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H4.SMR/193 - 30

"COLLQUE INTERNATIONAL SUR LA SCIENCE DES MATERIAUX POUR L'ENERGIE".
(26 août - 11 septembre 1986).

"ON THE USE OF PHASE MATERIAL AS HEAT STORAGE APPLIED TO BUILDING AND AGRICULTURE".

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ON THE USE OF PHASE CHANGE MATERIAL AS HEAT STORAGE APPLIED TO BUILDINGS AND AGRICULTURE.

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CONTENT.

ABSTRACT.

Phase change materials presenting a high enthalpy of melting have long been known as potentially efficient heat storage medium. After a recent period quite fruitful in research and developpment of reliable chemical compounds and efficient exchanger configurations, it is clear that various factors still slow down the expected developpment of such sophisticated heat storage. Typical applications concerning space heating in buildings and greenhouses are discussed and some suggestions on the future of PCM storage in a period of cheap energy are presented.

INTRODUCTION : A short historical survey.

Storing heat or cold on a modest scale is as ancient as the history of mankind, but in general this was simply achieved by heating up or cooling down ordinary inert materials (stones, earth, water) and by keeping it in a protected and confined space. A rare exception involving phase change processes is offered by a practice of ancient Romans who would carry down glacier ice from the neighboring alps to urban sites in order to prepare refreshed beverages and to keep refrigerated delicate foods for the rich class.
Thus if we track down the methods used for storing heat or cold, from these old times, we mainly find examples related to the search of a better thermal confort in residential buildings, through the use of thick stone walls or heavy slabs, and thick earth berms on roofs, and little use of what is now called phase change material (PCM). The recent (last 30 years) interest on such exotic ways of storing heat must be related to the modern evolution of human activity, starting with the industrial revolution of the last century : ancient brilliant civilisations took place in southern latitude (mediterranean shores, central america, south asia) characterized by a mild or warm climate ; but the use of coal and oil as a powerful means of producing mechanical energy (through newly invented thermodynamic engines), offered the opportunity to develop human activity in colder climates, with the generalization of space heating. The same process was more recently repeated by introducing industrial activity in hot and arid regions (in particular oil extraction) with the help of active cooling of buildings by heat pumps.

Following a similar tendancy, the agricultural sector now tries to develop out-of-season productions to meet the growing demand for a wider variety of foods.

By going further and further away from the natural conditions (in terms of ambiant temperatures and agricultural yields), the energy demand of the residential and the agricultural sectors increased steadily (not to speak of the industrial sector itself which of course followed an even faster evolution).
Heat storages started to become common auxiliaries of heat generators, and their nature varied with the type of source.

Whenever the energy source was a fossile or synthetic fuel or electricity, hot water tanks were enough to take care of a mismatch between a regular heat production and fluctuating demands. And this explains why water heating systems dominate throughout residential and industrial sectors (over air heating systems).

But last decade political events and subsequent tensions on the price of fossile fuels started a reassessment process of all possible technics able to improve the efficiency of energy consuming systems or to derive energy or heat from renewable sources (sun, wind, waves, biomass)

By doing so, more attention was paid to the temperature level of the storage and to its incidence on the efficiency of the thermal system. In particular, the renewed interest on heat pump systems emphasized the potential benefits that could be derived from isothermal storages ; while a popular approach, taking advantage of passive solar energy gains in house heating, stressed the need to smooth out temperature swings due to sharp variations in radiative flux.

Besides this, the development of large nuclear plants which produce, in some countries, up to 60 % of the total electricity, creates a situation where the offer is too rigid to adapt easily to the fluctuating demand (on a daily basis).
In order to improve that situation, reduced electricity rates have been created at night time, to promote heat storage technics able to take in charge the heat load during day-time.

All these factors explain why much effort has been devoted during the last ten years to develop new forms of heat storage, with improved heat capacity and better defined outlet temperatures, by means of highly performing phase change materials and sophisticated exchange geometries. However the practical impact of these new technics can be found deceivingly modest compared with the potential benefits that were predicted. The aim of the paper is to try to analyse the reasons for the present situation and to indicate in which directions some development of PCM should still be expected in the near future.

II SPECIFIC FEATURES EXPECTED FROM PCM :

1) High energetic density.

As mentioned before, efficient heat storages have long been used which were simply based on large volumes of water or rock beds. What specific feature of PCM and which circumstances should make this new way of storing heat or cold preferable ? The answer will be most easily provided by the illustration given by Fig. 1 which shows the amount of heat stored in water and in Na OH, H_2O, a typical phase change material for medium temperature application (melting temperature 64°C).
From this, it is obvious that a situation where the temperature of the water can freely fluctuate between 70°C and 20°C (supposing it can be efficiently used at any temperature) will not allow sodium hydroxyde to offer a very interesting bonus : it will merely allow to increase the heat capacity of a storage tank of equal volume by 50 % to 100 %, provided some efficient heat exchanger has be designed and introduced inside the storage.

However, if the user requires to have a nearly constant temperature (for example 55°C for domestic use) from the beginning to the end of the storage discharge period, the situation is quite different : then, the amount of heat usable from the water tank is only a small fraction of the previous one, namely 1/3, which means that the PCM storage offers 5 times to 7 times more usable heat in a given volume.

The comparison can even be more dramatic in some specific applications , as storing excess solar heat in a greenhouse for night heating. In that case, greenhouse internal temperatures usually do not exceed 20 to 25°C under sunny winter days, and average temperature required for the active night-time phase of the photosynthesis might be between 10 and 15°C. Given the 3°C to 4°C temperature gradient necessary to generate heat transfers between the air and the storage, it is clear that the temperature swing of the storage cannot exceed 4° to 5°C . In which case a water storage can only store 5 kWh/m^3 compared with 50 to 60 kWh/m^3 for some inorganic compound carefully selected for its adequate melting point, like some calcium chloride or Glauber's salt derivatives (fig.2).

2) Melting temperature range.

In such circumstances, an essential feature expected from PCM is to undergo complete melting over a narrow temperature range (a few degrees C). This is in general achieved in inorganic compounds, but can be far from being true with common organic PCM like paraffins , as Fig. 3 shows it (Ref 3).

3) Thermal conductivity.

Contrary to water storage, where the same fluid can be used simutaneously to carry the heat from the source and to act as storage medium, and where convective motions take place along exchanger surfaces, in PCM storages one usually separates the heat transporting fluid from the storage medium, to preserve its chemical composition and avoid corrosion. In addition, in the heat extraction process, a solid phase develops at the surface of the exchanger. Therefore a good thermal conductivity in the solid phase is an important feature of PCM, and care must be taken in avoiding too thick volumes of storage materials between successive heat exchange surfaces.

None of these remarks is new, and non exhaustive lists of known physical properties of most promising chemical materials has been established long before (Ref 1-5)
But it is interesting to make a difference between optimum theoretical values derived from purest grade materials, which can often be only observed in the first fusion-solidification process, and actual values concerning lower cost "industrial grade" materials or materials that have been physically or chemically modified in order to solve well known problems of incongruency, or nucleation. While we refer the reader to the abundant list of potential PCM quoted in ref.3 and 4 ,we rather present in Table I a few examples of characteristic phase change materials in the low temperature range .

From this can be drawn the following conclusions :

Organic materials, besides their higher cost and inflammability offer the lowest energy density per unit of volume and the lowest thermal conductivity (in the solid phase). Salt hydrates can offer much better prospects in terms of cost, compactness and conductivity ; but once various problems of incongruency and nucleation are solved, all energy densities fall in the range from 70 to 80 kWh/m³ in spite of higher theoretical values for some of them (pure Glauber's salt).

Furthermore, the thickening agents, that are often necessary to prevent segregation and to disseminate nucleating agents in the whole storage volume, tend to decrease the thermal transfers through the PCM, both in the liquid phase (since convective motions are reduced) and in the solid phase (since solidification in the presence of thickener may give rise to a porous solid medium). This explains why the figures quoted for the solid phase conductivity are often reduced with respect to those of pure cristals (0.7W/m°K instead of 1.1 for stabilized Glauber's salt for example)

In table I is quoted $KF, 4H_2O$ because it has long been proposed as a particularly suitable PCM storage component for low temperature applications (18° for greenhouses). This PCM is representative of the gap which exists between supposedly well known physical properties of salt hydrates and practical applicability : in fact nobody has ever found an effective nucleating agent for this nice congruently melting hydrate (subcooling always exceeds 8°C even in presence of Al_2O_3) (Ref 5) and there is no evidence that the production cost of this PCM can be brought down to a low value.

III PRACTICAL PROBLEMS ENCOUNTERED WITH APPLICATIONS OF PCM TO HEAT STORAGE :

1) Incongruency.

The problems of incongruency of some salt hydrates is sufficiently well known (Ref6-8) to allow us to go quickly through them. As the most promising inorganic material for low temperature heat storage appeared very early to be Glauber's salt, M. TELKES performed pioneer work to prevent phase separation during repeated cycles. Works by D. CHAHROUDI (Ref 9) are often quoted to mention various thickening agents adapted to various salt hydrates. As said before, the action of nucleating agents and their spreading inside the PCM volume is strongly helped by the presence of the thickener.
We thus mainly list in Table II the presently available stabilized PCM (developed by various laboratories with repeated thermal cycles tests) and simply mention that the thickeners actually used (when any) are not necessarily those quoted in the literature (Ref 6, 9): for example, the thickening agent

developped by CNRS (10) for calcium chloride is a needle shaped kind of diatomeous earth called Synedra, while Calor Company researchers use a cross-linked polymer resin to fight segregation in Glauber's salt. Other methods make use of additives (generally anhydreous salts) to modify the phase diagram and shift away undesirable hydrates liquidus slopes, (This is the case with Dow Chemical TESC 81° compound at 27° (Ref 11) or to create local eutectic like C.N.R.S. Serrolithe compound at 24,5°C (Ref 66) both predominantly made of Calcium chloride hexahydrate.

Table II only contains inorganic PCM which happen to be much cheaper than organic compounds (Calcium chloride for instance is a product of the Soda industry and is presently sold at $ 0.2/kg for preventing ice formation on roads, and Glauber's salt is not more expensive ; on the other hand, paraffins usually cost more than $ 1/kg).
This however does not necessarily means that no organic PCM can be found on the market : for instance, Addison Product Co. of the U.S. proposes Solar Therm, (12) a heat storage around 59°C, based on a paraffin ; and in the field of refrigeration Cristopia Cie (France) produces large thermal storages at temperatures between - 30°C and 0°C based on the use of various organic PCM encapsulated in spheres. (13)

2) Chemical agressivity.

Inorganic compound turn out to be more agressive towards their enveloppe than paraffins or polyethyleneglycol for instance. In particular, $CaCl_2$, $6H_2O$ can be destructive towards cement and concrete (Ref 14). A discussion on this topic can be found in Ref (15) and (16). As a rule, plastics and glass are usually found to be resistant. But even thick glass envelopes can be destroyed by the gigantic stresses created during cristallisation by hydrate cristals which happen to have molecular adhesion with the inner surface (17). Whenever metal (even stainless steel) is used, an internal coating must be used, and even then, it has been noticed that local puncture of the coating results in corrosion progress (Ref 18)

Plastics happen to be insensitive to most chemical agressions by salt hydrates. The weak surface adhesion with growing cristals prevents breakage under solidification stress. Among the most commonly used plastics can be quoted, from cheapest to costliest

High density Polyethylene	PEHD
Polyvinyl chloride	PVC
Polypropylene	PP
Polyurethane	PU
Polyester	PES

PEHD offers a bonus in terms of thermal conductivity (twice better than others) and barrier to vapor. PVC is easy to use in shorts series because it can be sealed by a PVC dissolution. PP is chosen for its good resistance to temperature (up to 120°C). PU has be used to make thin non-rigid encapsulation of sperical pellets (Ref 19). PVC and PP can be thermo-formed into large dimension units. PE and PEHD can mainly be blown in shape after injection or extrusion , within smaller dimensions, which is more costly en terms of investment but can result in a high production capacity.
Polyester can be chosen for its ability to create rigid and semi-transparent pouches filled with clear salt hydrates like TESC 81 or Serrolithe 24.5 (Ref. 66).

In all circumstances, the plastic envelope must be sealed airtight so that no water admixture or loss can ever modify the water content of the hydrate : the melting temperature and the phase change latent-heat content crucially depends on the precise composition of the mixture.

IV SHORT CLASSIFICATION OF ENCAPSULATION GEOMETRIES :

Plastic envelopes mentioned before as the most convenient ones for inorganic materials can be rigid or non rigid. It is possible to imagine two kinds of non rigid encapsulations : one that will simply take the form of a bag, made with complex laminated foils (metal + plastic) to be set on horizontal trays for making a simple plate heat exchanger (20-22) ; the other one, more tricky, assumes one can wrap spherical solid PCM pellets by a dipping method (19-23), and take advantage of dilatation during melting to preserve the spherical shape.

But the ability of the film to resist to the severe stresses created by piling up pellet beds is under question.
Most practical solutions make use of rigid plastic containers which do not require specific structures to be arranged into simple heat exchangers.
Among all possible rigid geometries, it is possible to make a distinction according to their behavior in the presence of volume change of their PCM content.

1) Effect of volume change.

It can be noticed from the literature {Ref3-4} that most PCM undergo a volume contraction when solidification takes place, and this is fortunate for the container. This change of volume is usually close to 15 % for organic as for inorganic PCM, with a few exceptions like polyethylene glycol E 1000 (dilatation of 1 %) and most nitrate hydrates which exhibit only 5 to 6 % volume contraction.

The containers will usually not be 100 % filled with the liquid phase material, for simplicity and security. So that a void exists from the beginning in the container. It is important to notice that this void affects very differently various geometries as show in Table IV .

Except for the case of long vertical cylinders, the void affects the exchange surface more seriously than the volume. Its effect can even be dramatic (50 % reduction) for thin plates which loose the PCM contact on their upper surface, except for exceptional conditions of surface adherence.

It is possible to estimate the shape of the free surface of the solid after solidification with some simplified assumption : let us suppose strong adherence on the surface of a vertical cylinder of great length in the y direction

The differential equation for the function y (r).

$$2 \pi r h \varepsilon \frac{dr}{dy} = - \pi r^2$$

is solved into $y = - 2 \varepsilon h \text{ Log } r/R$ where ε is the contraction rate

Thus the solidification takes place with a deep well in the center of the container, down to its bottom, as suggested by Fig.4 .
But it still does not really modify the wet surface of the container (unless the adherence hypothesis does not hold).
This contraction process may be however at the origin of a simple method to prevent phase separation in a slightly incongruent material like $CaCl_2$, $6H_2O$: {Ref 24} mentions that no phase separation is observed after a few hundred cycles when $CaCl_2$, $6H_2O$ is prepared with a slight excess of water (between stoechiometric and peritectic points). It might be that the stirring process produced by the creation of the well, and evidence by calorimetry by J.D. SYLVAIN {Ref 25} is enough to prevent density stratification and subsequent segregation in such a container

Another effect of volume change can be evidenced in plastic prismatic containers with a square section and large vertical height. Such PVC containers filled with calcium chloride {Ref 26} have exhibited opposite deformations at the top and at the basis, due to depression at the top during solidification and excess of pressure at the bottom during melting, thus making them unsuitable for being assembled side by side in a regular way, or even to be included inside a concrete wall (the contact with concrete would be poor in the upper section Fig5).
As a result, cylinder with circular basis seem to be the only suitable geometry in such applications. But this,of course,restricts the ability to increase the ratio S/V of the exchange surface to the internal volume, unless one choses small diameters (at the price of a small capacity per container).

A solution consists in modifying the flat plate geometry to make it mechanically resistant to deformations, by means of welded internal bridges or contacts like shown in Fig (6). Such a geometry can be obtained by a variety of different approaches (by assembling corrugated plates for example as it will be described below) and gives the benefit of reducing the negative effect of volume contraction on the wet surface.

V-MAIN THERMAL CHARACTERISTICS OF PCM STORAGE UNITS

The storage geometry influences both external heat transfers from the source and internal heat transfers through the di-phasic medium. On the outside, mainly 3 types of physical conditions can occur :

i) convective heat transfer by a liquid or a gaz ,
ii) conductive heat transfer through a solid medium (PCM envelope imbedded into concrete),
iii) direct radiative gains or emission on the surface .

On the inside, two types of processes take place :

i) melting process at the contact of the envelope ,
ii) solidification process at the contact of the envelope when melting takes place, two cases can happen : either the PCM in its liquid phase is able to undergo convective stirring, or its viscosity (due to thickening agents) is such that heat transfers take place by pure conduction through the static liquid medium. When solidification takes place, heat transferstake place by pure conduction through the solid medium.

Finally, we can mention the heat resistance opposed by the envelope itself, which is in general quite weak.

The literature is rich in various experiments and estimates on the previous heat transfer processes.

a) Influence of internal convective motion in the heating process of the PCM.

Most of them concern organic PCM because they are ready to be used and easier to manipulate in laboratory tests than salt hydrates.

Effets of heat transfer enhancement during charging processes were evidenced on naphtalene in an horizontal cylindrical tube of 4 cm diameter by K. KATAYAMA et al {Ref 27} ; they observe an increase of heat transfer by a factor between 2 and 3 (with respect to pure conduction) during melting due to convection motion of the liquid in the annulus region Fig .7 .

In a rectangular box geometry filled with cytoparaffin, J.P. BARDON and al {Ref28} observe a more modest increase (of the order of 50 %) of the melting rate due to convective motions, and successfully accounts for this by Nusselt correlations valid for laminar and transition modes.

C. BENARD et al {Ref 29} report a 25 % increase of melting rate compared with pure conductive mode in a geometry of a vertical box submitted to direct radiation gain.

In the case of a finned type exchanger immerged in myristic acid, A. ABHAT {Ref 30} observes just enough convective motion to compensate for the difference of heat conductivity between liquid and solid.

Convective motions inside hydrate salts were also evidenced, by B. CARLSSON and G. WETTERMARK {Ref 31} in calcium chloride hexahydrate and by L. KELLER {Ref 32} in sodium hydroxyde monohydrate (Fig . 8) with immerged heat exchangers.

In all these cases, the smaller heat conductivity of the liquid phase is more than compensated by free convective motions, so that heat transfer coefficient during charge periods can exceed that of discharge .

Morever , the density difference between solid and liquid phases can reduce the distance between the surface of the envelope and the solid to be melted. This will happen whenever the geometry of the container allows for free motions of the solid, provided the liquid phase is not too viscous, and the lower part of the container also receives heat.

A detailled discussion in the case of horizontal tubes is given by E. M. SPARROW and G. T. GEIGER in {Ref 33}. In the case of paraffin, the downward motion of the solid accountsfor a 50 to 100 % increase of melting rates, which in turns shows that convective motion in the liquid are not sufficienlly strong to make the transport distance irrelevant.

In the case of inorganic salts, we find less evidence of free falling solid effect in the literature. One reason is that not many unthickened salt hydrates can be used repeatedly without phase segregation, another one being that the cristal structure is sufficiently intricated to hold the partly melted solid phase in place (for example, in the case of $CaCl_2$, $6H_2O$, the fusion process takes place on the surface of needle shaped hexagonal cristals, leaving their arborescent structure intact until most of the solid has disappeared).

This situation is not dramatic since heat conductivity of salt hydrates is 3 to 4 times larger than those of organic PCM.

As a result it will be more reassonnable to analyse thermal characteristics of PCM storage geometries in the frame of purely conductive internal exchanges, assuming heat conductivities in the range 0,5 to 0,7 W/m°C for the liquid and the solid phase as well.

The following discussion assumes that heat exchange takes place through an external convective exchange coefficient he, an enveloppe of thickness e and conductivity λe, a PCM material of conductivity λm. The adopted geometry is that of a sphere of radius r. An empirical contact resistance $R_c = 6.10^{-3}$ introduced between all liquid and solid phases was fitted from observed results in a sphere of 7.5 cm diameter (Ref 13).

Let $x = \frac{\rho}{r}$, where ρ denotes the radius of the fusion front and 0<x<1 is a measure of the fusion rate of the storage content.

Then, in a simplified approach assuming steady heat transfers, one can define a conductant factor K(x), in W/m²°K, expressed as

$$1/K(x) = \frac{1}{he} + e/\lambda e + R_c\ (1+1/x^2) + r/\lambda m\ (1/x-1)$$

A few important features can be extracted from this elementary expression.

i) the term e/λe contributes to a resistance comparable to a thickness of (2·e) or (4·e) of the PCM material itself, which is not dramatic, given the value of e (10^{-4} to 2.10^{-3}m).

ii) K (x) is strongly dependent of the fusion rate x when he is large (convective exchange with a liquid he ≈ 300 W/m²°C) but does not vary as much when he is small (convective exchange with air : 10 to 30 W/m²°C). This is illustrated by curves of Fig. (9).

This means that large differences in the convective coefficient do not necessarily imply large differences in $\overline{K}$ (calculated as the value of K (x) for an average PCM melted fraction).

Therefore, we can even say that the main characteristics of phase change materials (their constant temperature during melting of solidification processes) is better exploited in a PCM storage exchanging heat by air convection rather than by convective exchange with a liquid, provided that a sufficient surface of exchange has been offered for the heat transfers.

In any case, the conductivity of the phase change material, even in the best conducting salt hydrates, affects the heat transfers in a way that reduces the gap between air and liquid convective exchange coefficients : Table III shows in fact that convective exchange coefficients as far apart as 20 and 200 W/m²°K give rise to degree-hours factors much close together (a factor 2 to 3 only separates them).

In the case of radiative transfers (corresponding to direct solar gains on the PCM storage for example) or transfers by solid conduction (PCM storage embedded in a heated solid medium) the situation is similar to one with very high convective exchange coefficient, and therefore the transfered heat flux will be strongly dependant on the melted fraction of PCM, unless some clever device allows to take advantage of the above mentioned "free falling solid" process in the course of melting.

3) Influence of the storage configuration on convective transfers.

Once a given S/V characteristic range has been selected, it is possible to improve the convective transfers by modifying the flow pattern around the PCM containers. Three factors can be combined to act in this direction:

i) the compactness C of the storage : which is measured by the ratio (overall volume) / (PCM volume). The compactness is a factor of increase of the front fluid velocity :

$$v^{(1)}_{fluid} = v_{front} \cdot {}^{1}/_{(1-C)}$$

ii) The tortuousness ζ of the flow lines (Fig 10), which measures the increase of flow line length :

$$\zeta = d'/d$$

$$v^{(2)}_{fluid} = v^{(1)}_{fluid} \cdot \zeta$$

An illustration is given by the replacement of spheres by oblate ellipsoïds in a storage bed (Ref 34-35); Fig. 11. In that particular experiment, the ζ factor was increased from 1.5 (for spheres) to rougly 2.0 with the use of a triaxial geometry 1 : 2 : 3 for the containers. The resulting increase in fluid speed is close of 30 %.

iii) Disrupting the boundary layers in the flow pattern.

This effect, which is used in finned type exchangers, can be helpfull in PCM storages : instead of using thin container plates with large surfaces tangential to the flow, it is more effective to create singularities that destroy laminar boundary layers developed on surfaces of the containers.
This is achieved in the pebble geometry discussed in ii), and actual measurements, in Fig. 12, show that heat transfers are much better reproduced with the Nusselt correlation of a single sphere, in a turbulent flow :

$$Nu = 0.31\ Re^{0.58}$$

rather than by the usual Nusselt correlation valid for turbulent flows in ducts :

$$Nu = 0.036\ Re^{0.8}$$

The Reynolds numbers corresponding to this experiment were slightly above the turbulent threshold.

For larger Reynolds numbers, the situation can be reversed at some specific values of the velocity, due to depression effects in the back side of the obstacles, as it was observed by MOLKI (Ref 36) in a corrugated duct.

The question of augmented convective transfers by corrugations is certainly not yet completely understood, and its analysis is related to the difficult problem of the stability of fluid flows and the properties of organized vertex flows (Ref 37)

One can conclude nonetheless that disrupting the flow pattern inside the storage volume is in general favorable to heat transfers, but results of course in higher head loss.

VI- EXAMPLES OF COMMERCIALLY PRODUCED STORAGE COMPONENTS.

The list is not exhaustive but gives a brief insight to the existing technology.

1) Small diameter cylindrical tubes.

- 38 mm diameter, 1 meter long PP cylinders (Calortherm { 38 }).

$S/V = 100\ m^2/m^3$

proposed PCM contents : various salts derivated from stabilized Glauber's salt with melting temperatures of 7°C, 18°C, 31°C ; sodium acetate trihydrate (48°C and 58°C) and sodium pyrophosphate (70°C).
Suggested applications : heat storage banks in convective air exchange.

- 50 mm diameter, 0,8 m or 1,10 m long cylindrical tubes, by Sunzorb (Calortherm { 38 }).

$S/V = 80\ m^2/m^3$

propose PCM content : stabilized Glauber's salt (31°C)
Suggested application : stacks of directly insolated horizontal tubes behind glazing Fig. (13).

2) Cylindrical tubes of large diameter.

a) 9 cm diameter, 2 m long HDPE tubes.

Producers : Thermalrod 27 by EMI inc. { 39 }
Thermol 81 by PSI Energ Syst. Inc. { 40 }
or Blue Lakes Engineering { 41 }
Heliotube by Heliopin International { 42 }

$S/V = 44\ m^2/m^3$

PCM content : $CaCl_2$, 6 H_2O with additives (27°-28°)
(Dow Chemical TESC 81 or Solvay Chliarolithe)

Suggested use : direct solar gain applications or centralized heat bank.

b) 12 cm diameter, 0,6 m long metal tube.
Producer : Boardman Energy System Inc. (43)
S/V = 36 m^2/m^3
PCM contents : various Glauber's salt derivatives at 7°, 17°, 23°, 25°, 27°, 32°C.
Suggested use : direct solar gain applications.

c) 11 cm diameter, 18 cm long metal
Producer : Texxor Corporation (44)
S/V = 46 m^2/m^3
PCM content : $CaCl_2$, 6 H_2O + additive (27°C)
Suggested use : direct solar gains applications or centralized heat banks

3) Flat box configuration.

a) 30 cm x 60 cm x 5 cm PE box
producer : Valmont energy system (45)
S/V = 50 m^2/m^3
PCM content : stabilized Glauber's salt 31°
Suggested use : convective heat exchanger - storage or direct gain solar component.

b) 60 cm x 60 cm x 5 cm polymer resin box "Sol. Ar. Tile"
Producer : Archit. Research Corp. (46)
S/V = 90 m^2/m^3 (1 side only)
PCM content : modified Glauber's salt (23°C)
specific use : storage tile for ceiling

c) 2 cm thick flat bag in laminated complex plastic foil ("Heat-Pac").
Producer : Colloidal Material Inc. (22)
S/V ≈ 100 m^2/m^3
PCM content : stabilized Glauber's salt (31°C)
Suggested use : storage bag to be set on horizontal
racks (heat central bank or ceiling tiles)

d) 1 m x 1,20 m x 4,5 cm PE flat box "Thermo-phase"
Producer : Holiday Energ. Product. (47)
PCM content : $CaCl_2$, 6 H_2O + additive (Dow Chem.) 27°C
Suggested use : component for convective heat exchanger storage

e) 40 cm x 60 cm x 1 to 4 cm fiberglass pouch "Sun-lite".
Producer : Solar component corporation (48)
S/V : 160 or 80 m^2/m^3 according to use .
PCM content : $CaCl_2$, 6 H_2O + additives, 27°C
Suggested use : translucent storage component for direct solar heat and
daylight in buildings.

3) Complex structures for augmented convective heat transfers.

We refer here to non-connex volumes in which both mechanical properties of the container and convective heat transfers on its surface are improved by the use of specially designed surface corrugations.

a) Enerphase panel 50 cm x 36 cm x 6 cm
Producer : Dow Chemical Corp. (11)
S/V : 80 m^2/m^3 (counting all sides together)
40 m^2/m^3 for practical applications
PCM content TESC 81 ($CaCl_2$, 6 H_2O)
27°C
Suggested use : passive solar component to create phase change Trombe walls in light constructions.

b) See also in this section Thermophase panel mentioned above.

4) Spherical encapsulation.

a) PE or PP 7,5 cm diameter spheres.
Producer Cristopia France (13)
S/V : 80 m^2/m^3
PCM content : NaOH, 1H_2O (64°C)
$CaCl_2$, 6 H_2O (TESC 81)
Application : large dimension H_2O (0°) ; various PCM (from-30to + 90°C)
liquid-exchange heat stores for heating and cooling industrial
applications.

b) PCM Pellets in soft coating (latex) 1 to 3 cm diameter.
Producer : Pennwalt Corporation (23)
S/V ≈ 200 to 700 m^2/m^3
PCM content : Calcium chloride
Glauber's salt
Paraffins

Application : additives for concrete.

5) Large containers with internal heat exchangers.

a) Calmac Heatbank : PE tank 1,20 m diameter x 1,20 m high with 1500 m PE
12 mm tubing for heat exchange.
Producer Calmac manuf. Corp. {Ref49}
S/V : 50 W^2/m^3
PCM content : ice, Glauber's salt eutectic at 17°C,
$CaCl_2$, 6 H_2O (TESC 81)
Na_2 S_2 O_3, 5 H_2O at 48°C
Mg Cl_2, 6 H_2O at 115°C
Application : liquid exchanger heat storage for solar or other applications.

b) ENSM.Cezanne prototype storage tank {Ref50} similar technics to Calmac.

c) Heliopin "Spiro-accumulateur" {Ref42}.
Prototype using a spirally distributed extruded polypropylene double layer mat.
S/V : adjustable according to specifications
PCM : various (in particular calcium chloride, sodium acetate or sodium hydroxyde hydrates).

VII - ILLUSTRATIONS OF PCM STORAGE APPLIED TO SPACE HEATING.

As more and more PCM storage containers start being commercially available, it is not our purpose to account for all interesting applications in space or domestic hot water heating. A few configurations are selected and described below for their demonstrative character, and the availability of thermal data on them.

1) Direct solar gains on large diameter storage tubes.

One of the earliest solar house designed with a remote directly insolated low temperature PCM storage is French Grimaud Solar house completed in 1978 {Ref. 51}. Fig. 14 gives a brief insight of the Solar hybrid system assisted by a air to air heat-pump : for the sake of the experiment (this was the first full dimension, stabilized calcium chloride hexahydrate storage ever used in a domestic application), the storage volume was kept outside the house volume, in a doubly glazed greenhouse protected by north-east and north-west earth berms.

Storage container were 10 cm diameter standard PVC tubes painted black, filled with ANVAR-CNRS patented Chliarolithe {Ref 10} (stabilized $CaCl_2$, 6 H_2O).
The heating system consists in a closed air loop successively crossing the greenhouse and the house at a rate close of 7 vol./hour. A typical temperature record is shown in Fig. 15 : the storage goes through complete melting after a couple of sunny days ; but the heat extraction at night is obtained in two successives processes ; during the earliest part of the night, air is still heated to a temperature above 24°C by mixed convection on the storage ; for the latest part of the night, it is necessary to assist heat extraction by a heat pump, so that the greenhouse temperature can decrease below 20° and the temperature of the air blown to the house stays between 24 and 30°C. This is of course the consequence of having chosen, for simplicity reasons, a storage geometry characterised by a low S/V ratio. Nevertheless, the choice of operating a heat pump for part of the night after sunny conditions is not unreasonnable, since it will be used as an auxiliary heating system during bad winter conditions and since french electricity rates are reduced for night use. This house has been operating very smoothly since the time of its completion ; it is often quoted as a clever architectural solution for combining solar gains and a traditional building pattern.

2) Low temperature latent heat storage embedded in a solar wall.

The next step in integrating PCM solar systems in a building is of course to reproduce the well known technics of Trombe walls with the help of latent heat materials. The aim is to reduce the wall mass and to take advantage of the natural temperature control provided by the fusion-solidification plateau. This concept was experimented as early as 1978 on a reduced scale {Ref 52}. More detailed analysis was reported by various authors later{Ref 29&53) which confirm the benefits obtained with PCM both in terms of mass and confort. But it still appears that the main draw back of Trombe walls remains true with PCM storage : strong heat loss from the storage to the outside, and overall poor K value for the PCM Trombe wall under adverse weather conditions. With this in mind, a modified PCM Trombe wall was designed which combines the passive restitution mode with active solar gains, so that night heat losses to the outside can be reduced to a minimum ; this is how the so-called phase change diode wall was created, first in terms of reduced size prototypes {Ref 54}, then in terms of a full scale realization in the Cogolin Solar house {Ref 55}.

Again, this prototype house used 10 cm diameter PVC storage tubes filled with stabilized calcium chloride (Chliarolithe) but in this configuration, the storage tubes are heated by warm air convection on their outer half surface, while the other half is embedded inside concrete and act as a temperature buffer for the wall.

The south facing side of the wall is treated as an air collector and the storage side is protected from heat losses by the rigid insulation which supports the absorbers of the air collector Fig. (16).

This solar wall was monitored in the absence of any other source of heat in the house, and it was found that the coupled air collector - PCM storage system was able to reach an overall daily efficiency between 30 and 40 %, thanks to reduced heat losses of the storage, the collector itself made with a single selective glazing and an expanded steel absorber being able to operate with a 40 % to 45 % efficiency. Temperatures observed in the solar wall are shown in Fig.17 This solar wall of course only contributed to heating the adjacent (60 m²) main room, but it can make the heated volume confortable even without any auxiliary, through a low temperature radiant heating by a 25 m² wall. It should be noted here that the thermal resistance opposed by the concrete during the restitution phase is not a serious problem : it amounts to less than 25 % of the total resistance to the heat flux.

The concept of phase change diode wall has since evoluated and more recent prototype realizations were done with the help of double envelope (annular section) tubes much easier to include in a concrete wall.

3) Radiant slab based on the use of a phase change material.

This is of course the ideal application for low temperature phase change storage : a 10 to 15 cm thick slab leaves enough room to locate PCM containers and reach a very high thermal storage capacity ; the large available surface for heating the space allows for low heat flux and thus low temperature gradients inside the slab. Therefore the surface temperature of the radiant slab can be very precisely regulated by the phase change temperature plateau of the latent heat material.

The previouly mentioned double-envelope cylindrical geometry which is designed to encapsulate PCM in the annular volume and to manage heat transfer from an incoming fluid in the internal duct as Fig. 18 shows, is particularly suited to make phase change radiant slabs. A detailed investigation of possible annular geometries and relative dimensions was undertaken (Ref56) and a real scale application was realized in a solar house in Annot, France (Ref 57) (Fig. 19) using Chliarolithe (28°) as a storage medium.

The radiant slab, shown in Fig. 20 under construction, is intended to provide enough storage capacity, to keep the auxiliary heating (electric resistances imbedded into the concrete within close distance of the PCM containers) switched off during 16 consecutive hours (day-time electricity rate).

The operating modes for heating are the followings : in case of unoccupancy conditions, the house is maintained at a moderate temperature level by means of active solar contribution, large double glazing windows (totalling 24 m²) acting as air collectors with the help of internal shutters, while a fan forces warm air through the slab to charge the PCM storage annular containers and additional concrete mass ; when the internal ambiant temperature falls below a selected level, back up electric heat is provided to the slab at night. During occupancy, shutters are opened during the day and direct solar gains hit the slab from above, storing sensible heat in the upper concrete part of the slab. Given the outstanding insulation characteristics of the house, (wall, ceiling and floor K values close to 0,2 W/m² °C), the active solar system was able to keep the house safely above freezing by - 15°C outside temperatures. In the passive mode, where solar collection efficiency is at its best and night insulation still maximum, the house needs no auxiliary heat after 2 days of warming up. Under consistently overcast and cold periods, back up heat is provided at night exclusively. In terms of physiological confort, the so-called "radiant" heating by the slab (which of course includes convective heating as well) allows for moderate (18°C) air temperature and is felt by occupants as a most pleasant way of space heating. (In fact, the surface temperature of the floor oscillates between 21 and 23°C and is even not felt as the actual source of heating).

Fig.21 shows the result of numerical simulations in terms of isothermal lines in the slab.
The temperature filter effect provided by the phase change material is particularly efficient in this configuration.

4) Radiant ceiling with phase change materials.

The construction of a PCM radiant floor requires to be specially cautious in terms of possible container failure, since salt hydrates, and in particular calcium chloride reacts with concrete and decrease its mechanical resistance. In addition, contractors being liable for a long term (10 years) period may have a reserved attitude toward such new technics. Most probably, the development of PCM radiant slabs will be delayed until prefabricated, ready to use slab components are produced on an industrial level.

On the contrary, prefabricated ceilings can be designed in a much simpler and lighter way and do not enter in the category of building structures components. This is why there exists a symmetrical approach to the problem of radiant surfaces where PCM containers (usually pouches of laminated plastic complex) are simply set on horizontal trays which are placed as ordinary ceiling tiles . Two industrial manufacturers were listed in the previous chapter, which in fact represent the logical continuation of a now well known demonstration : MIT Solar building n° V, designed and instrumented by T. JOHNSON (Ref 58).

A nice feature with PCM ceilings is that thermal exchange with the space is easily achieved : the thermal contact of the PCM with the supporting structure being kept optimum by gravity. However, other features are more demanding : because of air stratification, the main heat exchange with the space below will be achieved by radiative transfers only, (i.e. only 50 % of what a floor can contribute with the same temperature surface) ; and most of all, the heat source should be directed to the ceiling, which is not all that easy when it is solar energy. The problem was solved in a clever way by means of properly oriented reflexive louvers placed in the double plane windows.

In terms of practical applications, this technics is remarkably adapted to retrofit operations, and all components of the system are now available on the market.

In terms of heat coverage and thermal confort, it is clear that solar gains actually stored are relatively modest and that occupants may suffer from a temperature stratification and a somewhat large temperature swing between day and night.

5) Latent heat storage for hot water production.

This is of course a very wide domain, but, as said in the beginning, latent heat storages will only be really usefull in particular situations where a large temperature swing for the produced water is excluded. This typically includes domestic hot water, hot water procuded by heat pumps, and hot water produced for feeding radiant slabs.

Having quoted a few industrial or prototype PCM heat tanks in the previous chapter, we will briefly mention here the performance observed with the "spiro-accumulator' tentatively developped by Heliopin (Ref 42) and tested by CNRS.

Fig 22 shows the geometrical design of the tank and its embedded exchanger. The nice feature about this design is that different potential applications, related to different temperature gradients during operations, can be defined, by simply varying the length of the polypropylene extruded mat spirally rolled up in the cylindrical tank.
The tested prototype, with a heat capacity of 7 kWh at 28°C (Chliarolithe PCM) was able to deliver water with a very stable temperature around 27°C, corresponding to a stable output of 650 W (Fig. 23), achieved with 8.4 m^2 of exchanger surface. It would be easy to deduce from such measurements an optimum geometry for storing 15 kWh around 45°C (for domestic hot water) or 100 kWh around 30°C for space heating by a radiant slab ; the larger unit being obtained for example by simply coupling smaller unit in parallel or series modes.

VIII - ILLUSTRATION OF PCM STORAGE APPLIED TO GREENHOUSES.

The idea of storing excess heat generated in greenhouses during sunny day times (in many cases, the optimum temperature conditions for a plant or a vegetable require to refresh the greenhouses by natural ventilation) and of using that heat at night for reducing energy consumption is not new.

During the last ten years, two kinds of approaches have been developped :

i) greenhouses with semi-transparent liquid collectors on roof (Ref 59)

ii) greenhouses with air-exchange heat storages (Ref 60)

The first approach gave rise to very sophisticated applications but its cost remains very high and it can mainly concern newly constructed facilities.

The second approach is more pragmatic and can be retrofilled to ancient facilities.
But as we mentioned in the beginning, the available temperature swings for heat exchanges with the storage are quite limited and the time delay for charging the storage is quite short (6 hours typically in winter). Therefore, the adequate PCM heat storage must

i) have a suitable melting point

ii) be encapsulated with very large S/V ratio containers.

The first requirement is now easier to fulfil : newly developed eutectic materials, either from Glauber's salt hydrates (38.43), or from calcium chloride hydrates (61-66), offer a wide range of possible fusion points (from 18°C to 25°C, almost degree by degree).

The second requirement is still a challenging problem, specially in terms of economics. Early experiments were performed with flat bags (1 to 2 cm thick) on horizontal trays, and the results of detailed monitoring have been published (62-64).
Several essential features can be singled out :

i) it is possible to extract and store a large fraction of the night usual thermal loads in southern latitudes of Europe, it is even possible to ensure complete autonomy for demanding production like roses under mild climates like in Israel (Ref 65) and in probably most countries of northern Africa.

ii) heat exchange processes in greenhouses are enhanced by evaporation-condensations effects ; but sanitary conditions for the vegetal may restrict the systematic use of nearly saturated ambiance environment.

iii) The performance of air exchange heat storages and the heat loss coefficients of greenhouse covers are closely related factors ; and a well designed solar greenhouse should integrate several features : solar transmission, air tightness, thermal insulation, CO_2 injection, humidity control (by humidification and de-humidification systems).
The present stage of developpment of C N R S designed Solar greenhouses includes the use of small dehumidifying heat pumps, CO_2 generators, and a new geometry for PCM encapsulation called "Serrodule" which will be shortly described now.

Serrodule geometry:

A container was designed with the aim of achieving good mechanical resistance to volume changes of the content, a large S/V ratio, enough content volume and the ability to be simply piled up to make 50 % compacity air heat exchangers. This container is made of two corrugated plastic shells which are welded together on the edges and on each opposite corrugation contact (Fig.24). The S/V ratio is a simple consequence of the amplitude a of the corrugations :

$$S/V = \frac{2.8}{a} \text{ in } m^2/m^3 \quad (a \text{ in } m)$$

for corrugations with a symmetrical pattern.

The volume of the container is the product of the projected area of the shell by the amplitude of corrugation $V = S_o \times a$.

Therefore such a design allows to select arbitrary combinations of volumes and S/V ratios, within the limits of usual thermo-forming equipments. Typical values of V and S/V obtained with PCV sheets and a standard plastic transformation machine are 2 dm^3 to 4 dm^3 and 200 m^2/m^3 to 300 m^2/m^3, higher S/V ratios being of course more expensive in terms of encapsulation costs.

Successive adjacent serrodules are piled up to form heat exchangers batteries (Fig.25) with a compacity varying between 40 and 45 % (depending on edges overlap). Air flow through the battery takes an helicoïdal pattern resulting from oblique incidence on corrugations (Fig.26). The tortuousness parameter can be varied by selecting different corrugation orientations with respect to the main flow direction.

Heat transfer coefficients are being investigated in a laboratory experiment shown in Fig (27) using a humidity controlled, heated air loop, in order to reproduce actual greenhouse conditions. Convective heat transfer and mass transfer contributions are shown in a few representative curves (Fig.28). A typical feature is the existence of two distinct processes, one in which water condensation occurs on the surface of the serrodules and sharply increases the charge rate, and a later one in which an evaporation process of the previously condensed water substracts its contribution from the purely convective part.

A real scale application of serrodule PCM storage applied to greenhouse heating was undertaken in a joint C N R S - I N R A programm. A 200 m² double layer extruded polycarbonate greenhouse (Fig.29) in France Montfavet I N R A station. A 2,5 ton, 100 kWh serrodule storage filled with a Serrolithe 22°C (66) compound was installed, and tomato culture was started in january 1986. The greenhouse temperatures and auxiliary fuel consumption were monitored and an illustration of the observed parameters is shown in Fig.30 . The main features are the following : temperature conditions to charge the storage are fulfilled in early march only, indicating that the outside temperatures and the heat loss coefficients of the greenhouse situated in the windy Rhone valley are two severe for a 22°C melting temperature point storage (a 20°C storage would be better suited). When temperature conditions and solar radiation are favorable, the heat storing proceeds quite efficiently though a combination of convective heat and mass transfer ; then, as it is usually done in professional greenhouses, a natural ventilation is allowed in the afternoon, to decrease both temperature and humidity before the night period ; this creates a situation where evaporation processes cancel the convective contribution to the storage : during this period fans are activated for merely drying up the storage. Whether this strategy, which is favorable in terms of phyto-sanitary conditions, has to be rejected or not on the basis of thermal efficiency remains a subject of discussion.

Nevertheless, the use of "serrodule" containers for PCM storage in greenhouse together with the emergence of new inorganic compounds with melting temperatures in the range 18°C to 24°C is a very promising evolution in a technic which already proved to be quite successful in saving energy in agriculture.

VIII - CONCLUSION

This rapid survey of some presently available technics applying PCM storage to space heating in buildings and greenhouses was not intended to be exhaustive. But it gives an illustration of the actual difficulties to introduce non conventional materials in a field where tradition has deep roots.

Phase change materials can indeed be the source of decisive improvements in the domain of heat storage, both in terms of temperature control and compactness. But the present stage of industrial developpment is still too primitive to really offer full advantage of genuine PCM properties.

With the exception of sub-freezing temperature storage for refrigeration applications, few examples of successful applications of PCM storage exist at present on an industrial level. Most proposed storage components enter in the category "ready-to-use" kits for passive solar applications, with modest thermal performance ; this means that the gap between the abundant theoretical literature on optimized heat exchanges with PCM and actual proposed geometries is still wide open. On reason is certainly the problem of production costs of well designed encapsulations : a favorable S/V ratio for a mechanically resistant envelope translates into a non negligeable plastic-weight/storage-weight ratio. As the cost per kg of rough plastics is already five times larger than the cost of PCM, it is clear that transformed-plastic containers tend to cost much more than their PCM content. Still, the packing industry has shown how scale factors can help reduce costs, and the wide potential market for PCM heat storages is in favor of such cost reductions.

In the near future, every specific problem encountered with PCM, namely

- safety against container failure,
- cost of encapsulation
- cost of transportation,
- problem of integration

can be resolved in an inexpensive way, since similar problems have been solved in other cases (safety of chemical containers, long experience of the packing industry, organized transportation of low added value products, prefabrication technics in buildings).

But the best advocate of PCM materials will certainly be

- the concept of thermal confort
- the security of some thermal self-sufficiency

much more than the prospect of saving energy and money on a long range, which should simply be a bonus.

TABLE I

Some characteristic low temperature inorganic and organic chemicals for heat storage by enthalpy of phase change.

	PCM formula	Melting temperature °C	enthalpy MJ/m³	conductivities λ (solid) W/m°C	Remarks
INORGANICS	H_2O	0°C	307	2.2	
	NaOH, 7/2 H_2O	15°C	340		supercoolin
	KF, 4 H_2O	18,5°C	330		"
	$CaCl_2$, 6 H_2O	29,5°C	290	110	incongruent + supercooling
	Na_2 SO_4, 10 H_2O	32°C	377	0.54	incongruent + supercooling
	$Ca(NO_3)_2$, 4 H_2O	43°C	240		supercoolin
	Mg $(NO_3)_2$, 6 H_2O	89°C	253	0.66	
ORGANICS	C_{16} H_{34} (hexadecane)	17,5	195	0,20	expensive low conductivity
	$H(OCH_2CH_2)n$ OH (polyethylene glycol 600)	20-23°	165	0.21	low conduc low enthal
	polyethylene glycol 1000	33-36°	169	0.17	" "
	paraffin 46-48	46-48°C	126	0.22	" "
	cyto -paraffin	54-56	105	0.27	" "

TABLE II

Non exhaustive list of PCM materials available on the market in 1986.

Stabilized	Content	T_f	Manufacturer
Glauber's salt and derivatives	$Na_2SO_4,10H_2O$ + thickener	32°C	Calor Alternative Energy G.B. Calmac Manuf. Corp. U.S.A. Boardman Energy Syst. Inc. U.S.
	$Na_2SO_4,10H_2O$ + thickener + NH_4Cl + KCl	23°	Calor Alt. Energy. G.B. Boardman En. Syst. Inc. U.S.
	$Na_2SO_4,10H_2O$ + thickener + NaCl	17°	Calor Boardman
	$Na_2SO_4,10H_2O$ + thickener	7°	Calor
Calcium chloride hexahydrate and derivatives	$CaCl_2,6H_2O$ + thickener (chliarolithe)	29°	Solvay Cie Europe *
	$CaCl_2,6H_2O$ + KCl	27°	Dow Chem. Cie & Texxor Corp. (TESC 81 X Bisol II)
	$CaCl_2$,hydrates + $KCl+NH_4Cl$	24,5°	Solvay & Cie Europe *
	$CaCl_2, 6H_2O$ + $KCl+NH_4Cl+$ nitrate + thickener	21,5°	Solvay & Cie Europe *
Others	$MgCl_2,6H_2O$	117°C	Calmac Manuf. Corp. U.S. Dow Chem. Cie
	$Mg(NO_3)_2 6H_2O$	89°C	Dow Chem. Cie U.S.
	$MgCl_2,6H_2O/Mg(NO_3),6H_2O$	58°C	Dow Chem. Cie. Calor
	$Na_2S_2O_3,5H_2O$	48°C	Calmac Manuf. Corp U.S.

* C.N.R.S. and Solvay patents.

TABLE III

Container characteristics S/V m²/m³		300	200	100	50	30
ø equivalent sphere (m)		0,020	0,030	0,060	0,120	0,200
ø equivalent long cylinder (m)		0,014	0,020	0,040	0,080	0,130
average $\overline{K}$ conductance W/m² °C	exch/liq	33.8	31.6	26.4	19.9	14.9
	exch/air	13.4	13.1	12.1	10.5	8.9
Requirement for complete phase change : ΔT x Δt °C x h	exch/liq.	7.4	11.9	28.4	75.4	168.0
	exch/air	18.7	28.6	62.0	143.0	281.0

Thermal characteristics of various dimensions of PCM encapsulations
(Hypothesis : Ls = 270 MJ/m³
he for convective exchange with liquids 200 W/m² °C
he for convective exchange with air:20 W/m² °C).

	filling rate (% volume)	100 %	99 %	95 %	90 %
% wet container exchange surface	long horizontal cylinder	100 %	93 %	85 %	80 %
	long vertical cylinder	100 %	99 %	95 %	90 %
	Sphere	100 %	94 %	86 %	80 %
	Thin plate	100 %	≈100 %	≈50 %	50 %

Table IV

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Brevet Belge C.N.R.S., 9002448, mai 85 et extension Brevet Européen; (Patent Pending)
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FIGURE CAPTIONS

FIGURE 1 : Comparison between water and NaOH, H_2O for DHW storage.

FIGURE 2 : Comparison between water and a calcium chloride derivative (Serrolithe 20°) for greenhouse heat storage.

FIGURE 3 : Comparison between Sunoco wax and $CaCl_2$, 6 H_2O (Réf. 3).

FIGURE 4 : Different solidification patterns in containers.

FIGURE 5 : Observed deformation in plastic tube of square section (Réf. 26).

FIGURE 6 : Various mechanical resistant flat geometries for PCM encapsulation.

FIGURE 7 : Free convection motions in the melted part of a PCM horizontal tube (Réf. 27).

FIGURE 8 : Heat flux through liquid or solid part of NaOH, H_2O PCM (Réf. 32).

FIGURE 9 : Global conductance through the melted part of a sperically encapsulated PCM for various external convective coefficient he ($R = 0{,}025$ m).

FIGURE 10 : Various values of tortuousness for different storage geometry.

FIGURE 11 : Increased flow velocity due to oblate ellipsoïdal sphape of encapsulation.

FIGURE 12 : a) air temperatures through ellipsoïdal PCM pebbles.
b) corresponding heat flux for charge and discharge (Réf. 34).

FIGURE 13 : Various direct gain applications of PCM storage tubes (courtesy of Calmac Corp. (49) and Héliopin (42)).

FIGURE 14 : Grimaud Solar house with Chliarolithe storage tubes in direct insolation.

FIGURE 15 : Typical temperature records in Grimaud solar house showing heat pump operating periods at night (Réf. 51).

FIGURE 16 : Cross section of latent heat diode wall constructed in Cogolin solar house.

FIGURE 17 : Typical temperature records in Cogolin solar house (without auxiliary heating). (Réf. 55).

FIGURE 18 : Cross section of double envelope PCM tube (Ref. 56).

FIGURE 19 : Annot hybrid solar house (alternatively direct gain or air-collector connected to PCM radiant floor) (Ref. 57).

FIGURE 20 : PCM storage radiant slab under construction in Annot solar house.

FIGURE 21 : Numerical simulation of isothermes in a storage slab with "double-envelope" PCM tubes (Ref. 56).

FIGURE 22 : "Heliopin spiro-accumulator" geometry.

FIGURE 23 : Temperature curves for heat exchange fluid and PCM storage during charge and discharge periods of "Heliopin-spiro-accumulator" (Ref. 42).

FIGURE 24 : "Serrodule" container with crossed-corrugated sides (C.N.R.S.).

FIGURE 25 : Array of "serrodules" for low gradient air heat-exchanger (C.N.R.S.).

FIGURE 26 : Schematic air flow pattern through a serrodule heat exchanger.

FIGURE 27 : Two partial views of the lab. test bench for serrodules in a humid air flow (C.N.R.S.).

FIGURE 28 : Typical results observed in heat discharge with mass transfer through a serrodule storage.

FIGURE 29 : I.N.R.A.-C.N.R.S. experimental greenhouse with serrodule PCM storage in Montfavet.
a) global view
b) heat store

FIGURE 30 : Temperature and heat flux data observed in Montfavet greenhouse.

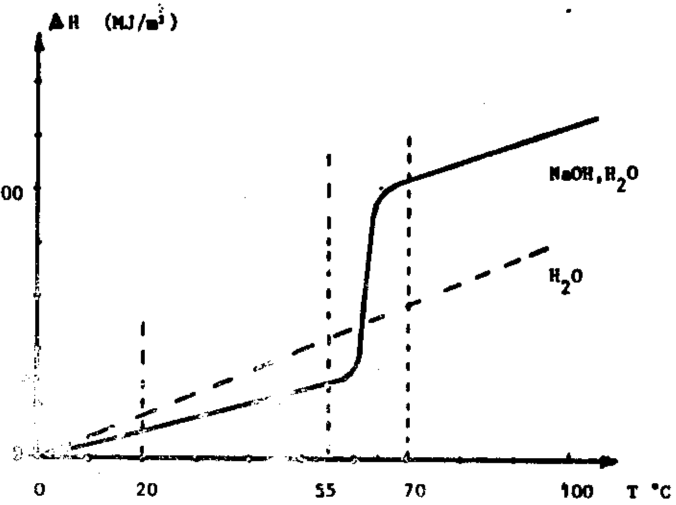


FIG. 1

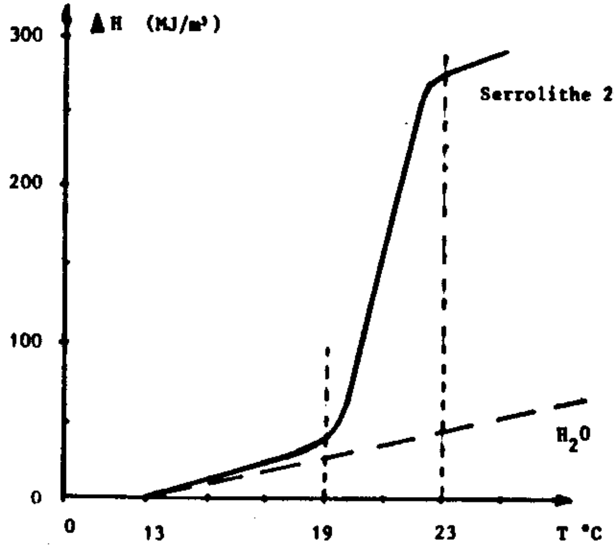


FIG. 2

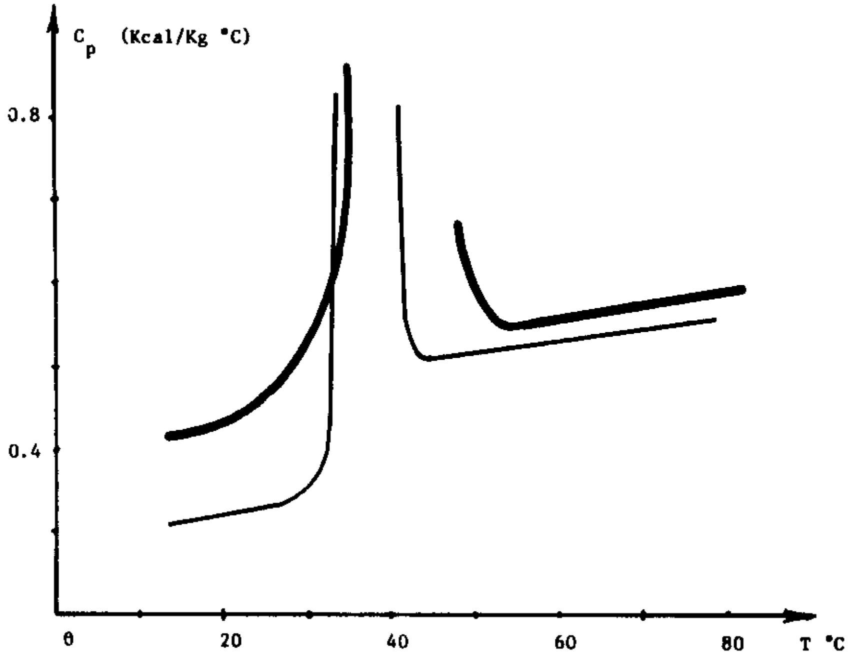
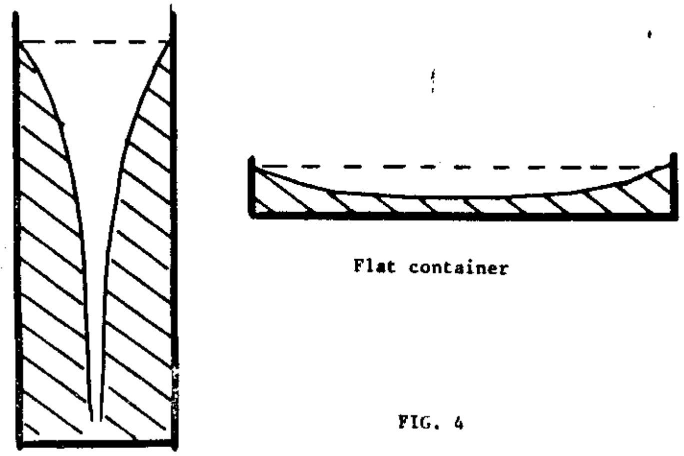


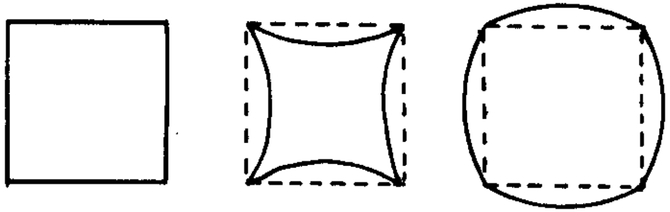
FIG. 3



Flat container

Long cylinder

FIG. 4



initial section

upper section

lower section

FIG. 5

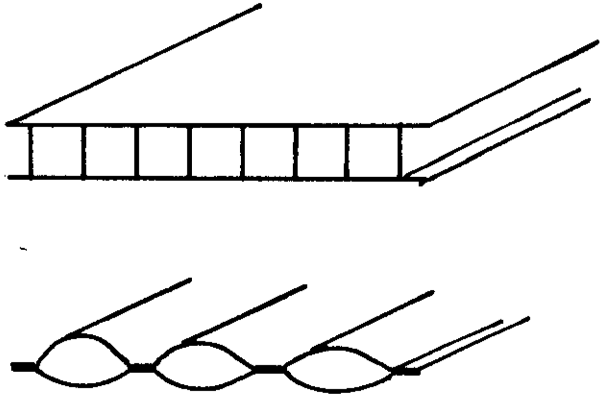


FIG. 6

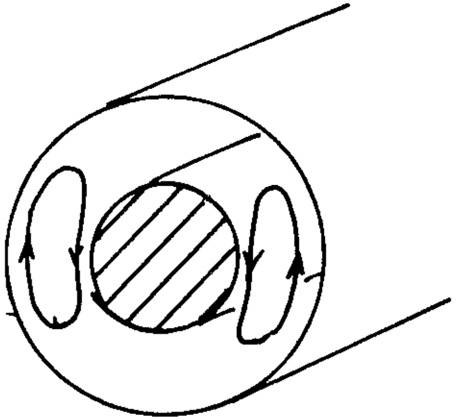


FIG. 7

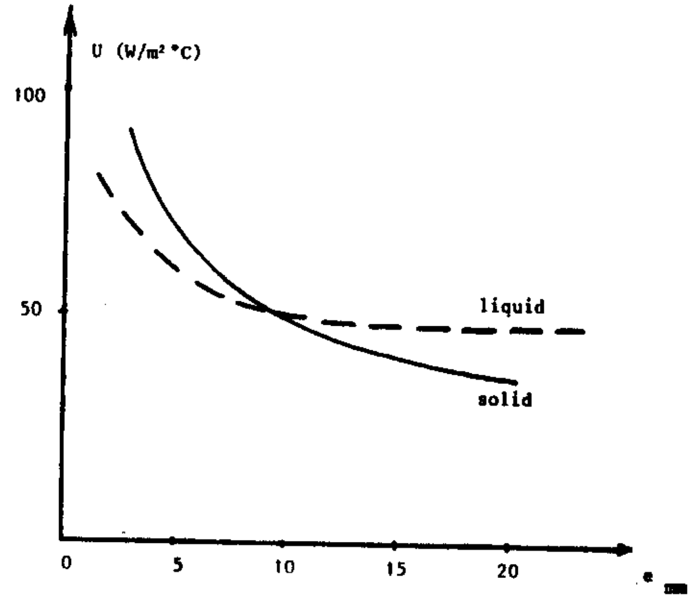


FIG. 8

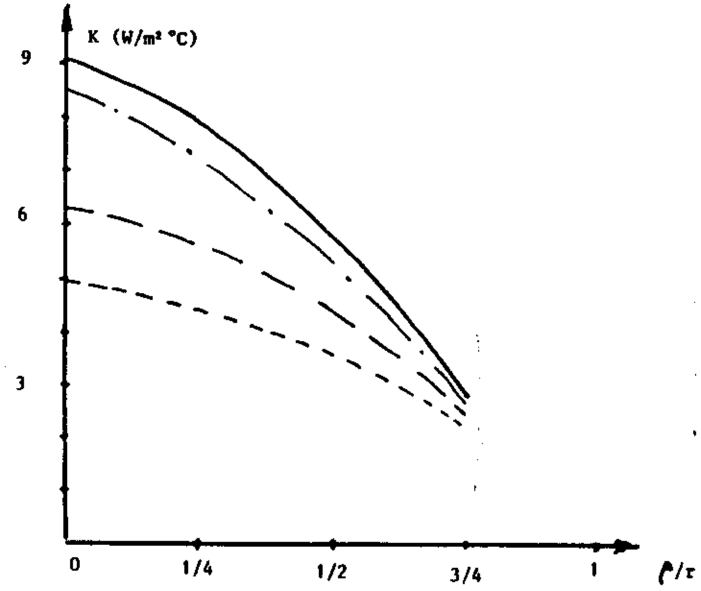


FIG. 9

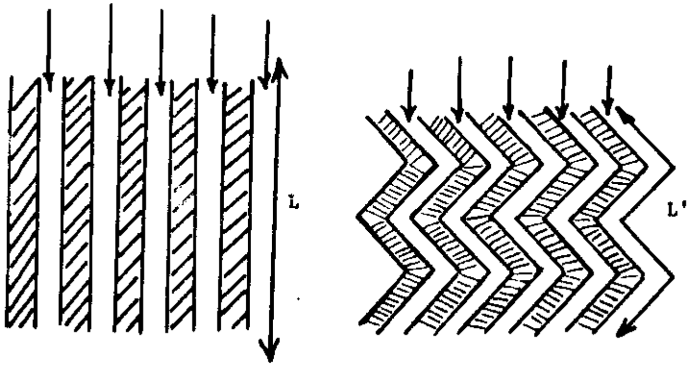


FIG. 10

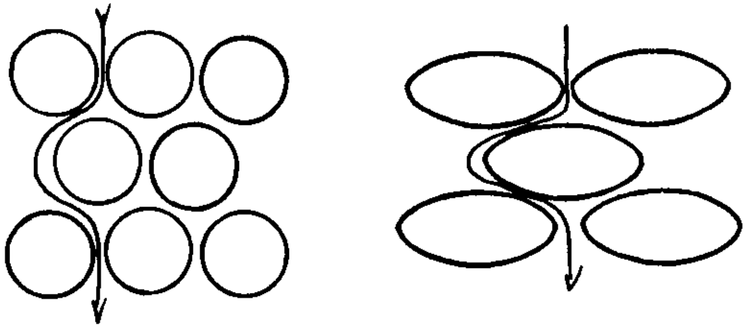


FIG. 11

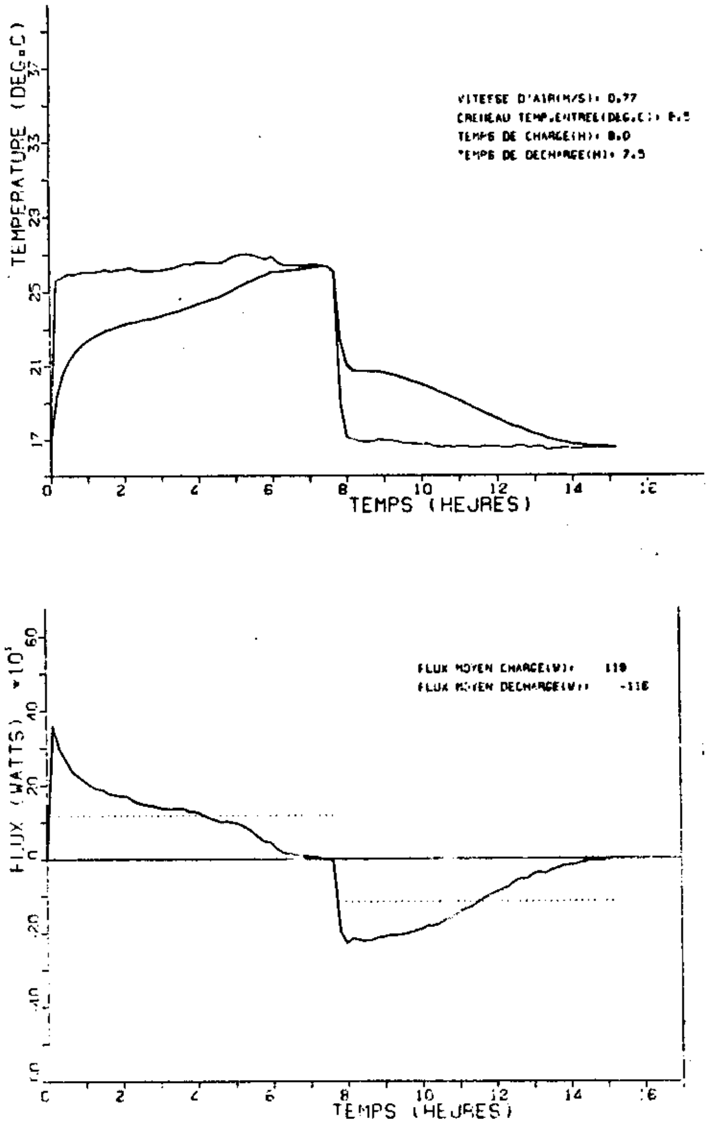

TEMPERATURE (DEG.C)
17
21
25
29
33
37
VITESSE D'AIR(M/S): 0.77
CRENEAU TEMP.ENTREE(DEG.C): 8.5
TEMPS DE CHARGE(H): 8.0
TEMPS DE DECHARGE(H): 7.5
TEMPS (HEURES)
0
2
4
6
8
10
12
14
16
FLUX (WATTS) *10¹
60
40
20
0
-20
-40
-60
FLUX MOYEN CHARGE(W): 119
FLUX MOYEN DECHARGE(W): -116
TEMPS (HEURES)
0
2
4
6
8
10
12
14
16

FIG. 12

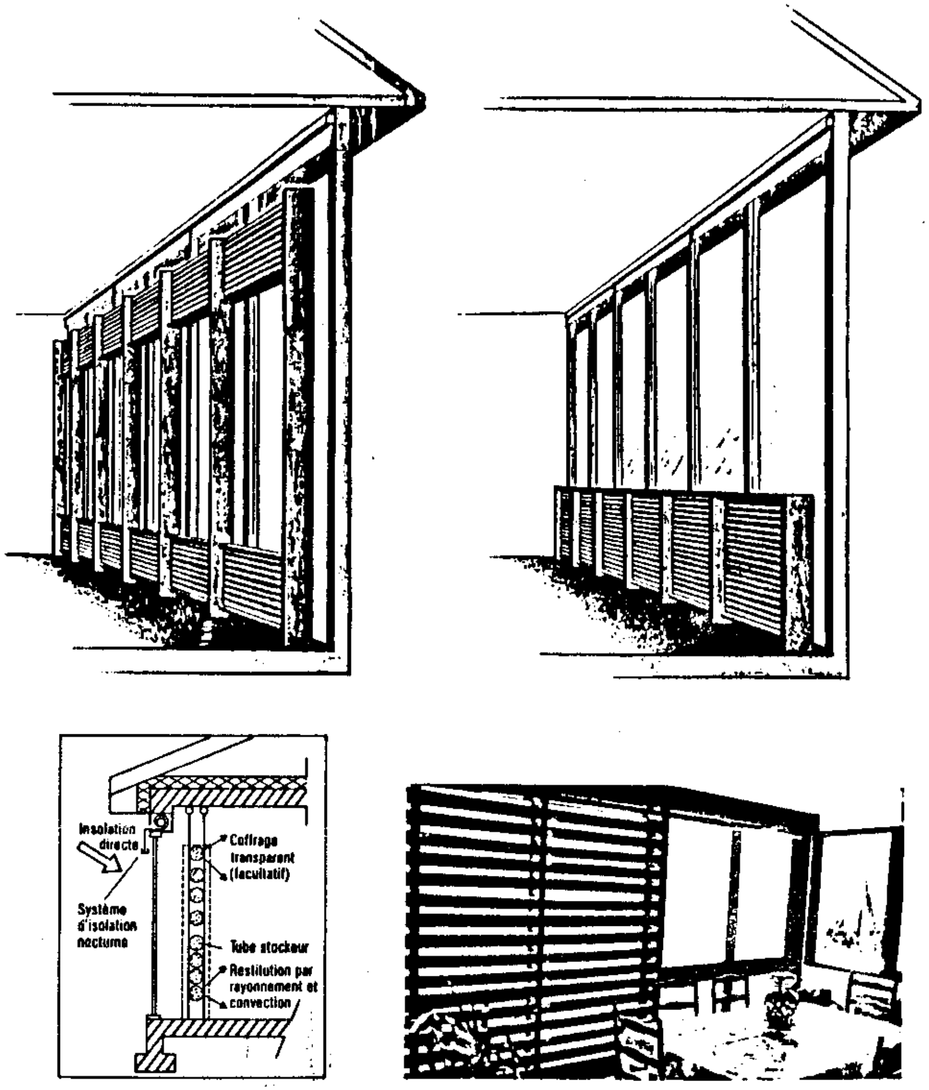

Insolation directe
Système d'isolation nocturne
Coffrage transparent (facultatif)
Tube stockeur
Restitution par rayonnement et convection

FIG . 13

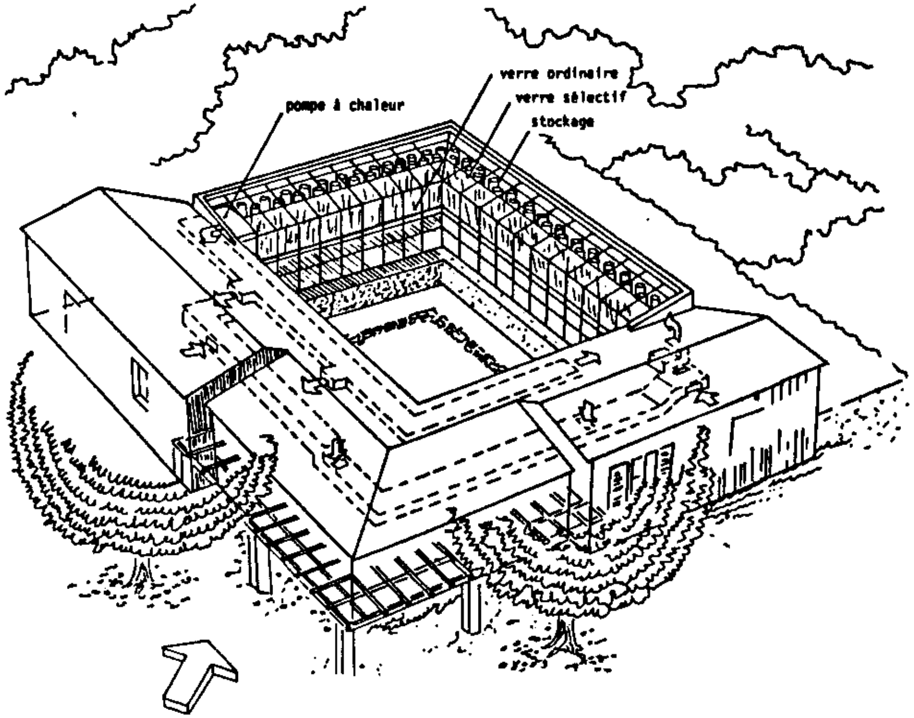


FIG. 14

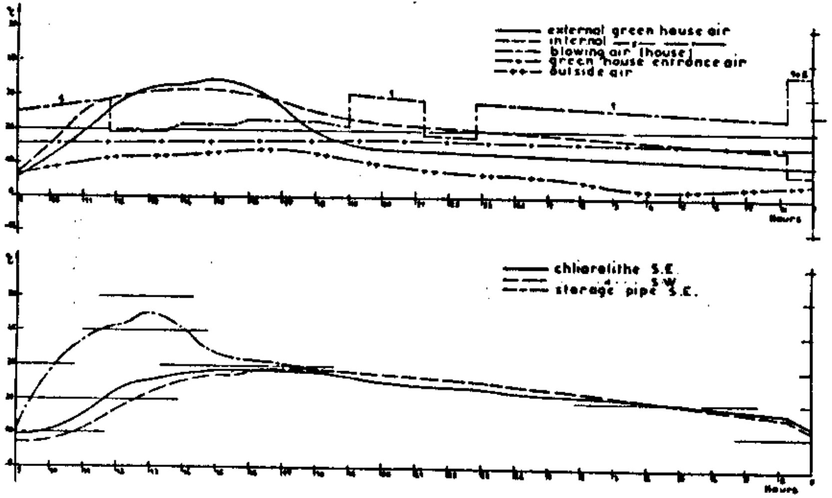


FIG. 15

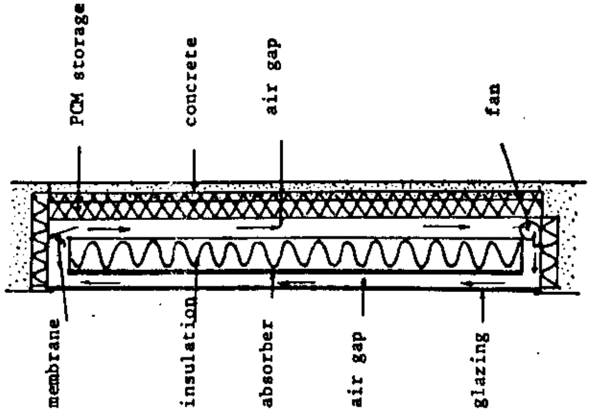


FIG. 16

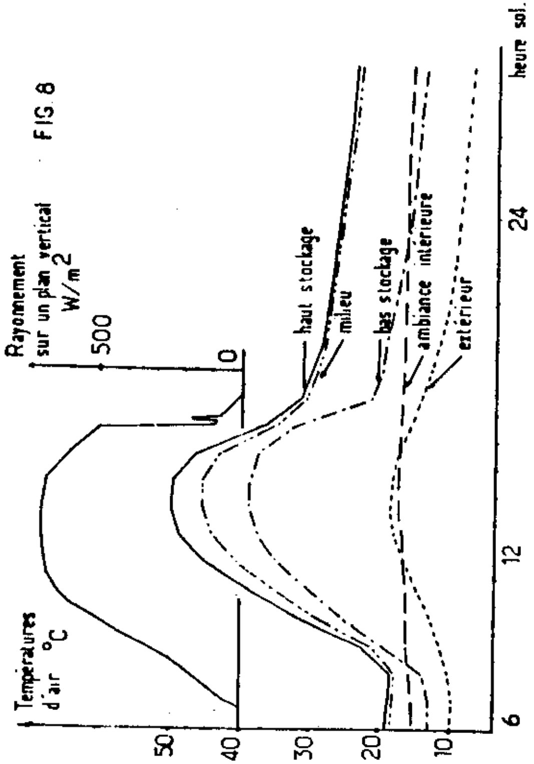
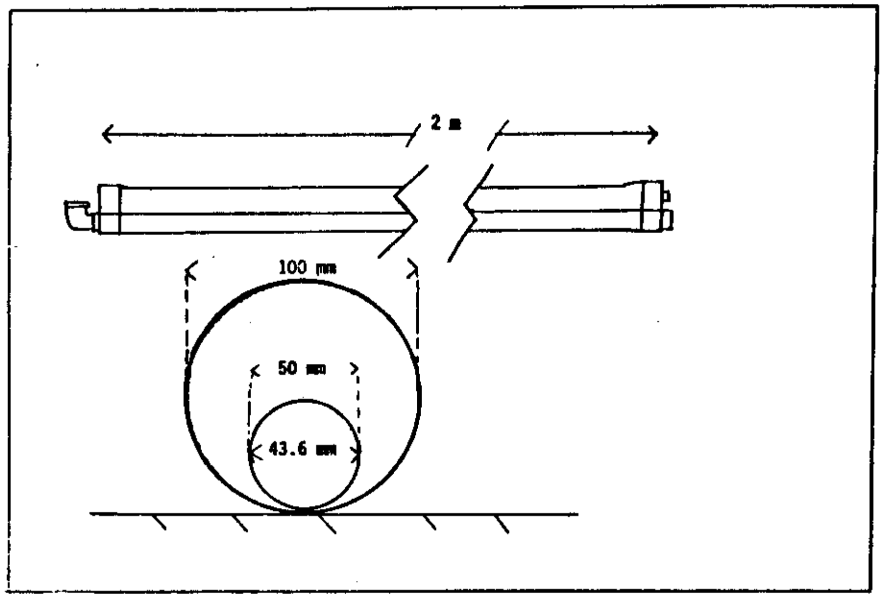
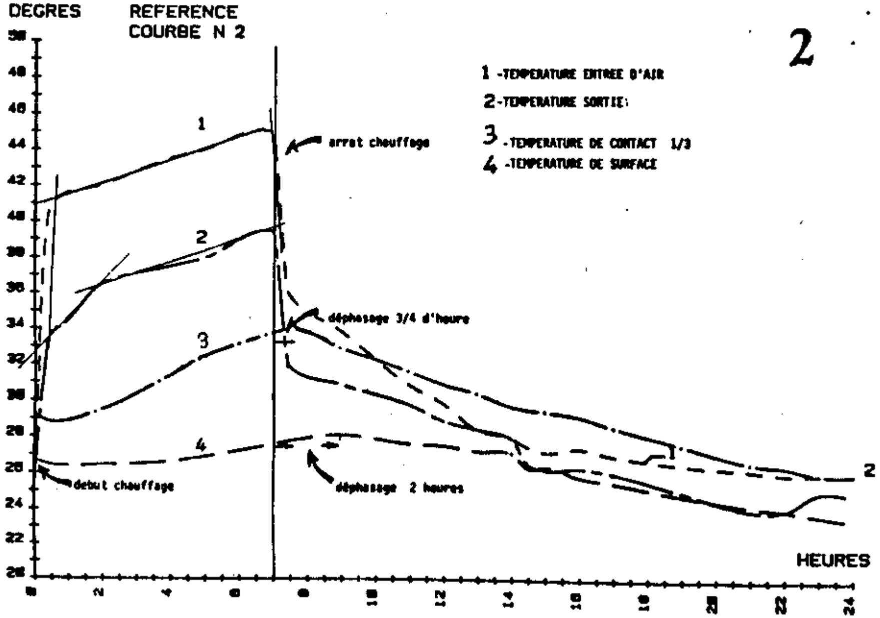


FIG. 17



Section of double envelope tube



Charge and discharge experiment with air

FIG. 18

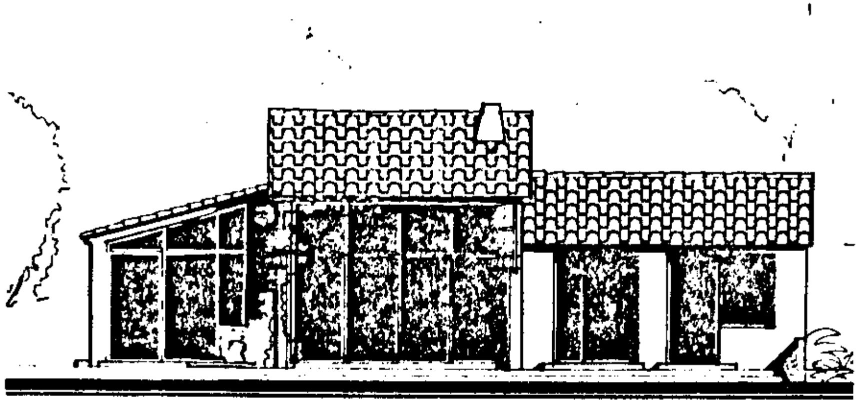


FIGURE 19

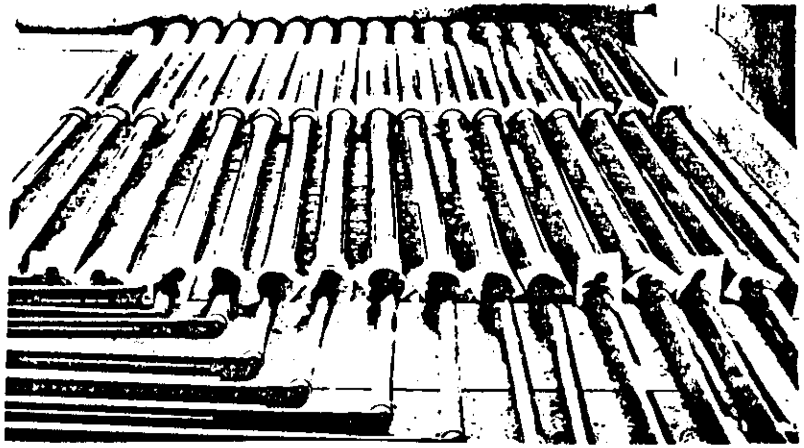


FIGURE 20

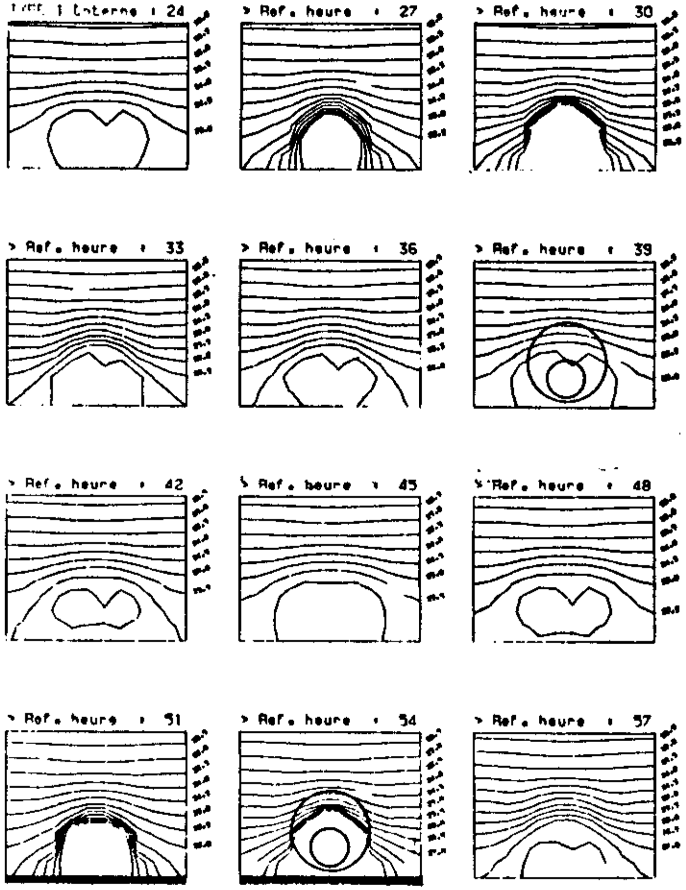


FIG. 21

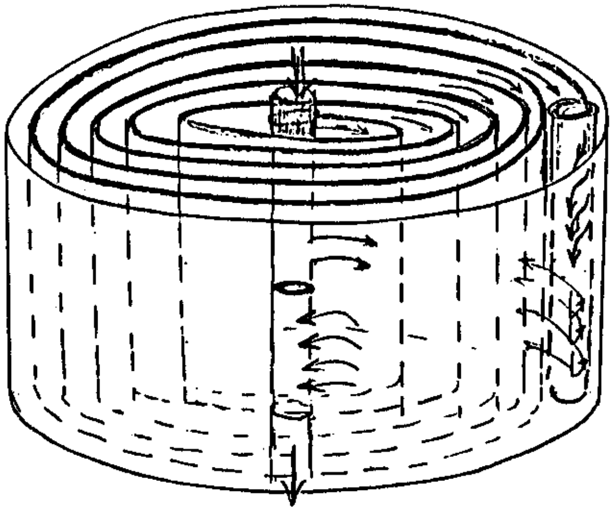


FIG. 22

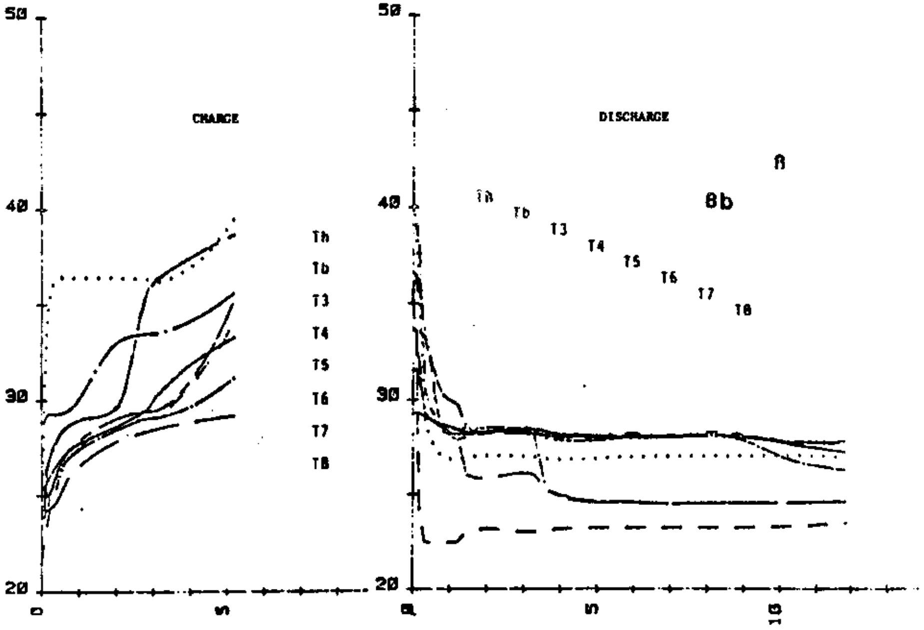


FIG. 23

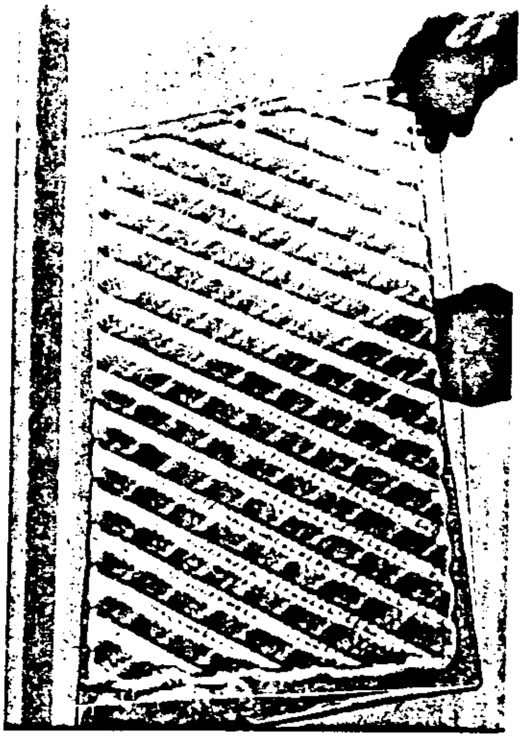


FIG. 24

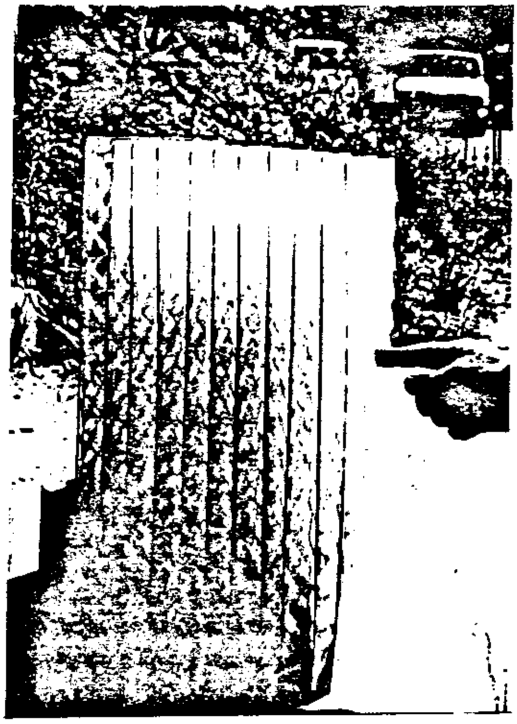


FIG. 25

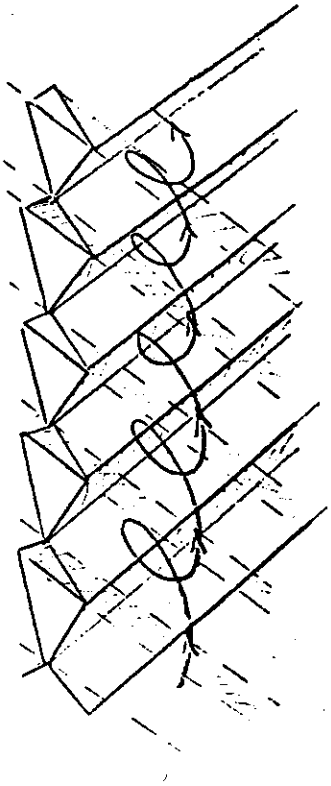


FIG. 26

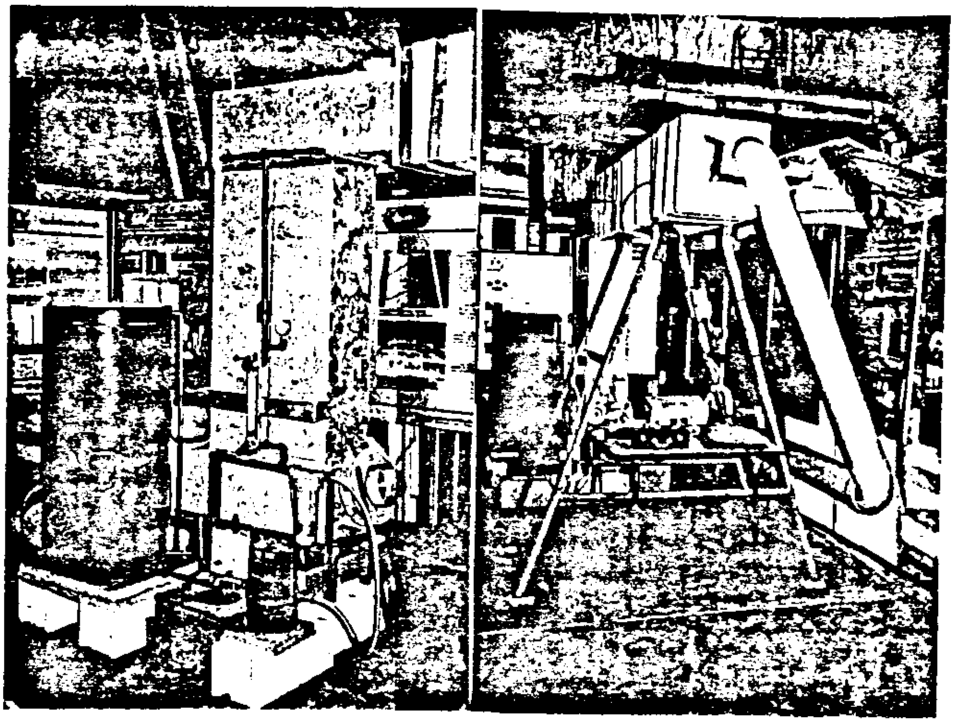


FIG. 27

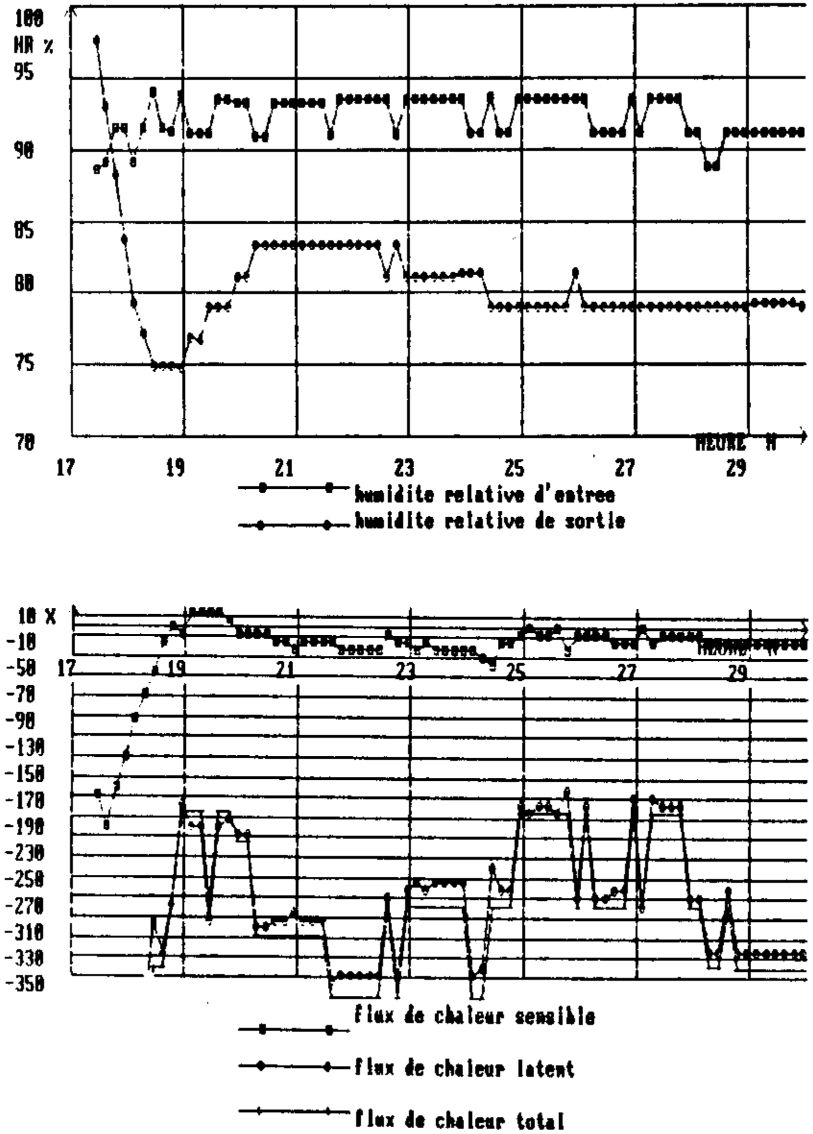

100
HR %
95
90
85
80
75
70
17
19
21
23
25
27
29
HEURE H
humidite relative d'entree
humidite relative de sortie
10 X
-10
-50
-70
-90
-130
-150
-170
-190
-230
-250
-270
-310
-330
-350
17
19
21
23
25
27
29
HEURE H
flux de chaleur sensible
flux de chaleur latent
flux de chaleur total

FIG. 28

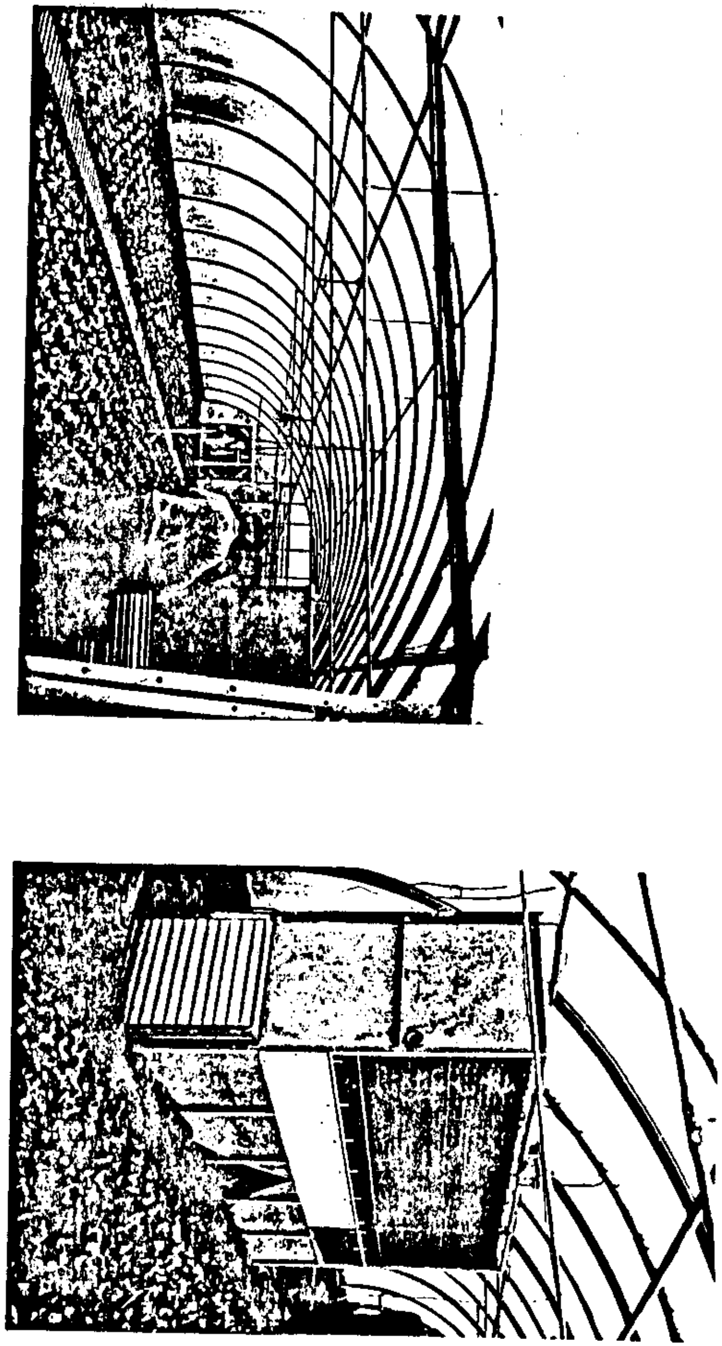


FIG. 29

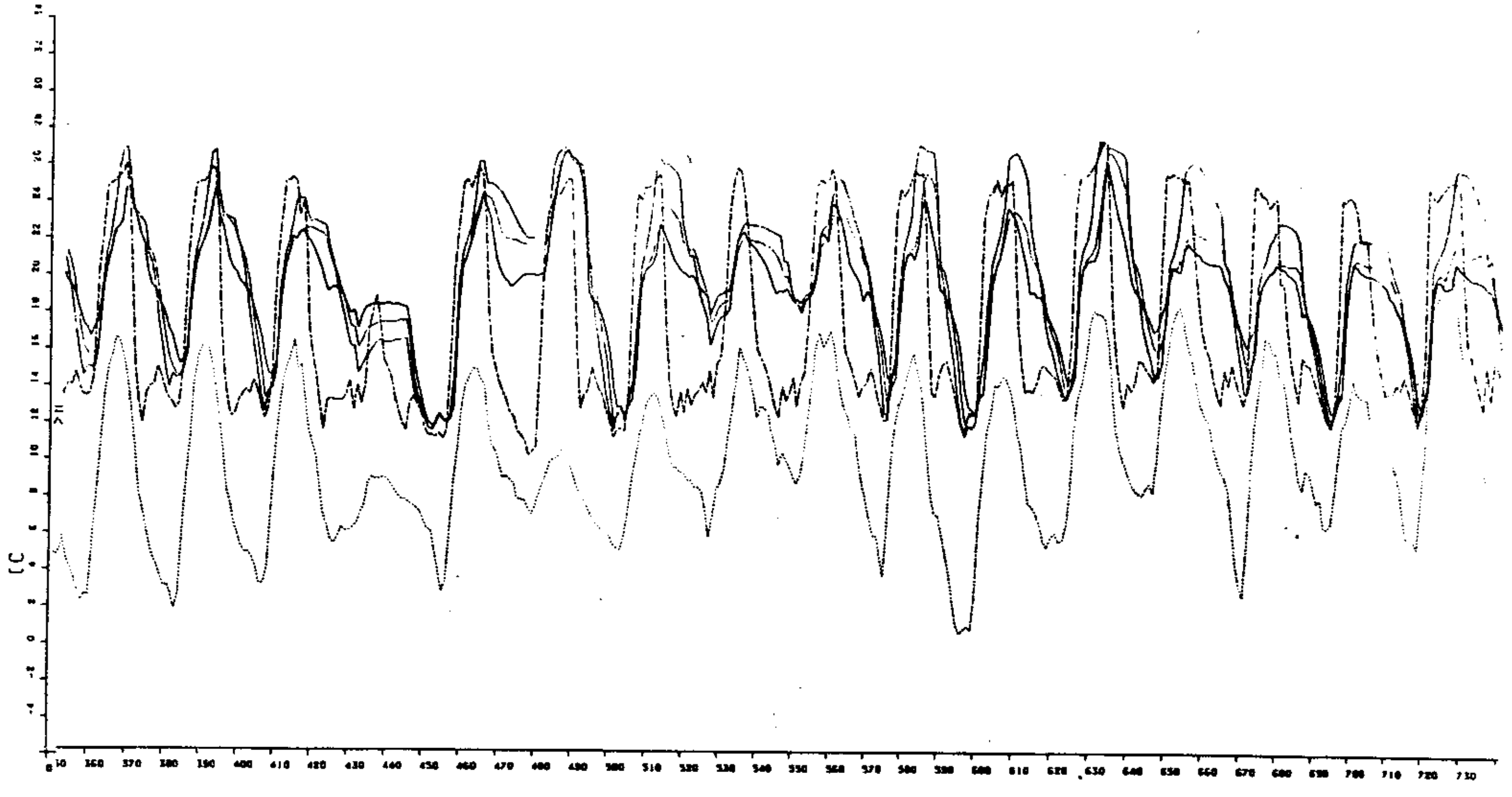


FIG. 30 a

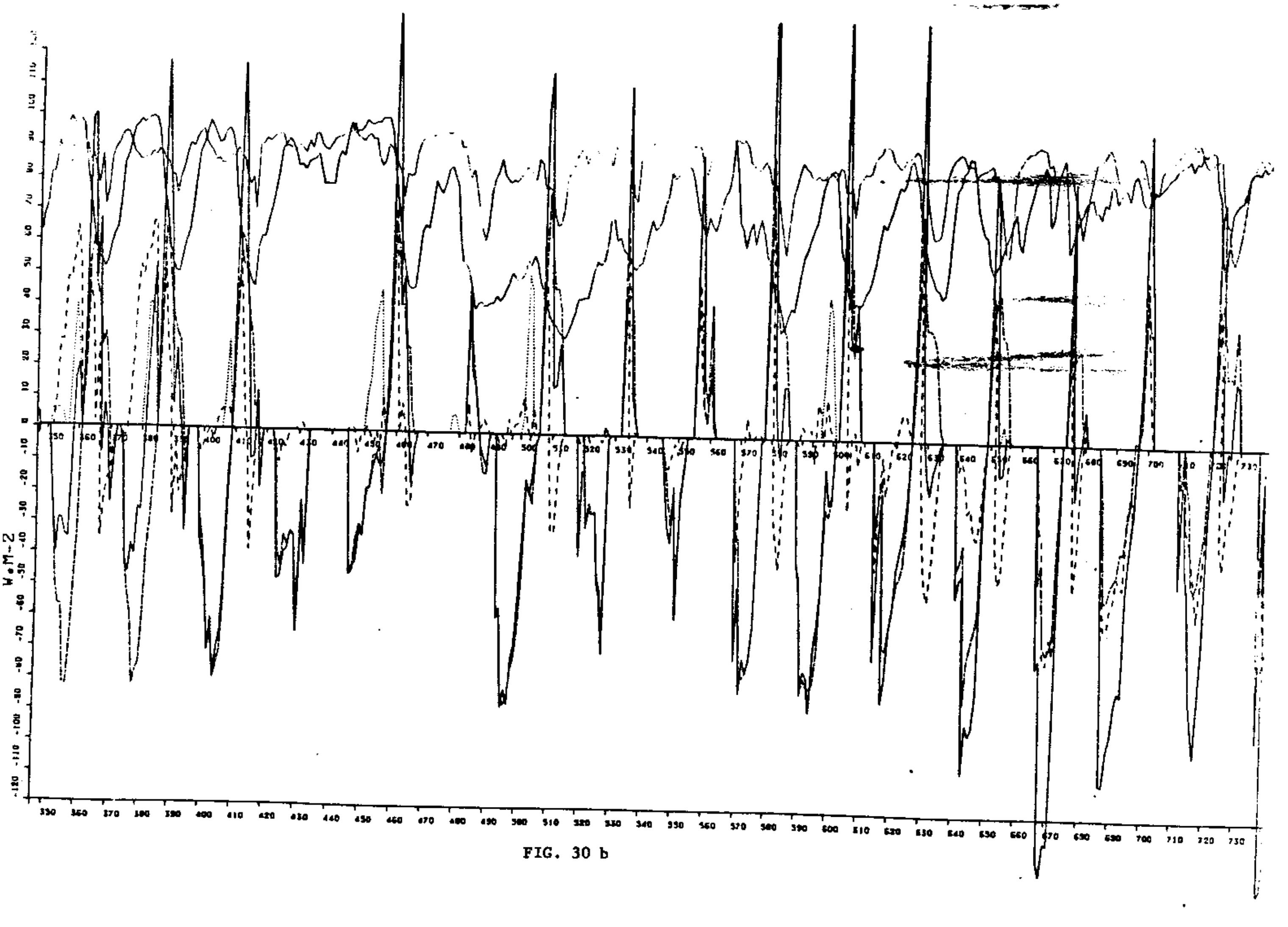


FIG. 30 b