MECHANICAL AND THERMAL PROPERTIES OF A THERMAL STORAGE MODULE WITH PHASE CHANGE MATERIALS DISPERSED IN CEMENT

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ABSTRACT

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At the Centre for Building Studies (Concordia University, Montréal), we are investigating the possibility of incorporating phase change materials in building components for space heating and temperature regulation applications.

The thermal storage module studied here, made from a mixture of fatty acids, cement, and water, was easy to produce. The melting point of the fatty acid mixture can be changed at will between -5°C and 70°C. Several compositions were tested and the best compressive strength obtained, 2.187 MPa after curing the samples for 28 days, was improved (to 4.4 MPa) when high early strength cement was used instead of normal cement. The tensile strength of the same mixture was found to be equal to 0.442 MPa after the same curing period. Additives, such as glass fibres and fly ash, produced only minor increases in strength. The compressive strength decreased linearly with temperature, between 25°C and 100°C, at a rate of 15 KPa/°C. The measured drying shrinkage is 50% larger than for cement mortar and should be considered in the design of the storage system.

Samples subjected to 200 freeze-thaw cycles (-5°C to 6°C) and to 80 thermal cycles (-30°C to 35°C) under U.V. light (254 nm wavelength) showed no spalling or damage. However, samples immersed in water and subjected to freeze-thaw were severely damaged after only 30 cycles.

The fatty acid used, a pressed stearic acid, has a melting temperature of 56.5°C and a heat of fusion of 144 J/g. Its thermal conductivity is equal to 0.190 W/(m.°C) and its measured specific heats are 1.81 (when solid) and 2.38 J/g.°C (when liquid). The thermal properties of the cured samples with 30-40% fatty acid by weight did not correspond to those of the pressed stearic acid. An infrared study did not reveal the cause of this effect. The cured samples had a high thermal resistivity (5.32 m.°C/W), comparable to that of hardwoods.

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CHAPTER I

INTRORDUCTION

Solar energy is considered by many scientists to be an alternative source of energy supply in several applications. Space heating and cooling consume large quantities of electricity and fuel which could eventually be replaced by energy from the sun. One important aspect of solar heating is the ability to store heat when provided for later use when required.

Several building components containing phase change materials have been proposed by researchers in the field of solar heat storage for house heating applications. The advantages of such components over other storage systems are many. First, they do not need to occupy needed living space since they can be stacked to form walls and partitions. Also, by varying the nature of the phase change material, these components could be made to suit a wide range of climates. Finally, their double use as partitions as well as heat stores could justify their cost of production.

Hydrated salts have been considered as phase change materials suitable for heat storage because of their low cost and appropriate thermal properties. However, a few years of research have uncovered many unfavourable characteristics such as supercooling, incongruent melting and gradual loss of heat storage capacity with thermal cycling. Research is still going on to improve their properties. Meanwhile, other materials have been proposed, including organic substances such as fatty acids and paraffins.

Fatty acids are more expensive than hydrated salts but their packaging costs are lower. They also are thermally stable, do not corrode, and are not affected by thermal cycling. At the Centre for Building Studies*, research is going on to investigate the possibility of incorporating fatty acids in cement components to produce a compact module for heat storage.

This thesis covers only the preliminary stages of the experimental research program being conducted to produce a feasible product. It has been divided into two separate but complementary parts.

Part 1 (chapters 2 to 4) is a general review on solar energy and heat storage systems. Chapter 2 is concerned with solar energy in general and its particular uses for space heating applications. Chapter 3 is basically important in understanding the aspects of energy storage in materials used in latent heat storage. Chapter 4 deals with fatty acids, candidates for latent heat storage. Many of their properties are presented in this chapter.

Part II describes the actual research performed on mixtures of a commercially available stearic acid, cement and water, and presents and discusses the results obtained. The scope and objectives of the experiment, the preparation of the samples and the testing procedure are all described in Chapter 5. The results, separated into "mechanical and physical properties" and "thermal properties and infrared spectrometry study" are dealt with in Chapters 6 and 7 respectively. A discussion concludes each of these chapters.

The conclusions and recommendations (Chapter 8) are reserved until the end. These are hoped to form the corner stone for the continuing research in this particular field in the future.

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PART I

CHAPTER 2

SOLAR ENERGY - A GENERAL OVERVIEW

2.1 HISTORICAL REVIEW

Time after time, man has been confronted with the need to search for new energy sources due to the scarcities of fuel supplies. The need of new energy alternatives has often spurred advances in solar architecture and technology. But, when abundant new sources of fuel were discovered, solar energy became "uneconomical" and dropped from sight. In some occasions, however, no alternative fuels were found. Such was the case in ancient Greece and Rome.

Centuries ago, in ancient Greece and later in the roman empire, forests were ravaged for wood, used in house and ship construction and for heating. Soon, many areas became totally denuded of trees and wood had to be imported and its use regulated. With fuel scarce and the sources of supply so far away, the ancient Greeks and Romans turned to an alternative source of energy supply: the sun, a reliable, harmless, cheap and renewable energy source. They learned to build their houses and planned entire cities to take advantage of the sun's rays during the moderately cool winters and to avoid the sun's heat during the hot summers. Thus, solar architecture flourished and people continued to rely on solar heating and cooling for centuries.

The knowledge of solar architecture was forgotten or deemed obsolete in the last century because of the effectiveness of recently developed central heating systems and the still more recent availability of an extremely convenient form of energy: electricity. But, in recent years, the public has once more become concerned about the rapid depletion and escalating costs of fossil fuels. There is also some fear about the environmental and safety risks associated with fossil fuels and nuclear power. These concerns have once more focused the attention on the potential of using solar energy in new and varied forms to meet society's growing energy needs; technological advances in several fields of science and engineering now make it possible to accelerate the use of solar energy to meet these energy requirements.

Solar energy is an intermittent energy source and its availability is affected by the day-night cycle, clouds, seasons and the changes in weather. Its use as an effective energy source for heating purposes is further complicated by the fact that the energy demand for most heating applications is out of phase with the availability of solar energy. The viability of solar energy as the main energy source can hence be established only by including a thermal store within the solar heating system. In addition, storing heat produces a desirable characteristic, that is, it reduces the temperature fluctuations inside the heated space, thus reducing discomfort.

Solar energy storage is a concept that has always formed part of the solar heating concept. K. Butti and J. Perlin (1) described a heat collection and storage technique, invented by the Greeks and passed on to the Romans. A shallow pit dug under the floor of a sunlit room would be filled with broken earthenware or other rubble and topped by a mixture of dark sand, ashes and lime, forming an excellent absorber of solar heat.

2.2 HEAT STORAGE SYSTEMS

With poor design, the house or building could overheat even on winter days. There are many ways to store the excess heat for later use to offset the use of purchased fuels. The simplest form of heat storage would utilize the structure of the house (or building) itself: its walls, floors, ceiling and interior partitions. Dense materials such as concrete and rock can increase the quantity of stored heat with small changes in room temperature. Light wood-frame houses store little heat and would require the addition of thermal mass, such as containers of water placed within the house or building, close to sunlit windows. Other techniques include filling the voids in concrete blocks with sand, gravel, concrete or water in vinyl containers, and the use of gravel or rockbeds in the crawl space below houses to store heat from the circulation of overheated room air through the beds.

The size of the optimal thermal storage system depends on the purpose for the solar heater. Thermal stores of small heat storage capacity can help neutralize the fluctuations on the load side introduced by minor interruptions in weather, like the appearance of clouds. Larger thermal stores can store enough heat while the sun is shining to meet the energy demands for a 24-hour period (daily or short-term storage) or a 4-month period (annual, seasonal or long-term storage).

Short-term storage is used in a dynamic process with a daily charge/discharge cycle and hence modifies the response of the solar heating system. In the following, we will only be concerned about short-term storage systems. Later, we will describe the techniques used to produce and test a particular latent heat storage component containing hydrated cement and a fatty acid.

Most short-term storage systems are used for solar space and domestic water heating. The application temperature of these systems generally varies between 20°C and 60°C.

2.3 SOLAR SPACE HEATING

The last few decades have witnessed a growing interest in solar space heating research. In 1938, M.I.T. started a research program that led to M.I.T. solar house I which began operating in 1948. The major components were rooftop collectors and a water heat storage tank. The heat collecting medium used was also water. The design called for seasonal storage. The results, from a technical viewpoint were generally positive, but those of the economic analysis were clearly unfavourable. Space heating research continued at M.I.T. with solar houses II and III. Meanwhile, Dr. George Löf installed a collector of his own design on a house in Boulder, Colorado, in 1945 and in 1948, Dr. Maria Telkes and Eleanor Raymond built the first house with heat storage in salt hydrates in Dover, Massachusetts (2). From 1950 on, research and construction of solar heating systems increased rapidly.

A large portion of residential and commerical energy consumption is used to heat occupied space. This application uses heat at moderately low temperatures, a fact that makes space heating one of the most cost-effective solar energy applications at the present time.

2.4 ACTIVE AND PASSIVE SOLAR SYSTEMS

Systems for solar space heating can be divided into two categories, active and passive. Active systems have mechanical devices such as pumps or fans to convey the heat between the solar collector, the heat store and the space to be heated. Passive systems lack such devices, the heat being distributed through radiation, conduction or natural convection.

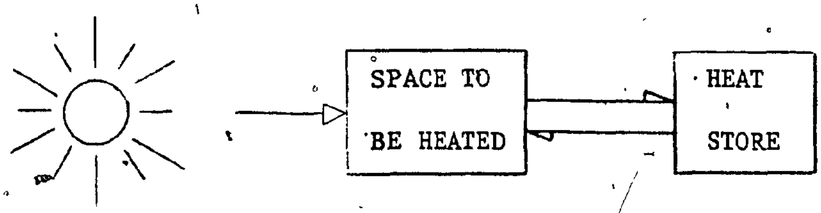
In passive systems heat is transported by non-mechanical means. The passive system operates on the energy available in its immediate environment and does not require external energy input such as electricity to power the fans and pumps which make active systems work. Passive systems have several advantages over active systems. They are less prone to breakdown, their maintenance costs are lower and no special installation skills are required. Some of them are also cheaper than active systems. Passive systems are more difficult to design. A poorly designed system can lead to unsatisfactory comfort conditions caused by excessive space temperature fluctuations.

It is worth mentioning that the inside air temperature for comfort in slab heated spaces is usually lower than in a space heated by conventional blowers or radiators. The vertical temperature gradients are also reduced, allowing for a lower thermostat setting while keeping the ankle temperature at a comfortable level, thus resulting in lower heating costs.

Both active and passive systems can use either air or water as energy transport medium. The advantage of air over water is that it is freeze-proof and does not cause corrosion. Also, airborne heat can have a lower temperature than waterborne heat, since no secondary heat transfer is required. However, its use requires large ducts.

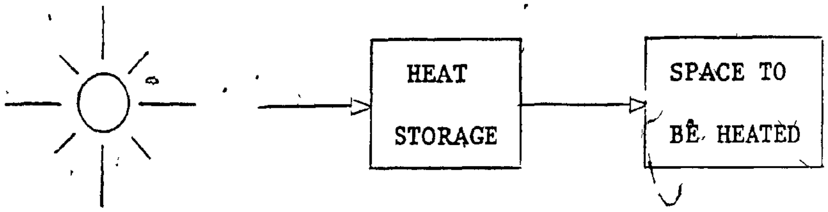
Active and passive systems are simple in concept and use. Three general concepts are mainly associated with passive solar space heating. These are:

A. Direct Gain



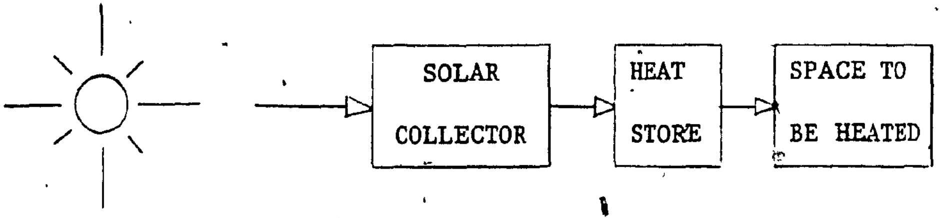
With the direct gain approach, the space becomes a live-in solar collector, heat storage and distribution system all in one. The design of south-facing glazing (the collector) and thermal mass is critical and the most common materials used for heat storage are masonry and water. The use of large glazing has two disadvantages: glare during the day and large heat losses during the night.

B. Indirect Gain



In this approach, sunlight first strikes a thermal mass which is located between the sun and space to be heated. The sunlight absorbed by the mass is converted to thermal energy (heat) and then transferred into the living space. There are basically two types of indirect gain systems: thermal storage walls and roof ponds.

C. Isolated Gain



The principle behind this concept is to isolate solar collection and thermal storage from the living space. This allows higher storage temperatures. The heat is drawn from the storage only when needed. The most common application of this concept is the natural convective loop system, that includes a flat plate collector and a heat storage tank or bed.

It is technically feasible to provide 100% of the energy needs of a building by solar energy. This, however, depends mainly on the climate and on the building losses and is usually not the economic optimum.

CHAPTER 3

HEAT STORAGE

Thermal energy can be stored in three different ways:

- Storage as sensible heat;
- Storage as latent heat; and
- Conversion into another form of energy, especially thermo-chemical storage.

3.1 SENSIBLE HEAT STORAGE

For a rise in temperature ΔT (^{o}C), the quantity of energy stored as sensible heat is:

$$Q = \int_{T_1}^{T_2} M.Cp.dT \approx M.Cp.\Delta T$$

where, Q = quantity of stored heat, KJ;

Cp = specific heat of storage medium, KJ/Kg.^{o}C;

M = mass of storage medium, Kg; and

$\Delta T = (T_2-T_1)$, the rise in temperature, ^{o}C.

The specific heat, Cp, varies with temperature and phase changes, but its value is assumed constant over the range of temperatures suitable for house heating applications. Often, the heat capacity per unit volume is of greater interest than per unit weight. Hence it is desirable that the substance should have a low molar volume. For example, Magnetite has the normal heat capacity for rock, but on the basis of volume, it has, owing to its high density, a value which is almost as high as that for water, as shown in Table 1 (3).

SUBSTANCE	J/(Kg.°C)	MJ/(m^3.°C)
WATER	4200	4.2
MAGNETITE	800	4.1

Table 1: Heat capacities per unit weight and volume of water and Magnetite

3.I.A HEAT STORAGE IN SOLIDS

Heat stores with solid material are often constructed according to the principle of a packed bed. In such cases, the storage unit is packed with solid bodies in direct contact with a heat-transfer medium which fills the space between the bodies. The material is usually rock and air is the usual heat-transfer medium.

Other forms of heat stores with solids include the Trombe wall and heat storage in the elements forming the structure of the building. Table 2 includes some of the solid materials commonly used in sensible heat storage.

Material	Density Kg/m^3	Heat capacity per unit weight, J/Kg.C	Heat capacity per unit volume, MJ/m^3.C	Thermal conductivity W/(m.C)	Ref.
Rocks, (granite)	2640	880	2.32	1.7-4.0	4
Cement, (portland)	1920	670	1.29	0.029	5
Brick, (building)	1970	800	1.58	0.70	5

Table 2: Properties of some solid media used in sensible heat storage.

3.1.B HEAT STORAGE IN LIQUIDS

Water is practically the only liquid which has been used to store heat at moderate temperatures. It is cheap, easily available, environmentally acceptable, has a high thermal capacity, and is backed by a well-developed technology. Water has also a few disadvantages: a high vapour pressure at increased temperatures and a tendency to contribute to corrosion in metallic containers in the presence of oxygen and/or salts in solutions.

In systems using water as a heat storage medium, water is usually also used as the heat-transfer medium from the solar collector to the heat storage tank, so that no heat exchanger is required between collector and storage element.

3.2 LATENT HEAT STORAGE

A change in phase is sometimes accompanied by large amounts of heat absorption or release, even though no change in temperature occurs (Figure 1). This heat is called latent heat of fusion if there is a solid-to-liquid phase change and latent heat of vaporization in the case of a liquid-to-vapour transition.

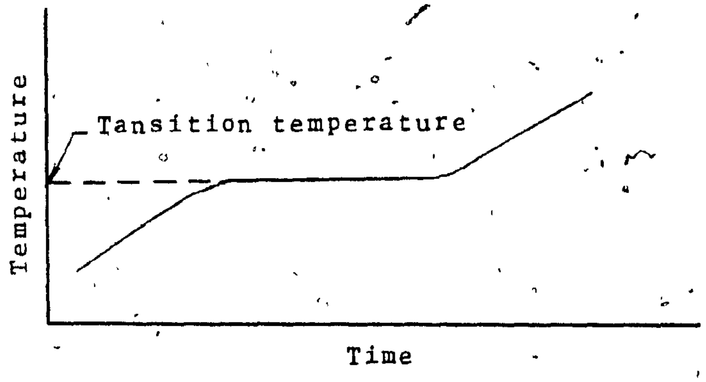


Figure 1: Time-temperature curve at phase change, with constant power input

Usually transitions from the solid to the liquid state are used, not only pure melting processes but also eutectic and peritectic transitions, as well as solvation processes. Transitions within the solid phase, e.g. order-disorder transitions, are also in certain cases accompanied by considerable latent heat (Table 3), and can therefore be used for energy storage. Transitions from the liquid state to the gaseous state are generally associated with considerably greater latent heats than are the changes referred to above. It is, however, only in exceptional cases that the storage of thermal energy through vaporization processes is feasible. The difficulties are connected with the degradation of the active surface of the dessicant after a few hundred drying cycles.

COMPOUND	HEAT OF TRANSFORMATION (Cal/g. (J/g)	TRANSFORMATION TEMPERATURE °C	MELTING POINT °C
Pentaerythritol	77.1 (322.8)	187.7	238
Pentaglycerine	46.1 (193.0)	81	197
NeopentylGlycol	31.3 (131.0)	43	126

Table 3: Order-disorder heats of transformation in solid media (7)

From the thermodynamic point of view it can be said that in phase transitions of the second order, e.g. order-disorder transitions and in dissolution processes, the heat is released within a temperature interval. In practice, however, the heat cannot be produced exactly at the equilibrium temperature owing to such factors as reaction kinetics and impurities (3).

In a melting process, the heat of fusion, ΔH_f, is equal to:

$$\Delta H_f = T_f \cdot \Delta S_f, \text{ in J/mole;}$$

where T_f = melting temperature, in K; and

ΔS_f = entropy change at melting, in J/(mole.K).

The majority of substances have at melting a ΔS_f-value which varies between 7 and 25 J/(mole.K). Water has especially attractive characteristics for heat of fusion storage, with a ΔS_f of 22 J/(mole.K), low molecular weight and a low molar volume (18 cm^3/mole); however, its melting point (0^oC) is too low for the majority of heat-storage applications.

3.2.A IDEAL CHARACTERISTICS OF LATENT HEAT STORAGE MATERIALS

The choice of a material for latent heat storage must be based on an appropriate trade-off between the following characteristics:

1. An appropriate melting temperature with a small melting range;
2. Similar melting and freezing curves;
3. A large heat of fusion;
4. A small degree of supercooling. Supercooling means a loss of quality as the heat will be produced at a temperature lower than the melting point. It makes a system difficult to control and can also impede the withdrawl of heat at the desired time. After extensive investigations, Dow Chemical Co. found only about 30 substances which spontaneously had no supercooling worth mentioning (7). Among these can be mentioned waxes and long-chained fatty acids.

   There are several ways to reduce supercooling. The addition of nucleating agents, the use of crystal-forming surfaces, mechanical stirring and ultrasound are some of these methods;

5. Large thermal diffusivity in both solid and liquid phases. The thermal diffusivity, α, is equal to:

$$\alpha = \frac{K}{Cp.d} \quad , \text{ in } m^2/s$$

where K = thermal conductivity, in W/(m.^{o}C);

Cp = specific heat, in J/(Kg.^{o}C); and

d = density, in Kg/m^3.

A high thermal diffusivity means that the material rapidly dissipates temperature gradients. A phase-change material with high heat capacity is preferrable for situations where the primary concern is energy storage and where possible large temperature changes would present no deleterious effect (8);

6. Small volume changes accompanying phase change and temperature rise. This requirement is made because of the danger of container rupture;

7. Reversibility; in multi-component systems several phases are in equilibrium with one another and there is then a risk of spontaneous and irreversible phase separations. Phase separation is a consequence of differences in density between the different phases. The reversibility depends on whether the material melts congruently or not and how the phases formed separate spontaneously from one another. Congruent melting means that only one solid phase is involved and that the compositions of the solid phase and the liquid are constant throughout the phase change. In incongruent melting there are more than two phases in equilibrium with one another. The solid phase may melt to a liquid of different composition, while at the same time a new solid phase is formed with a third composition. The temperature for incongruent melting is called the peritectic temperature;

8. Thermal and chemical stability after many freeze-thaw cycles;
9. No reaction between the phase-change material and the container;
10. The rates of thermal expansion in the solid and liquid phases should not be very different;
11. The phase-change material should not be toxic, flammable, explosive, or corrosive;
12. Availability and low cost;
13. High rate of crystal growth. The more complicated the crystal structure is, the more difficult will be the formation of crystals;
14. High thermal conductivity; the thermal conductivity in the solid phase and the heat transfer between the melt and the heat exchanger are often critical.

3.2.B PROBLEMS ASSOCIATED WITH THE DESIGN OF LATENT HEAT STORAGE SYSTEMS

The design of systems utilizing heat storage materials presents many problems (8). In phase change storage systems, separate fluid loops are needed to transfer the heat from the collector to the storage element. Also, expensive heat exchangers are sometimes required due to the usually low thermal diffusivities of the phase change materials. The corrosion of the container, the eventual destruction by repeated thermal cycling of the catalyst added to overcome supercooling, and incongruent melting are some of the problems which are encountered. Specially insulated containers may also be required if the storage temperatures are significantly different from ambient.

3.2.C EXAMPLES OF LATENT HEAT STORAGE MATERIALS

A. SALT HYDRATES

Salt hydrates are salts with water of crystallization. Many of them have appropriate melting temperatures and large heats of fusion. Salt hydrates, however, are not single-component systems and there is therefore a risk of formation of undesired phases and phase separation. For reasons of costs, only a few salts can be considered for use on a large scale. Supercooling is usual in the case of the pure substances but often it has been possible to reduce this through additions of nucleating agents (Table 4).

HEAT OF FUSION SYSTEM	NUCLEATING AGENT
$Na_2SO_4.10H_2O$	Borax
$KF.4H_2O$	Pumice, dry ice
$CaCl_2.6H_2O$	$SrCl_2.6H_2O$, SrO
$Zn(NO_3)_2.6H_2O$	$Mg(NO_3)_2.6H_2O$

Table 4: Examples of nucleating agents added to reduce supercooling

Two commonly used salt hydrates are briefly discussed below:

1. Sodium sulfate decahydrate ($Na_2.SO_4.10H_2O$ - Glauber's salt)

This salt is a byproduct of the potash production process and has two good characteristics: a high heat of conversion (215 - 253 J/g.), and a low price. Its conversion temperature (peritectic temperature), 31° - $32.4^{\circ}C$, allows it to be used in a central storage. Glauber's salt melts incongruently and gives a saturated solution as well as water-free sodium sulfate. The incongruent melting and phase separation are the two major problems associated with this salt hydrate. A few researchers have made some progress in solving these problems after several decades of research. It has also been noticed that its heat storage capacity decreases with thermal cycling.

2. Calcium Chloride Hexahydrate ($CaCl_2.6H_2O$)

$CaCl_2.6H_2O$ is a byproduct of the Solvay process. Its heat of fusion is 170 - 190 J/g. and it melts pseudocongruently at about 29.8°C. A tetrahydrate ($CaCl_2.4H_2O$) is thermodynamically stable within a temperature of about 2°C above the melting point of the hexahydrate. The major problem with the system is that the dissolution of any tetrahydrate formed takes place very slowly, even at temperatures exceeding the interval where the tetrahydrate is no longer stable. After a number of melting and crystallization cycles, a phase separation therefore generally appears. Tetrahydrate formation and precipitation reduce the heat-storage capacity after a number of cycles. To prevent the formation of the tetrahydrate, active components, such as $Ca(OH)_2$, diatomaceous earths, and $SrCl_2.6H_2O$, are added.

B. ORGANIC COMPOUNDS

Organic compounds can be used for heat-of-fusion storage from room temperature up to several hundred degrees. Usually, single-component systems are used and melting therefore takes place congruently. Supercooling is often moderate and, on a weight basis, the heat of fusion can be quite high. Oxidation and polymerization can become a problem after long use and fire risk is an obstacle to many applications. Some of these materials will be discussed in more detail in Chapter 4.

In Table 5 we compare most of the thermal properties of common phase

Material	Chemical formula	Group	Melting temp., C	Heat of fusion, KJ/Kg	Heat storage density, MJ/m^3.
Sodium sulfate decahydrate	$Na_2SO_4.10H_2O$	hydrated salt	31-32.4	215-253	300-372
Sodium thiosulfate pentahydrate	$Na_2S_2O_3.5H_2O$	"	48-50	200-209	335-346
Calcium chloride hexahydrate	$CaCl_2.6H_2O$	"	27-39	170-190	285-323
Disodium phosphate dodecahydrate	$Na_2HPO_4.12H_2O$	"	34.6-36.5	264- 281	403-427
Barium hydroxide octahydrate	$Ba(OH)_2.8H_2O$	"	78-82	265-300	657
Sodium carbonate decahydrate	$Na_2CO_3.10H_2O$	"	32-36	247-251	
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	"	117-120	165.6-172	250
Mixed calcium & magnesium hydrated chlorides	$CaCl_2/MgCl_2/H_2O$*	"	25	175	
Mixed sodium & magnesium fluorides	NaF/MgF_2**	Fluorides	832	615-625	1290-1370
Glauber's salt*** (eutectic)		-	13	146	215
Sodium hydroxide	NaOH	base	318-320	159-315	284-555
Ice	H_2O	-	0	334	305.8-308
Cross-linked, high density polyethylene		polymer	132	230	207
Octadecane	$C_{18}H_{38}$	paraffin	28	244	188
eicosane	$C_{20}H_{42}$	"	37		192
eicosene	$C_{20}H_{40}$	olefin	27		
Paraffin wax	mixture of 23,24&25 C-atoms paraffins	paraffin	50-52		167
Lauric acid	$CH_3(CH_2)_{10}COOH$	fatty acid	44-47	178-183	155
Stearic acid	$CH_3(CH_2)_{16}COOH$	"	69-69.6	199-240.8	
Pressed stearic acid (EMERY E400)	-	"	56.5	144	119
Paraffin wax (Sunoco P-116)		paraffin	47	209	161

Table 5: Properties of a few phase change materials

Density, Kg/m^3		Thermal conductivity, W/m C		Specific heat KJ/(Kg.C)		Thermal diffusivity, x10^{-6}m^2/s.	References
solid	liquid	solid	liquid	solid	liquid		
58-1460	1330-1460	2.25		1.76-1.78	3.30-3.31	0.87	4,29,30,31,32, 33,34,35
50-1730	1660	0.465-0.570		1.47	2.39		4,15,29,30,31, 32,33,36,37
34-1800	1560	1.09-1.10	0.54	1.44-1.46	2.13-2.32	0.44	4,30,31,33,34, 38,39,49
20-1522	1520	0.512		1.55-1.70	3.18	0.21	15,29,30,31,33, 34
2180				1.17			32,33
40-1442				1,88	3.35		31,33
60-1570	1442			1.59-1.72	2.24-2.85		4,33,49
							18
2570	2090	4.2-8.4	4.65	1,42	1.38	1.72	32,40,41
1470				1.42	2.68		4,36
2030	1760	0.92	0.92	2.00	2.09	0.23	32,42,43
17-920	998-1000	0.62	2.26	2.09-5.27	4.18-4.22	0.13	4,49
960	900	0.36	0.36	2.50	2.50	0.15	4,44
	756		0.15	1.45	1.70		38,45
			0.15				38
							38
840	770	0.20		1.67		0.14	46
	870	0.151	0.111-0.147	1.60			15,47
			0.160-0.172				13,34,47
949	823	0.19		1.81	2.38	0.11	
820	770	0.14		2.89	2.51	0.06	4,48

* 41/10/49 (% by weight)

** 67/33 (% by weight)

*** composition (% by weight): $Na_2SO_4.10H_2O$(74.5%), NaCl(6.7%), NH_4Cl(6.2%), borax nucleator(2.6%), thickener(7.9%), boric acid(1.8%), and tetrasodium phosphate(0.3%).

change materials, including salt hydrates and organic acids, to the properties of water.

3.2.D ENCAPSULATION OF LATENT HEAT STORAGE MATERIALS

A. MACRO AND MICRO-ENCAPSULATION

In micro-encapsulation, millimetre-sized units are used to increase the contact between the different components of the heat-of-fusion storage system. When larger units are used, the term macro-encapsulation applies. Micro-encapsulation is used to eliminate phase separations in incongruent heat-of-fusion systems. As the units are extremely small, the diffusion distance is shortened and a higher degree of reversibility is achieved. Encapsulation in small units can also be used to protect the storage medium from unfavourable reactions with external reagents, or to easily transport the storage medium in a more convenient form.

In addition to heat transfer, the changes of volume upon melting/solidification and the compatibility between the storage medium and the encapsulating material are factors which are considered in encapsulation.

Salt hydrates and organic substances can sometimes be stored in cans, if oxygen is excluded to avoid corrosion. Certain organic acids are not corrosive and do not have any effect on metals. Plastics are of great interest in low-temperature heat-of-fusion storage. However, their thermal conductivity is low, and organic acids have in some cases a tendency to dissolve plastics or react in other ways with them. Also, water difuses through the majority of plastics, resulting in concentration changes and loss of storage capacity for salt hydrates.

The Dow Chemical Co. (9) has investigated the macro-encapsulation of phase-change materials and found many interesting results. A mixture of stearic and palmitic acids melting at 60°C, for example, was found to be compatible with sulfonated polyethylene while high density polyethylene was found unsatisfactory for the encapsulation of the mixture.

B. ENCAPSULATION IN PREFABRICATED BUILDING COMPONENTS

This form of storage has the advantages of reducing the cost of installing the heat-storage units, and from the point of view of appearance. The matrix can also speed up the heat transfer to the centre and reduce the difference in heat transfer rates for melting and freezing.

On the macro level, it is easily possible to encapsulate the storage medium in plastic-lined cavities created in construction materials, such as concrete, for example. Also, it is in certain cases possible to replace part of the aggregate that constitutes 80% of the weight in a concrete mixture with a heat-of-fusion medium. One such material is "Thermocrete"*, a foamed concrete block filled with calcium chloride hexahydrate and sealed with a plastic coating (10, 11, 12).

3.3 THERMOCHEMICAL ENERGY STORAGE

Energy is stored by breaking some chemical bonds and replacing them with others in a chemical reaction. If the reaction is reversible, heat is stored when the reaction is driven in one direction (endothermic reaction) and discharged when proceeding in the opposite direction (exothermic reaction).

It is sometimes possible that charging and discharging take place at the same temperature, creating characteristics in the storage function

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* Registered trademark of Suntek Research Associates.

which resemble those of latent-heat storage.

If the endothermic reaction requires a catalyst, the reactants are stored separately and brought to react in the presence of the catalyst when necessary. The same is done with the products, to generate the energy stored when required.

Insulation is not required for the storage of the reactants and products, since no heat leakage will ever occur, and the energy content will not be affected by the length of the storage period.

Chemical reactions produce large quantities of heat, making long-distance transport of stored heat to the point of consumption economically attractive. Large entropy changes are desired to produce the required quantity of heat. Molecules which dissociate into many molecules of gas can give rise to high entropy changes. One such reaction is the decomposition of ammonium hydrogen sulfate with $\Delta S \approx 450$ J/(mole.K).

$$NH_4HSO_4 \rightleftharpoons NH_3 + H_2O + SO_3$$

Other promising reactions include decompositions of ammonium carbonate and ammonium bicarbonate at temperatures of 60° and 80°C respectively,

$$(NH_4)_2\ CO_3 \rightleftharpoons 2NH_3 + H_2O + CO_2$$

$$NH_4HCO_3 \rightleftharpoons NH_3 + H_2O + CO_2$$

These reactions seem to take place completely reversibly.

Thermodynamical heat storage is a new science and intensive research and development work are still required in many quarters; the results obtained so far are promising.

CHAPTER 4

FATTY ACIDS

Many researchers have already considered fatty acids as possible candidates for heat storage. Fatty acids occur abundantly in vegetable and animal fats. They are divided into:

- straight-chain saturated acids (alkanoic acids);
- straight-chain unsaturated acids; and
- branched-chain and alicyclic acids.

The majority of fatty acids are straight-chain compounds. In the following, we will consider only alkanoic acids. These acids are saturated fatty acids consisting (except formic) of an alkyl chain and terminal carboxyl group. They are conveniently represented by the formula R-COOH, and all members above acetic by the formula $CH_3-(CH_2)_n-COOH$. A few examples are presented in Table 6.

Chain length	Systematic name	Common name	Formula weight	Density (liquid) Kg/m^3.	M.p., °C	B.p., °C
12	dodecanoic	lauric	200.31	883	44.2	298.9
16	hexadecanoic	palmitic	256.42	853	62.9-63.1	351.5
18	octadecanoic	stearic	284.47	847	69.6-70.1	376.1
20	eicosanoic	arachidic	312.52	-	75.3-76.1	204.0

Table 6: Properties of common straight-chain saturated fatty acids (13, 14)

4.1 APPLICATION TO LATENT HEAT STORAGE

Lauric, stearic and palmitic acids are the most widely distributed saturated fatty acids found in nature. Lauric acid (15, 16) and stearic acid (10, 17) have already been used in prototype solar systems. Their use in solar heat storage has also been mentioned by a few authors (7, 15, 18). Palmitic acid, on the other hand, has not been seriously considered in heat storage. However, it is present in large portions in the commercially available stearic acid and thus indirectly forms part of stearic acid heat storage systems.

Lauric acid

Lauric is the saturated acid found most abundantly in nature. It is a crystalline solid with a faint fatty odor. It is practically insoluble in water (0.0055 g/100 ml of water at 20°C), freely soluble in diethyl ether, but less so in ethanol (1 g/2 ml) and propanol (1 g/2.5 ml). Its principal use is as ingredient of coconut oil base soaps. Lauric acid exhibits excellent melting-freezing characteristics. Only a small degree of supercooling (0.5-1.5 K) has been observed (15, 19). It also was not particularly affected by 130 thermal cycles (15).

Stearic acid

Stearic acid (13) is the highest molecular weight saturated fatty acid occurring abundantly in natural fats and oils. It is a waxy crystalline solid, practically insoluble in water (0.00029 g/100 g of water at 20°C), fairly soluble in chloroform (50 g/200 ml) and decreasingly soluble in carbon disulfide, benzene, carbon tetrachloride, ethanol, and acetone. Its use in solar heat storage will be more completely discussed in the chapters to come.

The transition temperatures for pure lauric, palmitic and stearic acids are higher than needed for space heating. However, commercially available fatty acids have lower melting points than the pure substances and some mixtures of these acids melt around 30°C, making them potential candidates for heat storage in passive solar energy. The phase behavior of mixtures of pure acids is further discussed in Ref. (20).

4.2 COMMERICAL PRODUCTION

Originally, the fatty acid industry was closely allied with the candle industry. The modern fatty acid production industry began with Chevreul's classical researches on the saponification of animal fats and the separation of fatty acids, between 1811 and 1825 (21).

The raw materials used in fatty acids production include tall oil, fish oils, vegetable oils and animal fats. Tall oil, a by-product of the paper and pulp industry, has become an important raw material in the fatty acid factory. Fish and other marine oils are hydrogenated and then converted into fatty acids while the use of vegetable oils is confined mainly to soapstock resulting from alkali-refining these oils. Animal fats, which constitute a large portion of the raw materials in the fatty acid industry are divided into four main types: edible tallow, inedible tallow, lard, and inedible grease. By custom, animal fats that are softer, more unsaturated, and have a titer lower than 40.5°C are designated greases if inedible and lard if edible. Animal fats are purchased using well-defined specifications. They constitute a primary source of stearic and oleic acids (22).

The industrial production of fatty acids follows in general the following steps:

1. Hydrolisis of fats, commonly known as "fat-splitting". Fat-splitting is the process of decomposing fats into acids and glycerol by subjecting them to a high temperature and corresponding pressure in the presence of water, or to a relatively lower temperature in the presence of a catalyst. The use of an alkali to saponify the fat and form a soap, followed by decomposition of the soap and liberation of the fatty acids by acidulation with a mineral acid, is termed saponification and was the first splitting process used in the fatty acid industry.
2. Distillation: fatty acids originating from different fat-splitting operations are highly colored and contain a variety of impurities, as well as unhydrolyzed fat. Distillation is the process by which these impurities are largely or totally eliminated.
3. Panning and pressing: this process is used to separate the solid from liquid acids, which differ markedly in melting points and solubility characteristics. Essentially, the process involves the crystallization of the solid acid fraction from a solution of liquid acids, in shallow trays or pans placed in rooms maintained at low temperatures ($\sim 3^{o}C$). The solidified cakes obtained are then subjected to high pressures in order to remove the liquid acids. This method is used principally for the separation of animal fatty acids to commercial stearic acid and commercial oleic acid. Its use in highly industrialized countries is being replaced by solvent-crystallization processes.

4.3 PROPERTIES OF FATTY ACIDS

4.3.A VAPOUR PRESSURE-TEMPERATURE RELATION

Through the application of thermodynamic principles, the vapour pressure-temperature relation can be derived and brought to the form:

$$\mathrm{Ln}\,p = -\lambda_o/(R.T) + 1.75\,\mathrm{Ln}\,T - (\epsilon\,.T)/R + C$$

where p = vapour pressure in mm. of Hg. at any optional absolute temperature T ($^{o}C + 273$);

λ_o = molecular heat of vaporization at absolute zero;

R = gas constant (1.985 cal/^{o}C);

ϵ = the temperature coefficient of the difference between specific heats in the liquid and gaseous states;

C = conventional chemical constant.

The values of λ_o, ϵ and C for lauric, palmitic and stearic acids are presented in Table 7.

Acid	λ_o	ϵ	C	λ_a	l_a, cal/kg.	T_a, K
lauric	23590	0.0349	11.408	13740	68.5	574.6
palmitic	26050	0.0326	11.568	15090	58.5	625.0
stearic	27280	0.0317	11.636	15860	56.0	647.0

Table 7: Calculated constants applicable to vapour pressure equation for higher aliphatic acids.

The results obtained using this equation have been found quite similar to results obtained by experimental procedures, as shown in Table 8.

Acid	Temperature, K	Vapour pressure, mm Hg.	
		Calculated	Experimental
lauric	484	55	50
	472	32	35
	465	27	27
	462	23	24
	451	14.4	13.2
palmitic	498	19.1	22.1
	493	15.8	15.7
	488	13.0	15.0
stearic	505	8.7	15.0

Table 8: Vapour pressure at different temperatures for several fatty acids according to Lederer (23).

Heat of Vaporization

The heat of vaporization at any absolute temperature T can be approximated by the equation:

$$\lambda = (\lambda_o + 1.75\,R.T. - \epsilon T^2)(1 - p/p_o). \quad (13)$$

where p_o = critical pressure, which lies between 30 and 40 atm. for the higher fatty acids.

In addition to the values of λ_o, ϵ and C, Table 7 contains values for the heats of evaporation at atmospheric pressure, λ_a, the heats of vaporization l_a of the fatty acids at atmospheric pressure in cal/Kg, and the absolute boiling points of the fatty acids at atmospheric pressure, T_a.

4.3.B DENSITY, MOLAR VOLUME AND DILATION

The molar volume, defined as the volume occupied by 1 mole of a substance, is calculated by dividing the molecular weight of a substance by its density. Table 9 lists experimental and calculated values of the molar volume, V_m, for 3 saturated fatty acids.

Acid	Density, Kg/m^3.	Molar volume, Vm, at 80°C, cm^3.	
		Experimental	Calculated
lauric	883	236.29	235.88
palmitic	853	304.56	304.88
stearic	847	338.85	339.38

Table 9: Densities and molar volumes of 3 fatty acids as liquids

The expansibilities and melting dilations of lauric, palmitic and stearic acids are also presented in Table 10 (24, 25).

Acid	Expansibility ml/g/°C.		Melting dilation			
			observed		calculated	
	solid	liquid	ml/mg	ml/mole	ml/mg	ml/mole
lauric	-	-	0.143	28.6	-	-
palmitic	0.00028	0.00097	0.181	46.4	0.182	46.7
stearic	0.00026	0.00097	0.186	52.9	0.186	52.9

Table 10: Expansibilities and melting dilations of 3 fatty acids

4.3.C SURFACE TENSION

Between particles of a liquid, as in solids, there are attractive forces which keep the liquid together, and these forces must be overcome by external forces if the particles are to be separated. These forces are molecular in nature and are exerted over only very short distances. The evaporation of a liquid entails overcoming these molecular attractive forces and the heat required for evaporation is a measure of the strength of the force. Table 11 represents the surface tension of Palmitic and Stearic acids at different temperatures (26).

Temperature, C	Surface tension, dynes/cm	
	palmitic acid	stearic acid
70	28.2	28.9
80	27.5	28.6
90	26.7	27.5
100	26.1	26.7
120	24.5	25.1
140	22.9	23.8

Table 11: Surface tension of palmitic and stearic acids

4.3.D THERMAL PROPERTIES

A. Melting, freezing and heat of fusion

Despite modern techniques of chromatography, melting point, or the related freezing point, is still a principal means of identifying, characterizing, and indicating the degree of purity of fatty compounds. Table 12 presents the melting and freezing points as well as the heats of transition of lauric, palmitic and stearic acids.

Acid	M.p., C	Freezing point, C	Heat of fusion Kcal/mole (J/g)
lauric	44.2	43.8	8.75(182.9)
palmitic	62.9	62.4	13.0(212.3)
stearic	69.6	69.4	16.36(240.8)

Table 12: Melting, freezing points and heat of fusion of 3 fatty acids (13, 25)

B. Specific heats

Roughly speaking, specific heats are greater where the structural order is less, where the molecular freedom is greater; hence they are normally greater for liquids than for solids. If, however, a rise in temperature involves a more than normal increase in freedom, specific heats may be abnormally large. Thus, for long-chain compounds some solids have greater specific heats than liquids.

* specific heats of liquids:

The specific heats of most liquid long-chain compounds at normal temperatures (25^{o} - 100^{o}C) are about 0.5 cal/g.°C. Singleton et al. (25, 27) reported that for:

Palmitic acid, $Cp\ (t = 63^{o}\ \text{to}\ 92^{o}C) = 0.4624 + 0.00175t$;

Stearic acid, $Cp\ (t = 70^{o}\ \text{to}\ 78^{o}C) = 0.4266 + 0.0018t$.

The value for lauric acid was found to change from 0.513 to 0.776 in going from 50^{o} to 250^{o}C (28).

* specific heats of solids:

For solid fatty acids, specific heats are mostly in the range 0.45 - 0.50 cal/g.°C. Singleton et al. (25, 27) found that for:

Palmitic acid, $Cp\ (t = -73^{o}\ \text{to}\ 40^{o}C) = 0.3831 + 0.0013t$

Stearic acid, $Cp\ (t = -120^{o}\ \text{to}\ 65^{o}C) = 0.4272 + 0.0018t$

All the values of the specific heats given above are in cal/g.°C.

PART II

CHAPTER 5: EXPERIMENTAL RESEARCH

5.1 GENERAL

Building components containing phase-change materials can be used either as solar heat storages or as physical temperature regulators. These can be distributed as passive storages throughout industrial and office buildings to absorb excessive internal heat gains and reduce cooling costs. They can also be used in Trombe walls to limit the rise of wall temperatures to a few degrees, thus controlling overheating during the day and reducing night-time heat losses.

Experimental modules containing phase-change materials have presented several problems. The epoxy seal on Thermocrete, for example, failed during aging tests and allowed phase-change material leakage (50). Also, in another experiment involving the encapsulation of $CaCl_2.6H_2O$ in concrete, the major problem has been that the addition of the heat storage material inhibits bonding between concrete and the aggregate (51).

5.2 MATERIAL SELECTION

In this experiment, we chose a block made from cement rather than concrete, with a fatty acid phase-change filler material. Fatty acids were chosen for three main reasons:

i- the phase-change melting point can be tailored to the specific application, anywhere in the range of -5°C to 70°C, by changing the components or their amounts in a mixture of fatty acids or their esters;

ii- for most of the mixtures tried, the surface tension of the fatty acid mixture, when liquid, was high enough and the cement pores were small enough that no liquid exuded from the pores. Thus, no plastic cover is required. Since no waters of crystallization are involved in the phase-change material, and the fatty acids are virtually insoluble in water (section 4.1), moisture has no effect on the heat storage modules, except in curing the cement;

iii- this type of module can be made in two steps (mixing and curing), rather than the five steps required for modules like Thermocrete (mixing, foaming, curing, filling, and surface sealing), which should lead to lower fabrication costs and faster scaling up to mass production.

For budgetary reasons, a particular commercial mixture, EMERY E400*, was chosen for the many samples used in the various tests. EMERY E400 is a pressed stearic acid containing over 60% pure stearic acid. The second major component is palmitic acid. This product also contains minor quantities of unsaturated acids (oleic and linoleic). Its melting point was found to be 56.5°C and its heat of fusion 144 J/g. There is very little difference in chemical properties between one saturated fatty acid and another, so most of the results can be considered representative for the whole group. The melting and freezing curves for EMERY E400 are shown in figures 2, 3 and 4.

Two types of cement were used. Type 10 (referred to as type I in ASTM**) is the most commonly used portland cement in the construction industry, while type 30 (ASTM type III), known as high early strength cement, is used when a higher strength in the early days of curing is required. Both types are produced by MIRON Inc., Montreal.

* Product of Emery Industries Ltd., Toronto, Ontario, Canada.

** American Standards for Testing Materials.

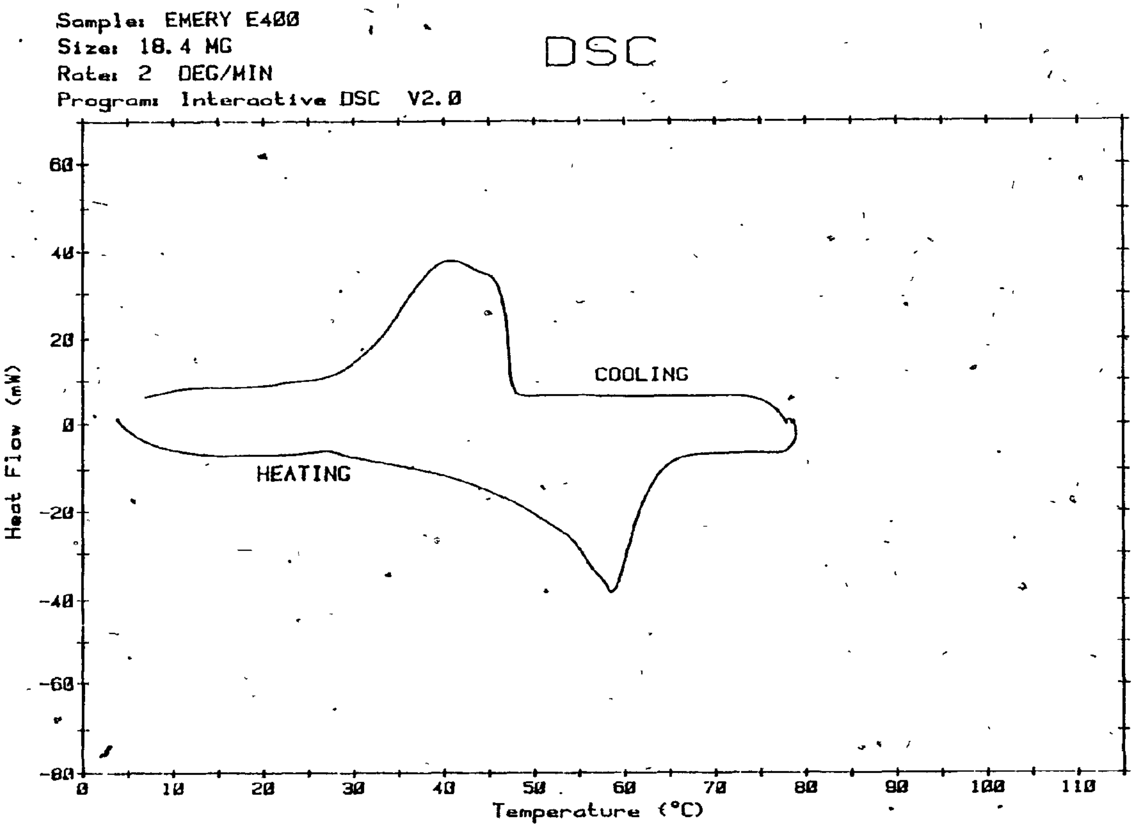

Figure 2: The heating/cooling thermogram of EMERY E400

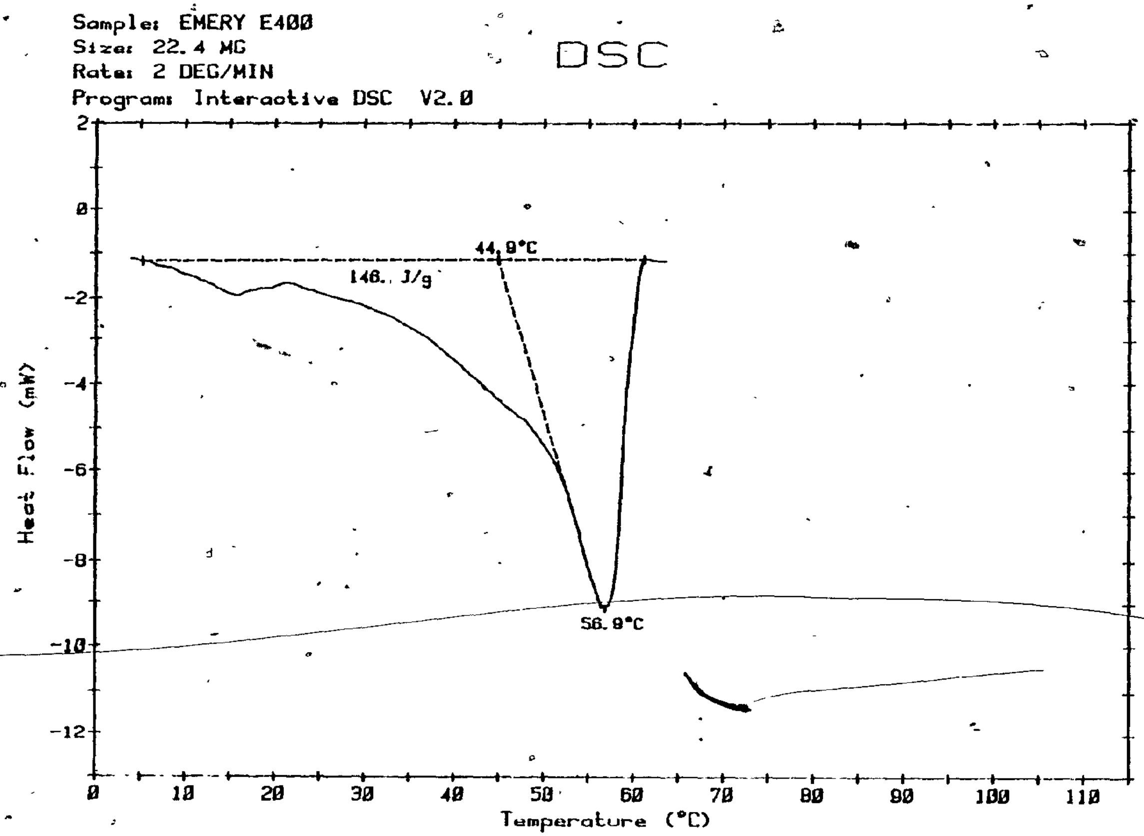

Figure 3: the endothermic peak representing the solid-to-liquid transition of EMERY E400

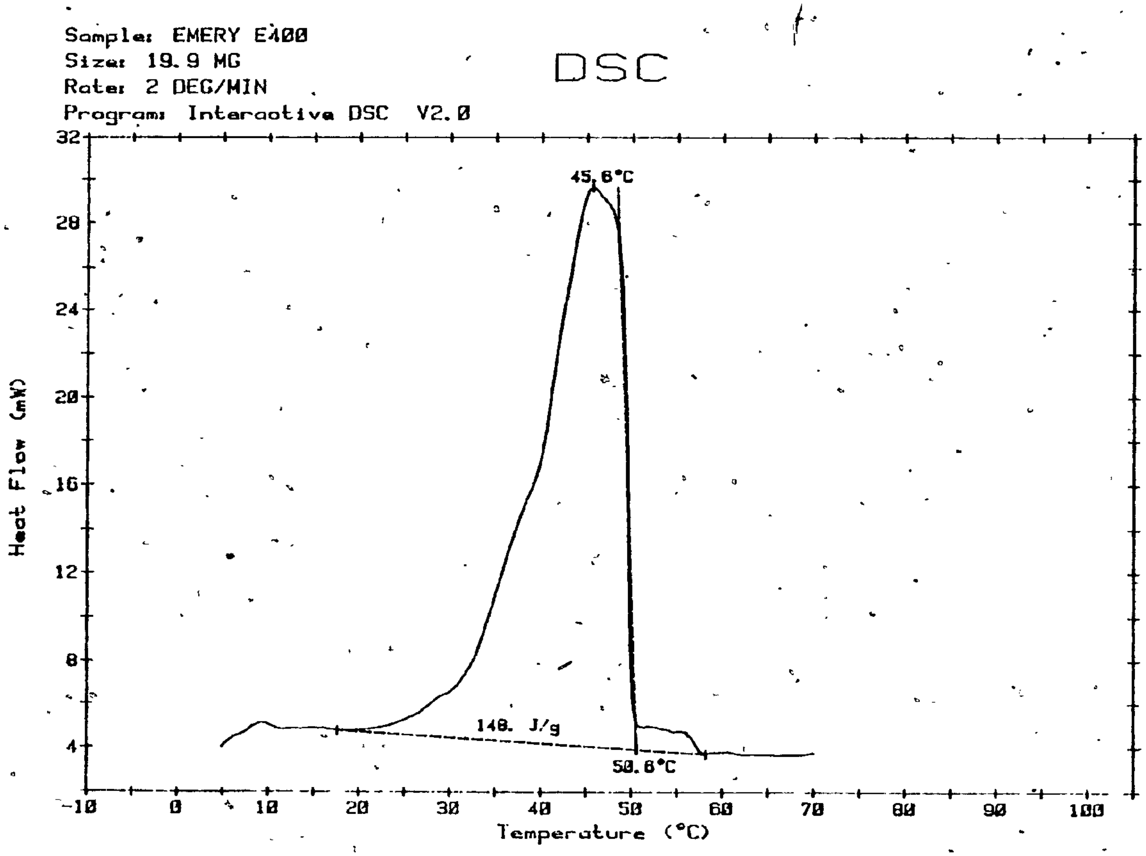

Figure 4: the exothermic peak representing the liquid-to-solid transition of EMERY E400

EMERY E400 costs 1.23 can$/kg. if ordered in large quantities (larger than 20 metric tons). 1 Kg of cement costs 0.095 can$ for type 10 and 0.105 can$ for type 30.

5.3 SCOPE OF THE EXPERIMENT

There is practically no limit on the number of experiments required to fully study and understand the properties and behavior of a new material. It is then necessary to clearly define and limit the scope of the experimental work and this can be achieved in two steps. First, the objectives of the experiment should be stated. These objectives define which material properties are important and which can be ignored. Second, restraints of many kinds can also limit the experimental work. These are generally time and the availability of test equipment.

Most of the tests and experiments that were performed to obtain the physical, mechanical, and thermal properties of the new thermal storage module were done at the Materials Laboratory, at the Centre for Building Studies*.

5.3.A OBJECTIVES AND TEST PROGRAM

In this case, it was easy to define the objectives of the experiment due to the nature and intended use of the tested material. These were to obtain and study the mechanical, physical, and thermal properties necessary to provide enough information on the possibility of use of these modules in latent heat storage. In order to meet these objectives, the following tests were done:

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* Concordia University, Montreal, Quebec, Canada

i- mechanical properties;

- using either regular (type 10) or high early strength (type 30) cement, find the cement/EMERY E400/water(C/F.A./W) ratio that gives the best compressive strength for the heat storing blocks with a worthwhile amount of fatty acid content;
- investigate the improvement in compressive strength achieved by such additives as glass fibres of different lengths and fly ash;
- find the tensile strength of the strongest mixture;
- determine the variation in compressive strength with temperature and test for leakage of liquid fatty acid at high temperatures;
- determine the effects of freeze-thaw cycling on the modulus of elasticity and check for durability under different temperature-cycling modes;

ii- physical properties;

- obtain the specific gravity, absorption and porosity of the mixture;
- determine its drying shrinkage;

iii- Thermal properties;

- check for the stability of the melting point and heat of fusion of the fatty acid used in the mixtures;
- obtain the specific heats, in solid and liquid forms, of EMERY E400 and two other commercial stearic acids;
- compare the thermal conductivities of the mixtures to those of EMERY E400 and dried hydrated cement;

iv- study the interaction between the cement matrix and the fatty acid filler, using infrared spectrometry.

5.4 EXPERIMENTAL PROCEDURE

5.4.A. PREPARATION OF SAMPLES

In accordance with ASTM C305-80 (Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency), the cement paste was mixed with either stearic acid or sand in a blender for eight minutes. For the reference cement mortar, a graded Ottawa standard sand, as defined in ASTM C109-80 (Compressive Strength of Hydraulic Cement Mortars Using 50-mm Cube Specimens), was used. It is a natural silica sand from Ottawa, Illinois, with a specific grading between no. 100 (150 μm) and no. 16 (1.18mm) sieves. The mixture was then poured into 5-cm cube molds, 7.62 x 7.62 x 36.10-cm molds, "dog bone" shaped molds (called briquettes), and into 20.32 cm (diam.) x 2.54 cm (height) disc molds. The mixture was cured in the molds for 24 hours in the humidity chamber at 23-24°C. By then, the surfaces were strong enough for handling and the samples were released from the molds and cured in lime-saturated water for periods ranging up to 27 days, according to ASTM C109-80.

5.4.B. TESTING EQUIPMENT AND PROCEDURES

5.4.B.1. Mechanical and Physical Properties

The 5-cm cube samples were tested to destruction for compressive strength in an INSTRON Model 1125 mechanical tester (Figure 5). As a set of 24 cubic samples made from the same mixture were being cured, three to six at a time were removed for compression testing. The range of mixtures with EMERY E400 tested for compressive strength was from C/F.A./W = 1/0.8/0.60 to 1/1.0/0.70 (ratios are in weight). Increasing the amount of fatty acid to more than the weight of cement in the mixture

Figure 5: the INSTRON Model 1125 mechanical tester

produced extremely weak modules. The water content was chosen for best workability. Two mixtures (C/F.A./W = 1/0.8/0.65 and 1/0.9/0.65) close to the maximum compressive strength found in this range were chosen for further tests.

To test for freeze-thaw spalling and bulk damage, two sets of three parallelepiped samples (7.62 x 7.62 x 36.10 cm) for each of the chosen pair of mixtures were cycled between 6°C and -5°C under a plastic covering, in an environmental chamber (Model C608, produced by Controlled Environments Ltd.). The cycle period was three hours and up to 200 cycles were used. A non-destructive acoustic test procedure was adapted. Using a SOILTEST Model CT-366C sonometer (Figure 6), the longitudinal resonance frequency was measured after every 15 cycles in temperature. The dynamic modulus of elasticity was calculated, according to ASTM C215-60 (Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens), using the following equation:

$$\text{Dynamic } E = D.W. \ (n)^2 \text{ , in Mpa}$$

where W = weight of specimen, Kg;

n = fundamental longitudinal frequency, Hz;

$D = 3.996 \cdot x\ 10^{-4} \ \frac{L}{b.t}$, S^2/cm^2;

L = length of specimen, cm;

t, b = dimensions of cross-section of specimen, cm.

This equation is slightly different from that given in ASTM. It has been modified to give the value of the dynamic modulus of elasticity in MPa instead of psi.

Three parallelepiped samples were also tested for freeze-thaw resistance in accordance with ASTM C666-73 (Resistance of Concrete to Rapid Freezing and Thawing). This test consists of immersing the samples in

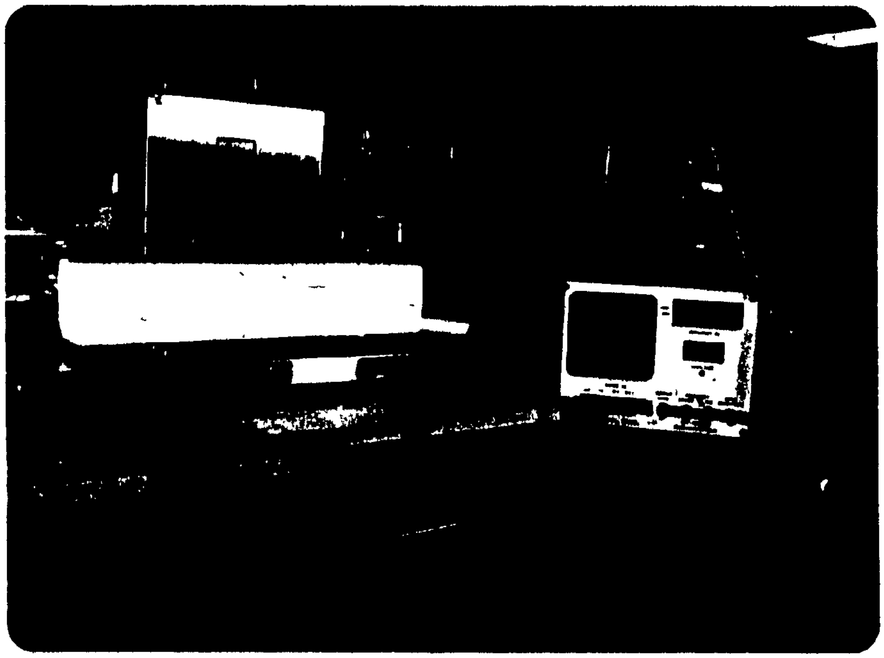

Figure 6: the SOILTEST Model CT-366C sonometer

water subjected to freezing and thawing (between -10°C and 10°C), in a SOILTEST Model CT-110 freeze-thaw tester, and then checking for the dynamic modulus of elasticity on the sonometer.

Four 5-cm cube samples were subjected to 80 thermal cycles (6-hour cycles between -30°C and 35°C) under an ultra-violet light source (wavelength = 254 nm) to check for possible damage under severe conditions.

Three briquettes ("dog bone" shaped specimens) of C/F.A./W = 1/0.8/0.65 were tested to destruction for tensile strength after 28 days of curing, in accordance with ASTM C190-72 (Tensile Strength of Hydraulic Cement Mortars).

Six 5-cm cube samples made from a C/F.A./W = 1/0.8/0.70 mixture were tested to destruction for compressive strength while being heated in the INSTRON oven, at 15°C intervals, between 25° and 100°C. The temperature was raised at a rate of 0.5°C/min to ensure uniform temperature distribution in the samples.

48 samples (C/F.A./W = 1/0.8/0.65) containing glass fibres and 30 samples of the same mixture containing different percentages of fly ash were also tested to destruction for compressive strength. A.J. Franklin (52) recommends a concentration of 2.2 g. of fibres/Kg. of cement upwards, with a preferred length of 3.2 mm to 28.6 mm, to improve the characteristics of mortar mixes during the critical stage of setting. Based on these recommendations, we used glass fibres 0.5, 1, 2 and 3 cm long in two different concentrations: 4g and 8g/Kg of cement. Also, fly ash was used to substitute cement in the mixture in amounts equal to 5, 10, 15, 20 and 25% of the weight of the initial portion of cement.

Two 5 cm cube samples of mixtures C/F.A./W = 1/0.8/0.65 and 1/0.9/0.65 were tested for specific gravity, absorption and porosity by weighing the samples when dry, after immersion, and after boiling, on a SARTORIUS model 2472 microbalance. The test procedure followed the steps described in ASTM C642-75 (Specific Gravity, Absorption, and Voids in Hardened Concrete). In addition, two 5 cm cube samples from a 1/0.8/0.65 mixture were kept on a blotting paper in a drying oven at 105°C. for 48 hours, to determine if the fatty acid would leak from such modules when liquid. Two 2.54 x 2.54 x 20.32 cm parallelepiped samples made from the same mixture were dried in air at an average temperature of 23°C for up to 25 days. The drying shrinkage of these samples was measured with a SOILTEST model CT-171 length comparator, following the procedure of ASTM C596-75 (Drying Shrinkage of Mortar Containing Portland Cement).

5.4.B.2 THERMAL PROPERTIES AND INFRARED STUDY

A DuPont 1090 thermal analyzer system was used to obtain most of the thermal properties. . The system was linked to a DuPont 910 differential scanning calorimeter (DSC) (Figure 7). Differential scanning calorimetry is the most widely used of all thermoanalytical techniques. Among others, the DSC can be used to study boiling points, melting points, liquid crystal transitions, heats of reaction, specific heat capacity, purity, glass transitions and reaction kinetics.

Generally, the samples used with this module weigh only a few milligrams (up to about 30 mg.) and are placed in aluminum or copper pans which can either be crimped or left open. The samples are generally heated in air, at rates ranging from 1°C/min. to 20°C/min.

The thermograms obtained can present a glass transition point, an endothermic peak, or an exothermic peak, represented respectively by points A, B and C in Figure 8.

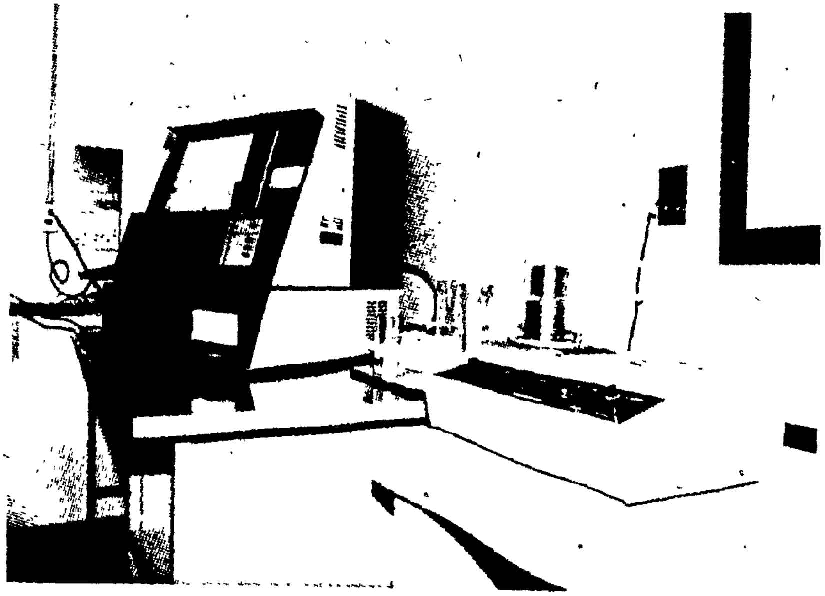

Figure 7: The DuPont 1090 thermal analyzer (back) and the DuPont 910 differential scanning calorimeter (front)

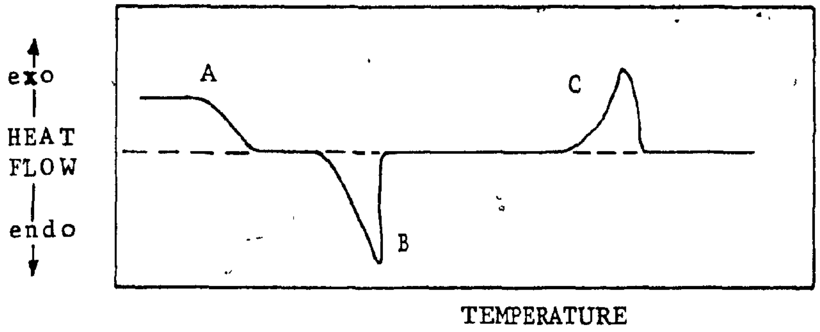

Figure 8: A thermogram showing the possible thermal responses

Generally, high rates of heating may coalesce two peaks occurring adjacent to each other. Ramachandran (53) recommends a rate of heating of 10 ± 1°C/min. for clay mineral studies. According to Mackenzie and Mitchell (54), a heating rate of 8–12°C/min. is appropriate for normal work. Pope and Judd (55) also agree on a heating rate of 10°C/min for most applications since it offers the best compromise between quality of resolution and time taken per experiment. For accurate temperature measurements, however, they recommend the lower heating rate of 2°C/min. In our research, slower heating rates were used where deemed necessary to clearly separate adjacent peaks and higher rates when no such accuracy was required.

Disc samples (20.32 cm diam. x 2.54 cm height) of EMERY E400, hydrated cement and C/F.A./W mixtures 1/0.8/0.65, 1/0.9/0.65 and 1/1/0.65 were tested on a DYNATECH model TCFGM-N4 Thermal Conductivity Instrument (Figure 9). In order to remove the hygroscopic moisture, the C/F.A./W and hydrated cement samples were dried for 48 hours in the oven at 105°C and cooled in dessicators for at least 24 hours before the test was done. The procedure used to measure the thermal conductivity (ASTM C177-76: Steady-State Thermal Transmission Properties by Means of the Guarded Hot Plate) consists of heating two disc samples of the same mixture, one on

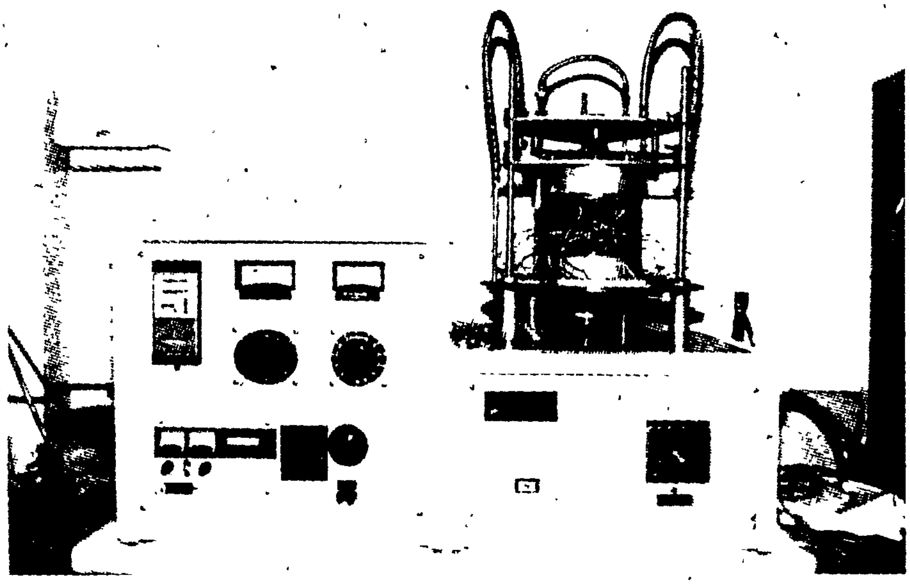

Figure 9: the DYNATECH Model TCFGM-N4 thermal conductivity instrument

top of and the other below a heating plate, on one side while cooling the other side. When both the hot and cold faces reach equilibrium, i.e. the hot and cold temperatures become constant, the thermal conductivity is then calculated using a simple equation involving the current and voltage supplied to the heating plate, the hot and cold temperatures, and the area of the heater (Refer to section 7.2.C). In these tests, the hot temperature was kept low enough to get average temperatures of the samples in the range 25° - 35°C.

To study the interaction between the cement and the fatty acid used, infrared spectrometry was used. IR spectra for the EMERY E400, stearic acid U.S.P., cement powder, hydrated cement and three C/F.A./W mixtures were obtained using a Perkin Elmer Model 599B IR spectrometer. The samples were prepared according to the pressed-disk method. This involves suspending the samples in a suitable matrix, dry potassium bromide (KBr) in this case, by mixing the ground samples with KBr and compressing the mixture in an appropriate die using a hydraulic press.

CHAPTER 6: MECHANICAL AND PHYSICAL PROPERTIES

6.1 COMPRESSIVE AND TENSILE STRENGTHS

Using type 10 cement, 7 mixtures between C/F.A./W = 1/0.8/0.6 and 1/1/0.7 were tested for compressive strength. The results, presented in figures 10, 11 and 12, show that mixture C/F.A./W = 1/0.8/0.65 has the highest compressive strength, 2.187 MPa, after 28 days of curing. This mixture contains 38% more water per unit mass than that required for maximum strength in a cement mortar (56). The tensile strength of the same mixture was found to be 0.442 MPa after 28 days of curing. The cement mortar composition (cement/sand/water = 1/2.75/0.485 in weight) was in accordance with ASTM C109-75 and the water/cement ratio (W/C = 0.35) of the hydrated cement was chosen after the recommendations of P. Maslow (56).

As expected, the compressive strength of the C/F.A./W mixtures was found to be less than the measured compressive strengths of the cement mortar and the hydrated cement (Figure 13). The use of type 30 cement increased the compressive strength of the cement mortar along after 28 days of curing by about 17%, a value higher than the 10% mentioned by Maslow (56), while the compressive strength of C/F.A./W = 1/0.8/0.65 doubled, after the same curing period, to reach 4.4 MPa (Figure 14). This strength is comparable to that of lightweight aggregate concrete, to Siporex, and to lightweight clay bricks (57, 58, 59).

The addition of glass fibres to the same C/F.A./W mixture, made with cement type 10, gave only a small improvement (~15%) in compressive strength after 28 days of curing (Figure 15). The best results were obtained with 2-cm long fibres. Doubling the concentration from 4g to 8g

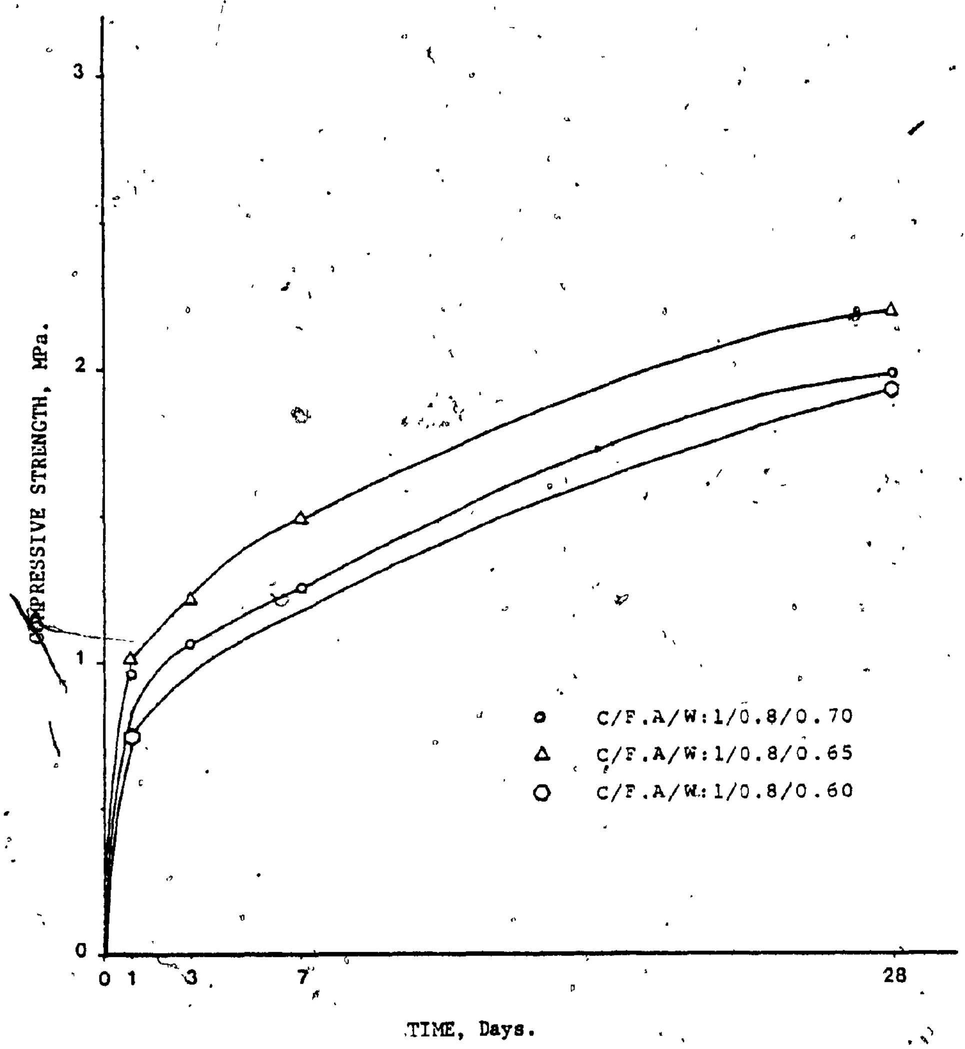

Figure 10: Compressive strength of three C/F.A./W mixtures (fatty acid/type 10 cement ratio = 0.8)

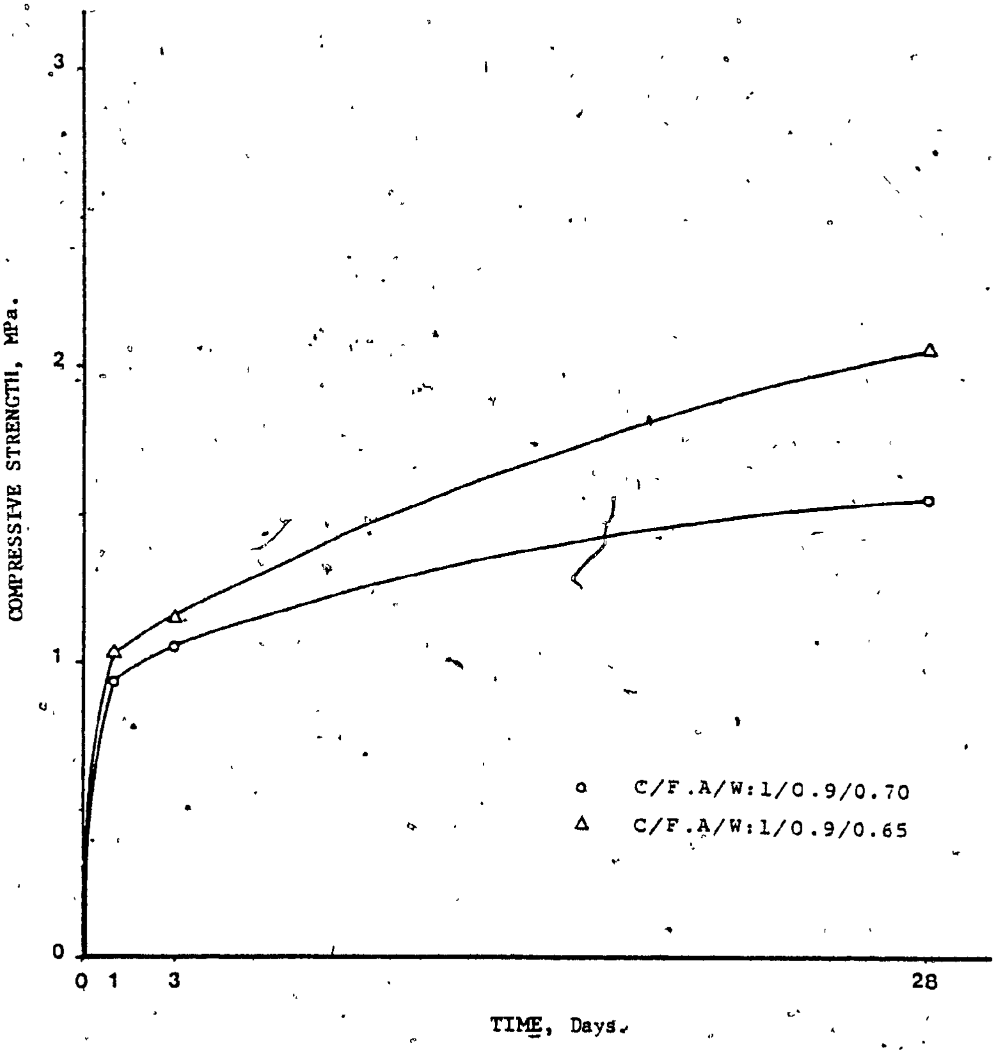

Figure 11: Compressive strength of two C/F.A./W mixtures (fatty acid/type 10 cement ratio = 0.9)

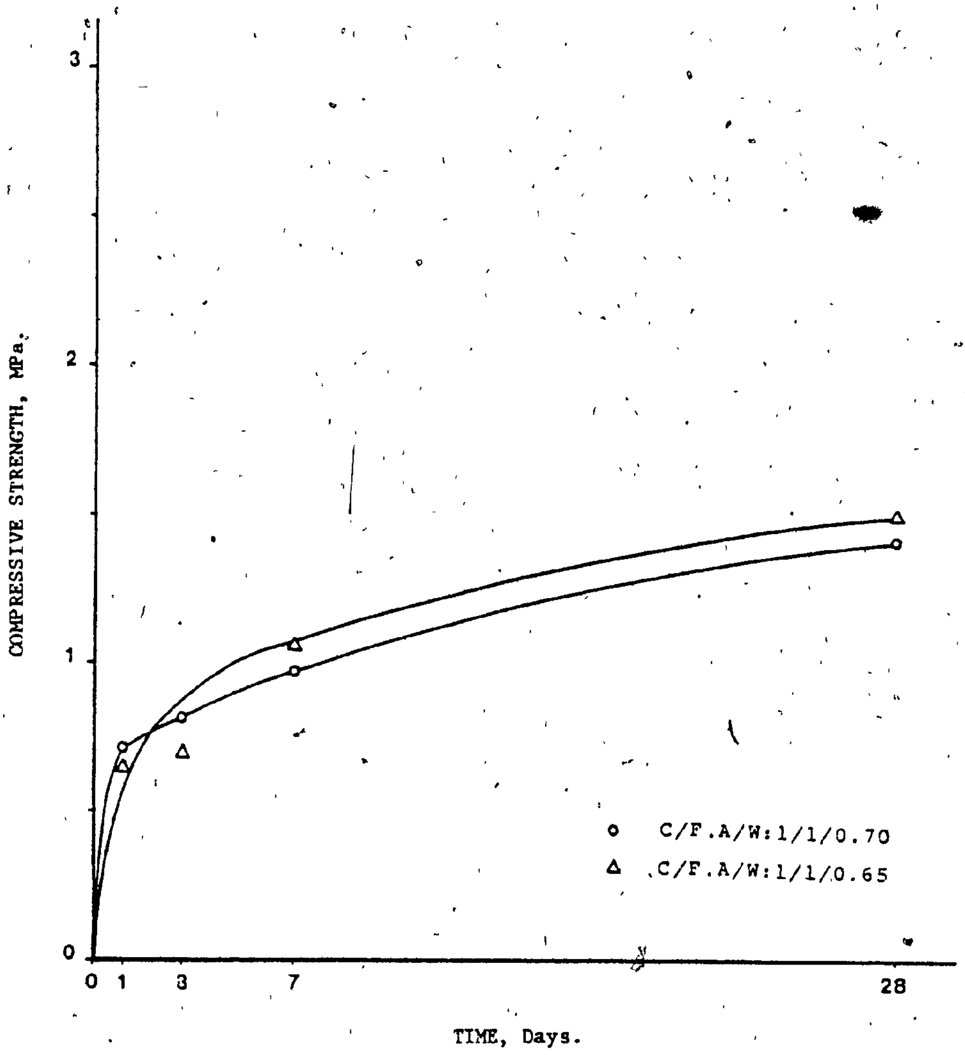

Figure 12: Compressive strength of two C/F.A./W mixtures (fatty acid/type 10 cement ratio = 1.0)

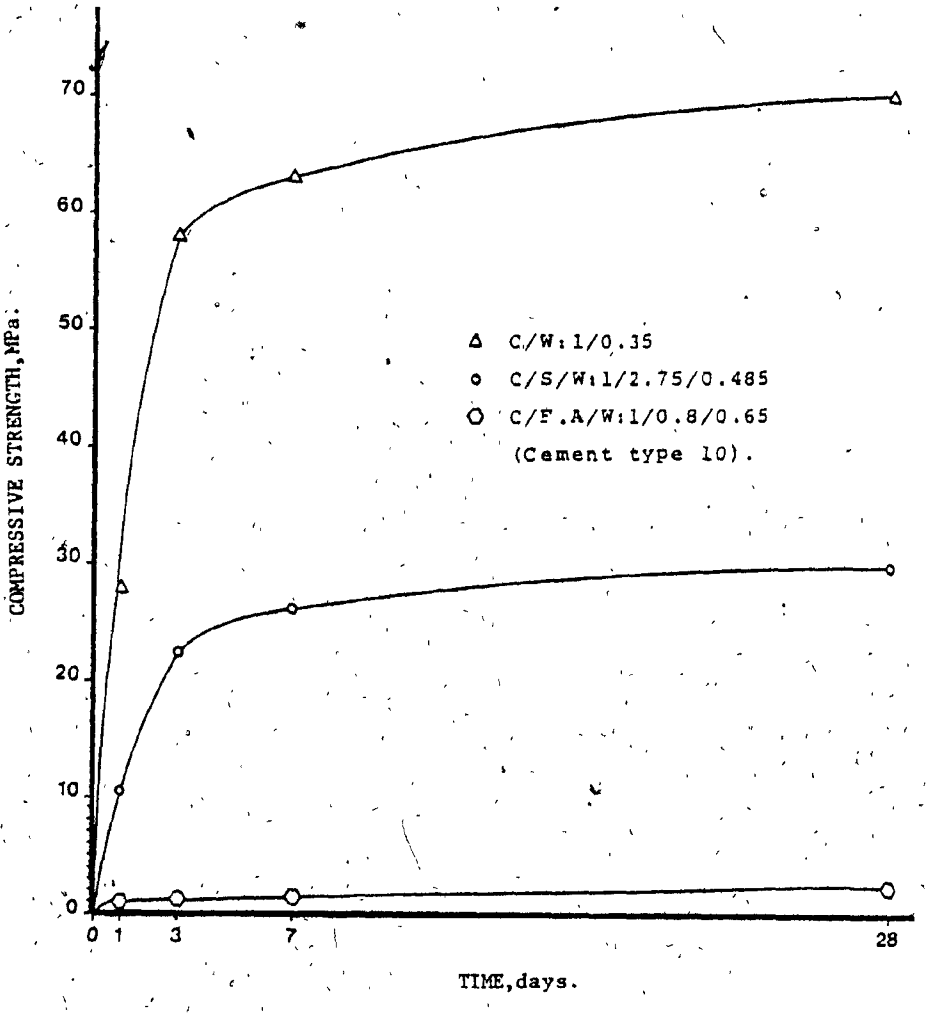

Figure 13: Compressive strength of C/F.A./W = 1/0.8/0.65, compared to the strengths of cement mortar and hydrated cement.

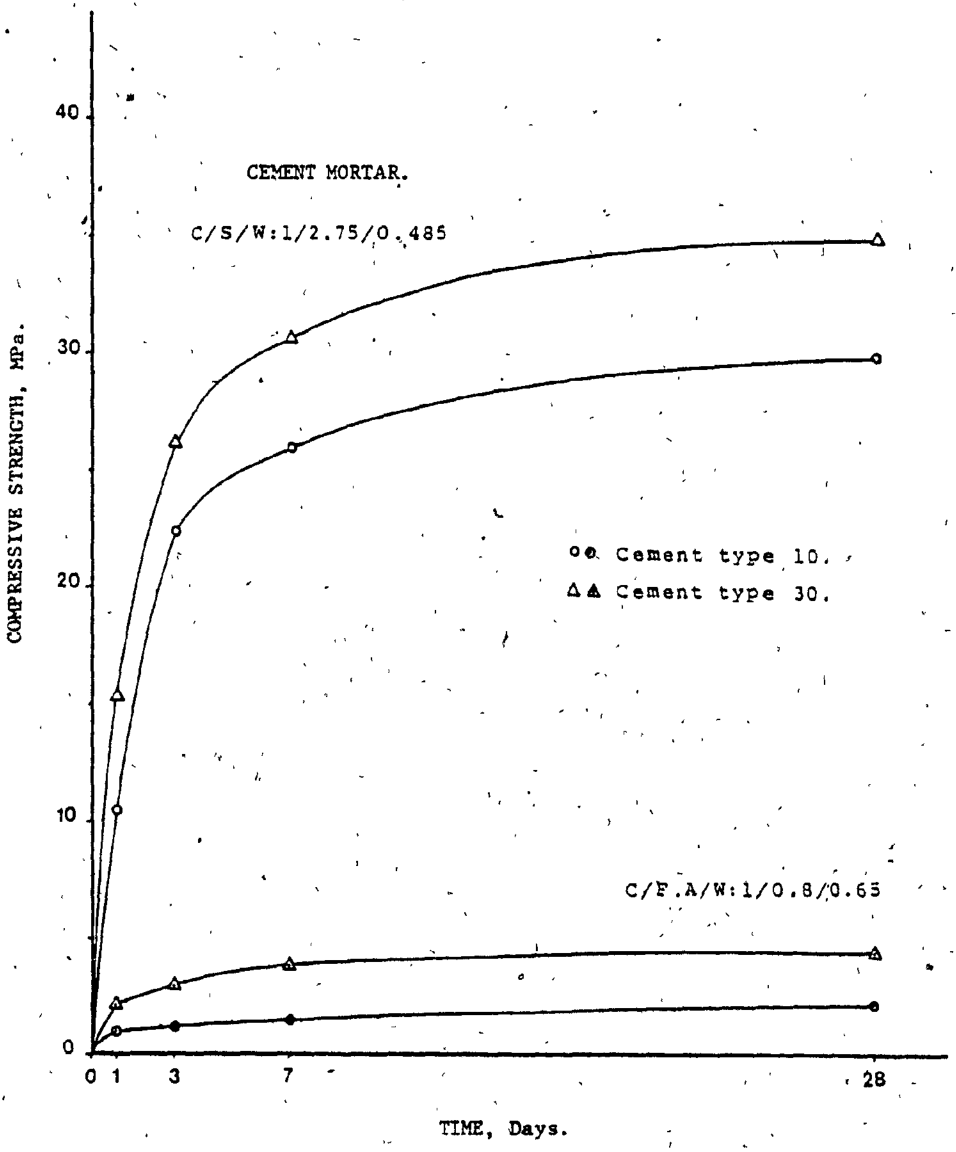

Figure 14: The improvement in compressive strengths of cement mortar and C/F.A./W= 1/0.8/0.65 caused by the use of high early strength cement (type 30).

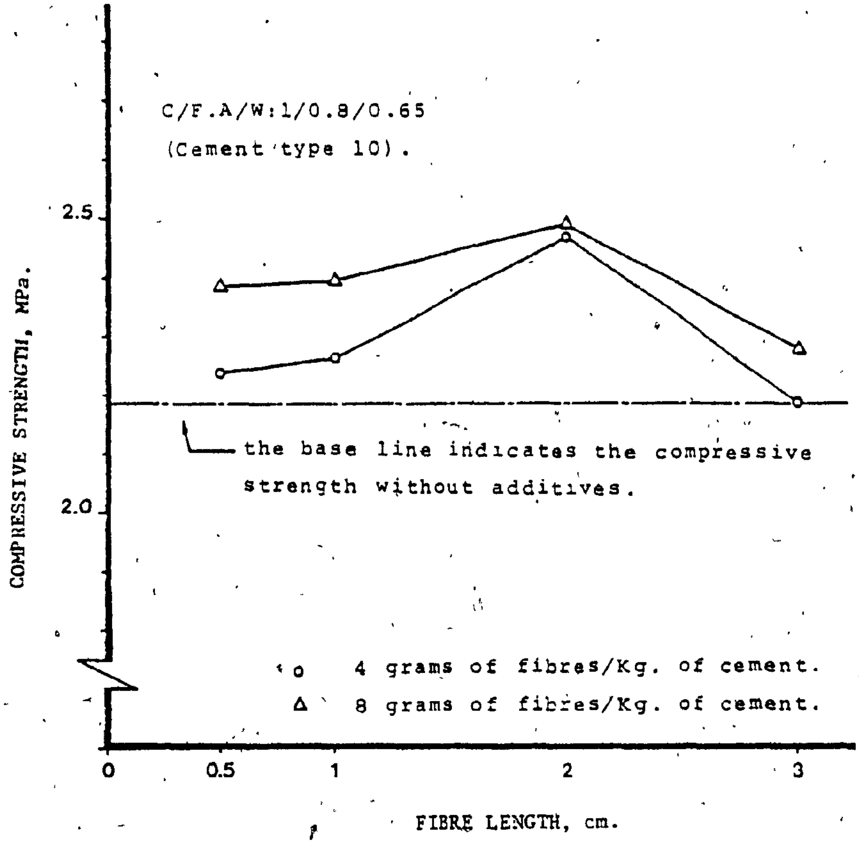

Figure 15: Compressive strength of C/F.A./W = 1/0.8/0.65, with two different concentrations of glass fibres of various lengths, measured after a 28-day curing period in lime-saturated water

of fibres per Kg of cement made virtually no difference to the compressive strength.

Replacing a portion of the cement by fly ash in the composition of the mixture caused a 25% increase in compressive strength after 28 days of curing, when the portion replaced was equal to 20% of the weight of the cement. The tensile strength, on the other hand, increased by only 3%. As reported by Kovacs (60), the addition of fly ash reduces the initial strength of the cement. The difference between strengths of plain portland cement and fly ash cement gradually disappears with advancing time of hardening and the strength of the latter eventually exceeds that of portland cement.

As expected, the compressive strength of the cured sample decreased linearly with increasing temperature (Figure 16), at a rate of 15 KPa/°C. At 100°C, the compressive strength was less than half of its value at 25°C. Also, no seepage of the liquid fatty acid onto the surface was observed for any of these samples, or for the two samples kept at 105°C for 48 hours in the oven.

In addition, an experimental error, causing the lime-saturated water in which a few test specimens were being cured to reach a temperature of over 50°C for about 8 hours, yielded interesting results. The specimens (3 days old) swelled and cracked, while their porosity increased and their strength decreased drastically. The cubes and briquettes were easily crushed by hand (Figure 17).

6.2 PHYSICAL PROPERTIES

The mixture of cement and fatty acid produced a lightweight material which, after drying and immersion, remained floating in a water bowl. Only

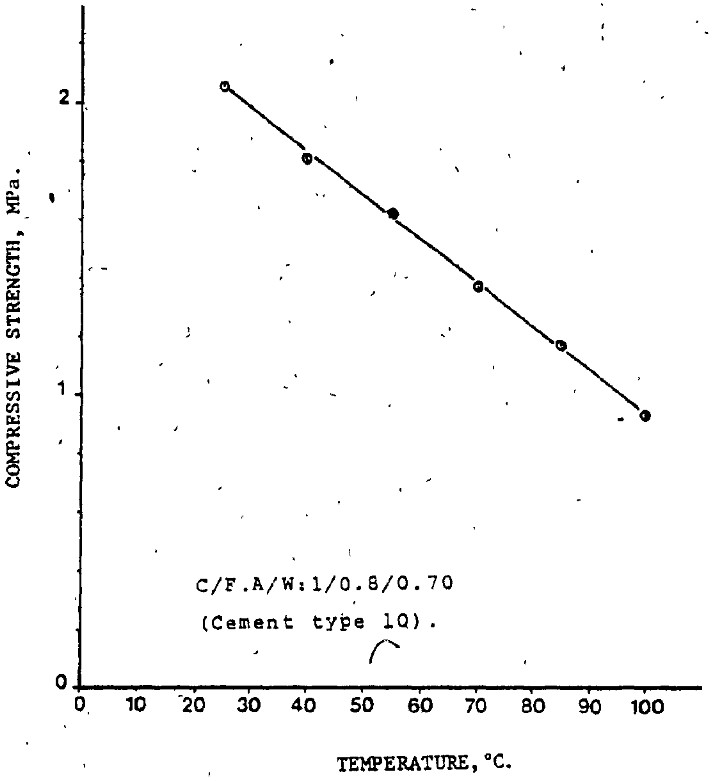

Figure 16: The variation in compressive strength of C/F.A./W = 1/0.8/0.70 with temperature.

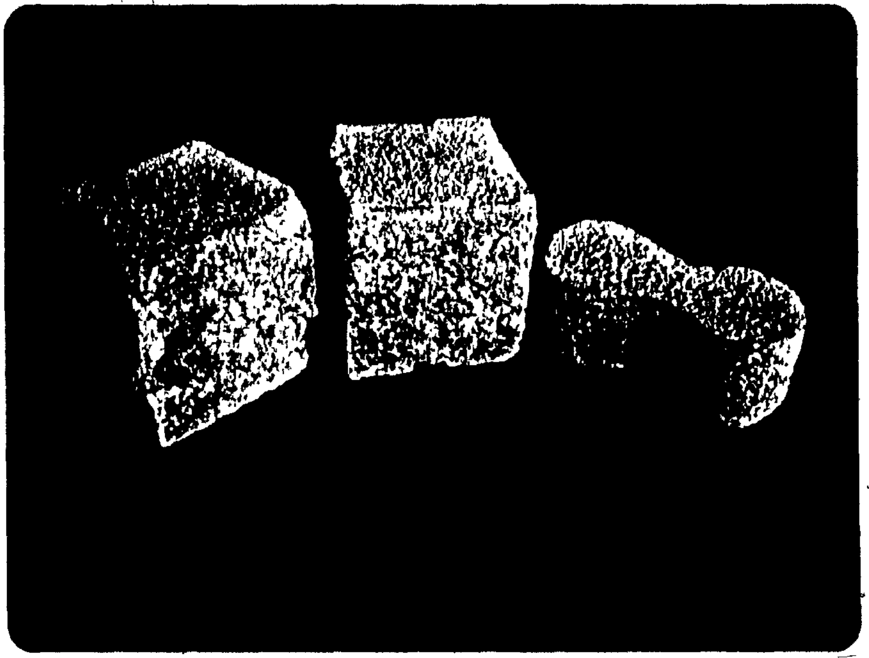

Figure 17: 3-day old C/F.A./W samples showing cracks and deformation after being submerged in water at 50°C for 8 hours

after boiling for 5 hours did the specimens settle below the water level. The values of the specific gravity and the porosity presented in table 13 show that the samples tested have a high degree of porosity (about 40%). A section through one of the samples shows a multitude of little hollow spheres (average diameter = 0.4 mm). These could have been formed by the lining of the inside of the pores with fatty acid material, due to surface tension forces between the fatty acid and the cement mixture. (Figure 18).

	C/F.A./W = 1/0.8/0.65 (volume 125 cm^3)	C/F.A./W = 1/0.9/0.65 (volume 125 cm^3)
oven dry weight, after 48 hours at 105°C, g.	121.0	122.1
saturated weight after immersion for over 2 weeks in water, g.	131.2	133.1
saturated weight after immersion in boiling water for 5 hours, g	177.0	183.5
apparent weight in water, after immersion and boiling, g.	35.9	38.9
absorption, during immersion, %	8.4	9.0
absorption, during immersion and boiling, %	46.3	50.3
bulk specific gravity (dry)	0.86	0.84
bulk specific gravity after immersion	0.93	0.92
bulk specific gravity after immersion and boiling	1.25	1.27
apparent specific gravity	1.42	1.46
volume of permeable pore space (voids), measured after immersion and boiling,%	39.7	42.4

TABLE 13: Results of the specific gravity, absorption, and porosity tests

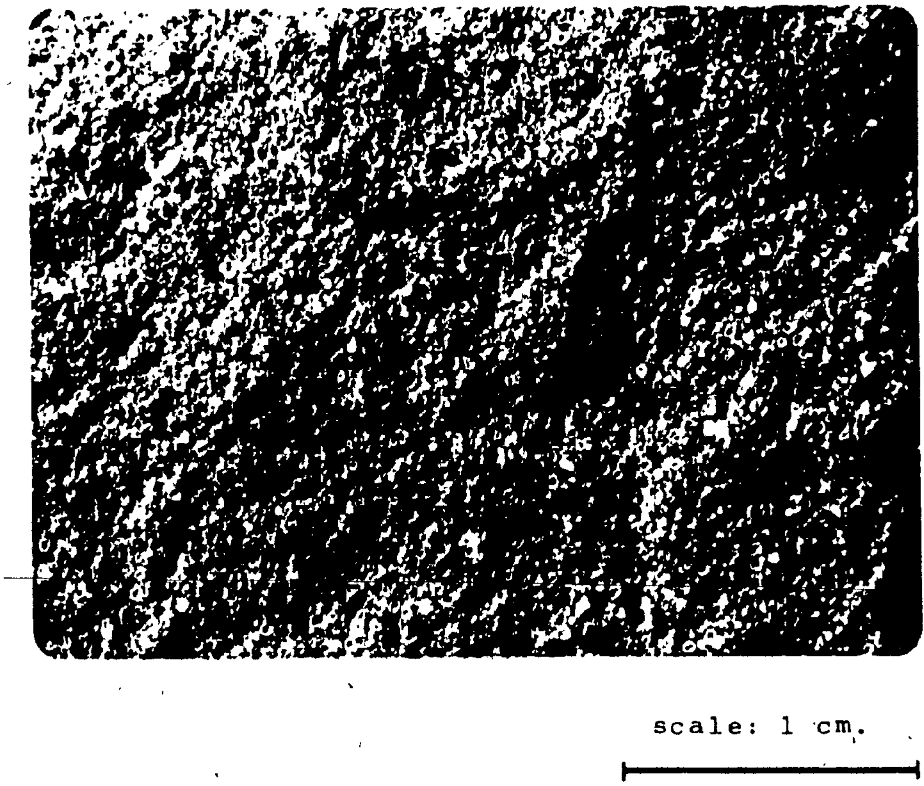

Figure 18: section through a cured C/F.A./W sample showing a large number of little hollow spheres

As shown in Figure 19, the drying shrinkage of mixture C/F.A./W = 1/0.8/0.65 is essentially complete in two weeks. The maximum observed, 0.335%, corresponds to about 1 mm shrinkage in a 30-cm block. This value is about 50% larger than the drying shrinkage of plain cement mortar (0.21% after 28 days) (56).

6.3 DURABILITY

No discernable decrease was found in the dynamic modulus of elasticity during temperature cycling between -5°C and 6°C for mixtures C/F.A./W = 1/0.8/0.65 and 1/0.9/0.65 after 200 cycles (Figure 20). However, the samples with more fatty acid showed signs of incipient spalling after about 150 cycles. Flakes of solids were easily peeled off the top face of these samples by the end of the experiment (Figure 21).

The parallelepiped samples that were tested for freeze-thaw resistance when completely immersed in water became soft and showed various degrees of swelling after only 20 cycles. After 30 cycles, the samples were badly damaged (Figure 22) and the test was then ended.

The 5-cm cube specimens kept under the ultra-violet light source did not show any sign of damage after 80 cycles between -30°C and 35°C. No signs of spalling or cracks were found.

6.4 DISCUSSION

The results obtained show that the mixture C/F.A./W = 1/0.8/0.65 gives the best compressive and tensile strengths. The principal characteristics are:

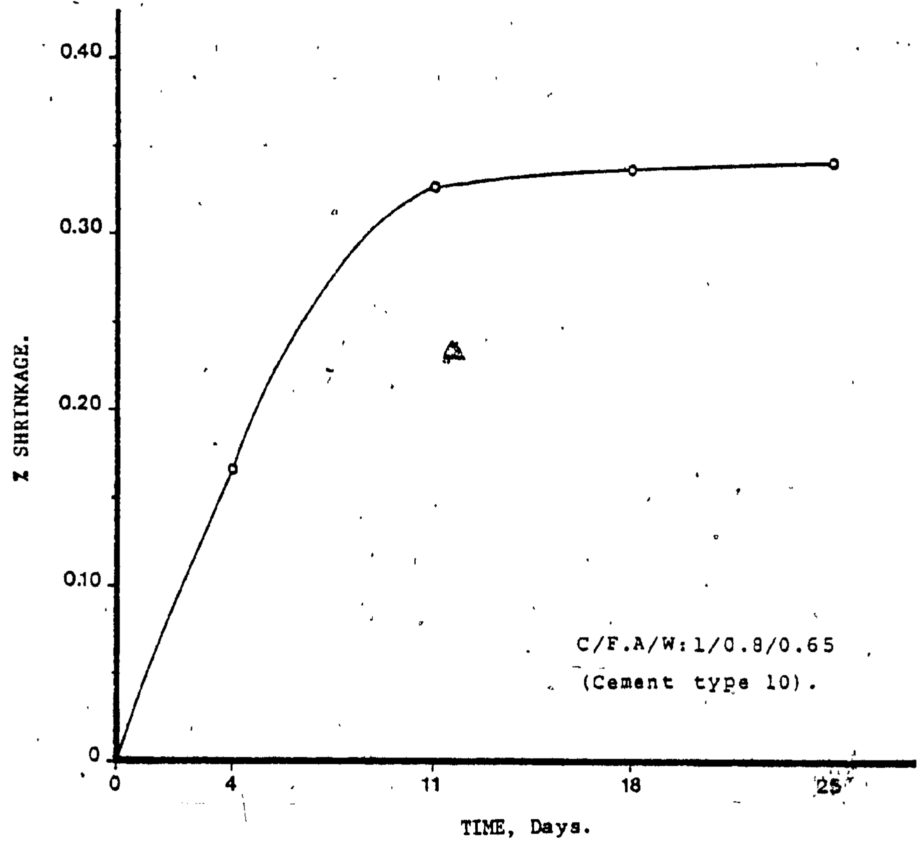

Figure 19: Drying shrinkage of mixture C/F.A./W = 1/0.8/0.65

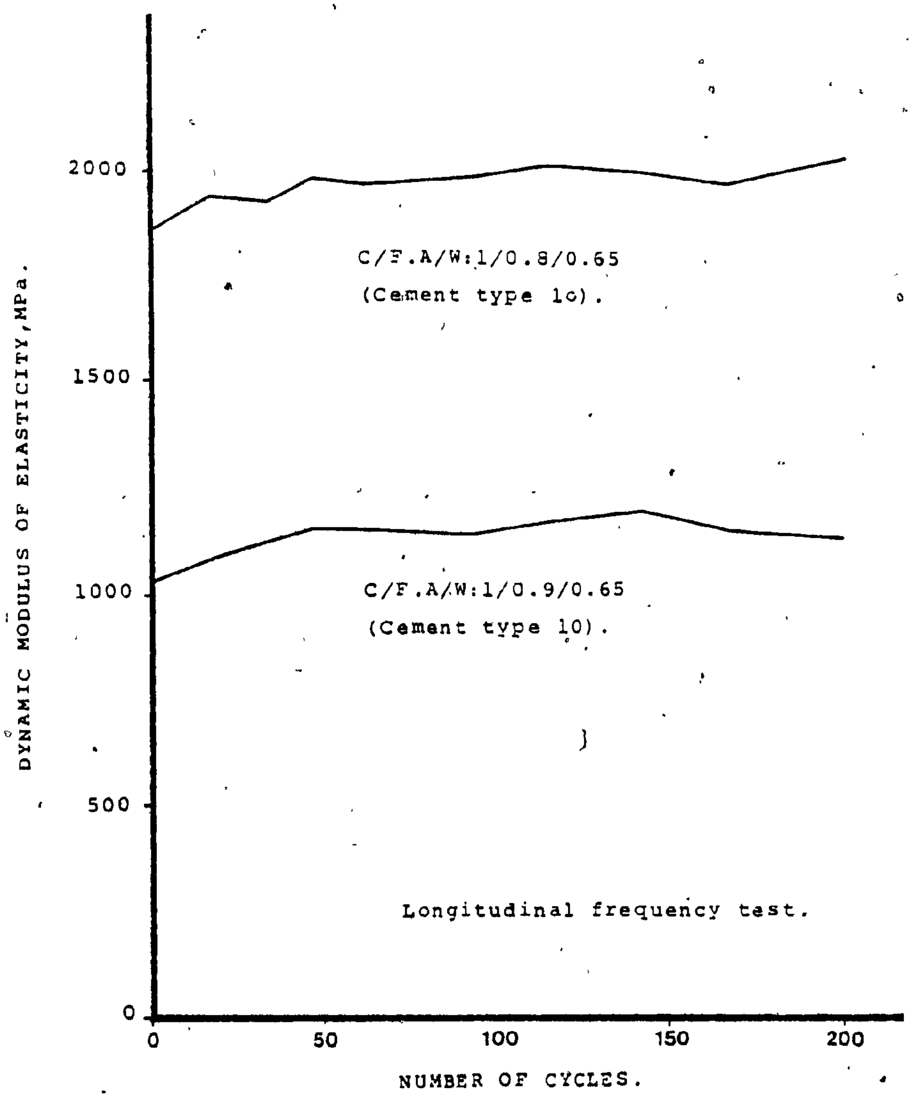

Figure 20: Variation of the dynamic modulus of elasticity of samples C/F.A./W = 1/0.8/0.65 and 1/0.9/0.65 with thermal cycling, between −5°C and 6°C.

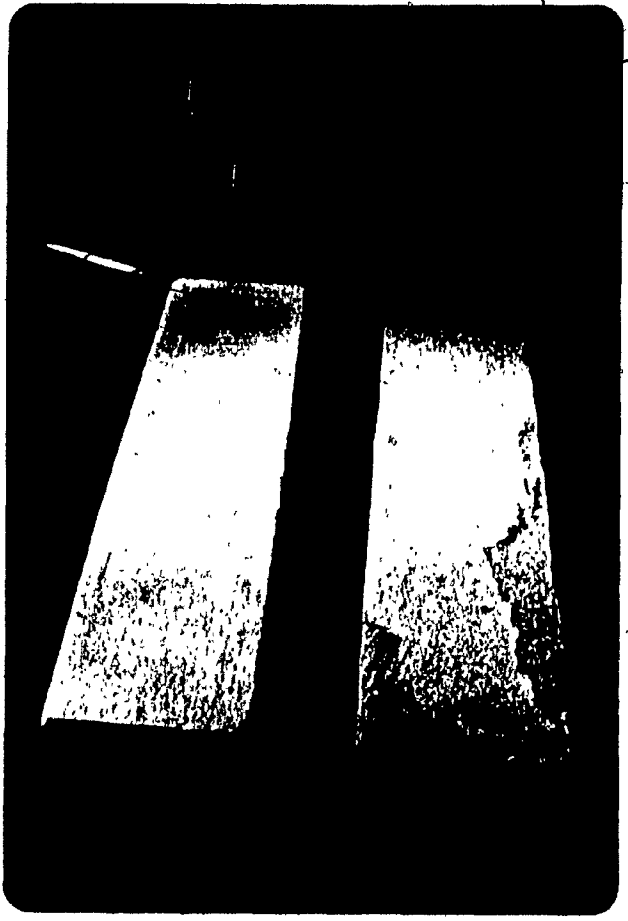

Figure 21: Effects of thermal cycling (between -5°C and 6°C) on a C/F.A./W 1/0.8/0.65 sample (left) and a 1/0.9/0.65 sample (right), after 200 cycles

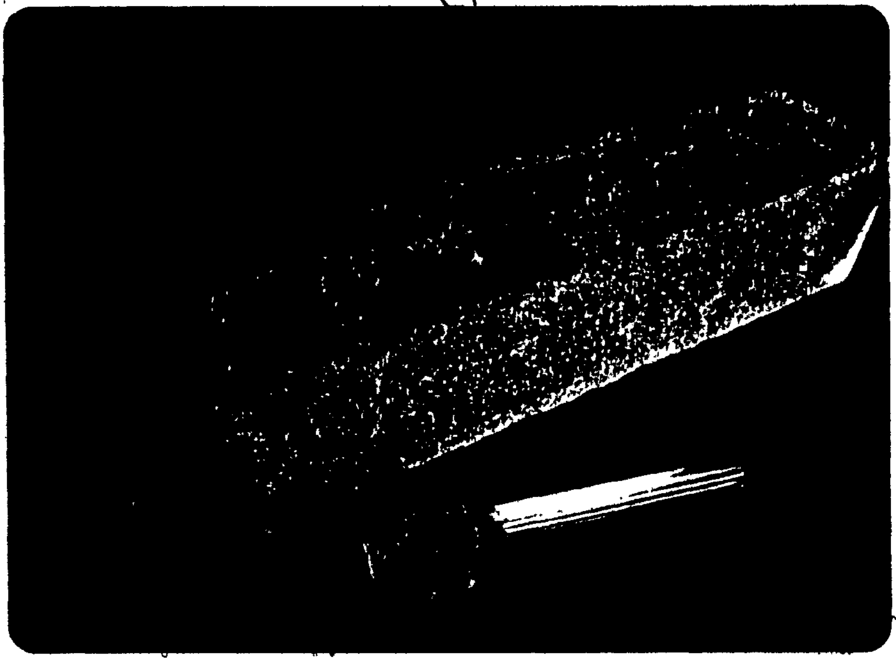

Figure 22: A soft and damaged C/F.A./W sample, after only 20 freeze-thaw cycles in water

i- light weight, which facilitates transportation and handling of the modules;

ii- strength; in this case, it was found to be worthwhile to use type 30 cement instead of normal cement in the fabrication of the modules. The compressive strength resulting from this substitution (4.4MPa) allows for the construction of higher walls using these modules. It should be noted that the strength of such a wall is also affected by workmanship, the strength of the mortar, the thickness of the mortar joints, the height of the unit module, the age of the mortar, and different other factors. Several equations attempting to relate the strength of the wall to the strengths of the unit and the mortar are presented in reference (67). These empirical formulas are based on test results, but can still be useful in practical applications.

Three of these equations are:

$$K_M = (\sqrt{1 + 0.15\,K_s} - 1)\,(8 + 0.057K_m)$$

$$K_M = 2\,\sqrt{K_s} + 3\,\sqrt{K_m}$$

$$K_M = 0.45\,\sqrt[3]{K_m\,K_s^2}$$

In these formulas:

K_M = strength of wall, in Kg/cm^2

K_m = strength of mortar, in Kg/cm^2

K_s = strength of modules, in Kg/cm^2

To obtain K_M in MPa, we have to multiply by 9.80665×10^{-2}. Using these formulas, we can find that it is possible to build non-bearing walls of considerable heights.

It was also found that the addition of glass fibres or fly ash did not improve the strength of C/F.A./W mixtures appreciably.

iii- durability; the resistance of the modules to up to 200 temperature cycles (between -5°C and 6°C) when covered with plastic and to 80 cycles between -30°C and 35°C under an ultra-violet light source prove that these mixtures are not easily affected by thermal cycling under low-moisture conditions. However, the failure of the samples after only 30 cycles of freeze-thaw testing when fully submerged in water indicate that these materials cannot be used for outside walls in cold climates due to the risk of damage caused by a combination of high humidity levels and wide temperature variations. This restricts their use to moderate and warm regions if they are to be used in outside walls. However, they can be used as indoor heat storages in all climates.

For applications in buildings, the occurrence of temperatures higher than 50°C is unlikely. At 50°C, the compressive strength of the heat storage modules ~~had~~ decreased about 35% below the room temperature value. This decrease can easily be accounted for in the design of the heat store.

CHAPTER 7: THERMAL PROPERTIES AND INFRARED STUDY

7.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC).

Differential thermal analysis (DTA) techniques constitute a powerful tool in determining the transformations in physical or chemical states occurring during the heating or cooling of a substance, and measuring the heats evolved or absorbed during these transformations. These techniques date back to 1887 when Le Chatelier devised a heating curve method which he employed in his study of clays and other minerals (62). Differential scanning calorimetry (DSC) is one of the most commonly used of these techniques. Its principles of operation are quite simple. If a sample and an inert reference are heated at a known rate in a controlled environment, the increase in sample and reference temperatures will be about the same (depending on specific heat differences), unless a heat-related change takes place in the sample. If this change does take place, the sample temperature either leads (evolves heat) or lags (absorbs heat) the reference temperature. In DSC, the temperature difference between sample and reference from such a heat change is directly related to the differential heat flow.

The DuPont 910 DSC system includes a cell base module and a DSC cell. The system's measuring unit is the DSC cell which uses a constantan (thermo-electric) disc as a primary heat transfer element. A silver heating block, capped with a silver vented lid, encloses the constantan disc. A selected sample and an inert reference are placed in small pans which sit on raised portions of the disc. Heat is transferred through the constantan disc to both the sample and the reference pans. Differential heat flow to the sample and reference is monitored by the chromel-constantan area thermocouples formed at the junctions of the constantan disc and the chromel wafers welded to the underside of the two raised portions of the disc. Chromel and alumel wires are connected to the chromel wafers at the thermocouple junctions to measure sample and reference temperatures.

The analysis programs we used in the tests were devised to calculate heats of fusion, heat capacities, and measure onset and peak temperatures. The onset temperature is the temperature at which the curve deviates from the base line to give an endothermic or exothermic peak. There are a few difficulties associated with the determination of this temperature, such as the shape of the peak and its width. The experimental peak width, for example, varies with the heating rate and thus the location of the onset temperature may be shifted at high heating rates. Peak temperatures, which are more easily reproducible, are therefore used in comparison studies. They are usually taken as the melting temperatures.

The thermograms obtained in one laboratory are not easily reproduced in other laboratories due to the many variables that should be accounted for. These variables are either instrumental, or due to the sample. The instrumental factors include, among others, the size, shape and type of the sample holder, the diameter and positioning of the thermocouples, the furnace, the heating rate, and the sensitivity of the recording system. The variations in the sample may be due to the method of drying, the amount used, particle size and crystallinity, packing density, thermal conductivity and heat capacity, swelling and shrinkage, etc.

7.2 THERMAL PROPERTIES OF THE FATTY ACID USED

7.2.A. THERMAL STABILITY

A sample of EMERY E400 was cycled between 0° and 70°C for 50 times using a heating rate of 5°C/min. A drop of 1.3°C in the melting point was measured between the first and second thermal cycles, accompanied by a decrease of 7 J/g in the heat of fusion. From the second and up to the 50th melting - freezing cycle, the sample exhibited good thermal stability, its melting temperature averaging 56.5 ± 0.3°C and its heat of fusion 144 ± 3 J/g (Table 14).

Cycle	Melting point, °C	Heat of fusion, J/g
1	58	152
2	56.7	145
10	56.3	147
20	56.7	145
30	56.2	142
40	56.5	142
50	56.4	144

Table 14: Effects of thermal cycling on the properties of EMERY E400

The initial change can be attributed to many factors. These include the presence of volatile impurities which require extra energy to evaporate; this possible explanation was later dropped when no loss in sample weight was measured between first and second cycles. The higher melting point of the first cycle may be due to the packing of the fatty acid in the pan. The presence of air pockets in the acid powder before the first melting may have impeded the heat flow through the sample and thus caused a time delay before reaching the maximum rate of melting.

The values of the melting point and heat of fusion of EMERY E400 reflect the degree of impurity of this acid when compared to the published values of the melting point (69°-69.6°C) and heat of fusion (199-240.8 J/g) of pure stearic acid.

The heats of reactions are equal to the areas under the endothermic or exothermic peaks, whatever the case may be. These areas are calculated on the DuPont 1090 Thermal Analysys system by the use of a data analysis program. The variations in the values obtained depend on the operator's choice of the 2 boundary points, a and b on the base line, which limit the area to be calculated (Figure 23A). The choice is not always as easy as presented in this figure as the peak takes different and varied shapes (23) (Figure 23, (B) and (C)).

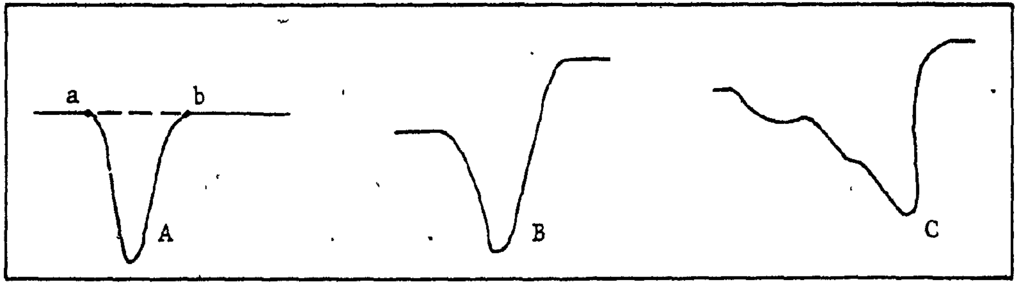

Figure 23: Some of the possible shapes of endothermic peaks

7.2.B. SPECIFIC HEAT CAPACITY

On the 1090 Thermal analysis (TA) system, the heat capacity is obtained by comparing the heat flow difference between sample and reference under 'blank' and 'sample' conditions. A 'blank' run is obtained by heating empty sample and reference pans. Under the 'sample' condition, the same procedure is repeated, under identical conditions, but with a weighed sample in the sample pan. At any desired temperature, the heat capacity, Cp, can be calculated as follows:

$$Cp = \left[\frac{60.E.\Delta qs}{Hr}\right]\frac{\Delta Y}{m} \quad \text{, in J/g. } {}^{o}C$$

where,

E = cell calibration coefficient, obtained from calibration runs on standard reference samples;

$\Delta qs =$ Y - axis RANGE setting, in mW/cm;

$Hr =$ heating rate, in °C/min;

$\Delta Y =$ difference in Y-axis deflection between sample and blank curves at temperature of interest, in cm;

$m =$ sample mass, in mg.

The results obtained at 20°C and 70°C for EMERY E400 and two other commercially available stearic acids are presented in table 15. Three samples of each product were tested and only the average values of Cp are reported. The specific heat was measured at the second heating cycle, using a heating rate of 5°C/min. Lower heating rates are not recommended since ΔY decreases with decreasing heating rate and the error in its measurement increases.

Stearic Acid	Cp, J/g. °C	
	Solid (20°C)	Liquid (70°C)
EMERY E400	1.81	2.38
U.S.P.*	1.67	2.42
Triple Pressed**	1.74	2.68

Table 15: Measured specific heat capacities of 3 commercial stearic acids

* Product of American Chemicals Ltd., Montreal, Quebec, Canada

** Product of J.T. Baker Chemical Co., Phillipsburg, N.J., U.S.A.

7.2.C. THERMAL CONDUCTIVITY AND DIFFUSIVITY

The value of the thermal conductivity is obtained using the following equation:

$$K = \frac{q}{A}\left[\frac{1}{\frac{(\Delta T)}{(\Delta x)top} + \frac{(\Delta T)}{(\Delta x)bottom}}\right], \text{ in } W/m.^{\circ}C;$$

where $q =$ voltage (volts) x current (Amp.), in watts;

$A =$ area of main heater, in m^2;

$\Delta T =$ sample temperature difference, in ^{o}C;

$\Delta x =$ sample thickness, in m.

The thermal conductivity of EMERY E400, obtained at an average temperature of 25°C was found to be 0.190 W/(m.°C). Low values for the thermal conductivity are an unfavourable characteristic of organic compounds when compared to the thermal conductivity values of salt hydrates (table 5).

The calculated value of the thermal diffusivity of solid EMERY E400, $0.11 \times 10^{-6}\ m^2/S$, is close to the thermal diffusivity of ice but also low when compared to salt hydrates.

7.2.D. MIXTURES OF PRESSED STEARIC AND LAURIC ACIDS

Stearic acid U.S.P. was mixed with lauric acid in different molar weight percentages. One particular composition, 30% stearic 70% lauric, was found to have an appropriate melting temperature for house heating applications. Its peak temperature and heat of fusion are presented in table 16, along with those of stearic and lauric acids. The thermogram of this mixture (Figure 24) showed only one endothermic peak, while most of the other mixtures presented two endothermic peaks (Figure 25).

Material	Heating rate, °C/min	Peak temperature, °C	Heat of fusion, J/g
stearic U.S.P.	1	51.6	216
lauric	1	42.5	189
70% lauric-30% stearic	1	31.8	197

Table 16: Properties of stearic U.S.P. and lauric acids and one of their mixtures.

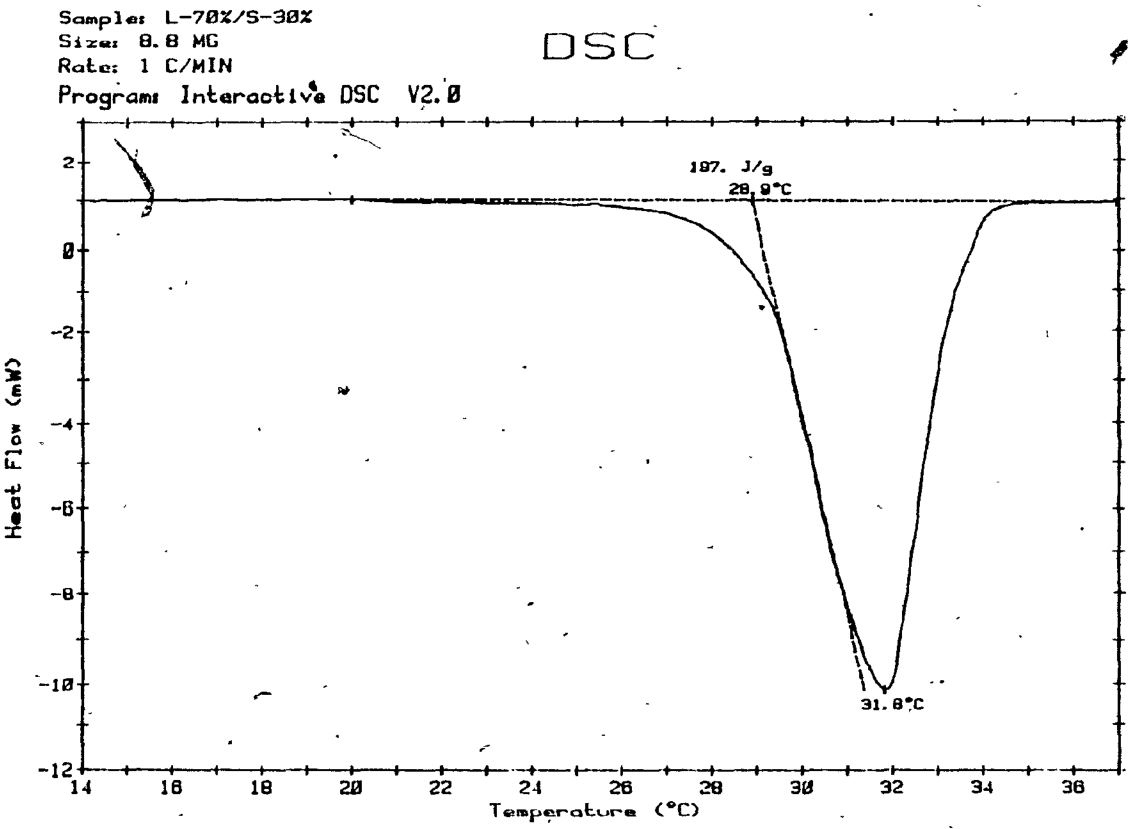

Figure 24: A thermogram of a 30% stearic-70% lauric acids mixture showing a single endothermic peak at fusion

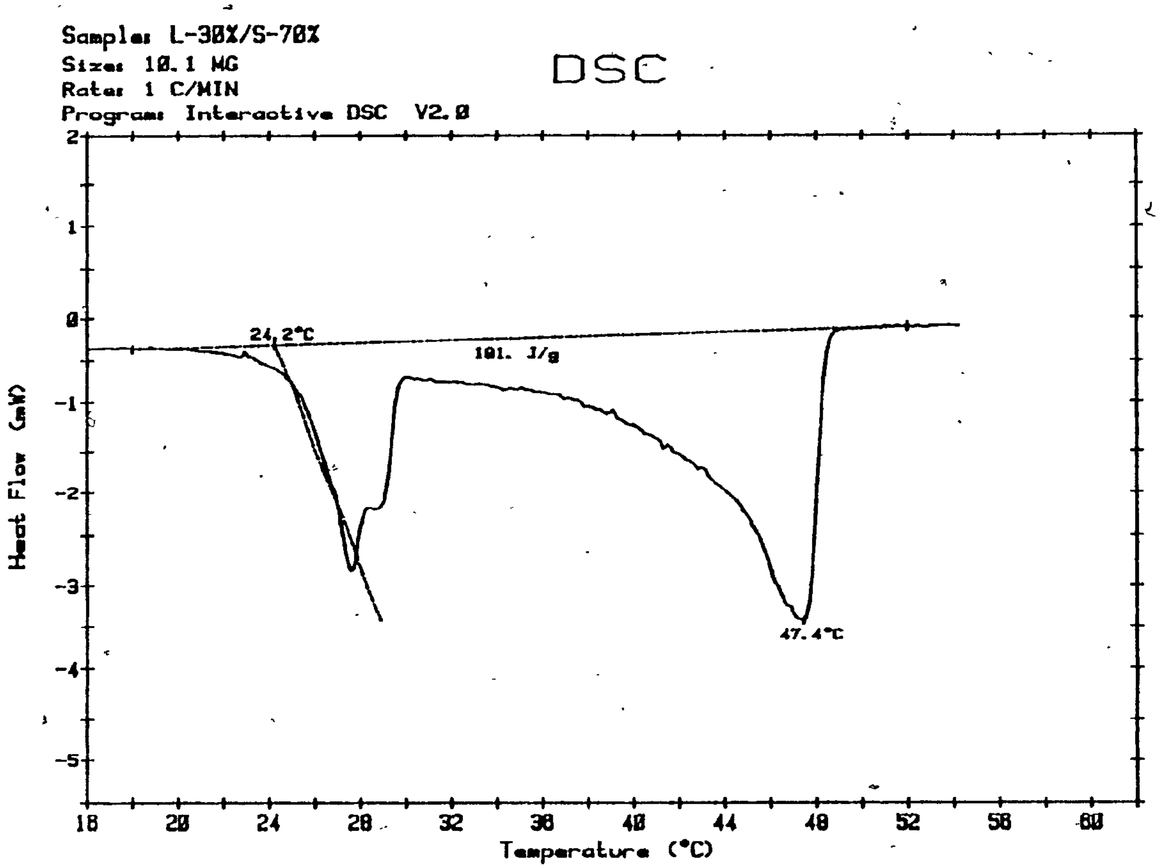

Figure 25: A thermogram of a 70% stearic-30% lauric acids mixture showing 2 distinct endotherms

7.3 PROPERTIES OF C/F.A./W MIXTURES

7.3.A CEMENT POWDER AND HYDRATED CEMENT

The thermogram of cement powder (Figure 26) presents two distinct peaks at 122° and 434°C in the 20°-440°C range and a shallow endothermic depression between 60° and 300°C, with a peak at approximately 170°C. The 122°C peak could be attributed to loss of the hygroscopic moisture that was not completely removed after drying the sample for 48 hours at 105°C. The flat endothermal depression at around 170°C and the 434° peak could be attributed respectively to the gradual dehydration of gypsum and to the $Ca(OH)_2$ formed during exposure to air, as explained by Ramachandran et al. (63).

The thermogram of hydrated cement (Figure 27) presents two coalescent peaks below 200°C, at about 160° and 190°C. These peaks could be equivalent to the peaks mentioned by Ramachandran (53). The first, occurring at 130°-140°C, is caused by the desorption of capillary water from the lime-silica gel, while the second (at 195°-200°C) represents the dehydration of the SO_3-poor member of the solid solution approaching $4CaO.Al_2O_3.13H_2O$. The endothermal peak obtained at 390°C might be due to the same cause as the peak obtained by Ramachandran at 415°-430°C, that is, the dehydration of $Mg(OH)_2$.

7.3.B. C/F.A./W MIXTURES

Samples of three mixtures (C/F.A./W = 1/0.8/0.65, 1/0.9/0.65 and 1/1/0.65), cured for 28 days and oven-dried at 105°C for 48 hours, were heated at a rate of 5°C/min. in the DSC cell. The samples were obtained by grinding chunks of the mixtures into powder. Two samples of each mixture were chosen to ensure uniformity in composition. It was estimated that 30 - 40% of the weight of these samples was fatty acid. The thermograms obtained were quite similar in shape (Figure 28) and showed

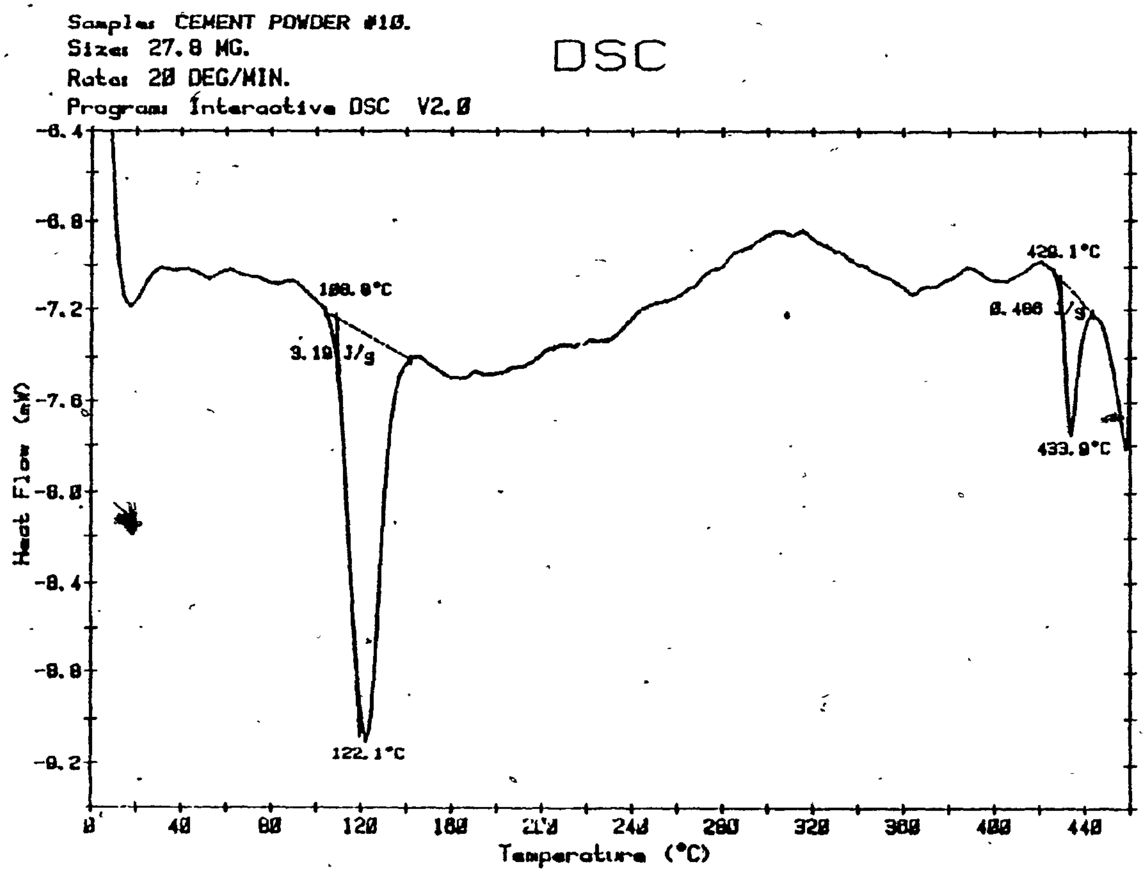

Figure 26: Thermogram of oven-dried type 10 cement

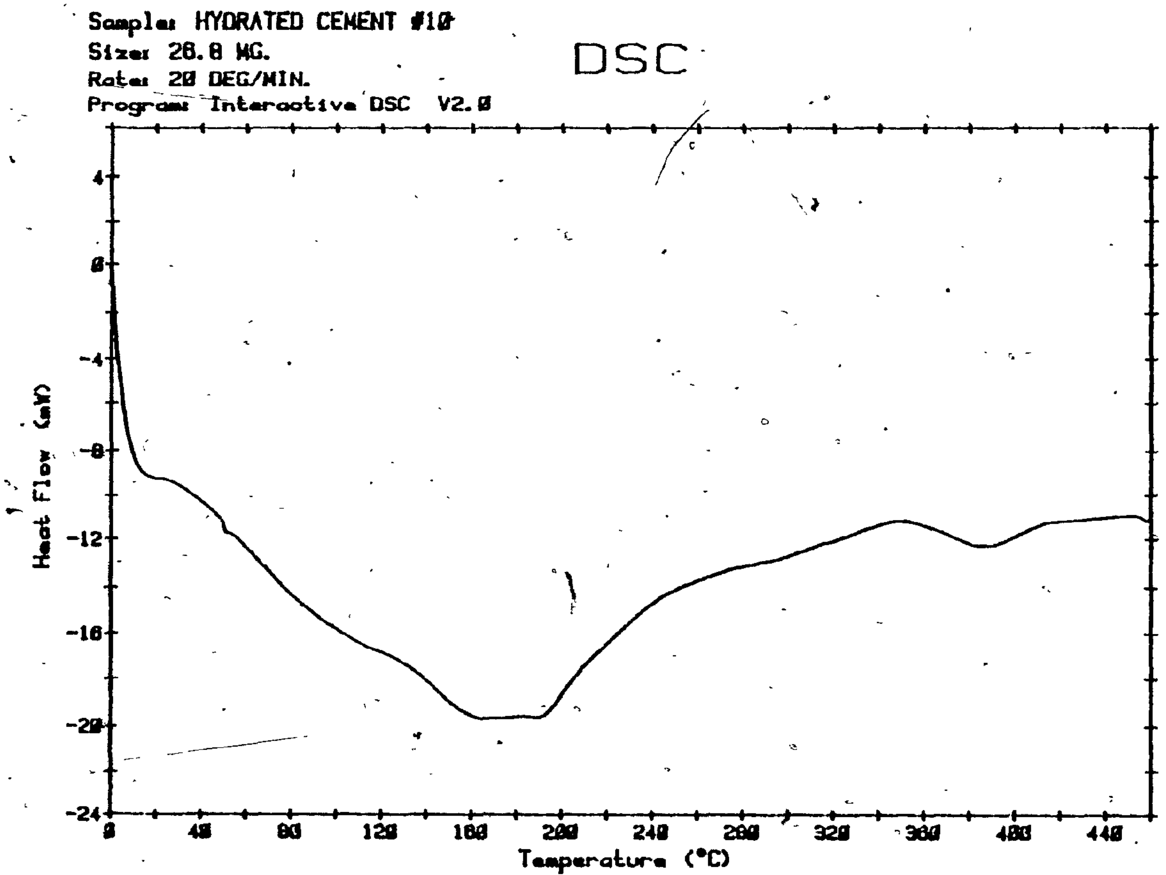

Figure 27: Thermogram of oven-dried hydrated cement, cured in lime-saturated water for 28 days

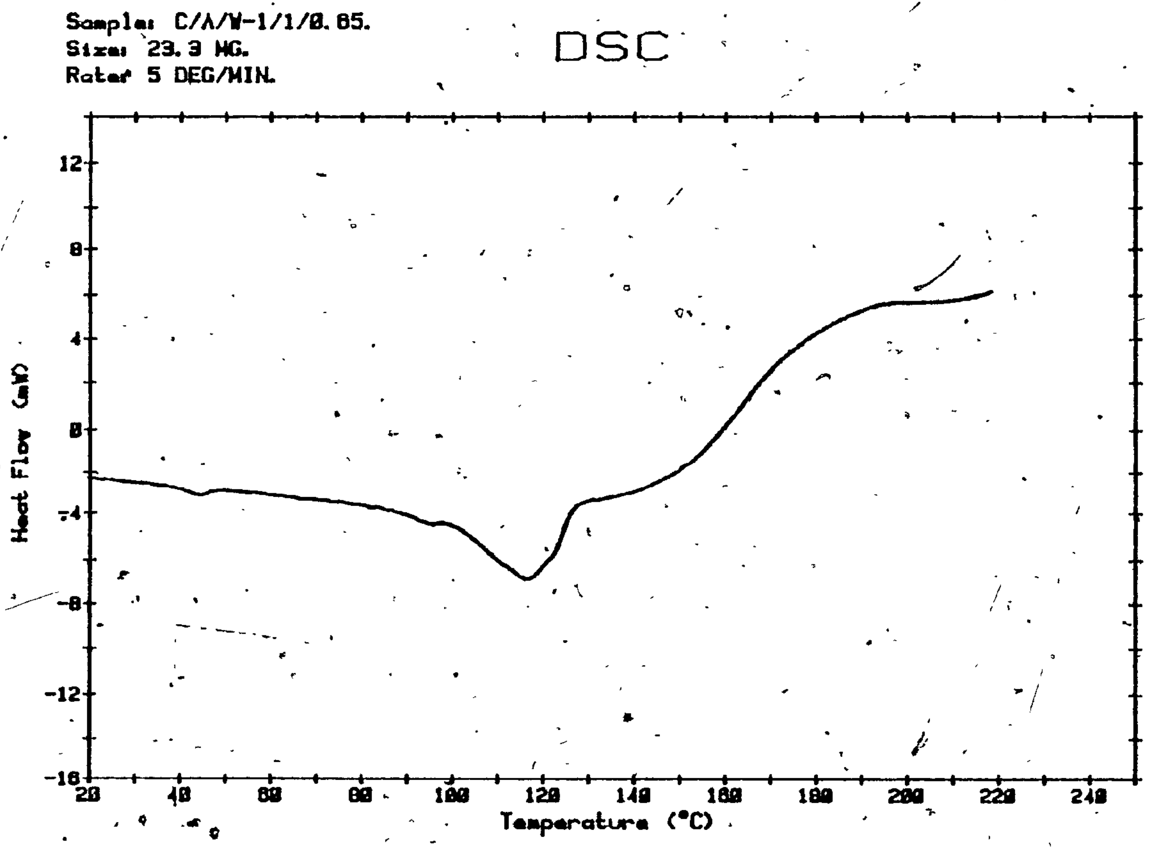

Figure 28: A typical thermogram of C/F.A./W mixtures

the following characteristics:

1. The absence of the endothermal peak around 56.5°C corresponding to the presence of the fatty acid;
2. The appearance at about 40°C of an endothermic dent of unknown origin. This endotherm, shown in figures 29, 30 and 31, is accompanied by a very small amount of heat absorption which could not be attributed to the fatty acid having, as found earlier, a heat of fusion of 144 J/g;
3. An endotherm at approximately 115°C, corresponding to the dehydration of the sample; and
4. A transition occurring between 170° and 190°C (Figure 28). The transition was accompanied by the release of heat and smoke, and the change of state of the sample from grey powder to a compact, dark and glassy compound.

The thermal conductivities of these mixtures (at ~30°C) were found to be slightly lower than the value obtained for solid EMERY E400. These values, presented in table 17 with those of EMERY E400 and hydrated cement, show a slight decrease with the addition of the fatty acid.

Material	Thermal conductivity, K (W/(m.°C))	average temperature at which K was measured
Hydrated cement	0.710	30
1/0.8/0.65	0.187	32
1/0.9/0.65	0.180	30
1/1/0.65	0.153	30
EMERY E400	0.190	25

Table 17: Thermal conductivities of cement, EMERY E400, and 3 C/F.A./W mixtures

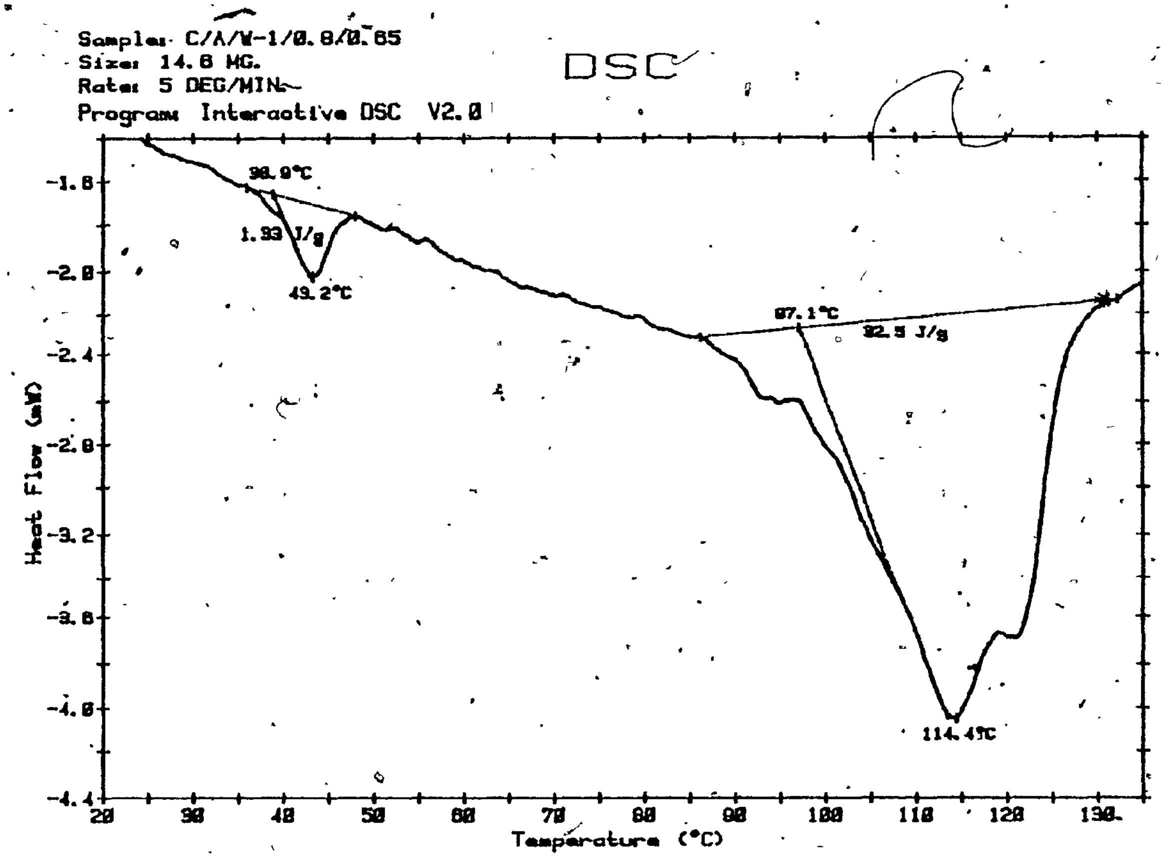

Figure 29: Thermogram of oven-dried C/F.A./W = 1/0.8/0.65, after 28 days of curing in lime-saturated water

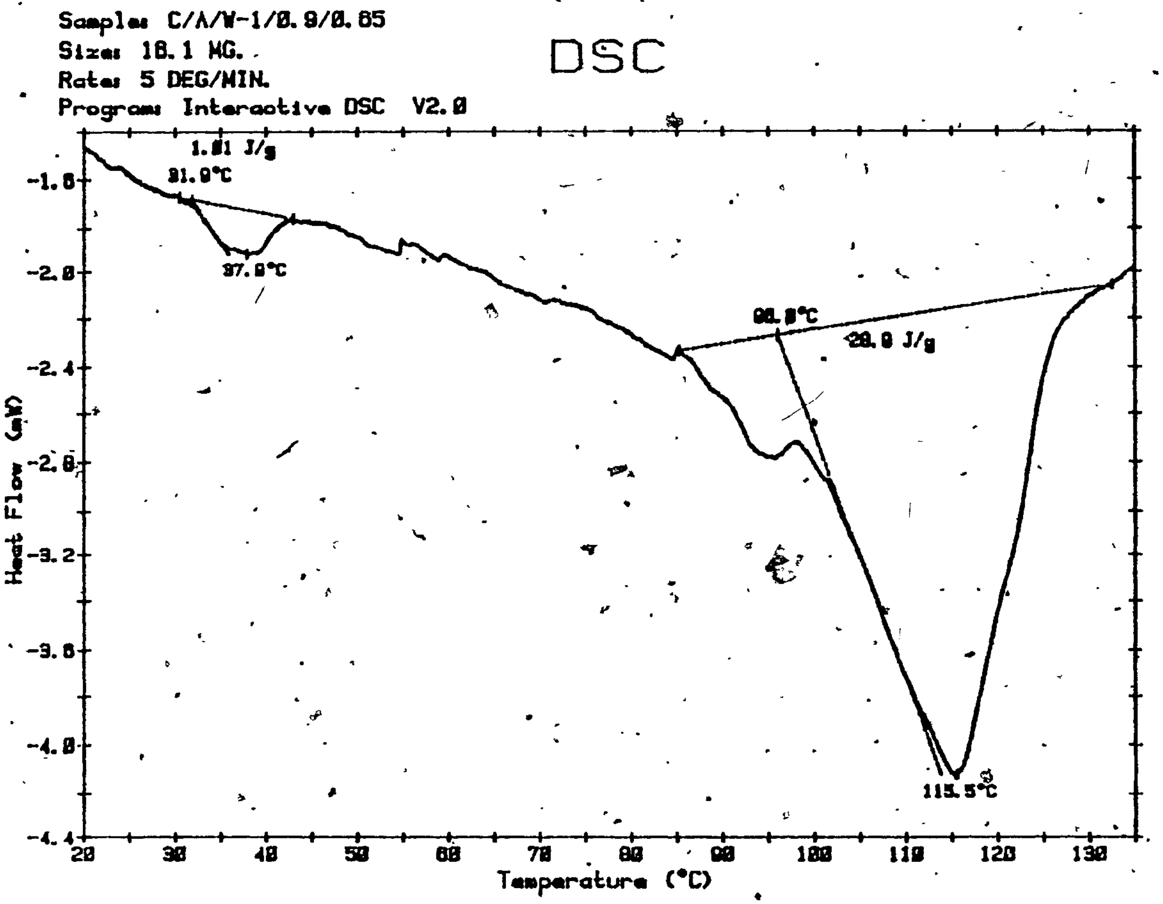

Figure 30: Thermogram of oven-dried C/F.A./W = 1/0.9/0.65, after 28 days of curing in lime-saturated water

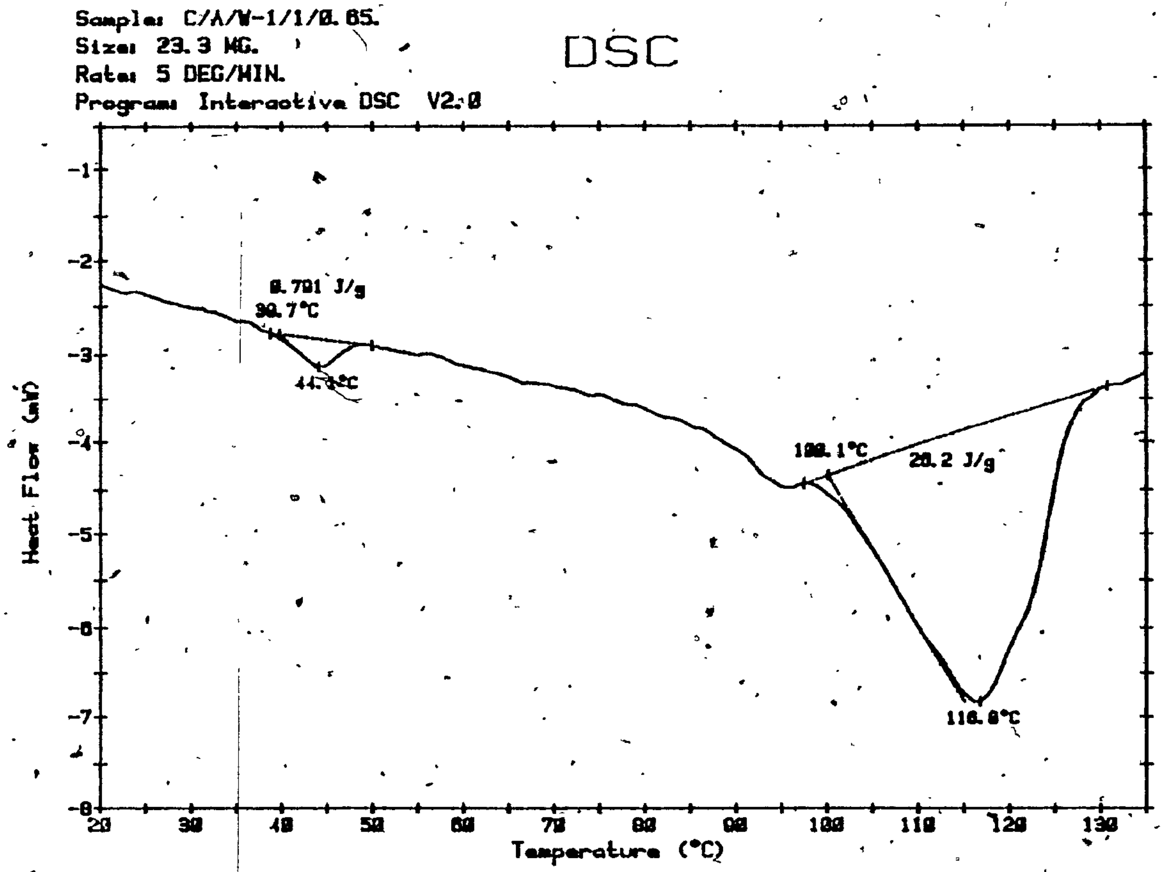

Figure 31: Thermogram of oven-dried C/F.A./W = 1/1/0.65, after 28 days of curing in lime-saturated water

The results of the thermal analysis of the C/F.A./W mixtures led us to believe that a possible chemical reaction might have taken place between the weak organic acids composing EMERY E400 and the lime present in the cement composition. Infrared absorption spectrometry was then used to investigate this hypothesis and the results are discussed in the next section.

7.4. INFRARED STUDY

Infrared absorption was used to study the interaction between EMERY E400 and cement in C/F.A./W mixtures. The infrared (IR) spectrum of EMERY E400 (Figure 32) corresponds to published IR spectra of pure stearic acid (64, 65). The most important characteristic of this spectrum is the C$=$0 band occurring between 1700 and 1725 cm^{-1} (65). Other less important characteristics include the C-H stretching at 2940 and 2860 cm^{-1} and a broad 0-H band in the 2500 to 3000 cm^{-1} range.

IR Spectra of type 10 cement in powder and hydrated forms were also obtained (figures 33 and 34). The cement powder spectrum agrees to a great extent to a published spectrum (67) of the same material. The spectrum of hydrated cement presents 2 peaks at about 1000 cm^{-1} and 500 cm^{-1} caused by Si-0 stretching vibrations as well as a band in the 1400 - 1500 cm^{-1} range which can be attributed to the CO_3^{2-} stretching mode. The occurrence of CO_3^{2-} can be explained by the partial carbonation of Ca $(OH)_2$ (69). IR spectra were obtained for mixture C/F.A./W$=$1/0.8/0.65 after 16 and 28 days of curing, and for mixture C/F.A./W$=$1/0.8/0.70 after a curing period of 28 days (figures 35, 36 and 37). In general, these spectra are similar in shape and are characterized by the shift and split of the C$=$0 band from the 1700 - 1725 cm^{-1} to 1545 cm^{-1} and 1580

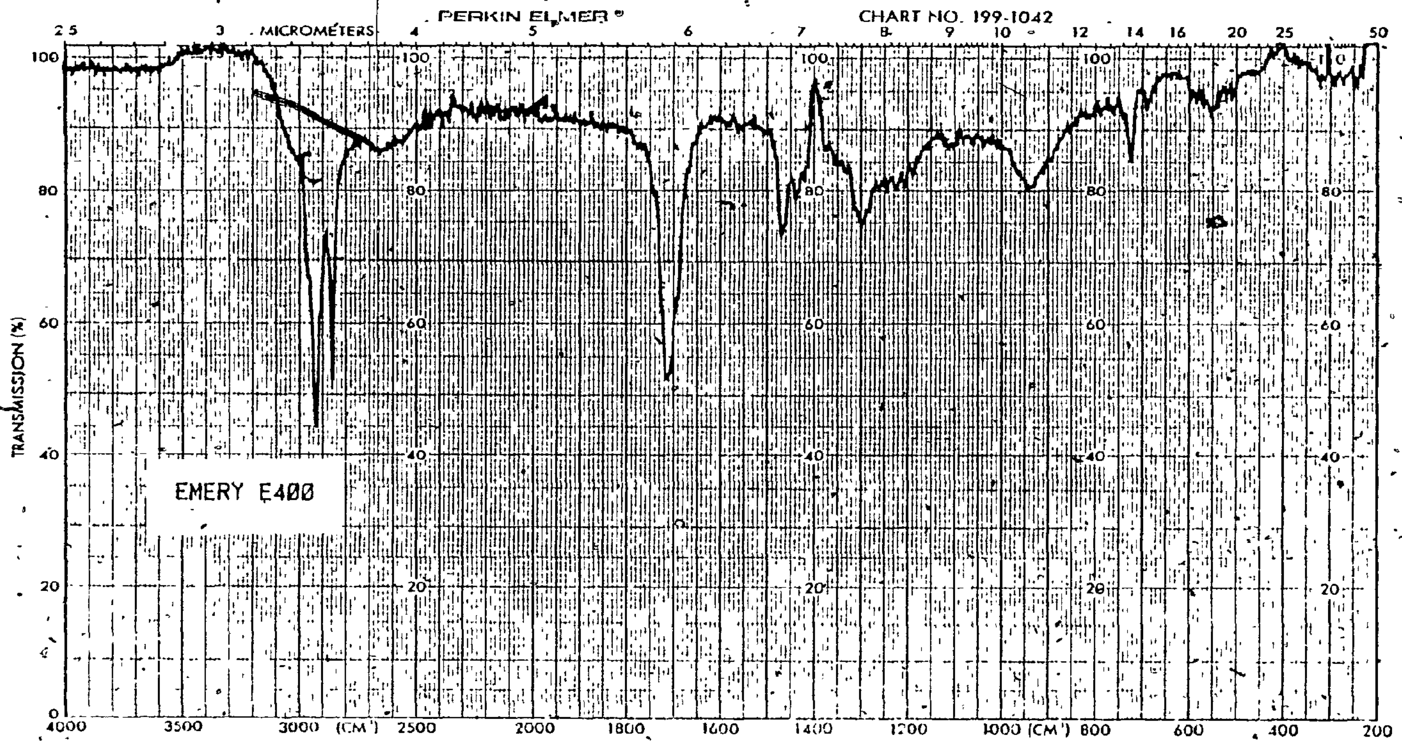

Figure 32: IR absorption spectrum of EMERY E400

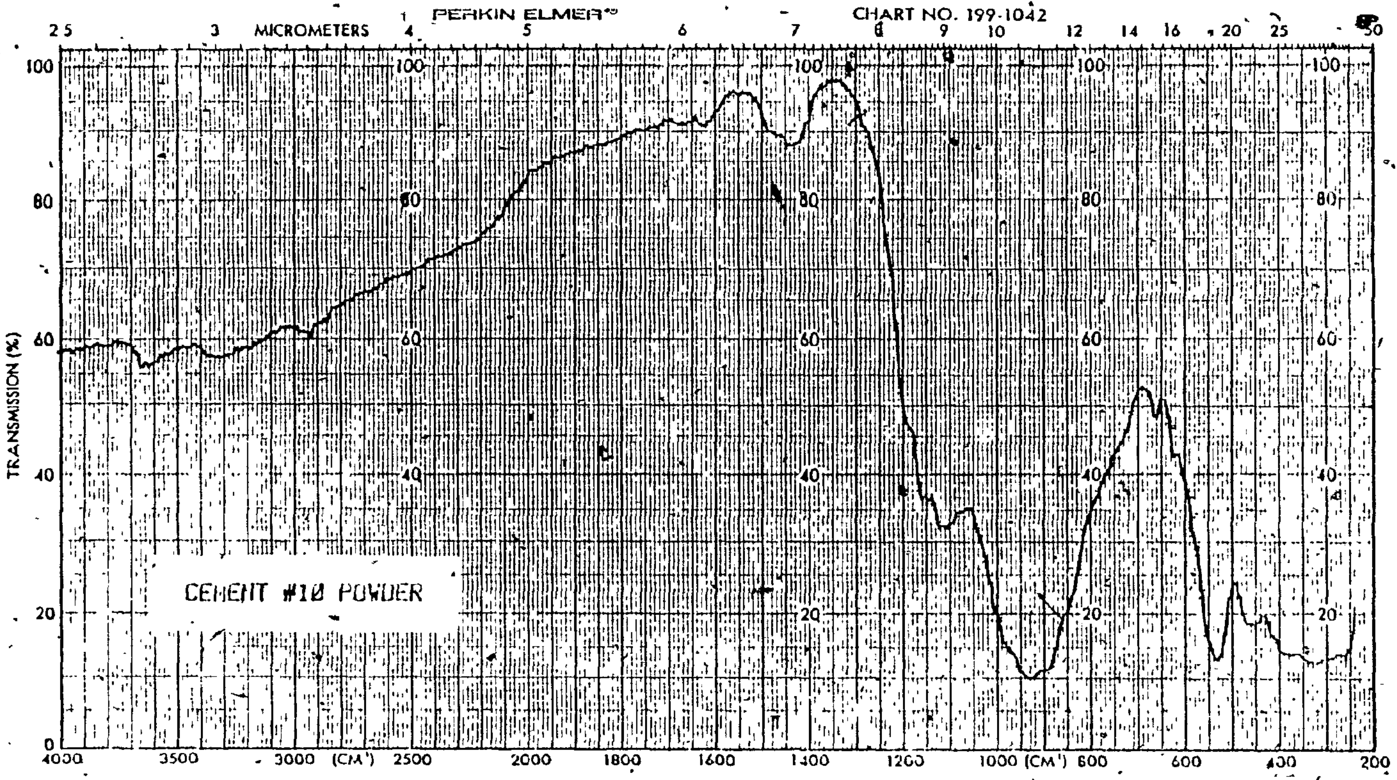

Figure 33: IR absorption spectrum of oven-dried cement type 10 powder

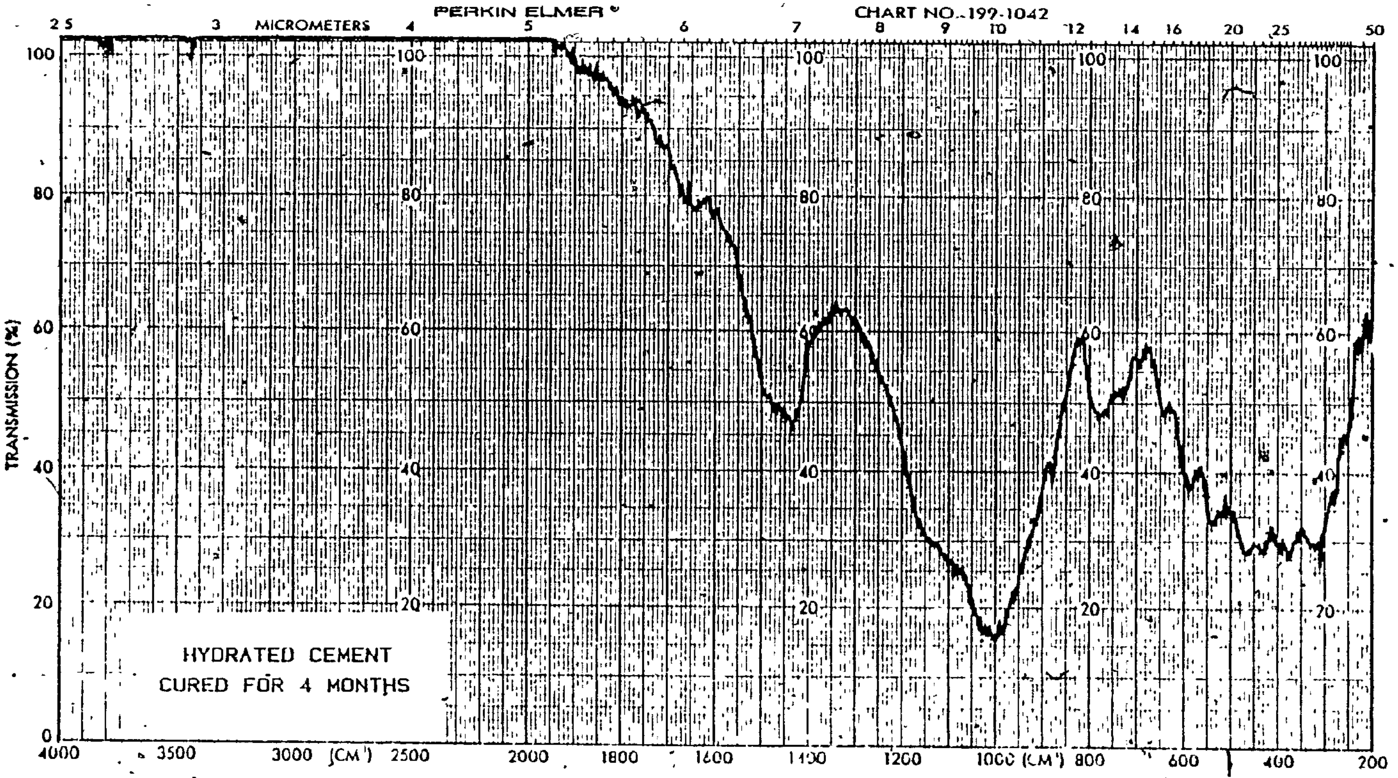

Figure 34: IR absorption spectrum of oven-dried hydrated cement

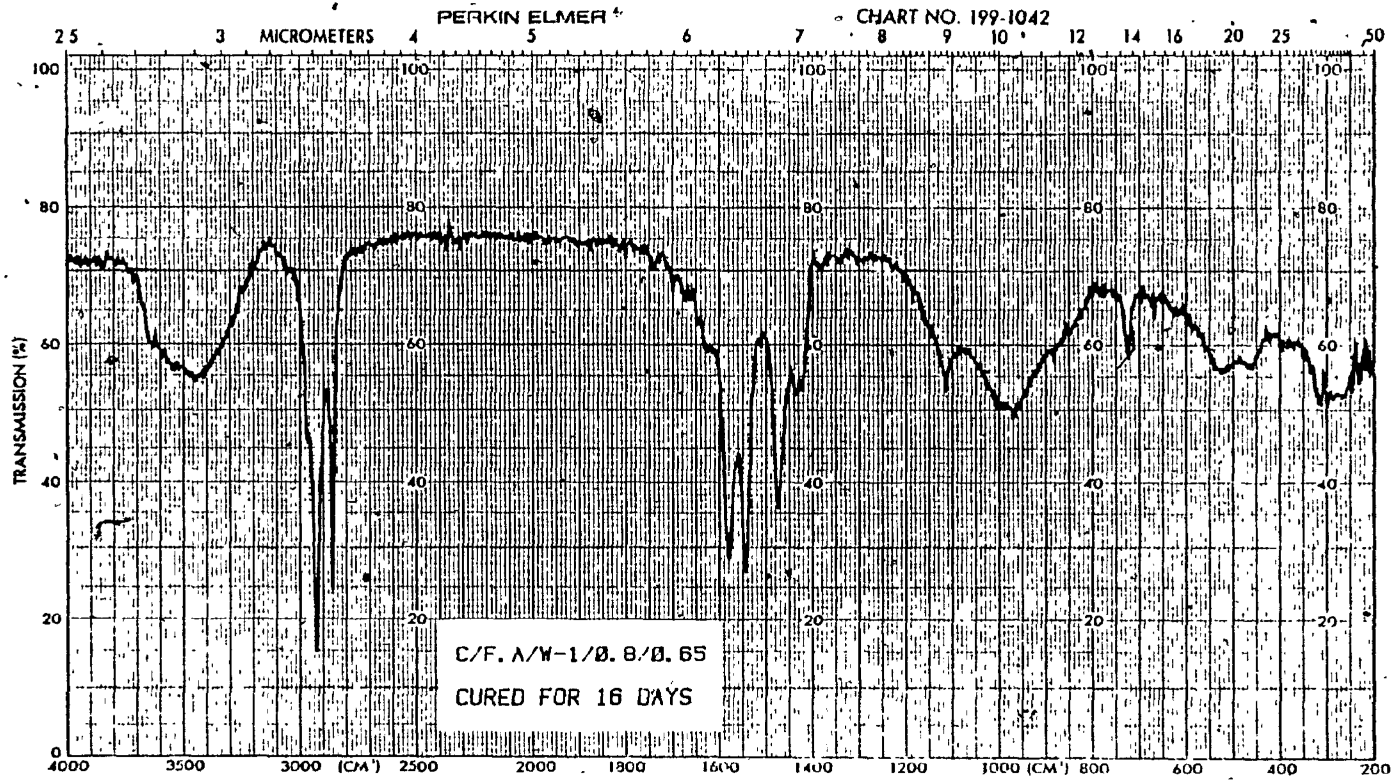

Figure 35: IR absorption spectrum of oven-dried C/F.A./W = 1/0.8/0.65 after 16 days of curing in lime-saturated water

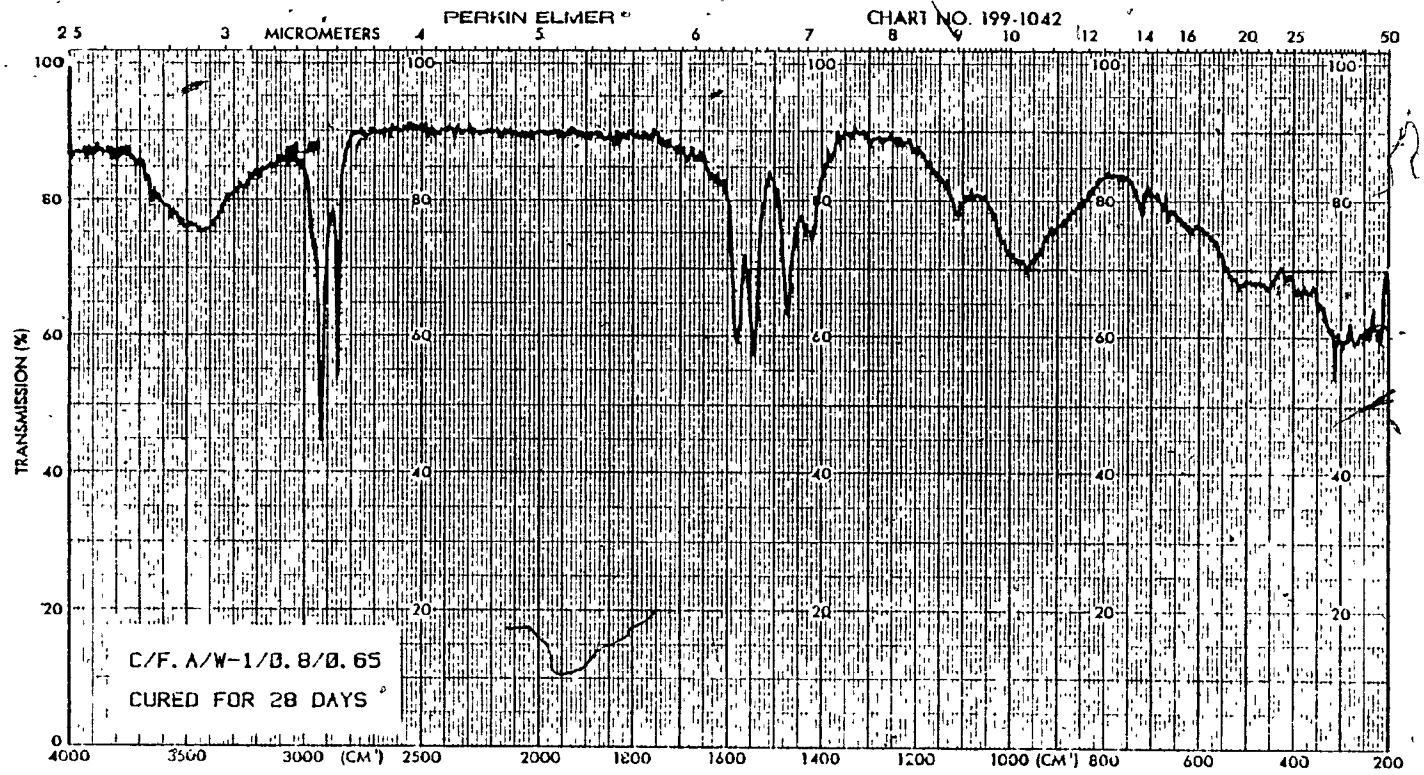

Figure 36: IR absorption spectrum of oven-dried C/F.A./W = 1/0.8/0.65 after 28 days of curing in lime-saturated water

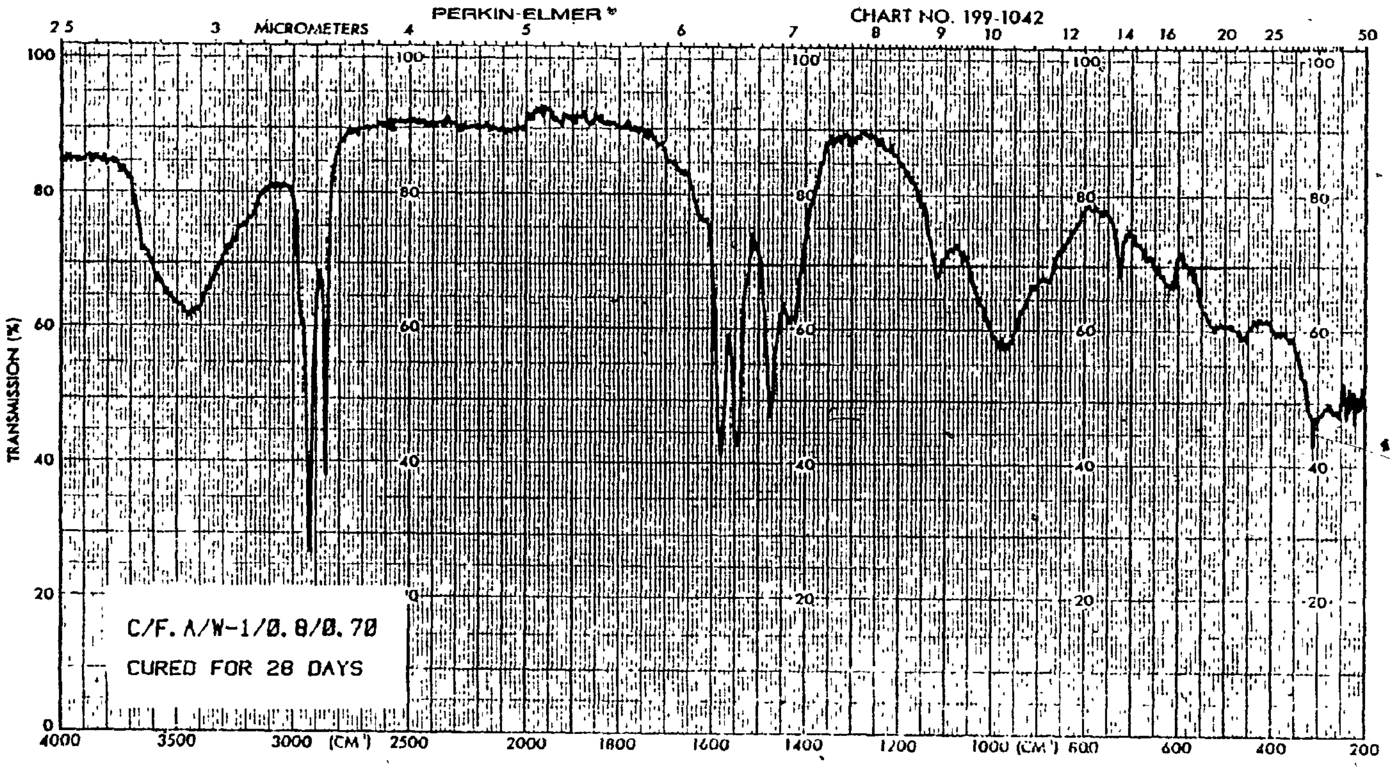

Figure 37: IR absorption spectrum of oven-dried C/F.A./W = 1/0.8/0.70 after 28 days of curing in lime-saturated water

cm^{-1} due to the possible formation of the carboxylate ion COO^- due to the presence of the fatty acid and water in the system. The bands which were found in the hydrated cement spectrum (at 1000 cm^{-1} for SiO_4 and between 1400 and 1500 cm^{-1} for CO_3^{2-}) are still present in the spectra of the C/F.A./W mixtures.

The results of the infrared absorption study were found to be unconclusive. In fact, the possible shift and split of the $C{=}O$ band means that a reaction at the carbonyl group did not occur and, if a secondary interaction ever took place, we were not able to reveal its existence using the spectra obtained in this study.

7.5 DISCUSSION

EMERY E400, like most organic compounds, has low thermal conductivity and diffusivity, which is a disadvantage when compared to salt hydrates. It is also more expensive than most of these salts. However, it is thermally stable, a fact that can make it cost competitive on a long-term basis with less expensive heat storage materials.

Mixtures of cement, EMERY E400, and water (C/F.A./W mixtures) did not present the thermal characteristics expected from a latent heat module because of a possible chemical reaction that has taken place between the components of the mixtures. The infrared absorption study was unconclusive and failed to reveal the existence of the reaction. The only clear indication on a chemical reaction taking place between the fatty acid and some of the cement components occurred when liquid fatty acid was mixed with cement powder. An appreciable amount of heat was released, indicating an exothermic reaction.

It was believed that cubes of fatty acid (average cube volume: 172 mm^3) mixed with the cement paste could help solve the problem of the chemical reaction between the different components. The resulting compound of reaction would cover and isolate the fatty acid cubes, thus preventing further interaction with the cement paste. The ratio of the weight of the EMERY E400 cubes to the weight of the cement in this new sample was 0.8, the same as in the C/F.A./W = 1/0.8/0.65 mixture. Less water was needed to make the cement paste (W/C = 0.5). The compressive strength of these samples, measured after 7 days of lime-water curing, was three times larger than for C/F.A./W mixtures. However these specimens present two major problems: leakage of the liquid fatty acid from surface cells and other cells connected to them, and thermal stresses in the samples, due to the thermal expansion of the fatty acid cubes, causing cracks in the cement matrix (Figure 38).

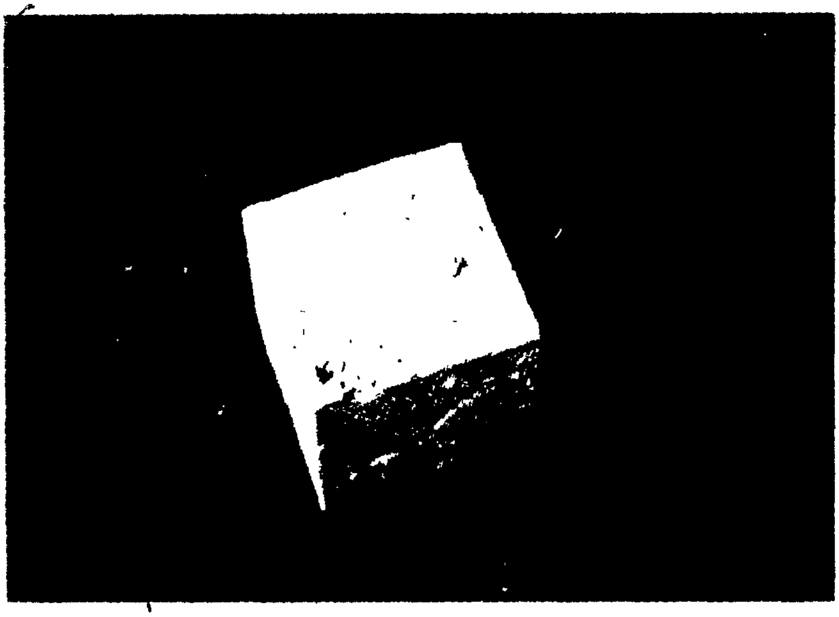

Figure 38: A cement cube containing EMERY E400 cubes showing cracks, and empty cells caused by liquid fatty acid leakage

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

Several conclusions can be drawn from the results of the study done on the heat storage modules during this preliminary phase of research. These are:

i- Cement/fatty acid/water (C/F.A./W) mixtures can be easily produced and molded into any desired shape. Their production process being the same as for cement mortars and concretes, no extra equipment is required. The best mixture* we found, C/F.A./W = 1/0.8/0.65, proved to have an appropriate combination of light weight and strength, which should reduce transportation and handling costs, and permit the stacking of the heat storage modules to appropriate heights.

ii- The poor resistance of this mixture to freeze-thaw cycling under humid conditions restricts the use of these modules to mild and warm climates if used in outside wall compositions. On the other hand, they can be used indoors as partitions in any climate if the living space temperature is kept within reasonable limits.

iii- The drying shrinkage of C/F.A./W = 1/0.8/0.65, though 50% larger than that of cement mortar, could easily be accounted for in the design of the heat stores.

iv- The use of high early strength cement instead of normal portland cement produced the best improvement in compressive strength, which increased from 2.187 MPa to 4.4 MPa. These values were obtained after a curing period of 28 days. Additives, such as glass fibres and fly ash, produced only minor increases in strength.

v- A commercially available pressed stearic acid (EMERY E400) was used in the mixtures mainly for reasons of cost. Still, the cost of $1m^3$

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* i.e. in terms of compressive strength.

of C/F.A./W = 1/0.8/0.65 is about 450 can.$, that is about eight times the cost of the same quantity of concrete (65 can.$/m^3). Pure substances are more expensive and their costs render their use in heat storage uneconomical.

vi- The thermal properties of C/F.A./W mixtures did not reflect the expected results. This was probably due to a suspected chemical reaction between the fatty acid and the cement. Infrared spectrometry was used to reveal the existence of such a reaction but, so far, the analysis of the IR spectra did not provide enough information as to the occurrence of any reaction. More advanced spectral and chemical analyses are required to clear this problem.

vii- One of the most important properties of C/F.A./W mixtures was their thermal resistance (5.32 m.°C/W) which was found to be equivalent to that of hardwoods (maple, oak, etc.) and four times larger than that of common brick (1.39m.°C/W), making this material a good thermal insulator.

8.2 RECOMMENDATIONS

The following recommendations should conclude this preliminary stage of research on this particular heat storage module, and open up new horizons for further research on the incorporation of fatty acids in building components. There are three main recommendations.

i- The first consists of a detailed chemical and spectral analysis to reveal the nature of the interaction between the fatty acid and the hydrated cement components. If any chemical reaction is found to occur between the fatty acid and any of the cement components, inhibiting this reaction should preserve the thermal properties of the fatty acid in the mixture.

ii- The use of acid-resistant cements should be considered. In this case, macro-encapsulation of the fatty acid in concrete tiles or panels made with these cements may produce appealing products in terms of thermal properties, appearance, and cost. Furan-resin, phenolic, and epoxy cements have proved to be resistant to fatty acids in general and to pure stearic acid in particular, even at temperatures reaching 120°C (70). These cements are more expensive than normal portland cement but, when mixed with sand, produce polymer concretes of lighter weight, increased tensile and compressive strength, excellent acid, alkali and moisture resistance and better strength-to-weight ratio than normal concrete.

iii- The third and last recommendation concerns the macro-encapsulation of fatty acids in sealed plastic bags which could be placed in hollow modules made of cement or concrete. In this case, research should be directed mainly to testing the resistance of these plastic bags to aging and thermal cycling.

A complete economical analysis should be performed to assess the feasibility of these products in terms of production costs and useful life. The first task, however, is to find a product that fits the basic requirements in terms of heat storage through continuing research.

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