEEL AEROSOL CANS

Figure 37

OUTLET AIR TEMPERATURE VS. TIME
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL CANS
 CHARGE CYCLES

Figure 38

OUTLET AIR TEMPERATURE VS. TIME
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL CANS
 DISCHARGE CYCLES

change for the next successive cycle. The shaded areas between the outlet and inlet air temperatures (shown only for 86 CFM in each case) was manually integrated and used to determine each charge (discharge) capacity. For the discharge profile, there is a significant spread in the initial outlet air temperatures. This is due to the variation of heat loss with air flow rate and results in different steady-state outlet air temperatures prior to the step change in the inlet air stream temperature. The temperature profiles for the lowest air flow rate for both charging and discharging are most similar to the nearly ideal latent heat type storage unit. This is attributed to the longer times available for better temperature equilibrium between the PCM and the passing air.

The reduced data with energy balance results for all runs are shown by Table XXI. The runs of similar air flow rates have been grouped. Each group has runs representing the charge and discharge cycles.

The charge (discharge) test times are shown as a function of the air flow rates through the storage unit (Figure 39). As mentioned earlier, the dominating heat losses from the storage unit to the surroundings work against charging, thus causing the prolonged charge times (13-28 hrs), especially at the lower air flow rates. The discharge times are controlled primarily by two opposing factors. Heat loss tends to decrease discharge times since it contributes to discharging the unit. Solid crystal buildup of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ on the inside surface of the cans tends to impede heat transfer from the molten cores to the air, causing an increase in discharge times.

Measured pressure drops across the storage unit are compared with theoretical values derived for air flow through a staggered arrangement of tube banks (Figure 40). A density difference for the different temperature air streams, charging and discharging, is reflected in the two theoretical curves shown. Measured values fall just above the respective theoretical curves because the pressure drop relationship does not account for the added pressure drop due to the bends in the air flow path through the storage unit. In designing a residential storage unit, typically one will select an air flow rate corresponding to the maximum allowable pressure drop, thus giving the shortest possible charge (discharge) times.

The heat loss during charging increases from about 10,900 KJ at 86 CFM to about 22,100 KJ at 52 CFM. The heat loss during discharging ranges from about 1/2 to 1/3 (5,700, KJ and 7,600 KJ) the heat losses during charging for

TABLE XXI

Test Results on Magnesium Nitrate Hexahydrate
Encapsulated in Steel Aerosol Cans

Run ^a	Air Flow Rate		Press. Drop ΔP (In. H ₂ O)	Air Heat Capacity C_{tf} (KJ/Kg °C)	Capacity Q_{in}, Q_{out} (MJ)	Energy Loss (MJ)	Corrected Capacity ^b CC, DC (MJ)	Percent of ^c Theoretical Capacity (%)	Design Rate DR (MJ/hr)	Test Time τ_c, τ_d (hr)	Time ^d Capacity (hr)
	CFM (Ft ³ /min)	m ³ (Kg/hr)									
2-19-C	86	130	.67	1.038	32.5	10.7	21.9	99	1.58	12.8	13.9
2-20-C	86	131	.68	1.041	32.7	11.2	21.5	97	1.59	12.8	13.5
2-19-D	86	146	.75	1.020	16.1	5.6	21.7	96	.87	8.1	25.0
2-20-D	85	143	.76	1.023	15.9	5.7	21.6	95	.85	8.1	25.3
2-10-C	74	112	.49	1.038	34.7	12.2	22.5	101	1.36	15.9	16.6
2-11-C	74	111	.49	1.038	33.7	12.1	21.6	97	1.34	15.3	16.1
2-10-D	73	122	.55	1.021	15.2	5.7	20.9	92	.73	9.1	28.8
2-11-D	73	125	.56	1.022	16.2	6.1	22.3	98	.75	9.2	30.0
2-12-C	61	90	.33	1.037	38.8	17.0	21.7	98	1.09	21.6	19.9
2-13-C	61	92	.34	1.036	39.4	18.2	21.2	95	1.11	21.6	19.0
2-12-D	61	104	.40	1.019	14.9	7.2	22.1	97	.62	10.4	35.7
2-13-D	60	100	.38	1.019	14.3	7.1	21.4	94	.59	10.4	36.0
2-14-C	52	77	.24	1.038	43.5	22.1	21.4	96	.93	28.2	23.0
2-15-C	52	77	.26	1.038	44.0	22.2	21.8	98	.93	28.3	23.4
2-14-D	51	86	.30	1.020	13.8	7.5	21.3	94	.51	11.6	41.8
2-15-D	52	89	.30	1.020	13.6	7.7	21.3	94	.53	11.5	40.2

^aC-Charge, D-Discharge

^bCC = $Q_{in} - \text{loss}$, DC = $Q_{out} + \text{loss}$

^c% = CC/TCC or DC/TDC

^dTime capacity = CC/DR or DC/DR

Figure 39

CHARGE (DISCHARGE) TIME VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL AEROSOL CANS

Figure 40

STORAGE UNIT PRESSURE DROP VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL AEROSOL CANS

equivalent air flow rates. The net increase in heat loss during charging with decreasing air flow rate is reflected by the increasing test times shown in Figure 39. Of course, the lower heat losses during discharging are simply a result of the lower temperature driving force ($\bar{T}_{unit} - T_a$) during the shorter test times. Using the integrated values of the temperature/time profiles for the charging (discharging) curves (Figures 37 and 38), the amount of energy delivered (Q_{in}) and recovered (Q_{out}) by the air stream were determined. The amount of energy stored in the PCM (charge capacity) is equal to the energy delivered to storage less the losses incurred ($Q_{in} - \text{loss}$). The discharge capacity is defined as the recovered energy by the air stream (Q_{out}) plus the losses. These two values need not balance, since the temperature spans defined by the testing procedure do not perfectly coincide. However, they should be close and will indicate any trends with air flow rate.

Two bar graphs are shown in Figures 41 and 42, illustrating the transfer of energy during charging and discharging, respectively, versus air flow rate for the cases of $Mg(NO_3)_2 \cdot 6H_2O$ (m.p. $89^\circ C$) and $CaCl_2 \cdot 6H_2O$ (m.p. $27^\circ C$) PCM's. The total height of each bar in Figure 41 represents the total energy delivered to the storage unit at a given air flow rate. This would be the energy delivered by a solar collector in actual practice. The shaded area of each bar represents the amount of the delivered energy which is lost. The remainder is the energy which is stored in the PCM. It can be seen for the case of $Mg(NO_3)_2 \cdot 6H_2O$ that the stored energy is fairly constant at about 22,000 KJ while the energy lost to the surroundings accounts for 33-51% of the total amount of energy delivered for storage. The case of $CaCl_2 \cdot 6H_2O$ shows losses that account for only 15-22% of the delivered energy while the stored energy is fairly constant at about 23,000 KJ. This clearly illustrates the heat loss problems incurred with higher-melting PCM's when using air as the heat transfer fluid. The slightly higher average of stored energy for $CaCl_2 \cdot 6H_2O$ is due to the higher heat of fusion, even though less PCM was used than for the $Mg(NO_3)_2 \cdot 6H_2O$ case. Figure 42 is the same type of bar graph except that the total height of the bars represent the amount of energy stored in the PCM prior to discharging (corrected discharge capacity). Note that this stored energy prior to discharge differs from the stored energy after charging since the temperature spans defined by the test procedure do not coincide. The shaded area still represents the loss, this time during discharging. The remaining energy represents

TRANSFER OF ENERGY vs AIR FLOW RATE

Figure 41

Figure 42

Loss

Total Energy Transferred To (From) Storage Unit

the energy recovered from the PCM by the air stream alone. The amount of energy recovered by the air stream is nearly 100% for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, but only 64-74% (26-36% loss) for the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It must be pointed out that the heat loss values for both cases are larger than that expected for a storage unit of optimum design containing the same amount of PCM. For these cases, there is a void fraction of about 0.7, compared with a minimum possible void fraction of about 0.5 (32% more surface area than needed for the given container arrangement). Of course, when scaling up to a higher capacity unit, the % loss value will be even less due to the smaller surface to volume ratio. For the higher melting PCM's, a liquid heat transfer medium should provide less heat loss to the surroundings than air, due to a lower void fraction in a tube bundle arrangement. The importance of adequate insulation is obvious.

Theoretical charge and discharge capacities (TCC and TDC) were calculated for the storage unit. Pertinent information and results are listed in Table XXII. The temperature range of the storage unit during the test was estimated using the minimum and maximum cutoff temperatures.

The theoretical and measured capacities for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were plotted against the air flow rate (Figure 43). Also, the losses were added to the measured heat discharged and plotted as the discharge capacity. Due to the large losses incurred, it was difficult to determine any trend of the charge and discharge capacities with air flow rate. The charge and discharge capacities were divided by the respective theoretical capacities (% capacity) and plotted vs. air flow rate (Figure 44). For the air flow rates used, the storage unit was able to charge and discharge an average of 97.6% and 95.1%, respectively, of its theoretical capacities. These values may be shifted up or down depending on the assigned maximum and minimum outlet air temperatures for terminating each test cycle. However, the difference between the percent capacity for charge and discharge is consistent with the observations of the temperature-time profiles for individual cans in the storage unit. At all the air flow rates, the unit was not discharged to the extent that it had charged by the end of the respective test times.

The maximum and minimum heat rates for each cycle were determined for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The maximum heat rate for charging (discharging) occurs immediately following the step change, where the difference between the inlet and outlet temperatures is at a maximum. The minimum heat rate occurs at the end of each test cycle. This value can be used as

TABLE XXII

Theoretical Charge and Discharge Capacities

Mg(NO₃)₂·6H₂O in Steel Cans

Mg(NO₃)₂·6H₂O

Fusion Temp., °C	89
Heat of Fusion, Cal/g	38
Specific Heat, Cal/g °C	0.60 (liquid)
	0.44 (solid)
Total Weight, Kg	100

Steel (Storage Unit Structure)

Specific Heat, Cal/g °C	0.10
Total Weight, Kg	125

	<u>Charging</u>	<u>Discharging</u>
Temperature Range, °C (Est.)		
High	94.83	about 102.00
Low	about 70.00	77.33
Theoretical Capacity, KJ ¹	22,231	22,676
	(TCC)	(TDC)

¹Not including specific heat of steel aerosol cans (<.3% of theoretical capacities).

Figure 43

CAPACITY (ENERGY) VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL CANS

Figure 44

% CAPACITY (ENERGY) VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL CANS

the design rate for the storage unit. These maximum and minimum heat rates are plotted as a function of flow rate (Figure 45). In actual operation the storage unit would usually exhibit a heat rate slightly greater than the minimum value, corresponding to a temperature near the fusion temperature.

A hypothetical plot (Figure 46) was made of the storage capacity in hours vs. air flow rate for this particular unit when charging (discharging) constantly at these maximum and minimum heat rate values. It is interesting to note that because of the excessive heat loss for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the actual charge profile corresponds closest to hypothetical at the minimum air flow rate, while the actual discharge profile corresponds closest to hypothetical at the maximum air flow rate.

C. Heat Storage Test Results $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ Eutectic.

The thermal energy storage unit used is shown in Figure 47. Pouches were fabricated from R-2 retort film (3.3 mil polyethylene, 0.35 mil aluminum foil, and 0.5 mil polyester), and filled with the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic.

Three-seam pouches (seams on one side and both ends) were used, because they survived thermal cycling better than four-seam pouches (seams on both sides and both ends). The pouches were made using a Vertrod impulse heat sealer (Model 20P-1/8" wide seal). The film was folded lengthwise and sealed on three sides, leaving a small filling section. After the pouch was filled with liquid eutectic, excess air was squeezed out of the pouch and the fill-hole was heat-sealed closed.

Pouches were laid on metal grills with their seams projecting horizontally (see Figure 47), and placed in the test storage unit. Nine thermocouples were glued between half-filled pouches and positioned in the subscale storage unit.

The temperature-time profiles obtained in testing this configuration resemble strongly earlier results for calcium chloride hexahydrate and magnesium nitrate hexahydrate. The profiles are not shown here because after the experiment some of the thermocouples were found to be rusted open, casting doubt on the data.

As mentioned previously, several pouches developed split seams, leaking a portion of their contents. The quantity of eutectic leaked was small, however, and should have little effect on the test results.

Figure 45

HEAT RATE VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL AEROSOL CANS

Figure 46

CAPACITY (TIME) VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STEEL AEROSOL CANS

Figure 47

THERMAL ENERGY STORAGE UNIT
MAGNESIUM NITRATE HEXAHYDRATE/AMMONIUM NITRATE EUTETIC
STORAGE MEDIUM, AIR-HEAT TRANSFER FLUID

A total of eight pairs of charge-discharge cycles (Runs 9 through 16) were evaluated at four air flow rates (59 through 89 cubic feet per minute, CFM). Profiles for the inlet and outlet air temperatures are shown in Figure 48 for the charging cycles and Figure 49 for the discharge cycles. The profiles are shown only for the test duration. Steady state was achieved before initiating the next step change.

The hatched areas between the outlet and inlet air temperature (shown only for the 89 CFM tests) was integrated numerically and used to determine the capacity. In each cycle it took significantly longer to charge the storage unit than to discharge it. The primary sources of this difference are heat loss from the system during the test, and the lower specific heat and density of the air during the charging cycle. The heat loss effect is approximately twice that of the variation in heat transfer fluid properties. In a scaled-up system with relatively smaller heat loss, the difference in charge and discharge times would be significantly reduced. Charge times would be shorter, while discharge times would increase, due to decreased heat loss.

One should resist the temptation to equate charge and discharge times observed in these tests with those attainable in an operating solar energy system. On a sunny day there are approximately 6 hours in which to charge storage. During charging, inlet air temperatures considerably higher than 67.5°C may be expected, and during discharge, inlet temperatures well below 32.5°C would always prevail. These factors would decrease charge and discharge times considerably. Also, several design options are available which affect the charging time: air flow rate, size of the PCM capsule, PCM melting point, and collector area (and thus temperature). For each solar system design, the number of hours required to recharge a fully discharged storage system should be optimized.

Table XXIII shows the reduced data from testing of the sub-scale thermal battery. Heat loss through the insulation is greatly reduced from that experienced with magnesium nitrate hexahydrate, due to the lower operating temperature. The energy balance is within acceptable limits indicating the accuracy of the experiments.

The relationships between test time, pressure drop across the thermal battery, and air flow rate through the battery become apparent in Figures 50 and 51. At the target pressure drop of 0.25 inches of water, 9-10 hours is required for charging. If needed, pressure drop can be lowered by reducing the number of containers in the direction of air

Figure 48

OUTLET AIR TEMPERATURE VS. TIME
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES
 CHARGE CYCLES

Figure 49

OUTLET AIR TEMPERATURE VS. TIME
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES
 DISCHARGE CYCLES

TABLE XXIII

Test Results on Magnesium Nitrate Hexahydrate/Ammonium Nitrate Eutectic
Encapsulated in R-2 Retort Film Pouches

Run ^a	Air Flow Rate		Press. Drop ΔP (In. H ₂ O)	Air Heat Capacity C_{tf} (KJ/Kg °C)	Capacity Q_{in}, Q_{out} (MJ)	Energy Loss (MJ)	Corrected Capacity ^b CC, DC (MJ)	Percent of ^c Theoretical Capacity (%)	Design Rate DR (MJ/hr)	Test Time τ_c, τ_d (hr)	Time ^d Capacity (hr)
	CFM (Ft ³ /min)	m (Kg/hr)									
3-9-C	89	153	.44	1.027	20.3	3.2	17.1	98	1.37	7.6	14.8
3-10-C	91	156	.46	1.027	21.1	3.6	17.5	100	1.40	8.0	15.1
3-9-D	89	172	.52	1.015	15.7	1.2	16.9	95	1.53	5.9	10.3
3-10-D	-	-	.53	-	-	-	-	-	-	-	-
3-11-C	81	139	.37	1.027	21.2	3.9	17.3	99	1.25	8.9	17.0
3-12-C	81	139	.37	1.027	21.5	3.4	18.1	104	1.25	8.7	17.2
3-11-D	81	156	.44	1.015	16.1	1.5	17.6	99	1.39	6.4	11.6
3-12-D	81	156	.44	1.015	16.4	1.2	17.6	99	1.39	6.6	11.8
3-13-C	71	122	.28	1.027	20.5	3.4	17.1	98	1.09	9.5	18.7
3-14-C	69	118	.26	1.027	21.0	4.0	17.0	97	1.06	9.8	19.8
3-13-D	69	133	.32	1.015	16.3	1.2	17.5	98	1.18	7.7	13.8
3-14-D	69	133	.34	1.015	16.7	1.5	18.2	102	1.18	7.5	14.1
3-15-C	59	101	.20	1.027	21.5	4.5	17.1	98	0.91	11.9	23.7
3-16-C	59	101	.21	1.027	22.5	5.4	17.1	98	0.91	12.5	24.7
3-15-D	59	114	.25	1.015	15.9	1.8	17.7	99	1.01	8.4	15.7
3-16-D	59	114	.25	1.015	15.8	1.8	17.6	99	1.01	8.3	15.6

^aC-Charge, D-Discharge

^bCC = Q_{in} - loss, DC = Q_{out} + loss

^c% = CC/TCC or DC/TDC

^dTime capacity = CC/DR or DC/DR

Figure 50

CHARGE (DISCHARGE) TIME VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES

Figure 51

STORAGE UNIT PRESSURE UNIT VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES

flow (presently 30), or increasing the void fraction in the storage bed. The first alternative would reduce the air velocity, and thus the film transfer coefficient, decreasing the capacity of the thermal battery. The second would increase the size of the storage unit, increasing hardware and space costs.

Theoretical charge and discharge capacities (TCC and TDC) were calculated for the storage unit. Pertinent information and results are listed in Table XXIV. Values of TCC and TDC vary slightly because of differences in the specific heat between the liquid and solid state of the phase change material. Both differ from the theoretical storage capacity of ASHRAE (94-77), TSC, in that the initial inlet temperatures and final outlet temperatures are used in the calculation instead of the initial and final inlet temperatures.

The theoretical and measured capacities for charge and discharge are plotted against air flow rate in Figure 52. Figure 53 shows the percent of theoretical capacity attained. The actual capacity is somewhat low in comparison with the previous experiments using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This is because the spacing between the racks holding the encapsulated PCM is greater than required for minimizing the pressure drop. A closer spacing would have made it difficult to insert the pouches in the racks. The system charged to nearly full capacity, but discharge capacity dropped off significantly, primarily due to heat loss during discharge.

The poor surface to volume ratio of the cabinet of the subscale thermal battery, accentuated by the high void fraction, 0.82, promotes excess heat loss. A full scale system with lower surface to volume ratio and less void volume should show a higher discharge capacity if adequate insulation were used.

As mentioned previously, reduction of the number of rows in the direction of air flow might have a negative effect on storage capacity. However, this system used roughly half the number of rows in the direction of air flow, but achieved results essentially equivalent to earlier tests with calcium chloride hexahydrate and magnesium nitrate hexahydrate. This is partially due to the extra heat transfer surface per unit weight of PCM. The composite film pouches (ignoring the seals) have a surface to volume ratio of 95 M^{-1} , versus 61 M^{-1} for the aerosol cans used with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 66 M^{-1} for the polyethylene bottles used with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Also, the configuration of this system is significantly different from the array of cylinders on an equilateral pitch used in the two earlier experiments. The relatively flat faces of the pouches, perpendicular to air flow, may have introduced significant turbulence, and the flat profile of the pouches insures that all the PCM is relatively close to the heat transfer surface.

TABLE XXIV

Theoretical Charge and Discharge Capacities

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ in Plastic Pouches

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic

Fusion Temp., °C	50
Heat of Fusion, Cal/g	31
Specific Heat, Cal/g °C	0.58 (liquid)
	0.48 (solid)
Total Weight, Kg	86

Steel (storage unit structure
including support racks)

Specific Heat, Cal/g °C	0.10
Total Weight, Kg	131

Temperature Range (approx.), °C	<u>Charging</u>	<u>Discharging</u>
High	58.75	67.50
Low	32.50	41.25
Theoretical Capacity, KJ	(TCC)	(TDC)
	17,483	17,798

Figure 52

CAPACITY (ENERGY) VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES

Figure 53

% CAPACITY (ENERGY) VS. AIR FLOW RATE
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ IN PLASTIC POUCHES

D. Heat Storage Test Results: Urea/Ammonium Bromide Eutectic.

The thermal energy storage unit used is diagrammed in Figure 54. The eutectic was encapsulated in polypropylene bottles. The bottles were laid horizontally on the racks used in the previous experiment. Nine bottles were fitted with glass thermowells projecting into the midsection. There were thirty rows in the direction of air flow compared with fifty-two rows used in the first two experiments using cylindrical containers.

The freezing point of the PCM was two degrees lower than expected and as a result the high and low set points for the inlet air were two degrees higher than specified in the experimental procedure. Due to time constraints, the set points were not adjusted to fit the new freezing point. The maximum and minimum outlet temperatures were adjusted downward 0.75°C to help compensate for the low freezing point and the high heat loss during charging.

The temperature-time profiles of a characteristic cycle are shown in Figures 55 and 56. It appears the unit charges almost completely before the outlet reaches the maximum charge temperature. However, on discharge there appears to be a substantial portion remaining frozen when the outlet temperature has dropped to the minimum discharge temperature. This observation was confirmed quantitatively when the charge and discharge capacities were calculated. Table XXV illustrates the method of calculating the theoretical charge and discharge capacities of the unit. Table XXVI presents the test results obtained on urea-ammonium bromide eutectic. The average charge capacity for all the runs was 94.5 percent of theoretical, but the average discharge capacity was only 72.8 percent of theory.

During charging there was some anomalous wavering of the bottle temperatures just after the temperature began to rise above the freezing point. This behavior was investigated further by observing the melting of the eutectic in a clear container. Temperature wavering was observed and appeared to be associated with crystals of eutectic falling onto the thermowell from an upper urea-rich layer as melting proceeded. In spite of the stratification discussed earlier in this report, the storage capacity on charging remained high, indicating that stratification had a minor impact on storage capacity.

Outlet air temperature profiles for three air flow rates are shown in Figure 57. Charge times ranged from just under ten hours at 91 CFM to just under nineteen hours at 55 CFM.

Figure 54

THERMAL ENERGY STORAGE UNIT: AMMONIUM BROMIDE/UREA EUTECTIC - STORAGE MEDIUM, AIR HEAT TRANSFER FLUID

Bottle Layout

Cabinet (1/8" Steel) 95Kg

Racks (Steel) 36Kg

Bottles Polypropylene

Diameter - .06M

Length - .17M

Wall - .75MM

90% Fill .42 Liter

Thermocouples

Positions ① → ⑨

In Slowest Cooling/Heating
Point Of Bottle

Figure 55: CHARGE CYCLE: AMMONIUM BROMIDE/UREA
EUTECTIC IN POLYPROPYLENE BOTTLES

Figure 56: DISCHARGE CYCLE: AMMONIUM BROMIDE/UREA
EUTECTIC IN POLYPROPYLENE BOTTLES

TABLE XXV

Theoretical Charge and Discharge Capacities:

Urea Ammonium Bromide Eutectic in Polypropylene Bottles

Weight of Eutectic 93.3 kg

Weight of Steel 131 kg

Temperature Range °C

	<u>Charging</u>	<u>Discharging</u>
High	85.5	95
Low	60	68

Theoretical Discharge Capacity (TDC)

20500 KJ

Theoretical Charge Capacity (TCC)

20100 KJ

Theoretical Storage Capacity (TSC)

22400 KJ

TABLE XXVI

Test Results Urea/Ammonium Bromide Eutectic
Encapsulated in Polypropylene Bottles

Run ^a	Air Flow Rate		Press. Drop ΔP (In. H ₂ O)	Air Heat Capacity C_{tf} (KJ/Eg °C)	Capacity Q_{in}, Q_{out} (MJ)	Energy Loss (MJ)	Corrected Capacity ^b CC, DC (MJ)	Percent of ^c Theoretical Capacity (%)	Design Rate DR (MJ/hr)	Test Time τ_c, τ_d (hr)	Time ^d Capacity (hr)
	CFM (Ft ³ /min)	m (Kg/hr)									
4-13-C	90	136	.56	1.063	24.8	5.9	18.9	94	1.37	9.8	13.8
4-14-C	91	133	.57	1.089	23.1	4.1	19.1	95	1.38	9.8	13.8
4-13-D	89	153	.65	1.034	13.3	2.5	15.8	77	1.26	6.5	12.5
4-14-D	89	151	.63	1.034	13.0	2.4	15.4	75	1.25	6.3	12.3
4-15-C	71	102	.33	1.085	26.0	6.2	19.7	98	1.05	14.0	18.8
4-16-C	71	104	.34	1.080	25.3	6.0	19.3	96	1.06	13.4	18.2
4-15-D	69	118	.40	1.030	11.9	2.6	14.5	71	.97	7.4	14.9
4-16-D	69	118	.40	1.033	12.0	2.6	14.7	72	.97	7.5	15.1
4-17-C	55	80	.20	1.082	29.4	10.7	18.7	93	.82	18.8	22.7
4-18-C	55	80	.20	1.085	29.0	10.6	18.4	91	.83	18.6	22.2
4-17-D	54	92	.24	1.033	11.4	3.2	14.6	72	.76	8.7	19.2
4-18-D	54	90	.24	1.036	11.1	3.1	14.2	70	.74	8.6	19.1

^aC-Charge, D-Discharge

^bCC = $Q_{in} - \text{loss}$, DC = $Q_{out} + \text{loss}$

^c% = CC/TCC or DC/TDC

^dTime capacity = CC/DR or DC/DR

Figure 57

CHARGE CYCLES, AMMONIUM BROMIDE/UREA
EUTECTIC IN POLYPROPYLENE BOTTLES

Six pairs of charge, discharge cycles were run. Profiles for the discharge cycles are shown in Figure 58. Steady state in the outlet air temperature was achieved before initiating a step change in the inlet air temperature. The stipled area between the inlet and outlet air temperatures was integrated numerically and used to determine the capacity. As in the previous experiments, it took significantly longer to charge storage than to discharge.

Referring again to Table XXVI, the heat loss approaches that obtained for the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ system, due to the high operating temperatures. The discharge capacity is consistently 23% less than the charge capacity, with an average deviation of 2.6% showing good repeatability. The 2°C temperature adjustment and the high rate of heat loss combined to terminate the discharge cycle with more than 25% of the stored heat not yet recovered.

Air flow rate has a minor effect on capacity and a more pronounced effect on test time, due to the high heat losses at the lower flow rates. The effect of air flow rate on test time and pressure drop is shown graphically in Figures 59 and 60.

E. Heat Storage Test Results, Two-Zone Stratified Unit:
Calcium Chloride Hexahydrate and Magnesium Nitrate
Hexahydrate/Ammonium Nitrate Eutectic.

The multi-zone heat storage unit, using two or more PCM's with different melting points, has several potential advantages. Higher grade heat can be collected during periods of availability and stored in a higher-melting zone, then lower grade heat can be collected over a wider period in lower-melting zones. The higher grade energy can then be used in applications needing a higher temperature. The low grade storage can be used as a preheat or for uses with less stringent temperature requirements, without degrading the high temperature store.

Multi-zone storage has the advantage that collection can proceed for a longer period of the day and under more overcast conditions than if only high grade heat were collected. Heat transfer fluid returns to the collector from the lower temperature storage zone, cooling the collector and increasing the efficiency. A disadvantage is that more complex controls with more ducting and dampers, or valving and piping, are required.

To study this type of storage, the two-zone unit shown in Figure 61 was set up. In practice, when changing from the charging to the discharging mode, one should reverse the flow through the storage unit. Provision should also be made to

Figure 58

DISCHARGE CYCLES
AMMONIUM BROMIDE/UREA EUTECTIC
IN POLYPROPYLENE BOTTLES

Figure 59: Test Time versus Air Flow Rate for Urea/Ammonium Bromide Eutectic in Polypropylene Bottles

Figure 60: Pressure Drop versus Air Flow Rate for Urea/Ammonium Bromide Eutectic in Polypropylene Bottles

Figure 61: Two-zone Thermal Energy Storage Unit: Calcium Chloride Hexahydrate and Magnesium Nitrate Hexahydrate/Ammonium Nitrate Eutectic Storage Media, Air Heat Transfer Fluid

bypass the high temperature section when appropriate to the operation. However, the test device had no provision for reverse flow, so two separate storage unit configurations were used, one for charging and another for discharge.

Two sections of the rack system used in the previous experiment were loaded with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in aerosol cans, and the third with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ eutectic in retort pouches. This arrangement might represent a system where most of the load can be carried by the lower melting material.

The inlet air temperature was step changed 45°C (from 16°C to 61°C). Therefore, there was an 11°C difference between the nearest melting point and the inlet air temperature in both the charge and discharge tests. Figures 62 and 63 show the response of the system to step changes in the inlet temperature. In the charge cycle all the PCM is apparently melted when the outlet air temperature reaches 49.75°C , three-fourths of the way between the initial temperature and the stepped inlet air temperature. In the discharge mode all of the calcium chloride hexahydrate containers had unused capacity when the outlet temperature reached a similar point (27.25°C). If the minimum discharge temperature is redefined as 21.6°C , about halfway between the inlet temperature and the PCM melting point, much of the calcium chloride hexahydrate is frozen.

Because of the way these tests were conducted, data were also available on operating in a "transposed" mode, i.e., charging with the air flow from low-melting PCM to higher-melting PCM and discharging with the reverse. Figures 64 and 65 show the effect of transposed operation. While roughly a hour's less charge or discharge time is observed, the storage capacity suffers 10-15%.

Table XXVII presents the data used to derive the theoretical storage capacity. Theoretical charge and discharge capacities were not calculated because more than one minimum discharge temperature was used. The reduced results of the tests are tabulated in Table XXVIII.

By discharging to 21.6°C an additional 25% of the theoretical capacity was extracted. Charging took 7.8 hours, while discharging took an average of 10 hours under the relaxed requirement.

Operation of the two-zone unit under test conditions was qualitatively as expected. Under charge, both PCM's began to melt at about the same time and were fully charged in roughly the same time frame. The design rate was higher than for the test unit containing only $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ eutectic, and

Figure 62: CHARGE CYCLE: TWO-ZONE THERMAL BATTERY, CHARGING CONFIGURATION

Figure 63: DISCHARGE CYCLE: TWO-ZONE THERMAL BATTERY, DISCHARGE CONFIGURATION

Figure 64: TWO-ZONE THERMAL BATTERY CHARGE CYCLES

Figure 65: TWO-ZONE THERMAL BATTERY, DISCHARGE CYCLES

TABLE XXVII

Theoretical Storage Capacity, Two-Zone Unit

Weight of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic

28.9 Kg

Weight of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

81.2 Kg

Weight of Steel

131 Kg

Temperature Range

High 61°C

Low 16°C

Theoretical Storage Capacity

31,700 KJ

TABLE XXVIII

Test Results, Double Zone Storage Unit: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in Aerosol Cans and
 $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ Eutectic in R-2 Retort Pouches

Run ^a	Air Flow Rate		Press. Drop ΔP (In. H_2O)	Air Heat Capacity C_{tf} (KJ/Kg $^{\circ}\text{C}$)	Capacity Q_{in}, Q_{out} (MJ)	Energy Loss (MJ)	Corrected Capacity ^b CC, DC (MJ)	Percent of ^c Theoretical Capacity (%)	Design Rate DR (MJ/hr)	Test Time τ_c, τ_d (hr)	Time ^d Capacity (hr)
	CFM (Ft^3/min)	m (Kg/hr)									
<u>Charging</u>											
5-10-C	91	156	.44	1.025	30.3	1.7	28.6	90	1.80	7.7	15.9
5-11-C	92	157	.44	1.020	30.7	1.4	29.4	93	1.80	7.9	16.3
<u>Transposed Charging</u>											
5-17-C	92	158	.44	1.026	26.7	1.1	25.6	81	1.81	6.8	14.2
5-18-C	92	156	.44	1.029	26.5	1.4	25.2	79	1.82	7.0	13.8
<u>Discharging to 27.25$^{\circ}\text{C}$</u>											
5-17-D	90	184	.54	1.007	18.4	.2	18.5	58	2.08	4.1	8.9
5-18-D	91	185	.55	1.007	18.6	.1	18.7	59	2.10	4.0	8.9
<u>Transposed Discharging</u>											
5-10-D	90	182	.55	1.008	15.5	.1	15.6	49	2.06	3.3	7.5
5-11-D	89	183	.55	1.006	15.5	.1	15.7	49	2.07	3.4	7.6
<u>Discharging to 21.6$^{\circ}\text{C}$</u>											
5-17-D	90	184	.54	1.007	27.4	-.3	27.1	85	1.04	10.5	26.0
5-18-D	91	185	.55	1.007	26.5	.2	26.7	84	1.05	9.4	25.3

^aC-Charge, D-Discharge

^b $\text{CC} = Q_{in} - \text{loss}, \text{DC} = Q_{out} + \text{loss}$

^c% = (CC or DC)/TSC

^dTime capacity = CC/DR or DC/DR

was reached at a lower temperature. We would expect a higher collector efficiency. On discharge, the high temperature zone was exhausted well before the first bottles of the low temperature PCM. The low temperature zone seems capable of supplying heat at a "set back" level for a considerable time period.

F. Discussion of Heat Storage Test Results.

Of the five subscale thermal energy storage devices assembled and tested, all used air as the heat transfer fluid. Four used single phase change materials with melting points of 27, 50, 76, and 89°C. The fifth used two phase change materials, one melting at 27°C and the other at 50°C. Interpretation of the results was important for subsequent system choice, design, and economics.

Computer simulations on the operation of phase change materials in solar heating systems have previously been carried out by Morrison,⁷ and Jurinak,⁸ at the University of Wisconsin. Morrison compared the performance of two PCM's, a paraffin wax melting at 46.7°C and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (Glauber's salt, m.p. 32°C), with rock storage and water storage. The effects of storage mass, surface area for heat transfer in storage, collector quality, collector size, and climate on the fraction of the heating load carried by the solar system were addressed. A load of 1000 KJ/hr°C and an air flow rate of 44 kg/hr m² were used. He concluded that a PCM storage mass between 7 and 25 kilograms per square meter of collector should be used for both materials in either Madison or Albuquerque. Little gain in the solar fraction was achieved above 25 kg/m² and it dropped off quickly below 7 kg/m².

Glauber's salt consistently gave about 2% higher solar fraction than the wax, because its lower melting temperature resulted in more efficient collector operation. Use of rock-bed storage resulted in slightly higher solar performance, supplying approximately 1% more of the heating load. From 200 to 400 kg/m² of rock was required. The difference in solar fraction is small enough that the choice between rock and latent heat storage should be decided by cost and space considerations.

⁶ Morrison and Abdel-Khalik, Effects of Phase-Change Energy Storage on the Performance of Air-Based and Liquid-Based Solar Heating Systems, Solar Energy, 20, 57-67 (1978).

⁷ Jurinak and Abdel-Khalik, Properties Optimization for Phase-Change Energy Storage in Air-Based Solar Heating Systems, Solar Energy Laboratory, University of Wisconsin-Madison, Madison, WI 53706.

Storage mass reduction was not as pronounced when comparing latent heat storage to water storage in liquid systems. Mass requirement for the PCM was 50% that of water.

In Jurinak's study the effect of varying the freezing point of the phase change material on the performance of a solar heating system was investigated. In this system the blower for the solar storage unit was activated when the room temperature fell below 70°F (21°C) and an auxiliary heater was activated if the room temperature fell below 65°F (18°C). A second auxiliary heater was turned on if the air stream returning from storage was at less than a minimum utilization temperature. Storage mass per unit collector area was maintained at 20 kg/m² for a PCM with the properties of wax except for a variable freezing point. The air flow rate was kept constant at 44 kg/hr per square meter of collector area.

When the minimum utilization temperature was set at room temperature, the fraction of the load supplied by solar reached a maximum when the storage medium freezing temperature was 24°C (75°F), with a sharp drop at lower and a very gradual drop at higher temperatures. As the minimum utilization temperature was increased to 30 and 35°C, the optimum freezing temperature increased to 28 and 30°C, respectively, while the solar portion dropped from 47% to 43 to 41%. System performance was improved and control simplified when continuous circulation of room temperature air was allowed.

Morrison and Jurinak's conclusions were based on year-long simulations using an infinite transfer unit model, a storage unit model with effectively infinite surface area for heat transfer between the storage medium and the heat transfer fluid. The number of transfer units, NTU, is defined by the following equation:

$$NTU = \frac{U A}{\dot{m} C_{tf}} \quad (\text{Dimensionless}), \quad (11)$$

where U, the overall heat transfer coefficient, is equated to the air film heat transfer coefficient (based on an isothermal storage medium perpendicular to air flow), A is the surface area for heat transfer, and $\dot{m}$ and C_{tf} are the mass flow rate and the specific heat of the heat transfer fluid, respectively.

Morrison modeled systems with 1, 10, and ∞ transfer units in a two-week simulation. The model with infinite NTU showed improvement in the heating load supplied by solar of less than 1%, compared with the model with NTU=1, and only one fifth of one percent versus NTU=10. Based on these results, the rest of his modeling was done with the less costly infinite NTU model.

The simple model used in these simulations yields an upper limit of what might be expected in actual operation. Corresponding simulations, using a storage model based on the response of a thermal battery to a step change in the inlet air, could be used to generate a lower limit for solar heating system operation.

In order to compare our test conditions with those assumed in the Wisconsin studies, values of NTU were calculated for each of our five storage units. The values of air flow rate, CFM (ft^3/min), minimum area for air flow, CSM (m^2), heat transfer surface area, A (m^2), and container diameter, D (M), required for these calculations are given in Tables XXIX and XXX. The air film heat transfer coefficient, h_o was calculated from the following equation:

$$h_o = 9.406 K \left(\frac{0.001548 \text{ CFM}}{\text{CSM}} \right)^{0.6} D^{-0.4} \quad (12)$$

where K is a correction factor for non-ideal air flow, set equal to 0.6 for these calculations.

Also listed in Table XXX are the calculated number of transfer units for each air flow rate in each storage unit. If the air mass flow rate per square meter of collector is assumed to be 44 kg/hr m^2 , a mass of PCM per unit area of collector for each test can be calculated. These values are also listed in Table XXX.

All of the storage tests were conducted at NTU values of one or greater, except the tests at high air flow rates with urea/ NH_4Br , which fell slightly below one. Storage mass per square meter of collector ranged from 22 to 51, based on a mass flow rate of 44 kg/hr m^2 . Setting minimum values of unity for NTU and 20 kg/m^2 for the mass of storage per unit area of collector, our tests clearly fall within the bounds of the Wisconsin modelling program.

The relationship of NTU to the fraction of the theoretical capacity achieved in our thermal battery testing is plotted in Figure 66 for the four single zone test units. The batteries using cylindrical containers appear to behave in a predictable fashion; storage capacity increases as the number of transfer units increase. As the number of transfer units approaches infinity, the fraction of storage capacity usable on charge and discharge will approach unity. The unit using flat plastic film pouches shows a high capacity for the calculated number of transfer units. This could result from several factors: 1) the maximum distance from the surface to the slowest cooling or heating point is smaller than for a cylinder; 2) the arrangement of pouches used may create additional turbulence in the air

TABLE XXIX

Data Used to Calculate NTU Values

<u>Test Unit</u>	<u>Mass of PCM Kg</u>	<u>Heat Transfer Surface Area (A) M²</u>	<u>Minimum Area for Air Flow (CSM) M²</u>	<u>Diameter of Container (D) M</u>
1. CaCl ₂ ·6H ₂ O in HDPE Bottles	96.75	4.45	0.0128	0.061
2. Mg(NO ₃) ₂ ·6H ₂ O in Aerosol Cans	100.0	3.87	0.0088	0.066
3. Mg(NO ₃) ₂ ·6H ₂ O/ NH ₄ NO ₃ in Pouches	86.0	4.72	0.0208	0.0476*
4. Urea/NH ₄ Br in Polypropylene Bottles	93.3	4.81	0.065	0.060
5. Double-zone Unit CaCl ₂ ·6H ₂ O in Aerosol Cans,	81.2	3.26	0.0642	0.066
Mg(NO ₃) ₂ ·6H ₂ O/ NH ₄ NO ₃ in Pouches	28.9	1.57	0.0208	0.0476*

*The equivalent diameter of the pouches was calculated as the average of the width and the height.

TABLE XXX

Number of Transfer Units and
Storage Mass per Unit Area of Collector

Unit	Run	Air Flow Rate CFM	Number of Transfer Units NTU	Storage Mass per Unit Area of Collector Kg/m ²
CaCl ₂ ·6H ₂ O in HDPE Bottles	1-62-C	74	2.13	32
	1-62-D	74	1.87	28
	1-60-C	65	2.24	36
	1-60-D	63	2.00	33
	1-66-C	46	2.57	51
	1-66-D	46	2.24	44
	Average		2.18	
Mg(NO ₃) ₂ ·6H ₂ O in Aerosol Cans	2-19-C	86	2.45	33.8
	2-19-D	86	2.22	30.1
	2-10-C	74	2.60	39.3
	2-10-D	73	2.40	36.1
	2-12-C	61	2.88	48.9
	2-12-D	61	2.54	42.3
	2-14-C	52	3.06	57.1
	2-14-D	51	2.75	51.2
	Average		2.61	
Mg(NO ₃) ₂ ·6H ₂ O/ NH ₄ NO ₃ Eutectic in Pouches	3-09-C	89	1.79	24.8
	3-09-D	89	1.61	22.0
	3-11-C	81	1.86	27.3
	3-11-D	81	1.67	24.2
	3-13-C	71	1.96	31.1
	3-13-D	69	1.78	28.4
	3-15-C	59	2.11	37.4
	3-15-D	59	1.90	33.2
	Average		1.84	
Urea/NH ₄ Br Eutectic in Polypropylene Bottles	4-13-C	90	0.92	30.3
	4-13-D	89	0.83	26.9
	4-15-C	71	1.03	40.2
	4-15-D	69	.93	34.9
	4-17-C	55	1.14	51.2
	4-17-D	54	1.02	44.6
	Average		0.98	
Double-Zone CaCl ₂ ·6H ₂ O	5-10-C	91	.55	22.9
	5-10-D	90	.47	19.6
Mg(NO ₃) ₆ H ₂ O/ NH ₄ NO ₃	5-10-C	91	.59	8.2
	5-10-D	90	.51	7.0
Sum	5-10-C	91	1.14	31.1
	5-10-D	90	.99	26.6

Figure 66: The average fraction of theoretical charge and discharge capacity achieved in thermal battery testing versus the average number of transfer units.

stream, enhancing heat exchange; and 3) the method used to calculate the equivalent diameter (average of the width and the height) may be poor.

The physical properties of the storage media simulated by Morrison and those tested in our test device are listed in Table XXXI.

This tabulation shows the superiority of PCM's over sensible storage media in mass and bulk of material required. Among the PCM's, paraffin shows a disadvantage of organic PCM's, low density. Glauber's salt shows higher capacity per weight or volume than the other materials, assuming no degradation with temperature cycling, and assuming sufficient rate of rehydration during discharge. In actual use, considerably less capacity might be expected. The PCM's listed (other than Glauber's salt) are congruent melting or effectively so.

Of the PCM's listed, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$ eutectic, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, Glauber's salt, and paraffin wax are potentially useful for forced air systems. Previously, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was thought to melt too low to be of utility in a direct heating application. However, Jurinak's results suggest that 27°C may be near optimal. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ should definitely be demonstrated in a direct heating application.

G. Modelling Refinements: Calcium Chloride Hexahydrate Storage.

The computer model of a thermal energy storage unit, previously discussed in Section IV. D., was modified to fit the results of subscale testing and then used to predict the performance of full-scale systems. The effect of container diameter and thermostat setting was investigated.

1. Discharge Mode - Much the same as before, performance of a storage unit was modelled by following 0.05 hour slugs of air through 18 segments of the storage unit. In the discharge mode, the temperature and the fraction of PCM in the molten state at the beginning of the time period was used to determine the rate of heat flow from the storage medium segment to the air slug, giving the air temperature leaving the segment. The total amount of heat transferred to the air stream was then used to calculate the temperature and fraction of PCM remaining molten at the end of the time period.

The effects of the sensible heat of the liquid storage medium, the latent heat of phase change, and the sensible heat of the solid storage medium were accounted for separately.

TABLE XXXI

Physical Properties of Storage Media

	Properties	CaCl ₂ ·6H ₂ O	Na ₂ SO ₄ ·10H ₂ O	Sunoco P116 Paraffin Wax	Mg(NO ₃) ₂ ·5H ₂ O/ NH ₄ NO ₃ Eutectic	Urea/ NH ₄ Br Eutectic	Mg(NO ₃) ₂ · 6H ₂ O	Rock	Water
Specific Heat of Solid	C _s (KJ/kg °C)	1.38	1.92	2.89	2.01	1.59	1.84	0.84	
Specific Heat of Liquid	C _l (KJ/kg °C)	2.18	3.26	a	2.43	1.98	2.51		4.19
Thermal Conductivity of Solid	K _s (KJ/mh °C)	3.92	1.85	0.498	2.00	2.41	2.26	0.45	
Thermal Conductivity of Liquid	K _l (KJ/mh °C)	1.94	--	a	1.80	1.17	1.78		2.15
Freezing Point	T _m (°C)	27	32.0	46.7	50	76	89		
Latent Heat of Fusion	λH _m (KJ/kg)	193	251	209	130	151	159		
Density of Solid	ρ _s (kg/m ³)	1713	1460	786	1633	1551	1643	2400	
Density of Liquid	ρ _l (kg/m ³)	1523	1330	a	1553	1442	1553		1000
Heat Storage Capacity (Volumetric)	SCV (MJ/m ³) ^{b, c}	343	403	210	271	274	314	40	84
Heat Storage Capacity (Mass)	SCM (KJ/kg) ^b	223	303	267	175	190	202	17	84

^aAssumed equal to corresponding value for solid phase.

^bAssuming a 20°C temperature range bracketing the PCM freezing point.

^cUsing the liquid density.

When the phase change material was either all frozen or all melted, it was assumed to be isothermal and the overall heat transfer coefficient was calculated from the air film heat transfer coefficient and the thermal conductivity of the container wall. As the material froze it was assumed to freeze in concentric cylindrical layers inside the container. The air film coefficient, and the conductivities of the container wall and the crystal layer were used to calculate the overall heat transfer coefficient.

To fit the test results, supercooling was included in the model and the air film heat transfer efficiency factor, K , was adjusted. Supercooling was accounted for by keeping the medium in the liquid state until the empirical supercooling equation was satisfied:

$$\text{Supercooling, } ^\circ\text{C} = 1.0 + 2.0 (\text{cooling rate, } ^\circ\text{C/hr})^{0.4}, \quad (9)$$

In describing the air film heat transfer coefficient, an efficiency factor, K , is used to account for non-ideal situations. Usually, for air flowing past cylinders arrayed in a triangular pitch, a factor of 0.8 is employed to account for short circuiting. For cylinders placed one behind the other, $K=0.6$ is used. In our subscale unit an equilateral triangular pitch was used, but the flow section was so narrow that considerable edge effects might be expected. Using $K=0.6$ gave the best visual fit of the outlet air temperature as a function of time, as shown in Figure 67. This may reflect non-ideal heat transfer in the subscale storage unit or it may be an adjustment for inadequacies in the model itself.

The simulated discharge capacities average ten percent lower than the experimentally observed values. These would be raised about 1%, if $K=0.8$ were used. Thus this model gives conservative results in full scale simulation work.

2. Charge Mode - In computer modelling, the discharge mode was considered to be controlling. However, year-long simulations of solar energy systems will require a model of the charging mode as well. Figure 68 shows the results from a charging mode model analogous to that used for discharge. This approach ignores the resistance to heat transfer within the phase change material. A value of $K=0.6$ was assumed for the air film heat transfer efficiency factor. To improve the fit of the model, some account should be made of the resistance to heat transfer within the PCM, and K should be higher.

3. Full-Scale Storage Units - The charging mode should be more carefully modelled before results based on larger containers can be relied on fully. With this in mind, we proceeded

Figure 67

COMPUTER MODEL FOR DISCHARGING SUBSCALE
 $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ THERMAL ENERGY STORAGE UNIT,
SUPERIMPOSED ON TEST RESULTS. (SOLID LINES,
TEST RESULTS: BROKEN LINES, MODELING RESULTS.)

to examine the effects of container diameter and thermostat setting (inlet air temperature) for full-scale thermal energy storage units.

Three full-scale units of the type shown in Figure 69 were simulated in the discharge mode. An inlet air temperature of 20°C (68°F) was selected. Each storage unit contained 2368 kg (5220 lbs) of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, giving a total latent heat of fusion of 452 megajoules (428,000 BTU). This is roughly equivalent to the heating requirements for an average day in March in the Midwest. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ encapsulated in HDPE plastic tubes of three diameters, 3.5, 4.5, and 5.25 in., were simulated, with the results shown in Figure 70.

For 3.5 inch diameter pipes, after 1 1/2 days of discharge, 74% of the latent heat had been recovered, and the discharge rate had dropped to 9.6 MJ/hr. The 74% discharge point was arbitrarily selected to define the minimum discharge rate (design rate). The thermal batteries with larger diameter encapsulant tubes have lower design rates to deliver the same amount of thermal energy, 10% less for 4.5 in. tubes and 26% for 5.25 in. containers. This must be balanced against savings in filling, sealing, and handling costs when using larger diameter pipes.

The effect of varying the inlet air temperature (thermostat setting) was simulated for 5.25 inch pipes, with the results shown in Figure 71. The discharge rate again was calculated when approximately 74% of the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was frozen and the capacity expressed as the number of hours the design rate could be delivered.

Compared with the base design rate of 7.1 MJ/hr for 20°C inlet air, the minimum delivery rate drops 28% for a 22°C thermostat setting. If 24°C is selected, less than 45% of the PCM can be frozen, even after 3 days. Conversely, lowering the inlet air temperature improves the design rate - 30% for 18°C, and 59% with a 16°C thermostat setting.

These results illustrate the critical importance of thermostat setting on solar fraction. As the set temperature is raised, the discharge rate available from storage decreases. The gap between this rate and the load demand must be filled by auxiliary heat. For $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ encapsulated in 5.25 inch pipes, a thermostat setting above 22°C (72°F) will have a devastating effect on the fraction of heat supplied by the solar system. For the night time setback portion of the load, with thermostat settings of 18°C (64°F) or less, such storage should perform admirably. If higher thermostat settings are to be used, smaller diameter pipes should be employed to forestall a precipitous decline in solar fraction.

Figure 69

FULL-SCALE STORAGE UNIT
CALCIUM CHLORIDE HEXAHYDRATE
ENCAPSULATED IN HDPE CYLINDERS

Figure 70 SIMULATED DISCHARGE OF FULL SCALE THERMAL ENERGY STORAGE UNITS

Calcium Chloride Hexahydrate In High Density Polyethylene Pipes.
For Various Pipe Sizes, Air Flow 1200 CFM

Figure 71: SIMULATED DISCHARGE OF A FULL SCALE THERMAL ENERGY STORAGE UNIT: CALCIUM CHLORIDE HEXAHYDRATE IN 5.25 inch O.D. HIGH DENSITY POLYETHYLENE PIPES, FOR VARIOUS INLET TEMPERATURES OR THERMOSTAT SETTINGS

VIII. SYSTEM CONCEPTS AND ECONOMICS

Solar space heating systems were conceptualized using calcium chloride hexahydrate and/or magnesium nitrate hexahydrate/ammonium nitrate eutectic. Performance analysis and economic evaluation were performed. Of the six conceptual designs, one was chosen for further design and analysis. To minimize the number of parameters to be analyzed, a standard house (Table XXXII) was used in the evaluation.

TABLE XXXII

Solar Home Specifications

Floor Space	1800 ft ²
Load	12,600 BTU/DD, 1000 KJ/hr °C
Collector Area	538 ft ² (50 M ²)
Tilt	60°
Orientation	South Facing
Location	Madison, Wisconsin (4224°C Days)

Electric resistance heat backup was assumed in all cases.

A. Passive Solar System Using CaCl₂·6H₂O for Thermal Energy Storage.

In the passive solar system diagrammed in Figure 72, sunlight is collected in a conservatory and a portion of the energy is absorbed directly into the encapsulated phase change material. During collection, over-heating of the living space outside the conservatory is minimized with an insulated drape. When the sun is not shining, movable insulation (R-9) is used to minimize heat loss through the conservatory glazing. The load characteristics of the structure, listed above, can be maintained, because some of the windows that otherwise would face outdoors will face into the conservatory. The insulation between the conservatory and the rest of the home is opened when necessary for heating.

Heat is stored in 8550 pounds of CaCl₂·6H₂O encapsulated in sixty 6 5/8" O.D., high density polyethylene tubes, eight feet tall. These pipes are fabricated by filling to 90 percent of capacity with molten calcium chloride hexahydrate and heat sealing. The 0.189 inch wall provides a positive moisture

Figure 72: PASSIVE SOLAR SYSTEM USING $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ FOR
THERMAL ENERGY STORAGE

barrier and enough strength to withstand the pressure developed in the container during freeze thaw cycling. The pipes are placed vertically on the north side of the conservatory one-half inch apart. Black polyethylene is used with a flat or dull finish to enhance heat absorption. Thirty-six linear feet of the north wall of the conservatory is required for the storage system.

The conservatory is considered to be part of the living space, although overheating is expected during collection periods. When a more comfortable atmosphere is required while the sun shines, the movable insulation can be drawn. This will significantly reduce the fraction of the heating load carried by the solar system if it occurs frequently.

The estimated installed cost of this storage system is given in Table XXXIII.

TABLE XXXIII

Cost Analysis for Solar Collection in Conservatory

	<u>Dollars/ft² Glazing</u>
Glazing, two panes	2.5
Installation	1
Wall credit	-3
Movable insulation	<u>3.5</u>
Total Cost	\$4/ft ²

A credit of three dollars a square foot was taken for the fiber reinforced plastic glazing system, for replacing the south weather wall. For a glazing area of 538 ft² the collection/movable insulation portion of the solar system is estimated to cost \$2152. The additional movable insulation used to minimize overheating outside the conservatory is estimated to add \$1.00/ft² or \$538 to the system cost. Table XXIV gives the estimated cost of the passive solar heating system.

Based on Balcomb's⁸ results, the passive system should supply approximately two-thirds of the space heating load for this design.

⁸J. D. Balcomb and R. D. McFarland, "A Simple Empirical Method for Estimating the Performance of a Passive Solar Heated Building of the Thermal Storage Wall Type," in Passive Solar State of the Art, Proceedings of the 2nd National Passive Solar Conference, (MASEA, 2233 Gray's Ferry Avenue, Philadelphia, PA 19146).

TABLE XXXIV

Cost Analysis for Passive Solar System;
CaCl₂·6H₂O in HDPE Pipes

Storage System

Raw Materials

CaCl ₂ ·6H ₂ O, 8550 pounds at \$.05/#	\$ 428
HDPE Pipe, 800 pounds at \$.85/#	<u>680</u>
Total Raw Material Costs	1108
Filling & Handling, Est.	1108
Installation	<u>300</u>
Storage Cost	\$2516
Conservatory Cost	2690
Auxiliary Heater Cost	<u>2400</u>
Total Capital	\$7606

B. Forced Air Solar System Using CaCl₂·6H₂O for Thermal Energy Storage.

The forced air system diagrammed in Figure 73 uses a conservatory for solar collection in much the same way as the passive system described above. Rather than storing heat in the conservatory north wall, the heat is transferred to storage via an air stream. By careful design of the air flow system the need for secondary movable insulation between the conservatory and the balance of the living space may be eliminated.

Heat is stored in a storage bank with 5220 pounds of calcium chloride hexahydrate encapsulated in three hundred thirty-six 2 3/8" O.D. x .068" wall thickness HDPE pipes, 7 feet tall. The system is designed to give 0.17" H₂O pressure drop across the storage bed when 2400 CFM of air is blown through the collection system. For discharge, an air flow rate of 1200 CFM can be used in the heating system. The high air flow rate in the collection mode is required to minimize heat buildup in the conservatory. Table XXXV gives the estimated capital cost of this solar system.

Figure 73: FORCED AIR SOLAR SYSTEM USING $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ FOR
THERMAL ENERGY STORAGE

TABLE XXXV

Cost Analysis of Forced Air and Hybrid Solar Systems:
CaCl₂·6H₂O in HDPE Pipes

Raw Materials

CaCl ₂ ·6H ₂ O	5220 # at \$.05/#	\$ 261
HDPE Pipe	464 # at \$.85/#	<u>394</u>
Total Raw Material Costs		\$ 655
Filling and Handling, Est.		655
Installation		<u>300</u>
Storage Cost		1610
Conservatory		2152
Additional Ducts & Controls		800
Auxiliary Heating System		<u>2400</u>
Heating System Cost		\$ 6962

Based on the results of Morrison,⁹ Jurinak,¹⁰ and Taff,¹¹ this solar system can be expected to contribute 50 percent of the heating load for the house.

C. Hybrid Solar System Using CaCl₂·6H₂O for Thermal Energy Storage.

The "hybrid" solar system diagrammed in Figure 74 in many respects is similar to the forced air system described above. However, the storage system is discharged by natural convection. This system might have particular utility in retrofit situations where it is inconvenient to couple the solar system with the auxiliary heating system. For this analysis, the costs and performance are estimated to be the same as for the active forced air system (Table XXXV).

⁹ Morrison, *ibid.*

¹⁰ Jurinak, *ibid.*

¹¹ D. C. Taff, et al., "Passive Versus Active Collector Systems, A Comparative Study of Efficiency, Capacity, and Economics" in *Passive Solar State of the Art, Proceedings of the 2nd National Passive Solar Conference*, (MASEA, 2233 Gray's Ferry Avenue, Philadelphia, PA 19146).

Figure 74: HYBRID PASSIVE/ACTIVE SYSTEM USING $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ FOR THERMAL ENERGY STORAGE

D. Forced Air Solar System Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Thermal Energy Storage Coupled in Parallel with an Air-to-Air Heat Pump.

The heat pump assisted solar system diagrammed in Figure 75 is the same as the forced air system described in Section B above, except an air-to-air heat pump was added in parallel to the solar heating system. The heat pump can be used for cooling as well as heating, but only the heating contribution is treated in this evaluation. If a phase change material melting below the 24°C minimum recommended by Jurinak¹² were used for heating, the heat pump might be used in series with the solar system. The heat pump portion of the system is estimated to add \$1800 to the cost of the heating system resulting in a total capital cost of \$8762. In a northern climate such as Madison, Wisconsin an air-to-air heat pump may be expected to reduce electric consumption for heating by 25 to 50%; a reduction of 30% was assumed in this analysis. The performance of the solar portion of the system was assumed to be the same as for the forced air system discussed in Section B.

E. Forced Air Solar Heating System Using Encapsulated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ Eutectic for Thermal Energy Storage.

A solar system using encapsulated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic, melting at 50°C , is diagrammed in Figure 76. It has an advantage over the $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ system in that the load can be satisfied from storage regardless of the thermostat setting. However, collector efficiency would drop due to higher operating temperatures. Heat is stored in 6545 pounds of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic encapsulated in 3600 sixteen-ounce steel aerosol cans. These cans are enclosed in a heat storage cabinet which operates much the same as the heat storage test device used in our test program.

The estimated costs for this system are given in Table XXXVI. Based on the results of Morrison¹³ and Jurinak¹⁴ this system can be expected to supply 46 percent of the heating load with solar.

¹²Jurinak, ibid.

¹³Morrison, ibid.

¹⁴Jurinak, ibid.

Figure 75: HEAT PUMP-COUPLED SYSTEM USING $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ FOR
THERMAL ENERGY STORAGE, PARALLEL OPERATION

Figure 76: FORCED AIR SOLAR SYSTEM USING $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{NH}_4\text{NO}_3$
EUTECTIC FOR THERMAL ENERGY STORAGE

TABLE XXXVI

Cost Analysis for Forced Air Solar System,
Using $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ Eutectic

Raw Materials

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ Eutectic

6545 # @ \$.10/#, Est. \$ 654

Aerosol Cans 3600 @ \$.12 ea. 432

Total Raw Materials Costs 1006

Filling and Handling, Est. 1086

Installation 300

Storage Costs 2472

Collectors @ \$10/ft² 5380

Solar Ducts & Control 800

Auxilliary Heater 2400

Heating System Costs \$11,052

F. Double Zone Storage in a Forced Air Solar System.

A solar system using two encapsulated phase change materials melting at 27°C and 50°C is diagrammed in Figure 77. This system is similar to the forced air system using encapsulated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{NH}_4\text{NO}_3$ eutectic. However, additional ducting and more complex controls are needed to make use of the advantages of two-temperature-zone storage.

Hot air from the collector is first blown through the high temperature PCM zone to store high quality heat and then through the lower temperature PCM zone to store additional heat. By storing heat from the solar system at two temperatures, additional flexibility can be built into the heating system. For example, when night time setback is used, the low temperature storage material can be used to carry the load through the night and the higher temperature PCM can be used to reheat the structure to the comfort zone in the morning.

Figure 77: TWO-ZONE FORCED AIR SYSTEM USING MAGNESIUM NITRATE HEXAHYDRATE/AMMONIUM NITRATE EUTECTIC AND CALCIUM CHLORIDE HEXAHYDRATE FOR THERMAL ENERGY STORAGE

A more conventional flat plate solar collector must be used in this system to reach the temperatures required to charge the higher melting PCM. The flat plate collectors were treated as an add-on to the structure, and no credit was taken for replacement of a weather wall. This seems to be standard current practice. If the flat plate collectors could be integrated into the weather wall, the capital cost of this type of system would be reduced somewhat. A cost of \$10/ft² was assumed for the installed collectors. Table XXXVII gives the cost build-up for this heating system.

TABLE XXXVII

Cost Analysis for a Double Zone Solar Heating System

Raw Materials

CaCl ₂ ·6H ₂ O 2610 # @ \$.05/#	\$ 130
HDPE Pipe 231 # @ \$.85/#	196
Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ Eutectic	
3272 # @ \$.10/#, Est.	327
Aerosol Cans 1800 @ \$.12 ea.	<u>216</u>
Total Raw Material Costs	869
Filling and Handling, Est.	869
Installation	<u>400</u>
Storage Costs	2139
Collectors @ \$10/ft ²	5380
Solar Ducts & Controls	900
Auxilliary Heater	<u>2400</u>
Heating System Cost	\$10819

This storage system employs CaCl₂·6H₂O encapsulated in 2 3/8" O.D. HDPE low pressure pipes and Mg(NO₃)₂·6H₂O/NH₄NO₃ in steel aerosol cans.

The performance of this system is difficult to estimate accurately. The collector operating temperature will be higher than for storage using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ PCM alone, but less than for the nitrate eutectic alone. Collector efficiency should be intermediate between the two. The effect on the heating fraction supplied by solar can be estimated from the results of Morrison¹⁵ and Jurinak¹⁶ if an average freezing temperature is chosen, 38.5°C. Based on this assumption, for the double zone system approximately 48.5% of the heating load is met by solar energy. By operating with a night time setback of 5.6°C, a load reduction of approximately 10% would be expected. Assuming this load reduction does not change the total solar input, the fraction of the load carried by the solar system would increase to 54%.

G. Economic Analysis and Performance Comparison.

Economic comparisons were made of the six design concepts discussed above. For a meaningful comparison to be made, not only operating expenses should be considered, but all outlays necessary to amortize the capital invested in the heating system. Mortgage financing appropriate for families was employed. The economic bases for this evaluation are given in Table XXXVIII. The estimated yearly cost for each system is given in Table XXXIX. Estimates for heating systems using electric resistance heat, oil heat, gas heat, air-to-air heat pump without solar assist, and forced air solar using rock thermal storage are also listed for comparison.

None of the solar systems was optimized and the values given for system cost and performance are preliminary estimates. There is an apparent inconsistency in the performance estimates between the passive system and the forced air systems. The passive system is estimated to be 66% solar while the forced air system only 50% solar, even though both systems use the same type of collector to supply similar loads. An air flow rate of twice the value given by Morrison¹⁵ was used to cool the conservatory during collection in the forced air system, in order to maintain a reasonable temperature. This should result in added efficiency of collection. Therefore, the value given for the solar fraction in the forced air system may be low. In the simulation of the passive system¹⁷, 100% absorbance was assumed rather than the 90 to 95% that might be expected, so the value given for the solar fraction in the passive system probably is high.

¹⁵ Morrison, ibid.

¹⁶ Jurinak, ibid.

¹⁷ Balcomb, ibid., p. 384.

TABLE XXXVIII

Economic Basis

1. Financing is assumed to be for new construction - a 25 year mortgage at 9% interest. Factor for average yearly payment is calculated for after tax effect as follows:

Yearly payment factor =	.1018
Amount for principle 1.00/25 yr =	.0400
Thus amount for interest =	.0618
After tax intr. cost w/25% tax rate =	.0464
Prin. plus after tax interest cost =	.0864

2. Yearly property taxes and insurance are assumed to be 2.7% of the capital costs.
3. Maintenance is assumed to be 1.0% of the capital costs.
4. Supplemental heat is supplied at \$0.05 per KWhr for electric or \$.55/gal for #2 fuel oil. Natural gas is assumed to cost .30¢/ft³. Furnace efficiencies used were 100%, 70% and 80% for electricity, fuel oil or natural gas respectively.

TABLE XXXIX

Economics of Various Home Heating Systems

Heating System	Capital Cost	Fraction of the Heating Load Solar	Utility Costs, Heating		Yearly Mortgage Insurance and Maintenance \$/Year B	Operating Cost	
			\$/MM BTU	\$/Year A		\$/Year A + B	\$/MM BTU
A. Passive Solar CaCl ₂ ·6H ₂ O Storage Conservatory Collector	7,606	0.66	4.99	479	939	1,418	14.8
B. Forced Air Solar CaCl ₂ ·6H ₂ O Storage Conservatory Collector	6,962	0.50	7.33	704	859	1,563	16.2
C. Hybrid Solar CaCl ₂ ·6H ₂ O Storage Conservatory Collector							
D. Forced Air Solar CaCl ₂ ·6H ₂ O Storage with Parallel Air-to-Air Heat Pump Conservatory Collector	8,762	0.50	5.13	493	1,081	1,574	16.4
E. Forced Air Solar Mg(NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ Eutectic Storage Flat Plate Collectors	11,052	0.46	7.91	760	1,364	2,124	22.1
F. Forced Air Solar Double Zone Storage with Night Setback Flat Plate Collectors	10,819	0.54	6.74	583	1,335	1,918	22.1
G. Forced Air Solar Rock Storage Flat Plate Collectors	9,980	0.51	7.18	690	1,232	1,922	20.0
H. Air-to-Air Heat Pump	4,200	0.0	10.26	986	518	1,504	15.7
I. Electric Resistance Heat	2,400	0.0	14.65	1,408	296	1,704	17.7
J. Oil Fired Forced Air	3,000	0.0	5.61	540	370	910	9.5
K. Natural Gas	3,000	0.0	3.75	360	370	730	7.5

A useful figure for comparing various systems is the operating cost, either per year or per million BTU. This represents the home owner's expenditure for home heating, not only utility costs, but outlays attributable to the heating system: maintenance, insurance, property taxes, and mortgage payments, including income tax adjustments.

Both natural gas and oil are substantially less expensive than any of the other systems. The only conventional heating system that solar heating can compete with is resistance electric. The solar systems that compete favorably with electricity are the ones that have the solar collector integrated directly into the living space. This reinforces the conclusion that the high cost of presently-available collectors is a barrier to the adoption of solar systems.

When solar collection is restricted to within the living space, the choice narrows to one of the various $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ systems. The other PCM's store heat at too high a temperature. The differences in operating costs among these $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ systems are within the accuracy of the estimates, so the choice should be made on esthetic and engineering grounds. The passive system makes use only of radiation and natural convection for heat transfer, and is also the least understood from an engineering perspective. The hybrid system is also difficult to characterize, and probably most applicable to some retrofit cases. The heat pump system involves a complex three-way interaction between a solar system, a heat pump, and the auxiliary heating system. For the sake of simplicity the forced air system was chosen for further analysis. This is in keeping with the experience base of this contract.

IX. SYSTEM DESIGN

Widespread acceptance of solar space heating has been slowed by high costs, particularly for the solar collectors. In some designs the price of the solar system has been reduced by incorporating the collector into the southern weather wall, and in some cases by making the living space part of the collector. The system described in this section represents an effort to incorporate solar collection into the living space. In such a system the lighting, thermal, and humidity conditions in the home will be modulated by solar availability. If the operation of the system is viewed as an improvement over the way homes currently operate, it has a good chance of success in the housing market.

The system uses a room as a solar collector. Heat collected in the collection room is transferred via an air stream to storage and from there to the rest of the heated space. The glazing system is covered with movable insulation at night and during cloudy periods to minimize heat loss. The movable insulation may also be used to control overheating in the collection area during periods when the rate of collection exceeds the storage rate and the load. A collection room of this type has been termed an atrium, solarium, conservatory, sun space, or attached greenhouse.

A thermal energy storage system employing phase change material should use more than 7 kg of PCM per square meter of collector and have sufficient surface area to supply more than one unit of heat transfer.¹⁹ In the storage system chosen for this application, the heat transfer surface is more expensive than the storage medium. Consequently, a relatively large mass was used, while heat transfer surface was employed frugally. Relatively large containers were specified to minimize sealing and installation costs. Pressure drop through the storage system was set at a low level to minimize utility costs. The air flow rate for collection was set at twice the air flow rate for heating to maximize collector efficiency and collector room comfort. Table XL gives the specifications for this design.

A. Storage Sub-System.

In choosing a phase change material for heat storage in this system, the freezing point is a key factor. The PCM must melt low enough to allow operation of the collection room within a range comfortable for human occupancy, yet high enough to handle the heating requirements. Of the materials investigated under this contract $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ best fits this application (F.P. 27°C , 81°F).

High density polyethylene pipe was chosen as encapsulant for the PCM for several reasons. A sealed pipe can withstand the pressure variations caused by freeze-thaw cycling. The pipe wall in the sealed system offers a positive moisture vapor barrier to assure compositional stability of the PCM. The HDPE is compatible with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ with or without oxygen present. The pipe system can be used in a vertical arrangement, minimizing the cost of supporting the PCM in the air stream. Sealing the containers can be done with established technology from the gas pipeline industry.

¹⁹ Morrison, *ibid.*

TABLE XL

Solar Home Specifications, Forced Air Solar Heating System
Using $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ for Heat Storage

House	Single Family Detached in Madison, WI
Load	527 BTU/hr °F (1000 KJ/hr °C) 7.0 BTU/DD ft ² , house 0.98 BTU/hr °F ft ² , glazing
Collector/Conservatory	650 ft ² , vertical glazing Movable insulation R-9 Automatic operation
Storage - $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in 3.5" HDPE pipes	47 kg/M ² of glazing Discharge capability @ 1200 CFM Inlet air at 20°C (68°F) Outlet air above 24°C (75°F) Capacity, 380 MJ (360,000 BTU) Design rate, 9.6 MJ/hr (9100 BTU/hr) Hour capacity, 40 hr
Control Strategy	
Heating	Fan on at 22°C (72°F) @ 1200 CFM Auxiliary on at 20°C (68°F) Thermostat/sensor
Collection	Fan on at 38°C (100°F) @ 2400 CFM Fan off at 29°C (84°F) Sensor at hot spot in conservatory

Filling and sealing these tall containers is not yet state of the art in the packaging industry. Pipe butt fusion initially will be done by hand with heat sealers. Development of automated equipment would follow as market demand develops.

The cost of a storage unit, estimated in Table XLI, is based on a developed packaging industry. Although a design using larger pipes should show reduced costs, the amount of plastic required for the containers remains relatively constant for a given pressure rating. Therefore, in the cost estimate, where manufacturing costs are based on raw material costs, a container size sensitivity is not shown.

TABLE XLI

Storage Unit Cost, Forced Air System,
CaCl₂·6H₂O in High Density Polyethylene Pipe

Raw Materials

CaCl ₂ ·6H ₂ O @ \$.05/# ^a	\$ 261
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HDPE Pipe @ \$.85/# ^b	<u>387</u>
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Total	648
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Filling and Handling	648
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Installation	<u>300</u>
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Installed Cost of Storage Unit	\$1596
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^aF.O.B. Dow Chemical Co., Midland, MI

^bPhillips Driscopipe® 7600.

Three storage units were designed as candidates for use with this system, as shown in Table XLII. Each incorporates the same amount of PCM in different size pipes. As container size increases, the number of containers to be filled and sealed decreases. However, the capability of the storage unit to charge and discharge suffers. Based on our testing results, the three-inch pipe system was chosen for design of a prototype demonstration home.

B. House Plans.

An architect was retained to develop a house design compatible with the solar system. After several preliminary attempts, the sloped collector was abandoned for a vertical

TABLE XLII

Thermal Battery Designs for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in HDPE Pipe*

Nominal size (inches)	3	4	5
Outside diameter (inches)	3.5	4.5	5.25
Wall thickness (inches)	.100	.129	.150
No. of tubes	146	90	65
Surface area (M^2)	87	69	58
Weight of HDPE (pounds)	455	455	455
Weight of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (pounds)	5220	5220	5220
Number of rows in the direction of air flow	17	10	11
Number of pipes across air flow	9	9	6
Spacing between pipes (feet)	.0696	.0534	.0840
Weight of each container (pounds)	39	64	88
Storage bed length (feet) (does not include diffuser)	5.32	3.71	4.97
Storage bed width (feet) (does not include insulation)	3.43	4.07	3.39
Number of transfer units @ 1200 CFM	1.49	1.26	0.97
Pressure drop @ 20°C and 1200 CFM (inches H_2O)	.046	.046	.046
Pressure drop @ 40°C and 2400 CFM (inches H_2O)	.17	.17	.17
Floor area for storage bed (ft^2)	18.3	15.1	16.8

*Seven foot tall high density polyethylene pipe rated at 27 psig at 140°F, filled 90% with liquid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and sealed.

glazing wall. This change will: increase usable floor space, decrease summertime overheating, and decrease the cost for the glazing and movable insulation. The south exposure features two glazing walls, each angled at 22.5 degrees from the east-west axis. This opens up the house plan and makes it more successful architecturally. Figures 78 and 79 show the floor plan. The house is a bi-level design, built ideally on a lot sloping from north to south. The main entrance is at a stair landing midway between the first and second floors.

The livingroom, which acts as the second stage of the collector, has a cathedral ceiling design. This is an attractive architectural feature, and also adds height to the hot air collection duct to allow additional thermal stratification in the conservatory. The hot air collection duct is also used as the cold air return for the heating system. Figure 80 shows a section of the family room/livingroom conservatory. The hot air ducts act as the conservatory air supply for heat collection. An outside vent is used to avoid overheating early and late in the heating season.

The entire south wall of the house is glazed for solar collection. Nearly all the glazed surface can be insulated at night and during periods of cloudy weather, using insulating shades. The clerestory window at the peak of the living room and small portions of the glazing in each of the other rooms are left open during non-collection periods for architectural effect. Figure 81 shows an exterior view of the house. Glazing is carried within 18 inches of the roof overhang to make maximum use of available collection area. The collector wall in the family/livingroom area projects 4 feet further south than the rest of the glazing area. Though this will partially shade the adjacent collectors, it allows cross ventilation and improves the interior layout.

Six insulating shades are required, two single story shades in each of the wings, and two double story shades in the livingroom/family room area. To maximize collection efficiency, each shade will be controlled separately. For example, east shades might be open from mid-morning into early afternoon, and west shades from late morning to late afternoon.

This design is intended to demonstrate the best features of both active and passive solar heating. It uses a fan to transfer heat to and from storage, while it uses direct solar gain to the living area, a feature commonly associated with passive systems. It has the economic advantage of incorporating the collector glazing in the southern wall, coupled with the thermodynamic advantage of low temperature collection. The energy storage material is conveniently located in the utility room, minimizing the architectural constraints of the system.

Figure 78
Solar Home Design
Lower Floor Plan

LOWER FLOOR PLAN
VS. 1. 0. 4

Figure 79
Solar Home Design
Upper Floor Plan

-67-

Figure 80
Solar Home Design
Section

FIGURE 81
SOLAR HOME DESIGN
EXTERIOR VIEW

P R O P O S E D S O L A R H O M E F O R
 D O W N C H E M I C A L C O M P A N Y
 F R A N C I S E W A R N E R A R C H I T E C T
 F R I O L A N D M I C H I G A N
 R O V 1 9 7 8

We have used the term "conservatory" to describe the primary collection area, partially to emphasize that the conservation of heating fuels must become an integral part of building design. Conservatories traditionally have been used for wintering cold-sensitive plants. We could as well have used the name "solarium", to emphasize the direct heating of rooms used for living, or coined a term such as "heliatrium" to describe both its architectural and heating function.

X. UTILIZATION ACTIVITY

Calcium chloride hexahydrate is ready for demonstration testing in thermal batteries. Potential applications include: tempered water heat pump systems, solar heated greenhouses, retrofit solar heating systems using nighttime setback thermostats, passive solar heating systems, and active solar heating systems using a conservatory for collection. Macroencapsulated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is appropriate for all these applications. Several potential experiments are being considered or are underway.

We have supplied 2160 aerosol cans with 3850 pounds $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, to Pennsylvania State University. They are testing them in a forced air thermal battery in a 184 ft² greenhouse with 400 ft² added solar collector.

One of the present program investigators (PBH) is retrofitting his residence with a hybrid system using a Solar Room® collector. Heat storage will be in HDPE pipes filled with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

Dr. F. C. Wessling, Albuquerque, NM, will be testing HDPE plastic pipes filled with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a direct solar gain configuration.

We are supplying Stan Moore of Los Alamos Scientific Laboratory 1700 pounds of Dow Experimental Storage Material XFS-43076, a CaCl_2 product with additives, to be used to study $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a direct solar gain storage application.

Discussions have been held with a large number of other solar, heating, and manufacturing personnel. Many samples of XFS-43076 have been supplied to interested workers, and encapsulated samples have been sent to several organizations.