MACRO — ENCAPSULATION OF PCM

MASTER

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JUNE 1977 to SEPTEMBER 1977
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Oak Ridge, Tenn.

by
THE DOW CHEMICAL CO.
Midland, Michigan 48640

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MACRO-ENCAPSULATION OF HEAT STORAGE PHASE-CHANGE MATERIALS for Use in Residential Buildings

Fourth Quarterly Progress Report

June 29, 1977 - September 29, 1977

by

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Division of Energy Storage Systems

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16. Abstracts

Objectives are to assess the feasibility of macro-encapsulated PCM's for residential solar systems, to develop and evaluate such materials. Encapsulant materials under consideration are multilayer flexible plastic films, steel cans, and plastic bottles. PCM's under study are $Mg(NO_3)_2 \cdot 6H_2O$, naphthalene-benzoic acid eutectic, stearic acid, $Mg(NO_3)_2 \cdot 6H_2O$-NH_4NO_3 eutectic, and $CaCl_2 \cdot 6H_2O$. A test device has been constructed, and is being used to study the storage capability of $CaCl_2 \cdot 6H_2O$ encapsulated in polyethylene bottles.

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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 material.

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

Task 1 has been completed, and Task 2 efforts are in progress.

I. PHASE CHANGE MATERIALS

The PCM's under study are listed in Table I.

TABLE I

PHASE CHANGE MATERIALS SELECTED FOR STUDY

Materials	m.p., °C	ΔH, cal./g	Cost, ¢/lb.
$Mg(NO_3)_2 \cdot 6H_2O$	89	38 (a)	15 (est.)
Naphthalene + Benzoic Acid	67	29 (b)	15
Stearic Acid Mix	60	48 (b)	25
$Mg(NO_3)_2 \cdot 6H_2O + NH_4NO_3$	52	30 (b)	10
$CaCl_2 \cdot 6H_2O$	27	46 (b)	5

(a) Literature value

(b) Dow Chemical Company

II. ENCAPSULATING MATERIALS

The following packaging materials are being evaluated as encapsulants for these PCM's:

R-2 Retort Film, a laminate of 3 mil polyethylene, .35 mil Al foil, and .5 mil polyester.
Plastic Bottle, 16 oz. high density polyethylene.
Plastic Bottle, as above, inside surface sulfonated.
Aerosol Can, 2.5 x 6.5 drawn steel.

The Glaminate films, used for such applications as toothpaste tubes, were dropped from our investigation when it was found that the cost would exceed that of polyethylene bottles.

III. PROPERTIES OF PCM'S

The humectant properties of calcium chloride - water solutions were calculated from a vapor pressure equilibrium diagram for pure calcium chloride solutions and a psycrometric chart. The results are presented in Figure 1. Calcium chloride hexahydrate is approximately 50% $CaCl_2$ by weight. Solid hexahydrate shows an equilibrium relative humidity of approximately 35%, while liquid hexahydrate shows an equilibrium relative humidity of approximately 25%. This information is useful for determining moisture barrier requirements for encapsulant containers.

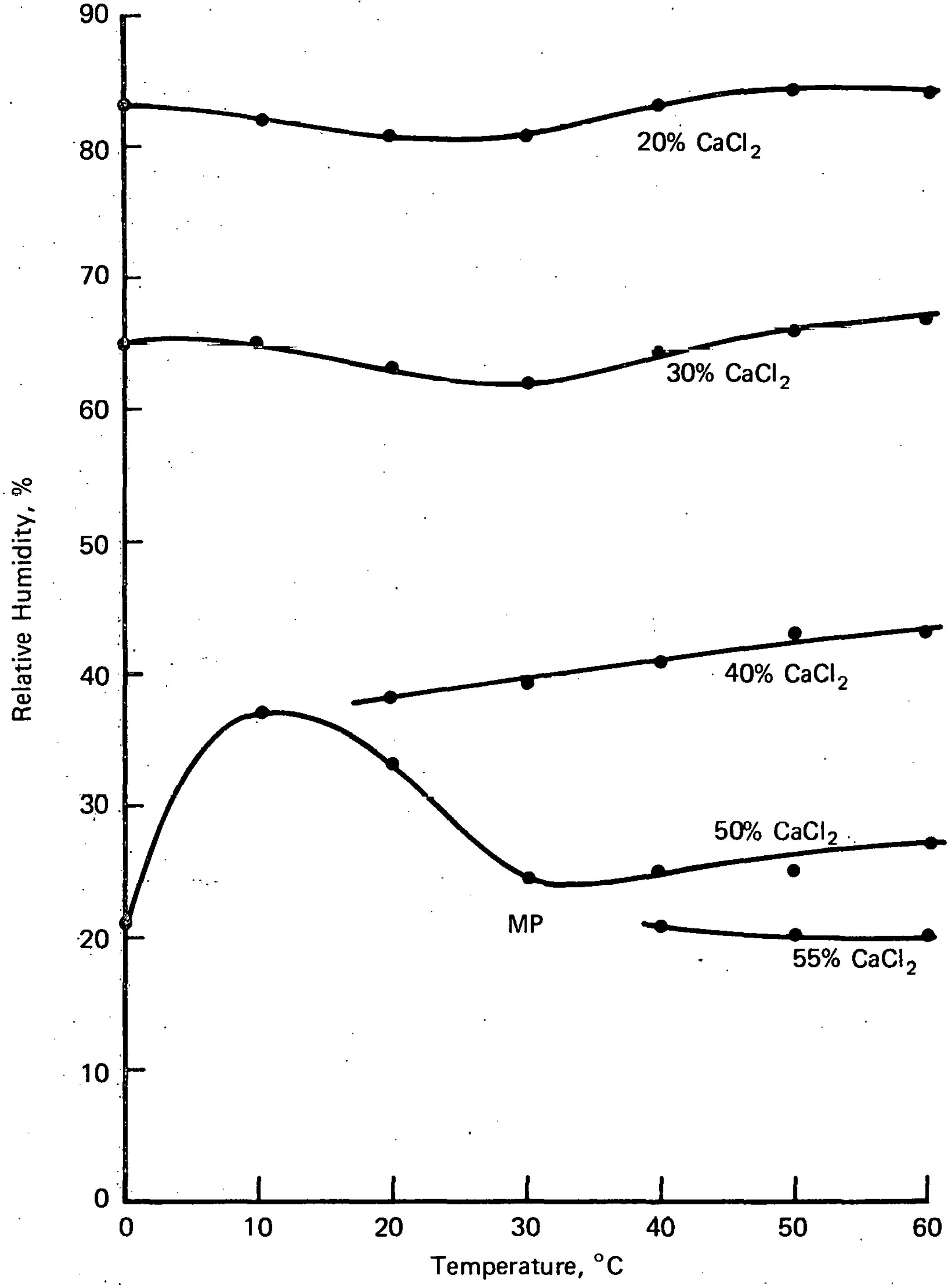
IV. HEAT STORAGE TEST DEVICE

The thermal energy storage (TES) test device is running, and charge/discharge tests are underway on HDPE bottles containing calcium chloride hexahydrate. Cycling of the calcium chloride hexahydrate from solid to liquid to solid started in mid summer, but system debugging, instrument breakdowns, and data reduction problems prevented completion of reliable energy balances on the first 55 "shakedown" cycles. Data are now being collected on a well cycled battery (starting with cycle 56). Three cycles have been completed at a flow rate of 130 kg./hr. Two more will be made at 152 kg./hr. and then two more at 95 kg./hr. When this series is complete, the thermal battery will be opened up and the polyethylene bottles will be examined for stress cracking, and other effects of cycling.

Cycling of the thermal battery prior to cycle 56 consisted of running with an inlet temperature of 44.5°C until the outlet temperature reached 36°C, then stepping the inlet temperature down to 9.5°C and running until the outlet temperature

Figure 1

HUMECTANT PROPERTIES OF CALCIUM CHLORIDE WATER SOLUTIONS



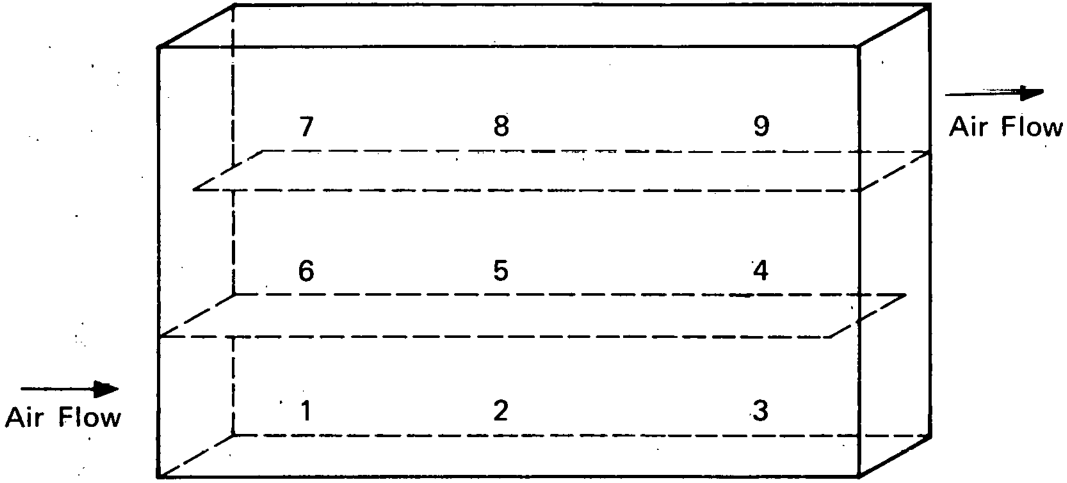
dropped to 18°C, and finally stepping the inlet temperature back up to 44.5°C. Starting with cycle 56 the cycling procedure was modified to correspond with the ASHRAE standard. Subsequent cycling consisted of a daily step change in the inlet air temperature. The primary aim of data collection is to complete an energy balance on the system to determine: 1) the capacity of the thermal battery on charge and discharge, 2) the rate at which the battery is charged and discharged, and 3) the amount of heat lost from storage to the surrounding air during the charge and discharge. To investigate supercooling, data were also collected on the temperatures of the calcium chloride hexahydrate in bottles at various places in the storage unit. Thermal wells were set in the middle of the bottle near the point that responds most slowly to variations in the air stream temperature.

A good understanding of what is happening in the storage unit during the charge and discharge cycle can be gotten by examining Figures 2, 3, and 4. Figure 2 shows the position of the thermocouple-equipped bottles in the storage unit progressing from number one near the air inlet through number nine near the air outlet.

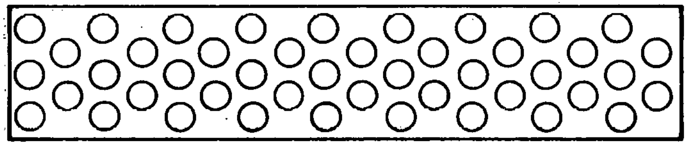
Figure 3 illustrates the charging cycle. The inlet and outlet air temperatures are shown along with eight of the nine bottle temperatures. The inlet temperature steps up to ∿44.5°C at the beginning and holds there. The middle of bottle number one heats quickly to the melting point and is completely melted before three hours have elapsed. Bottles located further into the storage unit stay frozen progressively longer; all but bottle number nine melt completely before the end of the cycle. Number nine takes another 80 minutes to melt completely. The order of melting of bottles six and seven is reversed. This is

Figure 2

POSITIONS OF THERMOCOUPLES IN THERMAL ENERGY STORAGE UNIT:
Calcium Chloride Hexahydrate In HDPE Bottles, Air Heat Transfer Fluid



Top View



Layout 0.24M Spacing Triangular Pitch
Minimum Possible Void Fraction .52

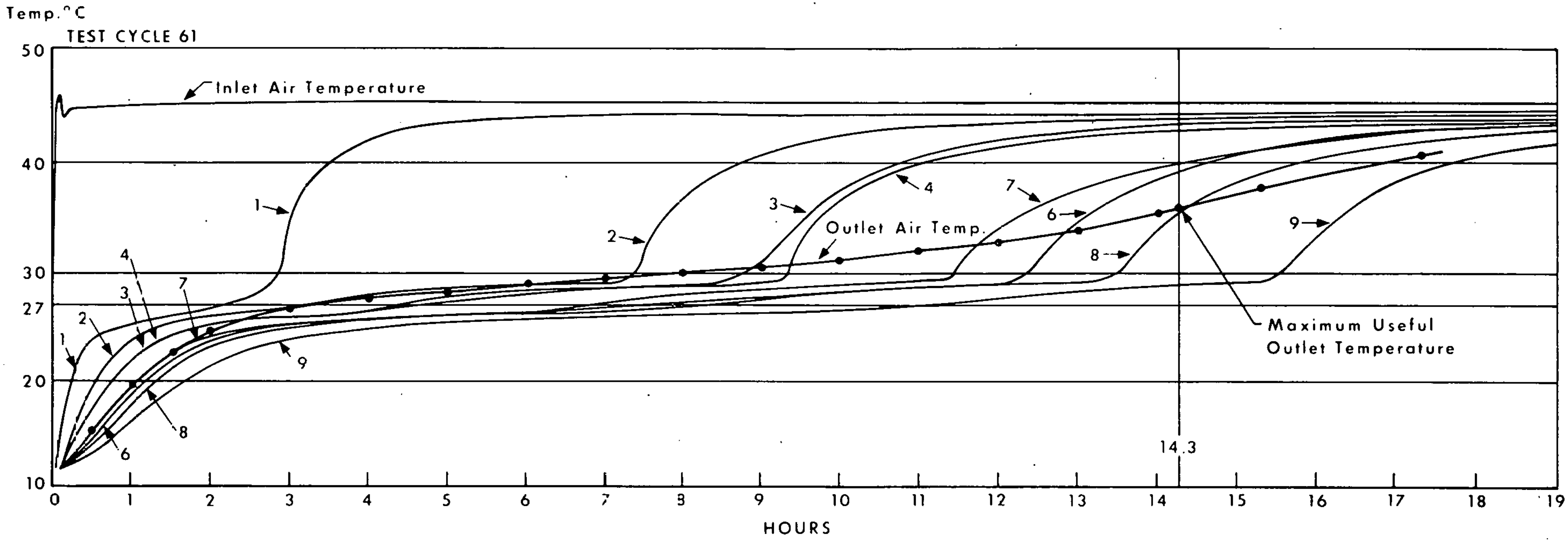


Figure 3: CHARGE CYCLE: Calcium Chloride Hexahydrate In HDPE Bottles

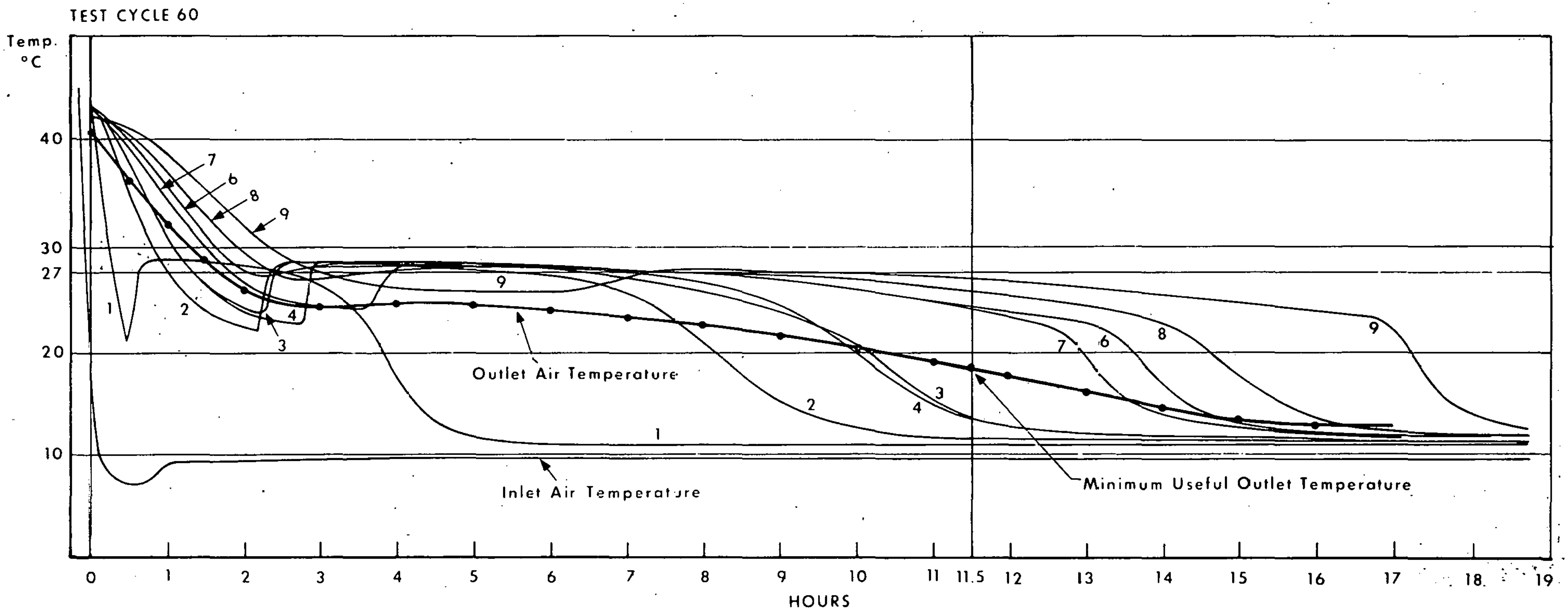


Figure 4: DISCHARGE CYCLE: Calcium Chloride Hexahydrate In HDPE Bottles

evidence of short-circuiting or variable heat transfer coefficients in the thermal battery. Both bottles are completely melted by the end of the cycle, so this should not reduce the charge capacity of the thermal battery. The outlet air temperature rises to the melting point within three hours of the start of the test, stays slightly above the melting point until much of the calcium chloride hexahydrate is melted, and then drifts up to the maximum useful outlet temperature. At that point the thermal battery is charging at the design rate. When the outlet air rises above the cutoff point (35.75°C for this design), the thermal battery charging rate drops below the design rate.

Figure 4 shows the discharge cycle. The inlet air temperature steps down to approximately 9.5°C and holds there. The material in bottle number one cools rapidly and supercools extensively, then warms to the freezing temperature as crystals form at the bottle wall, and is soon completely frozen. Bottles further into the thermal battery cool progressively slower, supercool less, and take longer to freeze up completely. Several bottles are not completely frozen at the end of the discharge cycle. Again, as in the charging cycling, there is evidence of a variable heat transfer coefficient or of short-circuiting, since the curves for 6 and 7 are reversed. The discharge capacity will be adversely affected by this effect, and by the bottles that aren't completely frozen when the outlet temperature dips to the minimum useful level. The magnitude of this problem appears exaggerated in Figure 4, since the temperatures are measured at the point that is the last to freeze in the bottle.

Supercooling has been monitored from the beginning of cycling and showed no tendency to increase. The amount of supercooling does vary from cycle to cycle for each bottle, as shown in Table II, and decreases from a high of around 8°C near the inlet to a low of around 1°C near the outlet. This behavior is favorable, because severe supercooling near the outlet would have a negative impact on storage capacity.

The energy balance for cycles 59 and 60 are summarized in Table III. The charging capacity is the amount of energy put into the thermal battery during the charge cycle, less the amount calculated to have leaked out through the insulation. The discharge capacity is the amount of energy retrieved from the thermal battery during the discharge cycle. The evident decrease in capacity represents run-to-run variation and is not a trend.

TABLE II

SUPERCOOLING OF $CaCl_2 \cdot 6H_2O$ IN THERMAL BATTERY, °C

	Position in Battery								
Freezing Cycle No.	1	2	3	4	5	6	7	8	9
2	X	6.9	4.1	2.1	1.5	0.8	0.7	0.6	1.0
20	8.9	5.7	4.0	4.4	3.0	1.6	1.9	1.0	0.6
57	X	4.3	3.2	3.6	3.1	0.3	2.5	1.0	1.2
58	6.0	5.2	3.3	3.6	1.4	1.1	2.8	1.9	1.5
Average	7.4	5.5	3.6	3.4	2.2	1.0	2.0	1.1	1.1

TABLE III

ENERGY BALANCE RESULTS FROM CYCLING A
CALCIUM CHLORIDE HEXAHYDRATE THERMAL BATTERY
USING AIR AS THE HEAT TRANSFER FLUID

	Charging			Discharging		
Cycle No.	Capacity (KJ)	Loss (KJ)	Time (Hr.)	Capacity (KJ)	Loss (KJ)	Time (Hr.)
59	25,200	2,000	14.7	23,000	1,300	11.0
60	25,600	2,800	15.4	22,400	1,100	11.5
61	24,700	2,000	14.3	23,300	1,100	12.0

A complete analysis of the energy balance will be made when cycling is complete on the thermal battery and the material balance has been closed.

Computer Simulation

A computer simulation program was used to evaluate the sensitivity of the storage capacity of a thermal battery similar to the one shown in Figure 2 to variation of several parameters: 1) thermal conductivity of the $CaCl_2 \cdot 6H_2O$ 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 rather than the three-pass unit diagrammed in Figure 2. 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 5 through 9. 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 $CaCl_2 \cdot 6H_2O$ 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.

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:

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

where: CFM = air flow rate

A = Air heat transfer constant

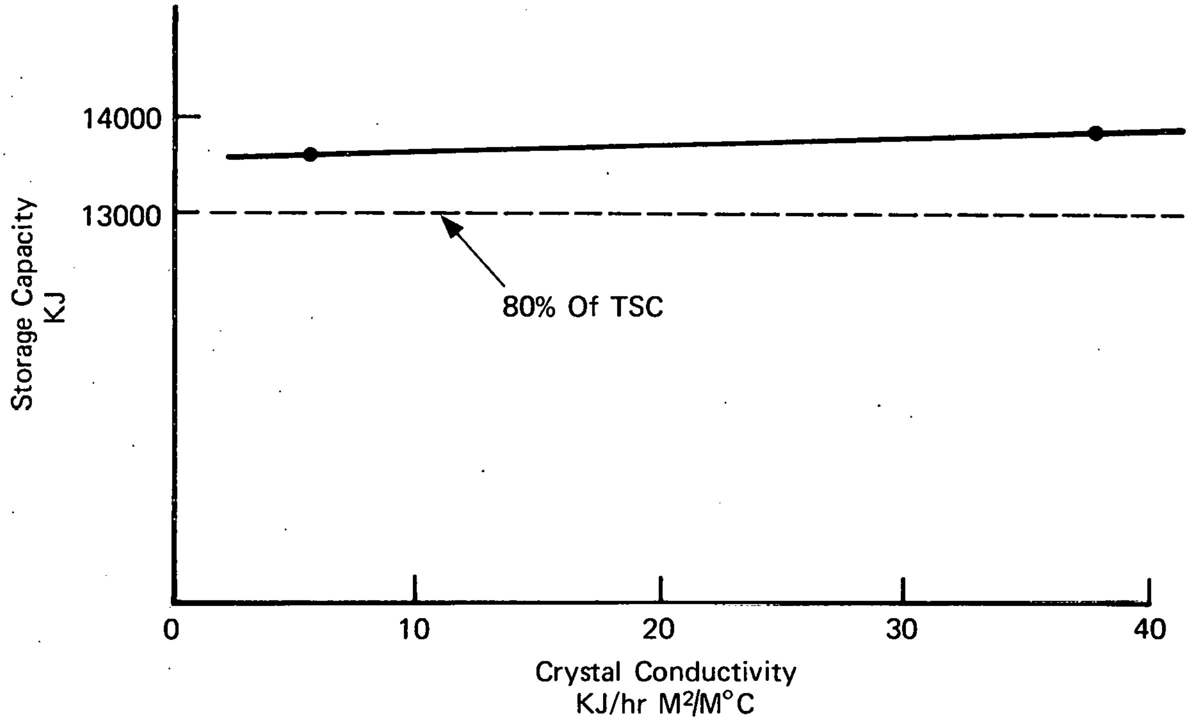


Figure 5: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Crystal Conductivity.

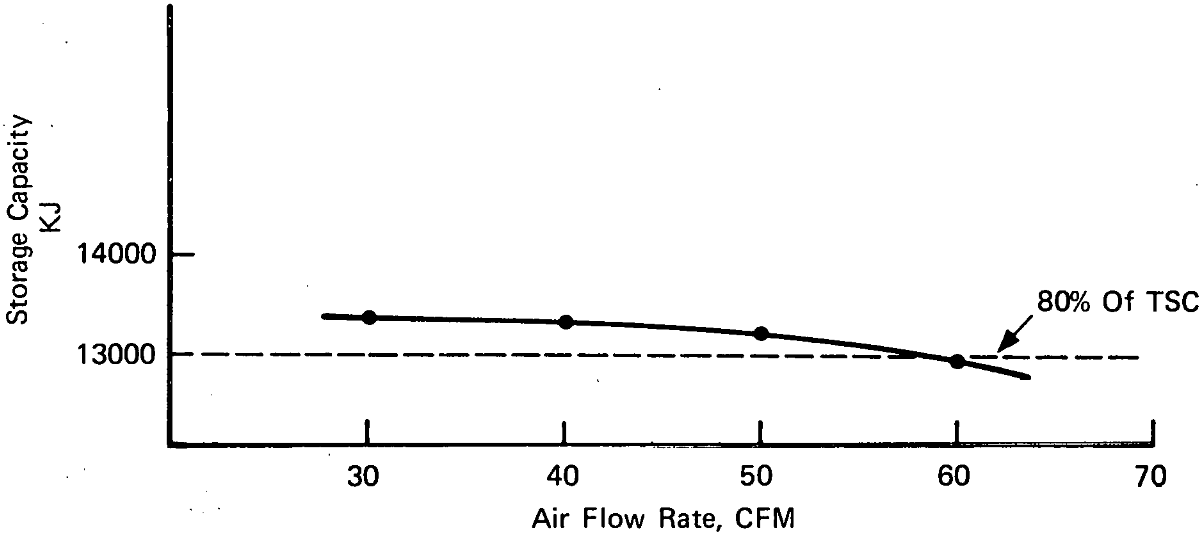


Figure 6: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Air Flow Rate.

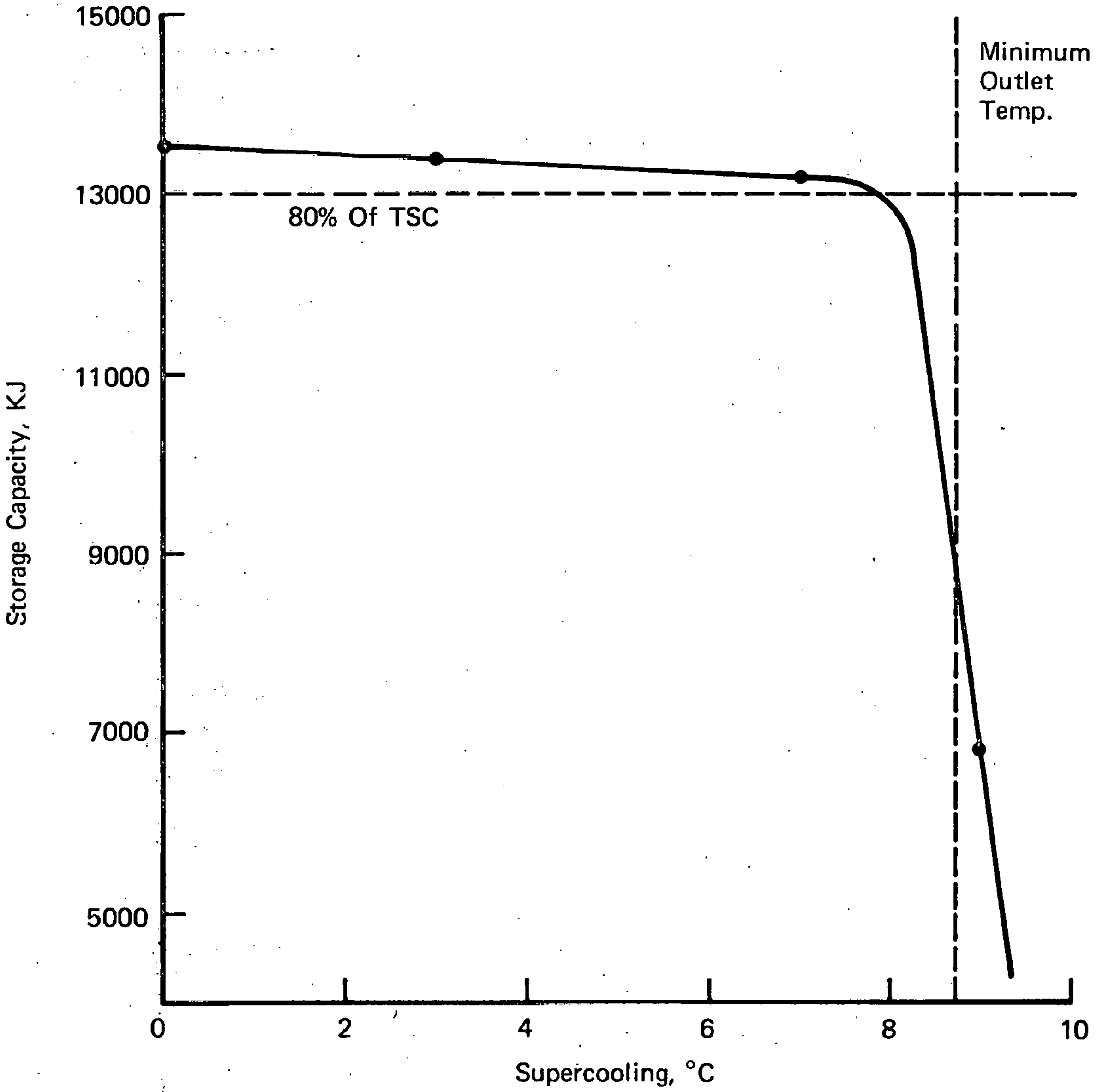


Figure 7: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Supercooling.

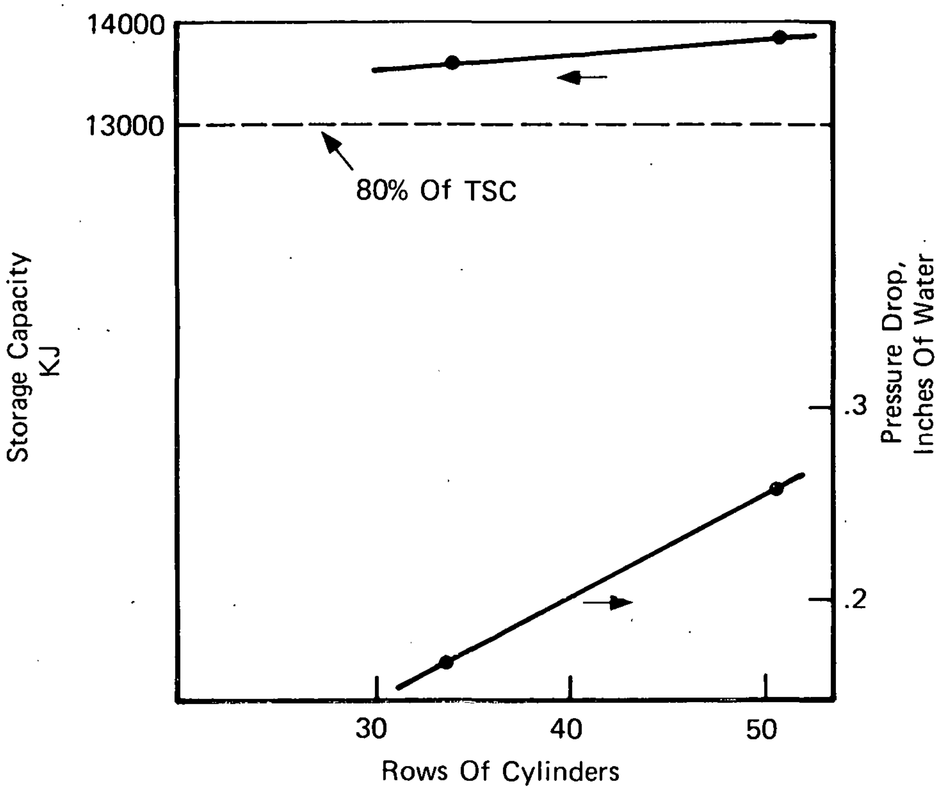


Figure 8: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Number Of Rows Of Cylinders In Direction Of Air Flow.

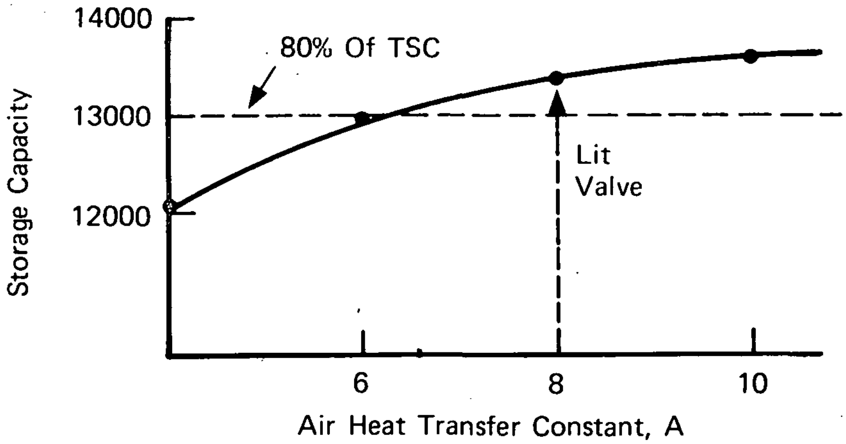


Figure 9: SENSITIVITY ANALYSIS: 2.4 Inch Cylinders Of Calcium Chloride Hexahydrate In Thermal Battery, Effect Of Air Heat Transfer Constant.

The calculated value for A is 8, assuming no short-circuiting. Figure 9 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 analysis did not address 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. Future simulation work will determine the sensitivity of storage capacity to cylinder diameter.

A simple design procedure was developed for calcium chloride thermal batteries based on the following assumptions: storage capacity 80% of TSC, pressure drop .25 inches of water, and design discharge rate exceeded for 50°F inlet air temperature and outlet air temperature above 65°F.

For normal storage capacities (10 to 30 hours) cylinders with a diameter of 2 to 3 inches are recommended. Using smaller diameter containers results in higher storage capacity for the same mass of calcium chloride hexahydrate, but container costs increase.

The following procedure was used to design a $CaCl_2 6H_2O$ thermal battery using air heat transfer fluid.

Design rate, DR, Btu/hr:

DR = CFM X 15.3

where CFM is the air flow rate, cubic feet per minute.

Capacity, C, hr.:

$$C = \frac{.8\ TSC}{DR}$$

where TSC is the theoretical storage capacity, Btu.

$$N_c = \frac{CFM \times C \times 3 \times 10^{-3}}{D^2\ h_c N_R}$$ - Storage capacity criterion

$$d = \frac{CFM\ N_R^{.5}}{2257\ h_c N_c}$$ - Pressure drop critieria (1)

D - the diameter of the cylinder, ft.

h_c - height of the cylinder or stack of containers on shelves, ft.

N_c - number of columns across air flow

N_R - number of rows in direction of air flow

d - spacing between cylinders, ft.

$L = N_R \times (D+d) \sin 60°$ - length of storage, ft.

$W = (D+d)(N_c+½)$ - width of storage, ft.

$H = h_c$ - height of storage, ft.

The length, width and height of storage do not include insulation or diffusers.

Calculation of void fraction:

$$\text{Void fraction} = \frac{A-B}{A}$$

$$A = \frac{(D+d)^2 \sin 60°}{2}$$

$$B = D^2\pi/8$$

---

1. Perry's Engineering Handbook, 4th Edition, 5-47, 48.

The value of the void fraction calculated by this equation gives a minimum limit for the void fraction of the entire thermal battery.

Figure 10 displays the results from a series of design calculations for a thermal battery to fit in a closet-sized area. The height of the storage unit in all designs is six feet. Void fraction, floor space requirements, and volume of storage bed are reported for different cylinder diameters and different numbers of rows in the direction of air flow. The floor space is shown as a rectangle, with the height proportional to the width and thc length proportional to the length of the thermal batteries. The more compact units are those with fewer rows and smaller containers.

The cylinders can be constructed by stacking shelves of containers or by using individual six foot tall cylinders. Figure 11 is a drawing of a closet thermal battery with 2-inch diameter cylinders and thirty rows in the direction of air flow. This design has the smallest void fraction, floor space, and insulation requirements of the nine design cases shown in Figure 10.

V. UTILIZATION ACTIVITY

A paper was presented, covering the work on this project, at the Annual Thermal Energy Storage Contractors' Information Exchange Meeting, Sept. 29 and 30, at Gatlinburg, Tennessee.

VI. PLANS

1. Complete the testing of the thermal battery (calcium chloride hexahydrate in HDPE bottles) and start life cycle testing of this PCM container combination.

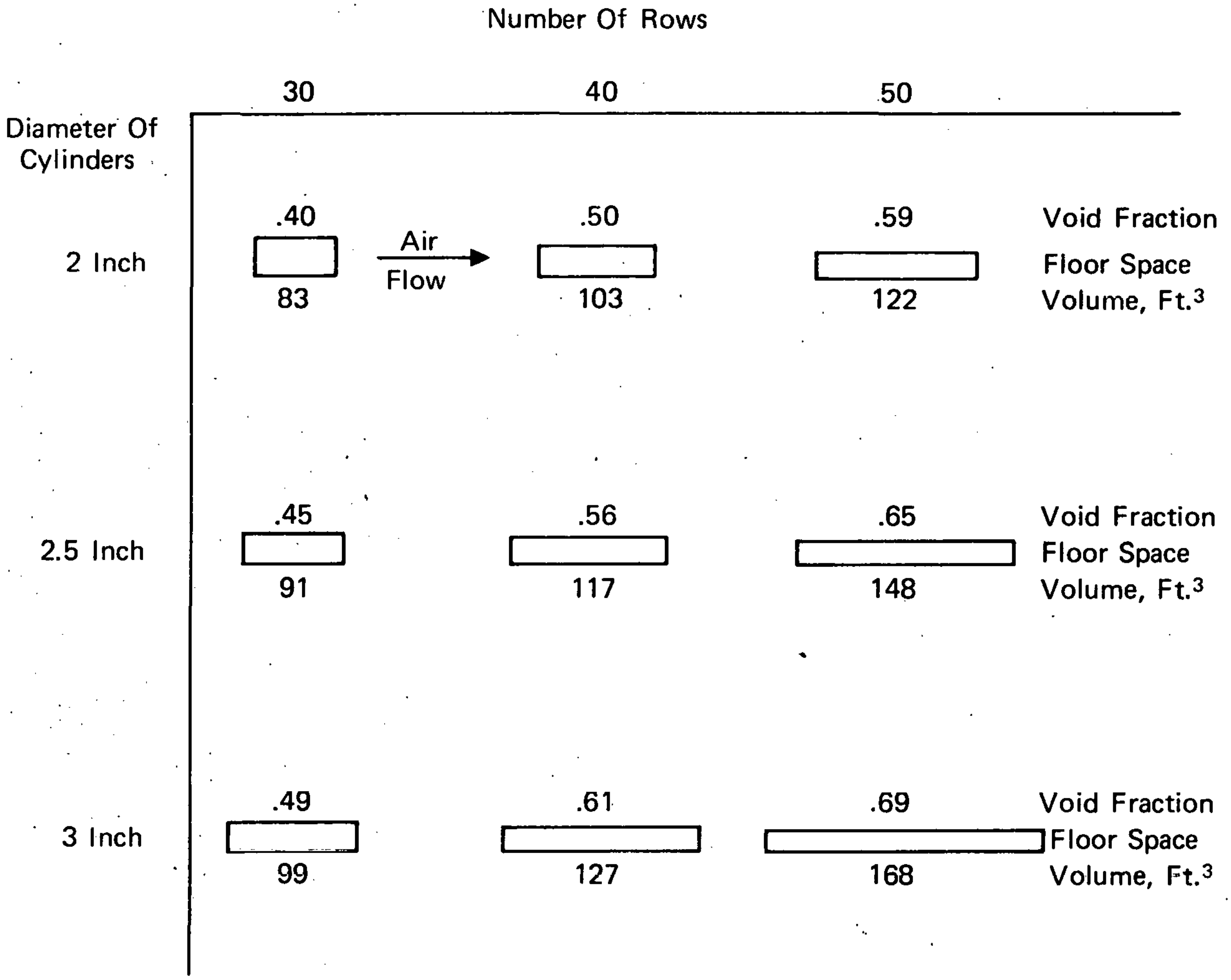
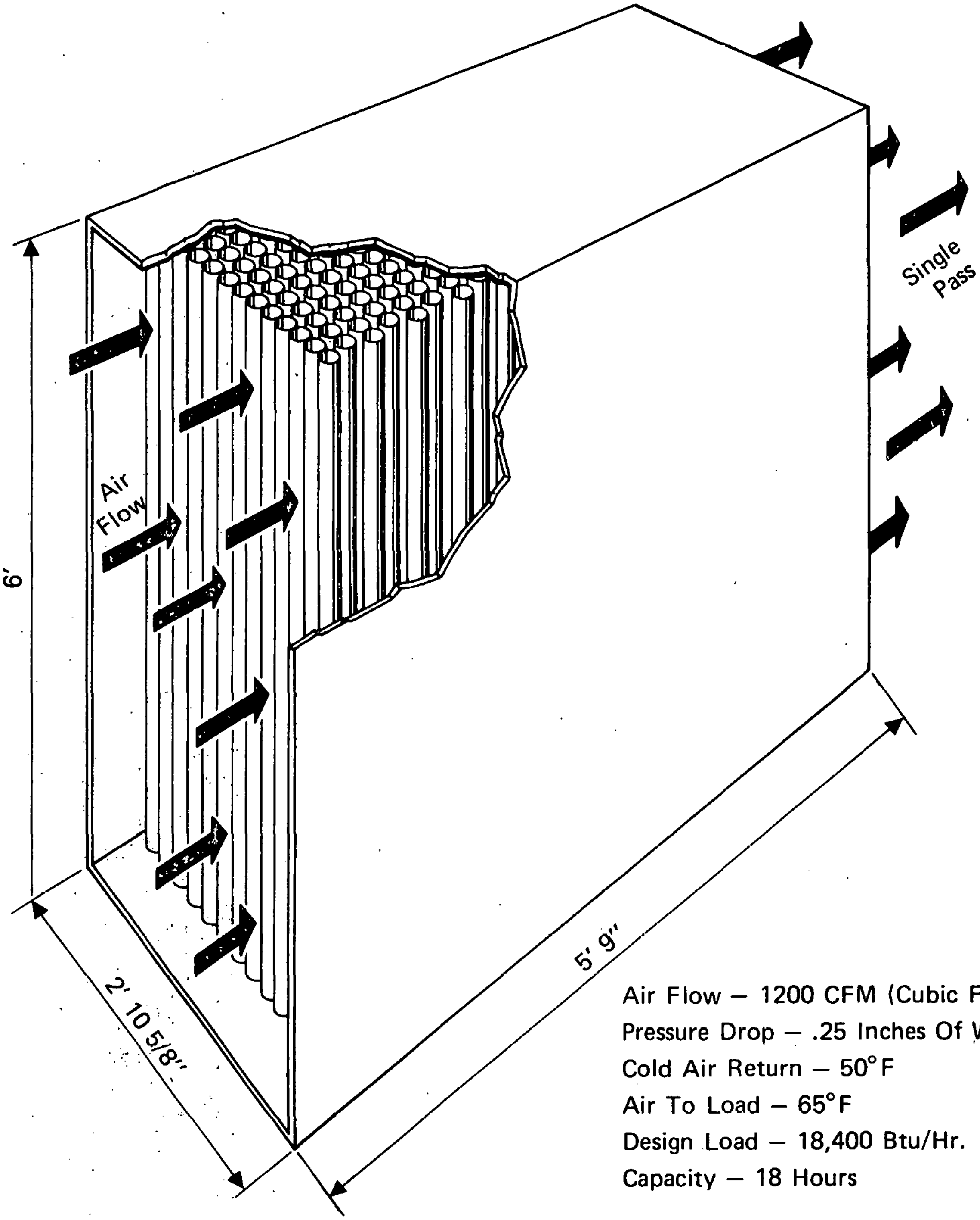


Figure 10: CLOSET STORAGE UNITS FOR NIGHT TIME SETBACK OR HEAT PUMP SYSTEM

CFM – 1200 Air Flow
Storage Capacity – 18 Hours
Cold Air Return – 50°F
Air To Load – 65°F
Pressure Drop – .25 Inches Of Water
Design Load – 18,400 Btu/Hr.



Air Flow – 1200 CFM (Cubic Feet Per Minute)
Pressure Drop – .25 Inches Of Water
Cold Air Return – 50°F
Air To Load – 65°F
Design Load – 18,400 Btu/Hr.
Capacity – 18 Hours

Figure 11: CLOSET STORAGE UNIT FOR NIGHT TIME SETBACK OR HEAT PUMP SOLAR SYSTEM: Calcium Chloride Hexahydrate Encapsulated In 2" Cylinders.

2. Evaluate the sensitivity of storage capacity to cylinder diameter.

3. Fit the computer model to the results of the thermal battery tests.

4. Move the thermal battery test device to the new laboratory building, and set up to run the next phase-change material (PCM)-container combination.

5. Sulfonate HDPE bottles for encapsulation of stearic/palmitic acid.

6. Update the economic analysis of thermal battery design.

7. Complete the hazard analysis of $MgNO_3 \cdot 6H_2O$ and $Mg(NO_3)_2 \cdot 6H_2ONH_4NO_3$ eutectic PCM's.

VII. CONCLUSIONS

The thermal storage test device is operating adequately and giving acceptable data. Tests on calcium chloride hexahydrate are nearly complete and appear encouraging.

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