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(NASA-CR-124214) THERMAL CONTROL AND
HEAT STORAGE BY MELTING AND FREEZING.
SPACE THERMAL CONTROL DEVELOPMENT
Interim Report (Lockheed Missiles and
Space Co.) 23 p HC $3.25 CSCL 20M G3/33

N73-22894

Unclas
17546

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**LOCKHEED MISSILES & SPACE COMPANY**
A GROUP DIVISION OF LOCKHEED AIRCRAFT CORPORATION
HUNTSVILLE, ALABAMA

HREC-5183-1
LMSC-HREC D162884

**LOCKHEED MISSILES & SPACE COMPANY**
**HUNTSVILLE RESEARCH & ENGINEERING CENTER**
**HUNTSVILLE RESEARCH PARK**
**4800 BRADFORD DRIVE, HUNTSVILLE, ALABAMA**

# THERMAL CONTROL AND HEAT STORAGE BY MELTING AND FREEZING

## INTERIM REPORT

## SPACE THERMAL CONTROL DEVELOPMENT

March 1971

Contract NAS8-25183

by

P. G. Grodzka
M. J. Hoover

**APPROVED:** George D. Reny
George D. Reny, Manager
Aeromechanics Department

J. S. Farrior
J.S. Farrior
Resident Director

## FOREWORD

This interim report is submitted in accordance with the provisions of Exhibit A of Contract NAS8-25183. The study was performed by personnel in the Aeromechanics Department of Lockheed's Huntsville Research & Engineering Center. The NASA-MSFC technical monitor for this contract is Miss B. Richard, S&E-SSL-T.

## SUMMARY

Current results of an experimental study of increasing phase-change material thermal diffusivity by means of solid fillers are reported. Aluminum honeycomb appears to offer the best improvement of any of the fillers investigated to date. Details of the experimental method developed in the present study for rapidly determining thermal diffusivities with a precision of about 10 percent are also reported. Further concepts regarding phase change material thermal diffusivity enhancement and of phase change material operation are discussed.

# CONTENTS

## Section 1
## INTRODUCTION

The science and technology of phase change material (PCM) thermal control and heat storage appears to be attracting a widening interest. A comprehensive bibliography on PCM technology is given in Ref. 1. For orientation purposes, however, the principle of PCM thermal behavior is briefly reiterated as follows: A PCM is a material which undergoes a phase change with a large accompanying liberation or absorption of latent heat. Ice cubes and water are an example of a simple PCM system. As long as any ice is present, the temperature of the ice-water mixture remains at $0^{\circ}C$. Heat from the surroundings is absorbed as latent heat of fusion and is used in melting the ice, without an elevation of temperature. Thus, the amount of the solid phase is decreased, while the amount of liquid is increased by an equivalent amount. The reverse process of freezing consists of an increase in the amount of solid phase, with the heat of fusion being given off instead of absorbed.

In the case of thermal control, a PCM material (such as water) is placed between a variable thermal environment and an element which is to be thermally controlled. By the processes of melting and freezing, an essentially isothermal control is maintained. Thus the PCM gives a reversible system which can act as either a heat sink or heat source, as required.

The advantages of this type of thermal control are many. No moving parts are required to maintain thermal control. Such a system could operate reversibly for indefinite lengths of time. The desired temperature for control can be picked from a wide selection of melting points offered by a variety of PCM candidates.

A number of development studies are currently being made across the country. Simple applications are already in use. Development studies are in progress for rather sophisticated applications. A number of material and design questions have been raised by investigators pursuing these studies. Among the most pressing are:

- Ways to increase thermal diffusivity of non-metallic PCMs without undue weight or space penalities.
- Limits of the thermal stabilities of the more exotic materials found to have some potential as PCMs.
- Effects of long-term thermal cycling on PCM stability and performance.

The present work is concerned with defining and generating the basic data needed to answer these questions for a broad spectrum of possible applications.

## Section 2

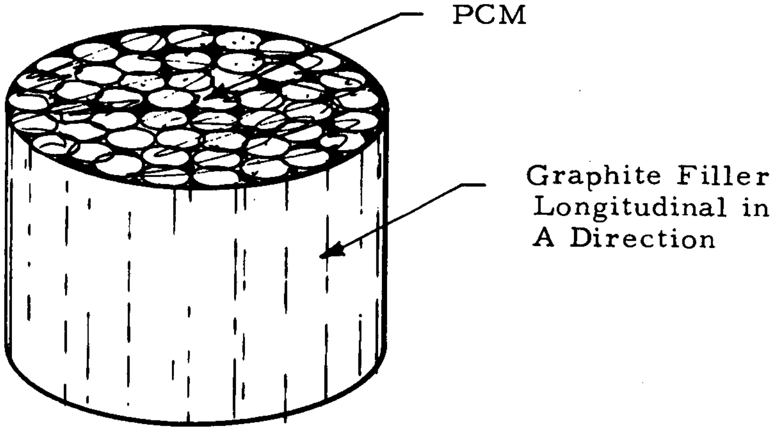
## PHASE CHANGE MATERIAL SYSTEM THERMAL DIFFUSIVITY

### 2.1 FILLERS AS THERMAL DIFFUSIVITY PROMOTERS

As is well known, the thermal diffusivities of most common non-metallic materials are about $10^3$ orders of magnitude lower than that of the metals. Liquids have slightly lower values than the corresponding solid. The obvious way to try to improve the thermal diffusivity of a non-metallic PCM, therefore, is to pack or fill it with an open structure of metal. Just what metal, how much, and what structure are questions to be answered. One consideration is that of weight, especially for space applications. Others are cost and PCM-metal compatability. With these considerations in mind, aluminum is the obvious choice. The question of just what configuration of aluminum filler results in optimum rate of heat transfer through the liquid, however, is not obvious and thus was investigated experimentally in some previous studies and also in the present study. Also not obvious is the optimum ratio of PCM to filler. If too much filler is used, the benefit of the PCM is lost; if not enough, the system thermal diffusivity will be too low. Again, the answer is to be sought in experimental determinations.

Although aluminum appears to offer the best combination of properties as a PCM filler of any of the rest of the metals, it will cause corrosion problems with some of the salt hydrate type PCMs. It might be possible to overcome the corrosion problem by judicious additions of additives such as sodium silicate which forms a protective film around the aluminum, but a really inert filler would be desirable. One possibility is a ceramic material. Although most ceramics have lower thermal diffusivities than metals, two ceramics – Beryllia (BeO) and Alumina ($Al_2 0_3$) – have surprisingly large values: BeO – 0.42 cm$^2$/sec, $Al_2O_3$ – 0.08 cm$^2$/sec (Al – 0.872 cm$^2$/sec). An open structure filler of BeO or $Al_2O_3$ would thus possibly offer advantages with some PCM materials.

Another possibility is pyrolytic graphite, a material characterized by extremely anisotropic physical properties. The difference in thermal diffusivity in the A and C directions is amazing: A direction – 10 cm$^2$/sec, C direction – 0.04 cm$^2$/sec. An open structure pyrolytic graphite filler constructed so that the PCM is in contact with the C direction and the A direction facing the heat flux input as in the following sketch, would be highly desirable.



Pyrolytic graphite has other desirable properties as a PCM filler. It is very inert to most chemicals and highly resistant to thermal shock.

The succeeding section reports results of experimental investigations designed to answer some of the questions just discussed. In brief, the experimental work consisted of varying PCM system thermal diffusivity by varying the filler amount, material composition, and physical structure. Measurements of thermal diffusivity of various PCM – filler systems were accomplished by means of a specially developed experimental apparatus.

## 2.2 DEVELOPMENT RESEARCH ON PCM/FILLER SYSTEMS CONDUCTED DURING PRESENT STUDY

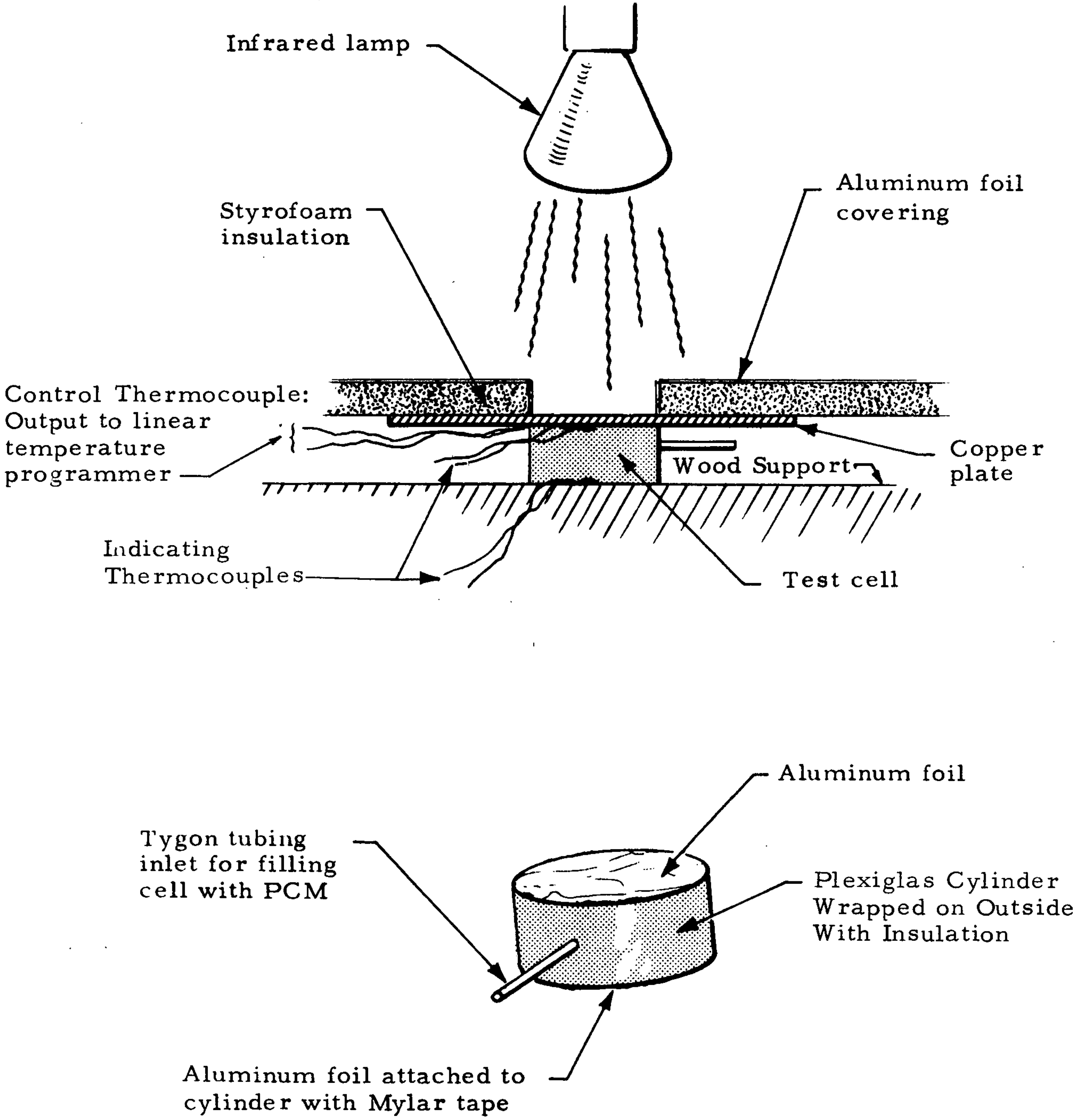
### 2.2.1 Development of Experimental Method for Determining Thermal Diffusivities

To be able to assess various ways of increasing PCM system thermal diffusivities, it was first necessary to develop a simple experimental apparatus in which the thermal diffusivities of pure and filled PCMs could be easily determined. A number of concepts were tried, with the experimental apparatus shown in Fig. 1 being finally selected as meeting the requirements of the present study.

The basis of the present method depends on maintaining a constant rate of temperature rise at the upper copper plate and on perfectly insulated side walls on the test cell. A constant heating rate is accomplished by feeding the output of the control thermocouple to a linear temperature programmer. The linear temperature programmer used in the present study is part of a Fisher Differential Thermal Analyzer (DTA) Model 316 unit. The programmer varies the current to the infrared lamp according to the control thermocouple input. The heating rate of the copper plate is thus maintained at a constant set value. With this experimental setup, the thermal diffusivity of a PCM system is determined from a knowledge of the constant heating rate, the constant temperature gradient through the PCM, and the height of the test cell. The equation relating these quantities is:

$$\alpha = \frac{\beta h^2}{2\Delta T}$$

where $\alpha$ is the thermal diffusivity ($cm^2/sec$), $\beta$ the constant heating rate ($^oC\ sec^{-1}$), h the cell height (cm) and $\Delta T$ the constant temperature difference between the top and bottom of the cell containing the test material.



Details of Test Cell Construction

Fig. 1 – Experimental Apparatus for Determination of Thermal Diffusivities

The test cell consists of a Plexiglas cylinder approximately one centimeter in height and 2.5 cm in diameter. Each end of the cylinder is covered with aluminum foil 0.0025 cm thick. A section of Tygon tubing inserted into a small inlet drilled into the cylinder serves for filling the cell with PCM material and as an overflow for expansion of material being heated. A hypodermic syringe proves to be a satisfactory tool for injecting material into the test cell. The wall of the cylindrical cell is wrapped with cotton string which is a convenient insulating material. The walls of the test cell are further insulated with polystyrene. The test cell is coated on top and bottom with heat-conducting silicone jelly. Heating from the top is employed to avoid convection.

It may be mentioned that the concept of measuring thermal diffusivities in the manner described is not original. The basic equation appears in Ref. 2 with regard to interpreting DTA data, however, and not as a method of measuring thermal diffusivity. In Ref. 3, explicit use is made of the same approach and equation for measuring the thermal diffusivity of polymer melts. The originality of the present work consists of adapting the method for rapid evaluations of a large number of composite material systems. The ease and low cost of the present method are also not to be overlooked. The accuracy and precision of the method for a one component PCM system can be ascertained from the following data:

| Substance | Thermal Diffusivity Values $cm^2/sec \times 10^{-3}$ | |
|---|---|---|
| | Observed | Literature |
| Water | 0.18<br>0.31<br>0.72<br>1.28<br>avg. 0.62 ± 0.38 | 1.35 (Ref. 4) |
| Glycerine | 0.43<br>0.63<br>avg. 0.53 ± 0.10 | 0.86 (Ref. 5) |

As can be seen, the accuracy and precision leave much to be desired. Also, in the case of composite systems, that is, PCM plus solid filler, further error arises from the positioning of the indicating thermocouples. If one thermocouple happens to sit or be placed just over the metal filler, it will register a significantly higher temperature than if it were placed directly over the PCM. The increase in data scatter when rigid fillers are used is evident from the following thermal diffusivity data for lithium nitrate trihydrate alone and with various fillers. The given PCM/filler ratios are by weight as shown in Table 1. Although the data for PCM plus filler is generally less precise than when no fillers are used, a definite trend is discernible. Rigid fillers increase PCM system thermal diffusivity more than the same amount of filler in powder form. Also a filler such as aluminum honeycomb which provides the heat input with a directional path appears to improve PCM system thermal diffusivity more than a filler such as aluminum gauze which allows heat to accumulate. Further research is indicated, however, before the latter conclusion can be accepted as fully valid. Possibly the honeycomb provides less resistance to heat passage because the cross section of metal is larger in the case of the honeycomb.

In an attempt to increase the precision and accuracy of the method, further sources of determinate error were sought and identified. For one, temperature differences between the top and bottom of the cell never were observed to come to constant values. Instead, the behavior shown in the following table with water as the test liquid was usually observed.

| $f(\Delta T)$ | $\Delta f(\Delta T)$ |
|---|---|
| 5.8 | |
| 12.7 | 6.9 |
| 19.4 | 6.7 |
| 25.0 | 5.6 |
| 29.8 | 4.8 |
| 33.8 | 4.0 |
| 37.2 | 3.4 |
| 40.4 | 2.2 |
| 43.1 | 2.7 |
| 45.5 | 2.4 |
| 48.0 | 2.5 |
| 49.9 | 1.9 |
| 51.7 | 1.8 |
| 53.3 | 1.6 |
| 54.5 | 1.2 |
| 55.7 | 1.2 |
| 57.0 | 1.3 |
| 58.1 | 1.1 |

## Table 1

## MEASURED VALUES OF THERMAL DIFFUSIVITY OF VARIOUS PCM-FILLER SYSTEMS

| PCM System | Thermal Diffusivity $cm^2/sec \times 10^3$ |
|---|---|
| $LiNO_3 \cdot 3H_2O$ with no filler | 1.80<br>1.20<br>1.40<br>0.87<br>0.18<br>1.80<br>avg. 1.2 ± 0.5 |
| $LiNO_3 \cdot 3H_2O$ + Aluminum powder + surface-active agent<br>8/1 PCM/Filler Ratio | 0.62<br>0.24<br>avg. 0.43 ± 0.19 |
| $LiNO_3 \cdot 3H_2O$ + Aluminum gauze<br>8/1 PCM/Filler Ratio | 0.62<br>2.0<br>3.0<br>avg. 1.9 ± 0.9 |
| $LiNO_3 \cdot 3H_2O$ + Aluminum honeycomb<br>8/1 PCM/Filler Ratio | 1.1<br>3.2<br>2.5<br>4.2<br>avg. 2.8 ± 1.0 |
| $LiNO_3 \cdot 3H_2O$ + Alumina ($A\ell_2O_3$) foam<br>8/1 PCM/Filler Ratio | 3.2<br>1.9<br>1.0<br>avg. 2.0 ± 0.7 |
| $LiNO_3 \cdot 3H_2O$ + Alumina ($A\ell_2O_3$) powder<br>8/1 PCM/Filler Ratio | 1.0<br>2.8<br>0.24<br>avg. 1.3 ± 0.9 |

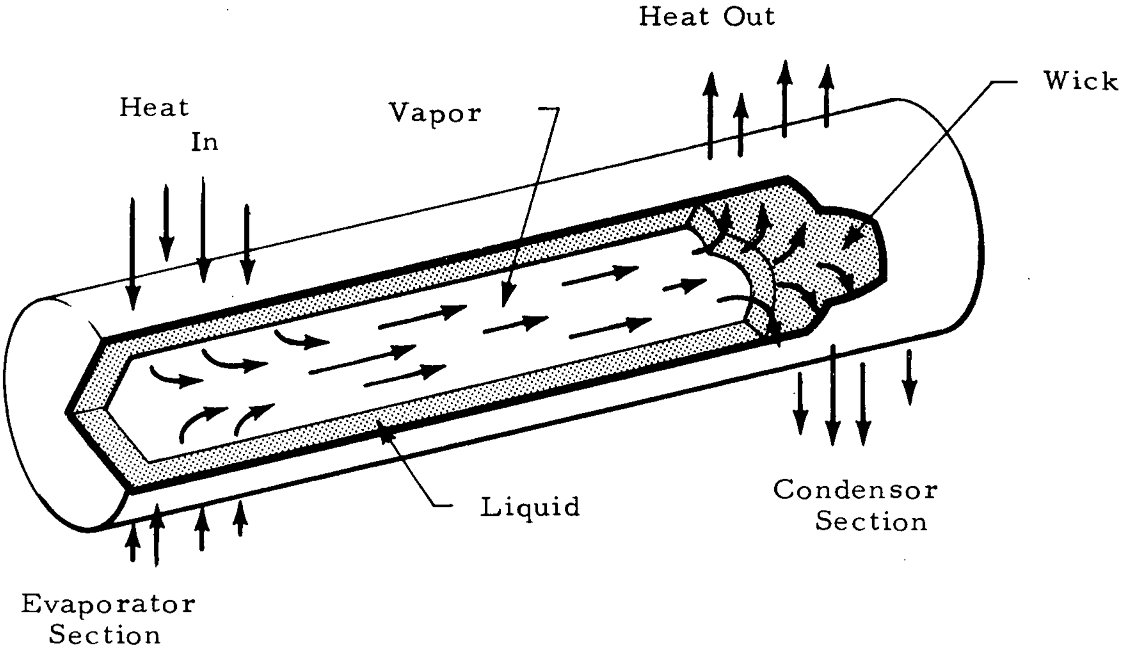
The symbol ($\Delta T$) represents the difference in scale readings of the thermocouples at the top and bottom of the cell, which can be converted into millivolts and subsequently to degrees centigrade. The differences are taken at one minute intervals. The term $\Delta f(\Delta T)$ represents the respective differences of $f(\Delta T)$. The meaning of the apparently constant difference between successive $f(\Delta T)$ values after about 15 minutes is not altogether clear at the moment. An attainment of a constant rate of heat leakage rise is one possibility. Another is that the thermal diffusivity is a function of temperature. Development of the present method into a highly precise and accurate method for determining thermal diffusivities will require further research of the posed possibilities. Considerable improvement in the precision of observed thermal diffusivity values was immediately noted, however, if a value of $f(\Delta T)$ is taken at the time when $\Delta f(\Delta T)$ becomes constant. For example, in the preceding table this value is 54.5. Thermal diffusivity values from data treated in this manner are shown in the following table for various systems.

| Substance | Thermal Diffusivity $cm^2/sec \times 10^{-3}$ |
|---|---|
| Water | 1.48<br>1.20<br>avg. 1.34 ± 0.14<br>(reported value of 1.35 (Ref. 4) |
| $LiNO_3 \cdot 3H_2O$ + Aluminum gauze<br>8/1 parts by weight | 5.2<br>4.3<br>4.3<br>avg. 4.6 ± 0.4<br>(by previous method, 1.9 ± 0.9) |
| Myristic Acid | |
| Solid | 2.44<br>1.87<br>1.84<br>avg. 2.05 ± 0.26 |
| Liquid | 1.33 |
| Acetamide | |
| Solid | 38.2 |

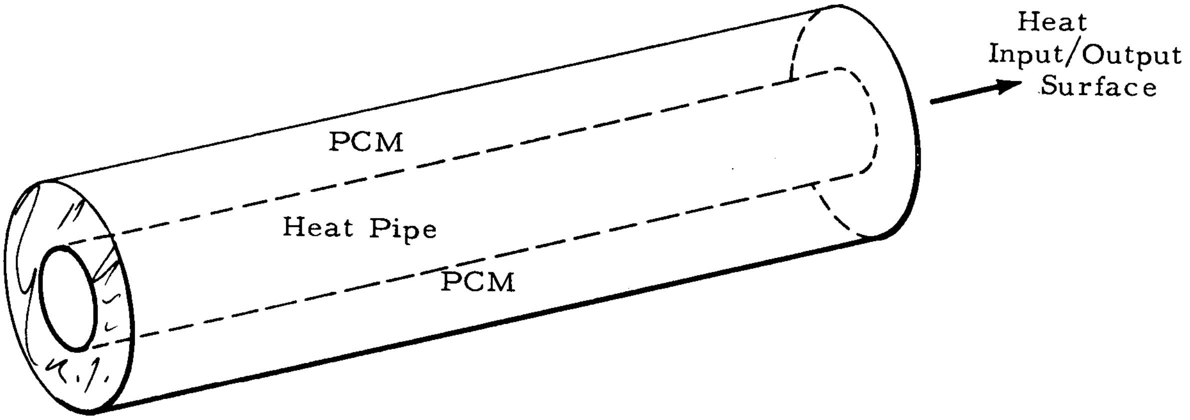
The precision of the method, it can be seen, has been increased to approximately 10% by the described data treatment.

## 2.3 HEAT PIPES IN CONJUNCTION WITH PCMS

The extremely high values of thermal conductivity observed in heat pipes naturally brings up the question of the advantages to be realized from heat pipe/PCM systems. A heat pipe might offer advantages for improvement of PCM system thermal diffusivity or as a heat transporter and a PCM as a heat sink. Just the brief consideration of the theory of heat pipes will be gone into here. Extensive reviews will be found in Refs. 6 and 7. A basic schematic of a heat pipe is shown in the following sketch.



Heat is absorbed as latent heat of vaporization at the evaporator end. The temperature of the evaporator end is at the vaporization temperature of the liquid inside the pipe. The vapor is driven by the temperature gradient to the condensor end where it condenses, giving up its latent heat of vaporization. The condensed liquid returns to the evaporator end by capillary action. Consider now the following arrangement of heat pipe and PCM:



A number of possible advantages could be realized from the arrangement for thermal control on spacecraft. Heat would be absorbed at some given temperature at the input surface and given out over the heat pipe/PCM interface. The PCM would melt, absorbing the heat. The absorbed heat would in essence be stored until rejected or used for other purposes. Possibly, the heat pipe would operate in a reversible manner. If so, the stored heat could be returned to the heat input/output surface if its temperature began to drop below the solvent boiling point. Thus the heat input/output surface would be maintained at a constant temperature. A reliable judgment, however, as to the advantages of a system composed of heat pipe plus PCM must await further study on the relative rates at which heat is transported by the heat pipe and the PCM.

## 2.4 ROLE OF CONVECTION IN PCM SYSTEM OPERATION

The presence of liquid and gaseous (bubbles) phases during PCM melting or freezing means that convection will be operative to varying extents, depending on the boundary conditions. The presence of convection increases the rate of heat transfer over what it would be if no convection were present. Convection, thus, is generally a desirable phenomenon in PCM operation. Convective theory, unfortunately, is not yet able to predict generally the type and extent of convection likely to occur in any given system. Detailed mathematical analysis or experimental data are usually required for specific instances. The work of Catton and Edwards reported in Ref. 8, however, does appear particularly pertinent to PCM operation because liquid convection in the presence of honeycomb fillers is explicitly considered. Cotton and Edwards consider the effect of insulating (phenolic-Fiberglas ) and conducting (aluminum) honeycomb on the extent of Bénard Convection. Bénard convection is a cellular form of fluid motion frequently exhibited by liquids whose horizontal extent is large in comparison to their vertical extent. The reader seeking further general information on convection is referred to Ref. 9. Figs. 2 and 3 illustrate that the onset of natural convection is inhibited by the presence of honeycomb filler, the inhibition being more pronounced with aluminum honeycomb than with phenolic honeycomb. Figures 4 and 5 show the corresponding extent of heat transfer.

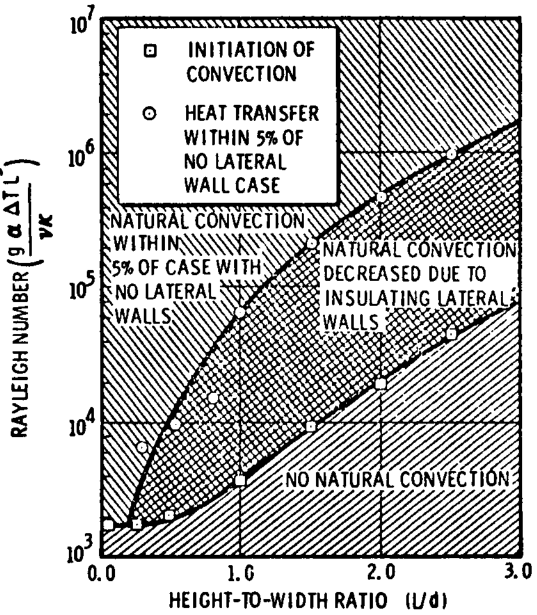


Fig. 2 - Region of Influence of L/D on Heat Transfer for Insulating Walls (Ref. 8)

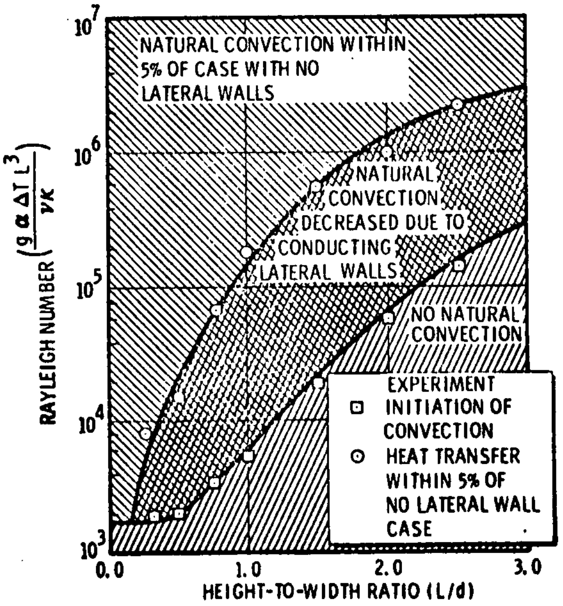


Fig. 3 - Region of Influence of L/D on Heat Transfer for Conducting Walls (Ref. 8)

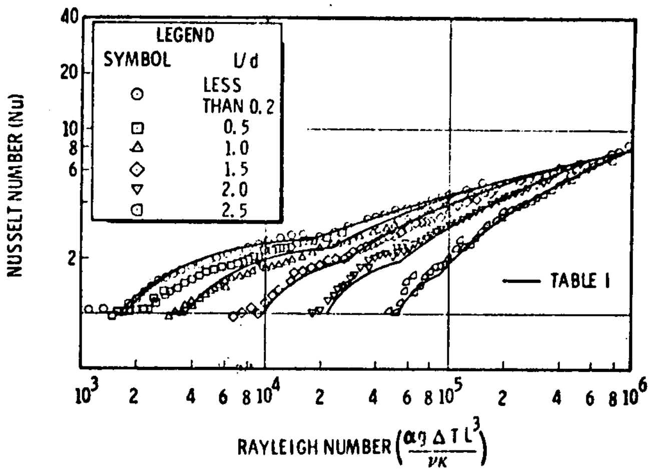


Fig. 4 - Heat Transfer through a Cell with Insulating Laterall Walls (Ref. 8)

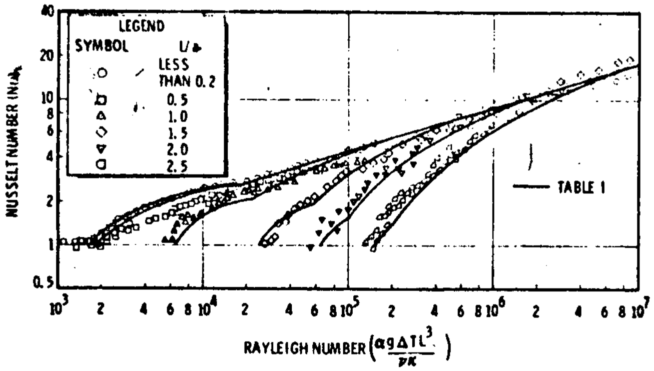


Fig. 5 - Heat Transfer through a Cell with Conducting Lateral Walls (Ref. 8)

# Section 3
# PCM SYSTEMS – LONG-TERM STABILITY

## 3.1 THERMAL CYCLING

Long-term thermal cycling can result in a number of deleterious effects. For example, PCM degradation can build up the concentration of impurities to a level which seriously interferes with efficient operation. Other deleterious effects of thermal cycling on PCM operation include eventual distruction of the nucleation catalyst and stratification of impurities. Because the effect of thermal cycling is so important for long-term PCM operation, an experimental testing program is currently in progress. The current work consists of packaging various PCM materials into small aluminum cannisters. The cannisters in which photography film is sold were found to be suitable, equipped as they are with an air-tight lid. The cannisters are then placed on a hot plate which is automatically turned on and off at set time intervals. The PCM operation before and after thermal cycling is determined by monitoring the temperatures at the top and bottom of a thermal diffusivity cell whose top is being heated at a constant rate.

## 3.2 CATALYST STABILITY

Very few specific nucleation catalysts are known. One of the very few which has been identified is the compound zinc hydroxy nitrate which apparently is a specific nucleation catalyst for the PCM candidate, lithium nitrate trihydrate. The long-term stability of this material in contact with molten lithium nitrate trihydrate, therefore, will soon be tested in the same manner as that in which the long-term stability of various PCMs is tested.

## Section 4
## PLANNED FUTURE ACTIVITIES

Refinements of the experimental apparatus and of the data processing to improve the accuracy and precision of the thermal diffusivity measurements are currently in progress. Construction of new cells designed to minimize heat leakage and to enable more accurate effective thermal diffusivity values to be measured for composite systems is planned for the near future. After a satisfactory design is achieved, a number of other filler materials and configurations will be evaluated. Also planned for the near future are a series of experimental tests of PCM performance after a long period of sustained thermal cycling.

A number of new, promising PCM candidate materials were identified in the course of the present study. Accurate heat of fusion data on these new candidates, however, are not available. The development of a simple calorimeter method to rapidly determine heat of fusion, therefore, is planned for the near future.

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