THE
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EVALUATION OF PHASE CHANGE MATERIAL FROM INDUSTRIAL WASTE FOR THERMAL STORAGE

A. Brandstetter

S. Kaneff

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A. Brandstetter
S. Kaneff

Research School of Physical Sciences
Australian National University

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Abstract

The use of phase change material (PCM) as a medium for thermal energy storage for solar space heating and similar applications constitutes a practical alternative to sensible-heat storage in such media as rock or water.

The objectives of the work reported were to define, formulate and critically investigate a PCM based on calcium chloride hexahydrate derived from an existing large-scale industrial effluent, called "distiller blowoff" (DBO), from ICI's soda ash plant in Osborne, S.A. Calcium chloride hexahydrate (CCH) melts at 30°C with a heat of fusion close to 200 kilojoules per kilogram.

Central to this work has been a calorimetric evaluation of this PCM, in which the long-term stability of formulated samples of CCH, prepared from DBO, was assessed in series of melt/freeze cycles by a unique method of continuous thermal analysis.

Findings were positive, also in regard to the potential of practical applications, such as off-peak electric space heating and greenhouse temperature stabilization. More fundamental aspects of PCM storage, such as factors determining the enthalpies of fusion and crystallization, as well as supercooling characteristics, also were part of this study.

SUMMARY

Objectives

The overall objective of this project has been to develop a cheap, compact thermal energy storage system based on inorganic phase change material. Calcium chloride hexahydrate (CCH), in particular as processed from waste brine - so-called distiller blowoff (DBO) - from the ICI Austrlia soda ash plant in Osborne, S.A., was selected for this project.

The principal objective pursued in this project has been the continuous calorimetric evaluation of the behaviour of PCM samples prepared from DBO, under long-term melt/freeze cycling. Design and testing of prototype PCM systems, including a greenhouse heat storage unit and a residential space heating system were related objectives.

Findings and Conclusions

This report presents a detailed account of an experimental study of the melt/freeze behaviour of calcium chloride hexahydrate phase change material for thermal storage. The central work consisted of a laboratory experiment involving continuous calorimetric monitoring of enthalpy variations in a small sample of this material. At the time of writing this sample has been subjected to more than 500 daily melt/freeze cycles in a variety of realistically simulated environmental conditions, and the principal finding has been that none of the various known deleterious degradation effects - notably phase separation and severe supercooling - need to occur in this material if suitably formulated. Since this sample was prepared from DBO, the principal conclusion to follow from this experiment is that this DBO, presently discharged to sea in very large quantity at the Osborne soda ash plant, is in fact a potential source of low-cost phase change material, suitable for use in a variety of space heating and similar applications.

One such potential application that has been explicitly selected for study and assessment in this project is a small greenhouse equipped with a heat storage system involving approximately 100 kg phase change material processed from distiller-blowoff. A monitoring and control system for this part of the project became operational recently and some preliminary data obtained are presented in this Report. Temperature stabilization through the PCM, with excess heat taken in during the day and released back during night time, could already be assessed - so far with only partial success because of encapsulation problems. Demonstration of energy-saving night heating will have to wait for later in the season. (Requests for special funding for this study have unfortunately been unsuccessful).

A second application currently studied, a local space heating system using close to 200 kg of CCH phase change material not based on the ICI distiller blowoff - designed and set up in collaboration with a private investor - has so far been proven totally successful.

This work has produced also results of theoretical value, presently in the course of preparation for publication in the scientific literature. This includes a study of the phase stability of CCH, as well as unusually precise data on transition temperatures and heats of fusion and crystallization for this phase change material.

Work description

The following two experimental setups have been used in carrying out our current investigations, in addition to the PCM processing and chemical analysis arrangements.

- a continuous calorimetric measurement laboratory setup, computer monitored and controlled, recording the behaviour of a 0.4 kg sample of PCM under daily, and other melt/freeze cycling regimes.
- a close-to-practical system, in the form of a small greenhouse, with some 100 kg of PCM processed from the Osborne distiller blowoff being cycled over natural ambient temperature variations.

The laboratory experiment was designed with a view to a perceived need for an assessment of the true storage capacity behaviour of CCH and other phase change materials in continuous operation under realistic thermal cycling conditions.

Distiller blowoff was brought from Osborne, South Australia, to Canberra in 44-gallon drums, courtesy by ICI Australia. The processing of this DBO into CCH was carried out last summer, using three evaporation pans of about 300 litre capacity each, ultimately producing a total of about 150 kg PCM.The larger part of this PCM is being used in the greenhouse PCM store with only preliminary results so far recorded. The main sample studied in the laboratory experiment which was produced from a small quantity of DBO received from ICI a year earlier, has at the time of writing recorded in excess of 500 melt/freeze cycles.

Potential for application and Patents

The scope for application of CCH phase change material (m.p. 30°C) has recently been conjectured here to be wider than anticipated, with the realisation that this PCM may be capable of providing suitable storage for a heat pump in both heating and cooling mode. One can see potential for patent rights relating to a special type of heat pump sytem with integral PCM store. Until lately it was not generally accepted that transition temperature close to 30°C might be suitable for a heat pump even in the heating mode alone. Interest in our concept was informally expressed by Siddons Industries of Heidelberg West, Victoria, a company who recently started manufacturing and marketing solar-boosted heat pump hot water systems.

In general, cost-effective solar space heating of necessity involves some form of heat storage for night heating, and CCH has the potential for being viewed as the most suitable storage medium. A private entrepreneur (W. Radford, see Ch. VII) who recognized this

potential has collaborated in setting up at the A.N.U. an off-peak electric small heating system based on a CCH phase change storage unit and using a commercial type room radiator. This system has operated impeccably several months now and has generated serious interest from potential investors.

Interest has been expressed also in relation to the small "domestic" greenhouse with integrated solar collector and PCM store, which was developed here within this project. Patent rights could apply to a number of novel aspects connected with this part of the project.

Recommendations

Our foremost recommendations are a) continuation of the ongoing experiment, now nearing cycle No. 600, to at least 1000 cycles, and b) scientific improvement and technical refinement of our unique "continuous thermal analysis" method in a second apparatus to be built.

Industrial applicability of the results of this project appears totally warranted, in a number of ways, in the light of the last paragraph, provided that adequate development of cost-effective production and marketing methods can be assured. This in turn depends on the time scale and magnitude of investiment in this new technology.

At least one product can already at this early stage be considered as ready for pilot line production and market introduction. This is the off-peak electric heating system with CCH phase change storage unit and commerical type room radiator which we developed in collaboration with Mr Warren Radford.

Future R,D&D, in addition to the above stated recommendations, should address among other the completion of the work begun on the "domestic" greenhouse with PCM stabilization, as earlier proposed for NERDDC funding. Early public acceptance of such products, which could potentially generate a relatively wide market in regions like the A.C.T., would accelerate the acceptance of other types of PCM-based systems, including solar space heating.

Furthermore, in a current (1987) NERDDC application we have proposed to investigate possibilities of development, testing and application of sodium acetate trihydrate as a phase change material for higher (58°C) temperature, for use, in particular, as a peak load buffer in the A.N.U.'s all-electric heating system.

I. INTRODUCTION

A potential major mode of utilization of solar energy is in active solar space heating. For most applications any conceivable technology evidently then involves some form of energy storage. This also applies to auxiliary uses of solar energy such as in heat pumps, where extreme inefficiencies due to ice formation could be prevented through the use of a suitable heat store. This requirement for thermal storage perhaps is the most outstanding problem of solar space heating, and latent heat storage is one of the few presently considered practical solutions. Analoguous storage solutions would apply also to non-solar situations, such as in waste-heat recovery and off-peak electricity systems, to name a few.

I.1. The principal objective pursued in this project has been to establish the suitability of a certain phase change material (PCM), derived from a large-scale industrial effluent, for space heating and similar applications. This PCM, calcium chloride hexahydrate (CCH) with minor additives, has its melting point near 30°C and has latent heat close to that of the ice/water transition, by volume. The material has been processed successfully from 'distiller blowoff' from ICI's soda ash plant in South Australia, with essentially no energy input other than solar evaporation.

Pure calcium chloride hexahydrate ($CaCl_2.6H_2O$) supercools severely and melts semi-congruently, gradually transforming to the tetrahydrate form. It is therefore not a practical PCM unless successfully stabilized. Much research has been devoted to this problem, worldwide (Carlsson [1979], Feilchenfeld [1984], Kimura [1984], Lane [1981], Telkes [1954]), and we have investigated methods proposed involving certain types of nucleation-promoting and phase-separation-inhibiting additives.

An apparatus was designed which allows continuous calorimetric evaluation of a sample of investigated PCM cycled between temperatures below and above the melt/freeze transition. In parallel, two close-to-practical systems using several hundred kilograms of PCM were run under more or less realistic environmental situations: a small greenhouse and a space heating system with simulated solar or rather off-peak electric, heat input.

While no long-term data have been obtained as yet from these two systems, the laboratory experiment has been highly successful in providing a large amount of meaningful data, having completed a total of over 500 daily cycles at the time of writing. Of special interest may be considered the heat of fusion observed in this experiment, being significantly above the currently accepted value of 190 kJ/kg; and the material's nucleation and supercooling characteristics and the mathematical modelling attempted here to reproduce these characteristics.

Our calorimetric assessment method, which judging by Abhat [1982] appears to have filled a gap in PCM experimental methodology, has provided us with required insight on additive dosage levels and into

actual system design parameters, such as heat transfer geometries and melt/freeze times. The aforementioned greenhouse application, which was developed and tested here over the last months, together with other applications promising cost-effective solar and/or off-peak electricity space heating solutions, have been designed on the basis of this gained insight.

I.2. Phase change materials for heat storage applications, in general, are categorized with some exceptions as organic or inorganic. The former include such well-known materials as paraffin (Bernard [1985]) or stearic acid (Arndt [1984]). Their main drawbacks are, generally speaking, relatively high cost, variable transition temperature and flammability.

Inorganic PCM's usually are hydrated salt complexes such as $CaCl_2.6H_2O$. Heat storage in hydrated salts for solar applications has been piorneered by Maria Telke since the early fifties, with sodium sulfate decahydrate ($Na_2SO_4.10H_2O$ - Glauber's salt) as her prime candidate. This material is notorious for suffering from severe incongruency problems - Na_2SO_4 separating out, irreversibly, upon melting - but has been proven amenable to stabilisation and PCM heat storage systems using this material are commercially available (Calor [1984]). Its transition temperature, 32°C is somewhat higher than CCH-based PCM.

I.3. Calcium chloride hexahydrate PCM - its chief advantage is its potentially very low cost. Its good safety characteristics in handling and operation then render it a favourite candidate where somewhat lower transition temperature is advantageous, such as in greenhouse and heat pump applications.

Over the 1985 summer period we have successfully tested a CCH production process based essentially on natural solar evaporation of the earlier mentioned 'distiller-blowoff' (DBO) waste effluent. As reported (Brandstetter [1982]), DBO is discharged to sea at the rate of 10 million litres a day, with each litre containing close to 0.2 kg CCH. Fig. 1 illustrates our experimental production process - to be described in detail in Chapter III - and Fig. 2 presents photographs of the installations and equipment used.

The detailed characteristics of CCH in general, and of the particular PCM samples and systems studied in this project, will be presented and discussed in the following chapter. From the practical point of view in relation to heat storage the main characteristics are summarized in the fact that one net cubic metre of this PCM is capable of storing 75 kilowatt-hour of latent heat, worth some $4 a day at current average electricity tariffs.

II. THEORETICAL/EMPIRICAL BACKGROUND

II. 1. The heat storage characteristics of calcium chloride hexahydrate vary with source material, manufacturing techniques and additives. In fact, pure $CaCl_2/6H_2O$ easily supercools by as much as 20 degrees and may be considered useless in regard to heat storage for this reason alone.

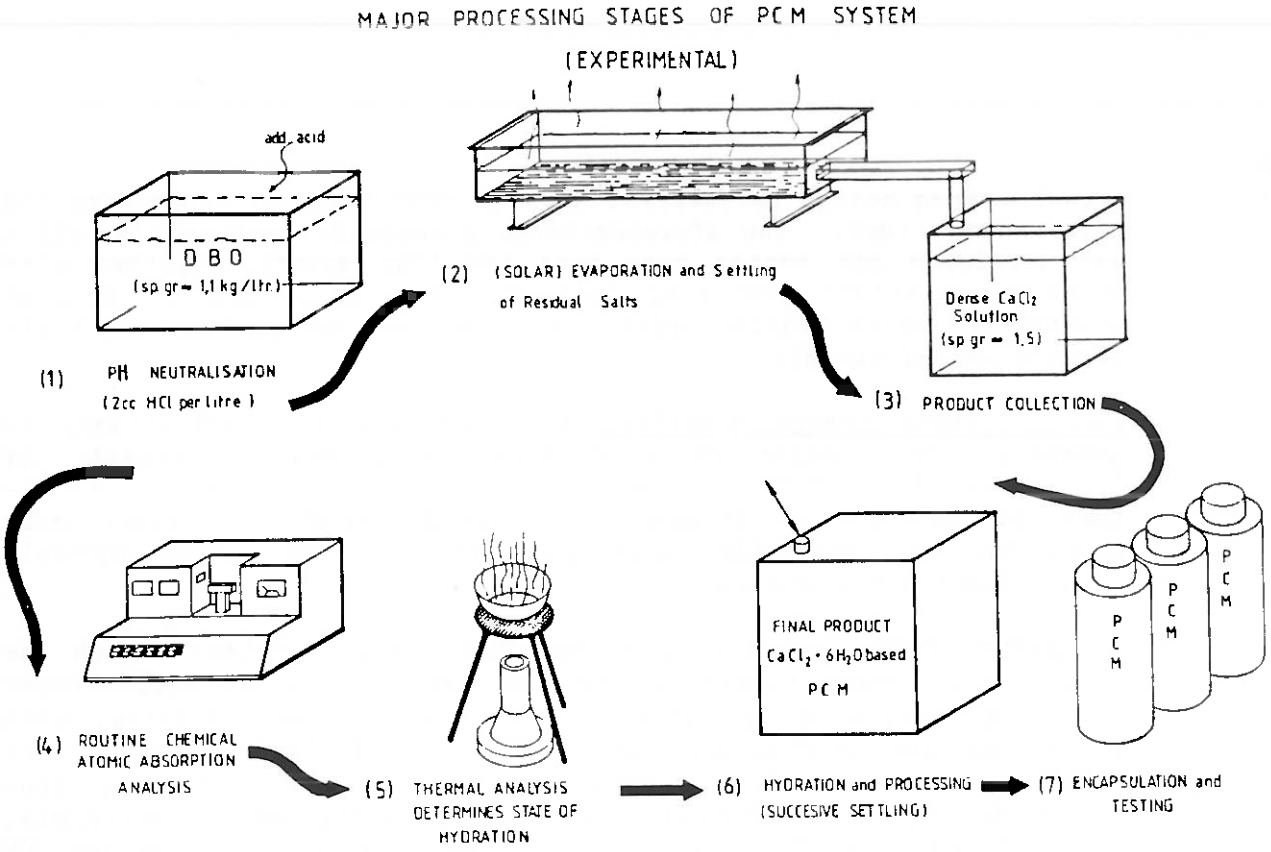


Fig 1 Schematic description of PCM processing stages, starting from "distiller blowoff" - for details see section III.2.

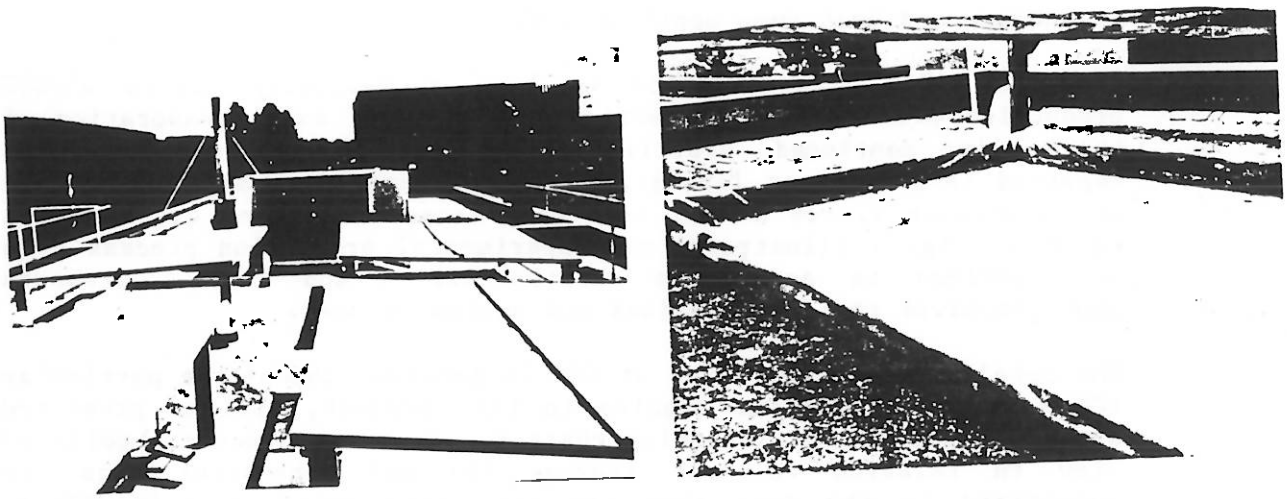


Fig 2 Left: solar evaporation ans on the roof of the Cockroft building. In the near background: warm-storage box with 44-gal drums. Right: final evaporation stage, with settled sodium chloride.

Calcium chloride forms stable hydrates with two, four and six molecules of water, as illustrated by the $CaCl_2$ solubility curve, Fig. 3: Above 30°C the solubility of the 4-hydrate, $CaCl_2.4H_2O$, becomes less than the 6-hydrate and the 4-hydrate becomes the stable species. Similarly, above 46°C the di-hydrate becomes the stable species.

At the 'peritectic' point, where the 6-hydrate and 4-hydrate parts of the solubility curve intersect (P in Fig. 3), the calcium chloride/water composition is 50.25/49.75 by weight, slightly below the 6-hydrate's stoichiometric composition of 50.66/49.34. Any composition just below 50.25/49.75 ("extra water principle") will exist, at equilibrium, either in the form of homogeneous solution, above 30°C; or below 30°C, in the form of solid (and/or supercooled liquid) hexahydrate with a small amount of 'supernatant' liquid.

An alternative representation of the $CaCl_2$ solubility curve, Fig. 3, is given in Fig. 4, where the abscissa and ordinate are interchanged, more commonly referred to as a 'phase diagram'. The added β-tetrahydrate form in Fig. 4 is more soluble than the "α" form and may be ignored so long as the 'extra water principle' is satisfied. Where conversely, water is deficient relative to the stoichiometric 6-hydrate composition, both these 4-hydrate forms can precipitate, with the β form more likely to appear at temperatures below, and the α form above 30°C. As noted already, and as can be inferred from Fig. 4, any α -tetrahydrate present will dissolve above 46°C; and similarly, any β -tetrahydrate present will dissolve above 38°C.

Thus, when heated to temperature higher than 46°C calcium chloride hexahydrate can be seen to melt "congruently", i.e. liquefy homogeneously, given enough time. Below 46°C, however, melting will be 'incongruent' (or rather 'semi-congruent') if the stoichiometric composition is below 6-hydrate; and may turn incongruent also, if for any reason - such as unduly delayed nucleation of the 6-hydrate - an amount of solid 4-hydrate should form out of below-6-hydrate solution, at sufficiently low temperature.

From the last observation it follows that a good nucleation promoting additve not only is necessary to minimize super-cooling - i.e. freezing at temperature lower than the melting point - but also to inhibit the formation of the 4-hydrate species and consequent 'phase separation'.

It has been found, moreover, that thixotropic additives (thickeners) exert an inhibiting effect on the occurrence of incongruences (Telkes [1975]), in first instance through retardation of gravity induced phase separation (microscopic solid particles drifting downward) and thereby allowing 4-hydrate crystals to re-dissolve or absorb extra water to form 6-hydrate.

Carlsson (1979) has proposed a different mechanism for the prevention of tetrahydrate formation: changing the chemical composition in such

a way as to increase the 4-hydrate solubility while decreasing that of the hexahydrate, thereby moving the peritectic point (point P, Fig. 4) towards the stoichiometric composition. Lane (1981) cast doubt on Carlsson's method, which consists of adding 2 wt percent stontium chloride hexahydrate, for example. One may observe in this respect that the 'extra water principle' (Furbo 1982) is almost equivalent to Carlsson's proposition in its effect since it too moves the actual composition towards (and even slightly beyond) the peritectic point and this at only the small expense of some extra solution not participating in the heat storage process. This will be discussed quantitatively in the following section.

From here on, in this chapter, we will discuss characteristics only of the 'technical' calcium chloride hexahydrate studied in this project as processed and formulated starting from the Osborne 'distiller-blowoff' (see above), and as from here on referred to as 'The Phase Change Material', or PCM.

In broadest terms these PCM characteristics are as follows:

- The transition temperature is close to that of pure $CaCl_2.6H_2O$, i.e. close to 30°C. Some variation in the melting point as well as in the crystallization temperature pattern will be discussed on the basis of the presented data in chapter IX (Annex). Sub-cooling amounts normally to 3-4°C.

- Latent heat of fusion as high as 220 kilojoules per kiologram has been observed in our laboratory experiment; as already reported (Brandstetter [1986]), well in excess of the usually quoted values of 170-190 kJ/kg (Abhat [1982]), but Feilchenfeld [1984] has reported a similar high value. It appears to be a characteristic of this material - and, probably, similar others - that the "heat of fusion", with its folded-in heat of hydration (Kimura [1984]), is not fully seen in each melt freeze cycle. This problem will be discussed in chapter III in conjuction with our continuous calorimetric evaluation data.

- From The Dow Chemical [1980] technical data sheet the values for the specific heat in the liquid and solid states have been taken to be 2.2 and 1.4 Joule/gram/°C, respectively, varying only insignificantly with temperature in the ranges of interest. These values have been verified against results obtained in our laboratory experiment as described in section III.

- The thermal conductivities are 1.10 and 0.54 Watt/m°C in the solid and liquid state respectively according to The Dow Chemical [1981] data sheet. In independent measurements using the method described by Brandstetter [1982] we found 0.95 ± 0.05 and 0.58 ± 0.03 Watt/m°C.

The specific gravities ("densities") are close to 1.50 and 1.70 kg/litre in the liquid and solid state respectively. Precise determinations of density in the liquid state at a particular temperature (around 33°C) are being used routinely to characterize the state of hydration of production samples of PCM.

Note that 1.5 ton of PCM, requiring a net volume of one cu.m., is capable of storing 75 kWH in latent heat alone, assuming a conservative 180 joule/gram (~ 45 kcal/kg) for this heat of fusion.

II.2 TEMPERATURE -COMPOSITION RELATIONS FOR THE CCH SYSTEM

The basic data for the relevant calculations are a) the molar weight of $CaC\ell_2$: 110.990 gr, and of water: 18.016 gr; and b) the solubility vs. temperature relation such as expressed by Fig. 3.

We shall use in particular the values given in Lange's Handbook of Chemistry [1973]. Table 1 shows (a) these $CaC\ell_2/H_2O$ weight ratios for 0,10,20 and 30°C, and our interpolations for 5,15,25 and 28°C based on Fig. 1. Added in Table 1 for convenient reference are (b) weight-percent values in grams $CaC\ell_2$ per 100 gram solution, and (c) the hydration values in mols of water per mol $CaC\ell_2$ corresponding to the weight ratios.

Table 1 - Saturation values for $CaC\ell_2$ in aqueous solution (from Lange's Handbook of Chemistry [1973])

Temperature T deg. C	weight ratio (a)	weight percent (b)	degree of hydration (c)
0	0.595	37.3	10.35
5	0.62	38.3	9.94
10	0.650	39.4	9.48
15	0.69	40.8	8.93
20	0.745	42.7	8.27
25	0.83	45.4	7.42
28	0.93	48.2	6.62
30	1.02	50.5	6.04

****

The point at 30°, for concentration 50.5 wt%, is just beyond the peritectic point, P (fig. 2), which according to Mellor [1946], citing Roozeboom [1889], is located at 29.8°C and has the weight percent concentration 50.25, as compared with 50.66 for the precise 6-hydrate composition. (Lane [1986] now quotes 29.45°C, at 49.62 wt%, for this peritectic point, and 29.6°C for the CCH melting point.). It should be emphasized that all the values in Table 1 specifically refer to $CaC\ell_2.6H_2O$ as the solid in equilibrium with $CaC\ell_2$ solution at the given concentration - temperature points.

When calcium chloride solution at or near the hexahydrate composition is cooled below freezing temperature, for example to 20°C, the final equilibrium state will as a rule feature a phase of "supernatant" liquid. This supernatant - and also interstitial - liquid actually is saturated solution in equilibrium with the solidified hexahydrate and as such its composition, at temperatures T <30°C, is as given in Table 1, independent of the relative amounts of solid and liquid present. This was verified by examining a number of samples of varying water content - both in excess and deficient relative to the hexahydrate composition - which all were found to have very nearly identical liquid phase compositions.

In a system of solidified CCH and supernatant liquid, weight fractions (s) and (ℓ), with $CaCl_2$ weight fraction X_s in the solid and X_ℓ in the liquid phase, the overall $CaCl_2$ weight fraction X is given by

$$X = (s)\, X_s + (\ell)\, X_\ell \qquad (1)$$

The weight fraction of supernatant liquid is thus given by

$$(\ell) = (X - X_s)/(X_\ell - X_s) \quad , \qquad (2a)$$

the ubiquitious "lever rule" (Abhat [1982], Kimura [1984], for example).

X_ℓ is as obtained from Table 1, (b), and X_s is the weight fraction of $CaCl_2$ in $CaCl_2.6H_2O$, i.e. 0.5066.

In terms of the degree of hydration H ((c) in Table 1) eq. 2a becomes

$$(\ell) = \frac{\dfrac{6.1606}{H + 6.1606} - 0.5066}{X_\ell - 0.5066} \qquad (2b)$$

Fig. 5 is a graph of eq. 2b for a number of temperatures, using the X_ℓ values given in Table 1, (b), and some additional values taken from the inset in Fig. 5 (and the conversion $X^{-1} = S^{-1} + 1$). These (ℓ) vs H curves are not exactly straight lines, although close enought to be mistaken for such.

The experimental points in Fig. 5 were obtained from a series of samples of known composition, in various containers ranging in size up to two litres, by weighing them and their supernatant liquid parts. This simplistic technique obviously ingores the interstitial part of the liquid and therefore as a rule undervalues (ℓ). Moreover, even though the weighing may be at room temperature, 20-25°C, the amount of supernatant liquid found in a sample reflects largely its amount at the time of its formation following freezing, at which time the temperature may have been much lower. Our data points close to the 0° and 10°C curves suggest this as a likely explanation, since some of the samples were in fact allowed to freeze outdoors.

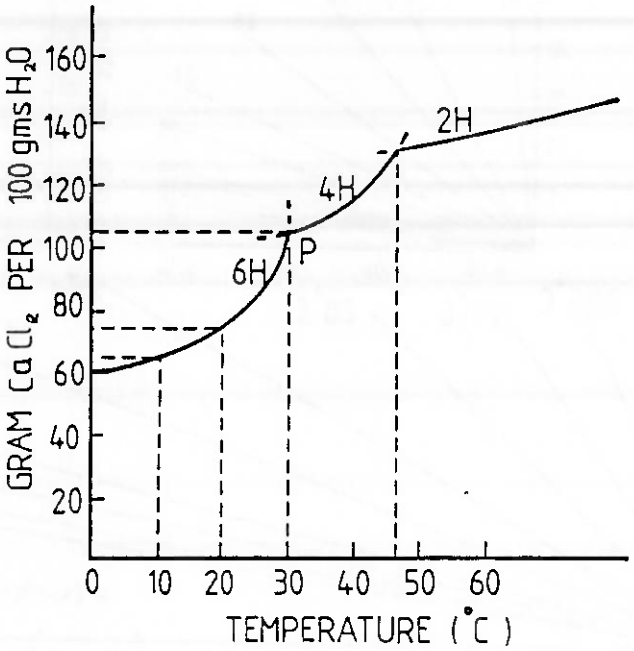


Fig 3 Calcium chloride solubility curve, after Pauling [1958].

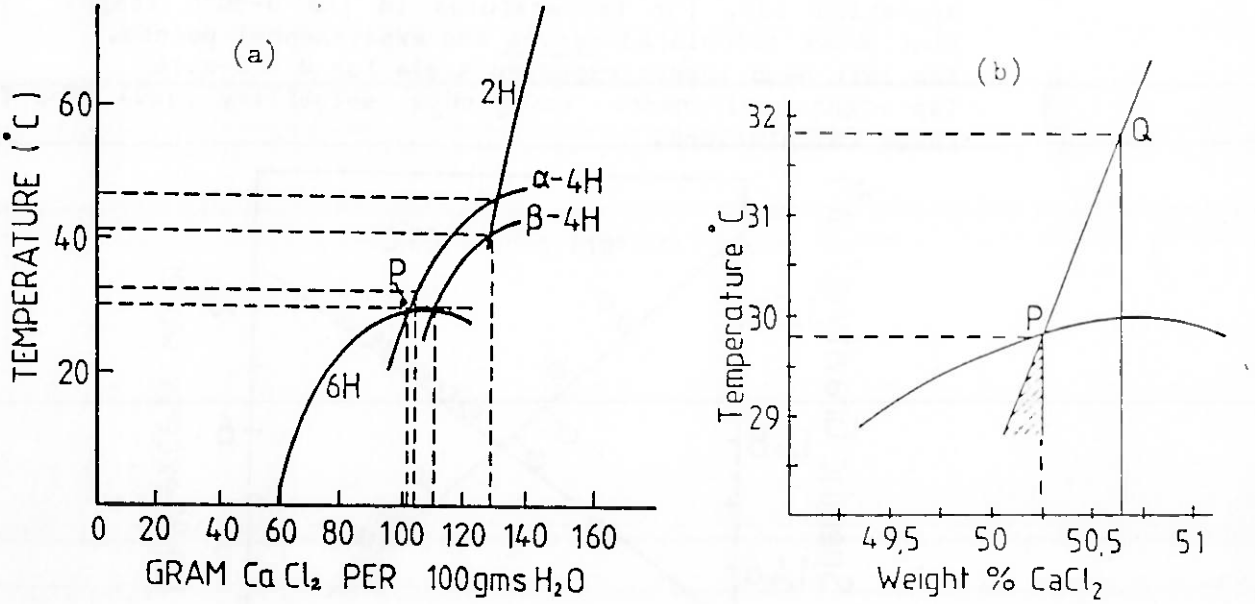


Fig 4 (a) 90-degree rotated mirror image of Fig 3, with added β-tetrahydrate curve

(b) like (a) - i.e. phase diagram of $CaCl_2$-H_2O system - in narrow concentration range around the hexahydrate. The hatched area indicates the metastable region where tetrahydrate can form due to supercooling of the hexahydrate.

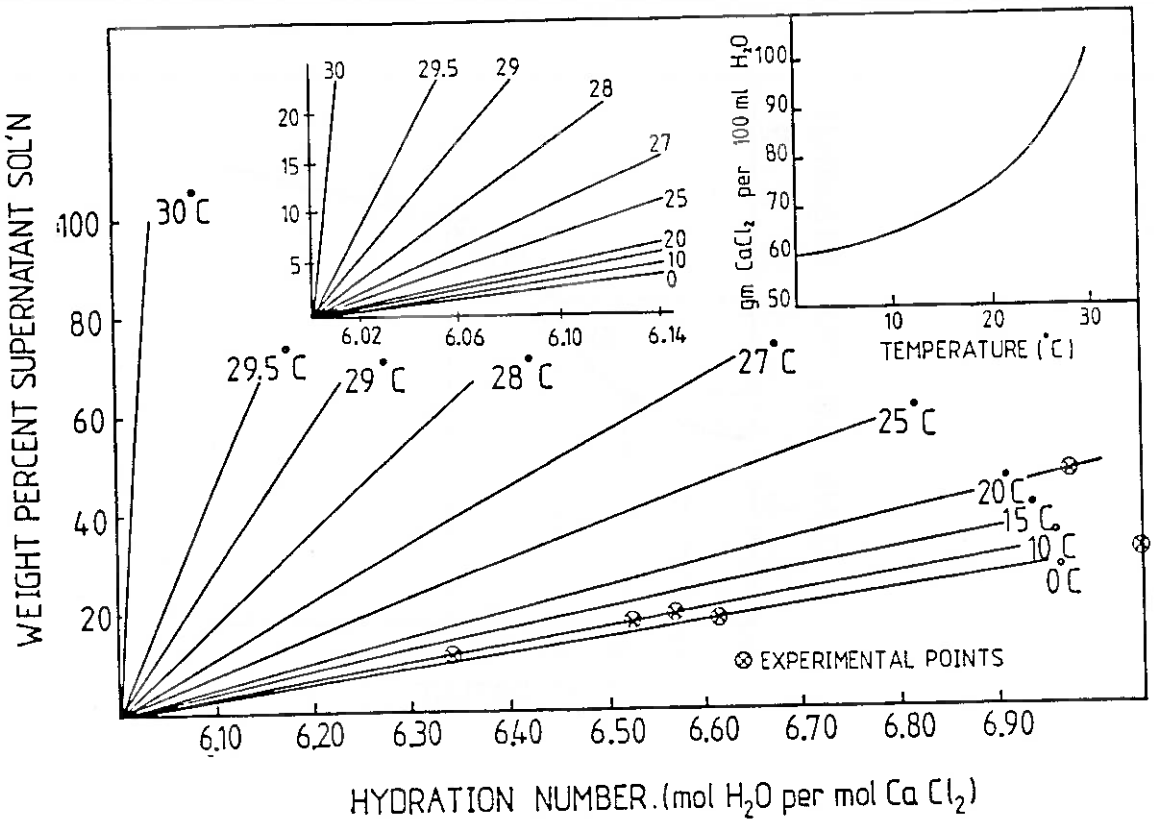


Fig 5 Weight percent supernatant $CaC\ell_2$ solution vs. degree of hydration (H), for temperatures in the 0-30°C range. The plot shows calculated curves and experimental points.
Top left hand inset: expanded scale for H = 0-6.14
Top right hand inset: $CaC\ell_2 \cdot 6H_2O$ solubility curve used for these calculations.

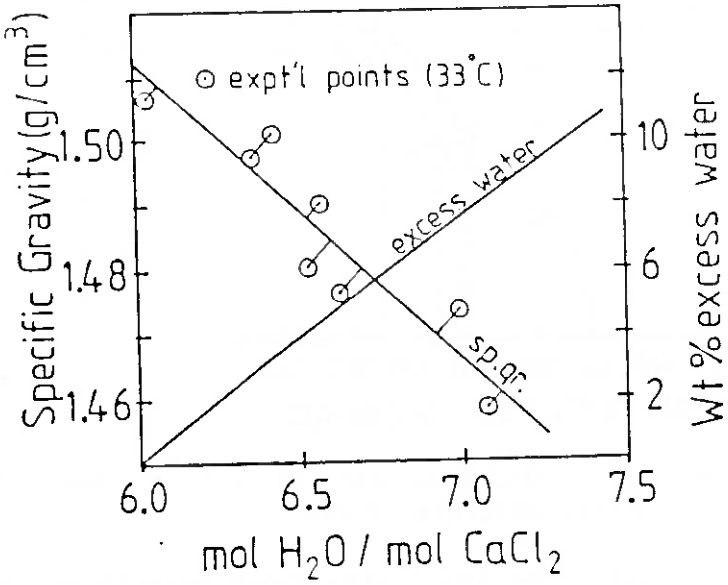


Fig 6 Calcium chloride specific gravity vs. degree of hydration, empirically determined for "technical" material near the $CaC\ell_2 \cdot 6H_2O$ composition. Also in this plot: weight percent excess water (right hand ordinate) for same abscissa.

A quantity of interest directly related to the fraction of supernatant liquid is the excess of water causing it. Up to the peritectic concentration this quantity is simply given by

$$\text{Weight percent excess water} = \frac{(H-6) \times 18.016 \times 100}{219.086 + (H-6) \times 18.016} \quad (3)$$

Fig. 6 presents this weight percent excess water function for convenient reference. Fig. 6 also offers an empirical relation of the density of $CaC\ell_2$ solution as a function of concentration. The temperature of 33°C at which the points determining this density relation were obtained was selected for practical reasons: since our samples of CCH usually were stored in a "hot box" at approximately this temperature, this curve provided for fast determination of concentration by simple weighing (to 0.01 grams) of a given volume (approx. 250ml) of any sample from this hot box. Actual states of hydration, for example to establish the density vs. H relation of Fig. 6, were determined by a de-hydration method, in which following the initial boiling-off the residual solid was subjected to 300-350°C for 15 minutes (see section III.1). The curve in Fig. 6 represents a best linear fit to the experimental points shown.

It should be noted that the material used, although essentially 'technical grade', containing in particular close to 0.4 weight percent $NaC\ell$ is relatively pure $CaC\ell_2$ aqueous solution, as evidenced by the transition temperature in excess of 29°C of its CCH form. The presented density vs H relation should therefore represent fairly closely pure $CaC\ell_2$ solution.

II.3 Tetrahydrate Formation and how to Prevent It

For correct evaluations in the region about the α-tetrahydrate peritectic point is it clearly helpful to redraw this region, Fig. 4, on a magnified scale such as in Fig. 4b. In this drawing points P and Q are placed in accordance with Fig. 1 of Lane [1981], purportedly after Roozeboom [1889], except that point P has here been located at exactly 29.8°C to comply with Mellor [1946], citing Roozeboom, as already mentioned.

It should be noted that very accurate location of melting points, etc., is here of little interest since we refer to technical CCH; and secondly that the β (and γ) tetrahydrate species (see Fig. 4) can safely be ignored so long as compositions above the hexahydrate, ie. above 50.66 wt%, do not occur; therefore 'tetrahydrate' in the following refers to the α- tetrahydrate only.

A $CaC\ell_2$ solution super-saturated with tetrahydrate at any point between P and Q, Fig. 5, will form a solid phase of weight fraction (s) given by

$$(s) = (X-X_\ell)/(X_s-X_\ell) \quad (4a)$$

with X_s = 0.6063 the weight fraction of $CaC\ell_2$ in $CaC\ell_2\ 4H_2O$. In terms of the hydration degree H

$$(s) = \frac{\frac{6.1606}{H+6.1606} - X_\ell}{0.6063 - X_\ell} \qquad (4b)$$

Of special interest here is H=6, the stoichiometric composition of the hexahydrate, which was the basic object of the work by Carlsson [1979] and criticism thereof by Lane [1981].

At temperture corresponding to the point Q (31.8°C, but Lane [1986] quotes 32.78°C) the weight fraction for saturation is 0.5066. At this composition the amount of solid tetrahydrate in equilibrium with the solution can be calculated through eq. 3b. With H=6 and X_ℓ = 0.5025 (the weight fraction for saturation of the tetrahydrate at the peritectic according to Fig. 4b), (s) = 0.040 is the weight fraction of precipitated $CaC\ell_2.4H_2O$.*

The weight fraction of liquid is thus 0.960 and its composition is that of tetrahydrate - saturated solution at the peritectic i.e. 0.5025 weight fraction $CaC\ell_2$, corresponding to hydration degree H=6.10. At 25°C this composition leaves 7% supernatant liquid, according to Fig. 5, but at 28° this becomes 18%, etc.

Disregarding for the present the possible formation of tetrahydrate in its metastable region at concentrations below peritectic we may then conclude that the optimal excess quantity of water is for concentration just, but safely, below the peritectic, such as H=6.14. This according to Fig. 5 would amount to a loss of 11% storage capacity at 25°C, 6% at 20°C, etc.

It follows that heat of fusion values measured over repeated cycles with a sample containing excess water should be increased by the appropriate factor, depending on the amount of extra water and the low-temperature level, to yield the true heat of fusion value, in distinction from the achievable heat storage capacity. Account of this is taken in the results presented in the following.

In the metastable region, the 'hatched area' in Fig. 4b, tetrahydrate can form due to supercooling of the hexahydrate or to concentration gradients creating regions where the tetrahydrate is stable. The prevention of these have been shown in our study to be possible, by a) minimizing the time span of hexahydrate supercooling - not necessarily the supercooling temperature differential, as discussed in the following section; and b) retarding any formed tetrahydrate in its descent to the container bottom. Having been formed 'legitimately' in a dense region, such tetrahydrate is then bound to traverse lower-density regions where it no longer is thermodynamically stable and only requires the necessary time to return into solution. Nucleating and thixotropic additives (Telkes [1975]) were found totally effective in preventing phase separation in our sample, as well as in a prototype space heating system employing 200kg of our PCM.

* with the 49.62 wt% peritectic composition quoted by Lane [1986] this value would be 9.4%.

II.4 Nucleation and supercooling

A number of distinct phenomena are strongly reflected in our temperature mapping data in the supercooling region:

- for nominally identical ambient conditions, the degree of supercooling (in degrees below the transition temperature) tends to vary significantly from cycle to cycle.
- following deep supercooling, the temperature at each of the monitored locations tends to restore itself very close to the transition temperature, often to closer than 0.1°C relative to the melting point, exhibiting a strong phenomenon of 'recalescence' (Lane [1986], p. 109) in terms of the steepness of the temperature rise.
- by comparing supercooling regions from different cooling regimes, it is apparent that the degree of supercooling tends to increase with increasing cooling rate. Closely related to this is the tendency for the time to reach the minimum of temperature to be invariant. Although this is far from being accurately borne out by observation, presumably due to the above-mentioned variation in the degree of supercooling even within identical conditions, the postulation of such an invariant time (for a given PCM sample) provides a convenient point of reference for theoretical investigation (Carden [1987]).

- Comparison of supercooling regions from different PCM formulations leads to the conjecture of the existence of a critical dosage of nucleator additive: at this dosage dwelling times in the supercooled state occur with broad distribution from close-to-zero up to many hours; whereas slightly above this dosage this dwelling time never occurs. It appears likely, moveover, that the degree of supercooling generally decreases with increasing nucleator dosage.

III. EXPERIMENTAL PROCEDURES

The experimental procedures applied in this project can be broadly classified in 4 categories:

- various general-type laboratory procedures, including temperature measurements, weight and density measurements, chemical (spectrophotometer) analysis, and thermoanalysis for water content.
- small and larger-scale processing of phase change materials, starting either from ICI 'distiller-blowoff' or from other base materials, including calcium chloride di-hydrate.
- the long-term laboratory PCM melt/freeze cycling experiment, including continuous year-long temperature mapping and thermal analysis, data recording on floppy disk, and data retrieval in various forms.
- the greenhouse heating implementation of a near-practical PCM system, involving a 100 kg PCM store in a computer monitored/controlled small 'makeshift' greenhouse.

These items will now be detailed.

III.1 General measurements

Four types of standard measurements are constantly used in this project:

- temperatures in the 0-50°C range, approximately, using thermistors, thermocouples, infra-red thermometry and mercury glass thermometers. In addition a special solid state element (LM35CH supplied by SEMTECH (NSW)P/L, PO Box 671, Lane Cove 2066), has been used lately in our experiment as part of a newly installed (locally made) high-precision temperature bath controller.
- density measurements, mainly used to determine quickly the states of hydration of PCM samples by use of a hydration vs. density graph (Fig. 6).
- spectrophotometric measurements, to determine chemical compositions, detect leakages, evaluate concentration gradients of additives, etc.
- thermoanalysis-type measurements, in which the total water content of a sample is evaluated by way of total dehydration of the sample in an evaporation pan over a bunsen flame. This, combined with fast, accurate weighing provides the accurate degree of hydration evaluation discussed above in relation to 'supernatant liquid'.

Temperature measurements are a principal part of the melt/freeze cycling experiment. There we use 12 copper-constantan (type T) junctions coupled to a reference junction of that type which in turn is thermally coupled to a precision thermistor (Yellow Springs Inc., 3000 Ω at 25°C, 0.1°C precision in the range considered) as described in Fig. 7. The resistance values of the thermistors are converted first to voltages (Fig. 8), which are measured with the 'Thermocouple multiplexer' interface (Figs. 9,10) to the computer. The reference temperature T_{ref} is obtained from this voltage by the function

$$T_{ref} = 16 + 0.91V + 0.0033V^2 \quad \text{(V in Volts)}$$

derived by a fit to the V(T) graph given in Fig. 8, based on the manufacturer's (tabulated) resistance vs temperature relation. This function is valid between 17 to 45°C to precision better than 0.5°C, but between 20-35°C the precision is better than 0.2°C.

All other temperature measurement precisions are coupled to this in absolute magnitude; however, as thermocouples with a common reference junction (thermally coupled to this thermistor), Fig. 7, these other sensors introduce practically no further error, in the range used, so that all relative precisions are high and restricted mainly by the precision of the conversion relations (V in millivolts):

$$\Delta T_{tc} = 0.107 + 25.654\ V - 0.5584\ V^2$$

$$V = 0.0017 + 0.03873\ \Delta T_{tc} + 0.00004\ \Delta T +^2$$

The reference temperature is monitored also by a 0-50°C mercury glass thermometer near the reference junction and the thermocouples are tested to measure near-zero deviation from the reference temperature in the 'quiescent' state. The thermocouple temperatures are actually

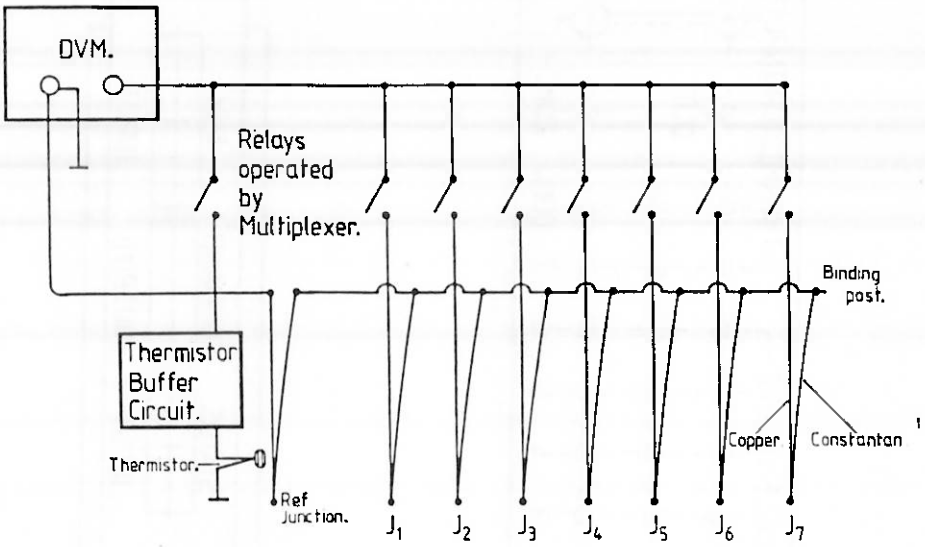


Fig 7 Thermocouple arrangement with reference junction thermally coupled to precision thermistor.

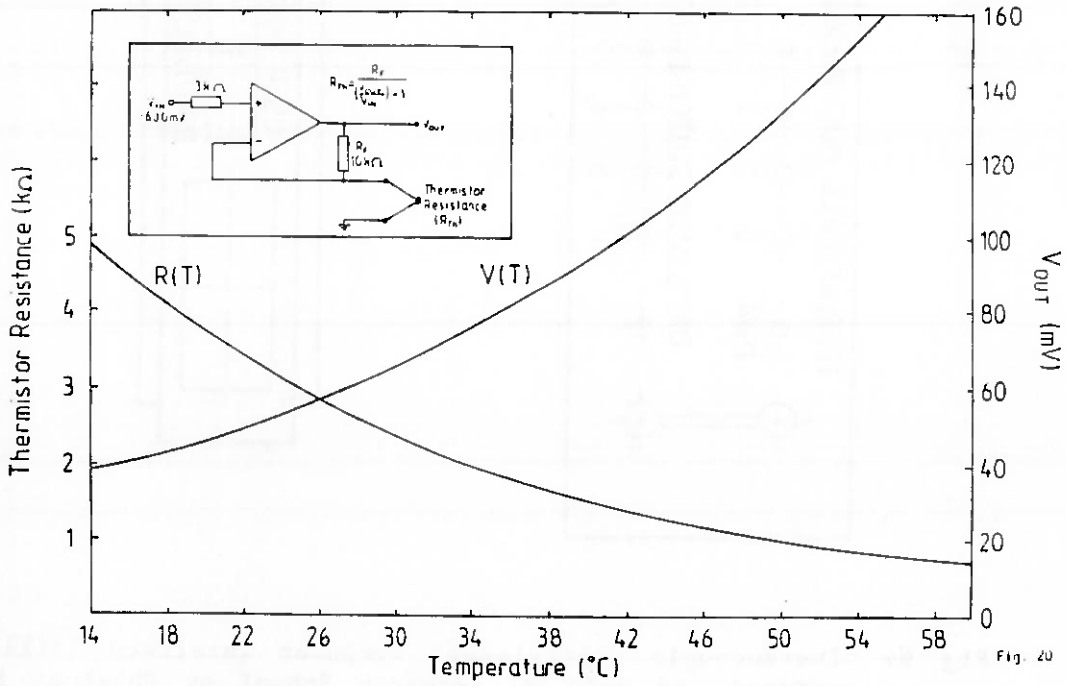


Fig 8 Thermistor resistance, R, and derived voltage, V (see inset), vs temperature T. (YSI 44005 precision thermistor, 3000 ohms at 25°C, by Yellow Springs Instruments Co., Ohio, USA).

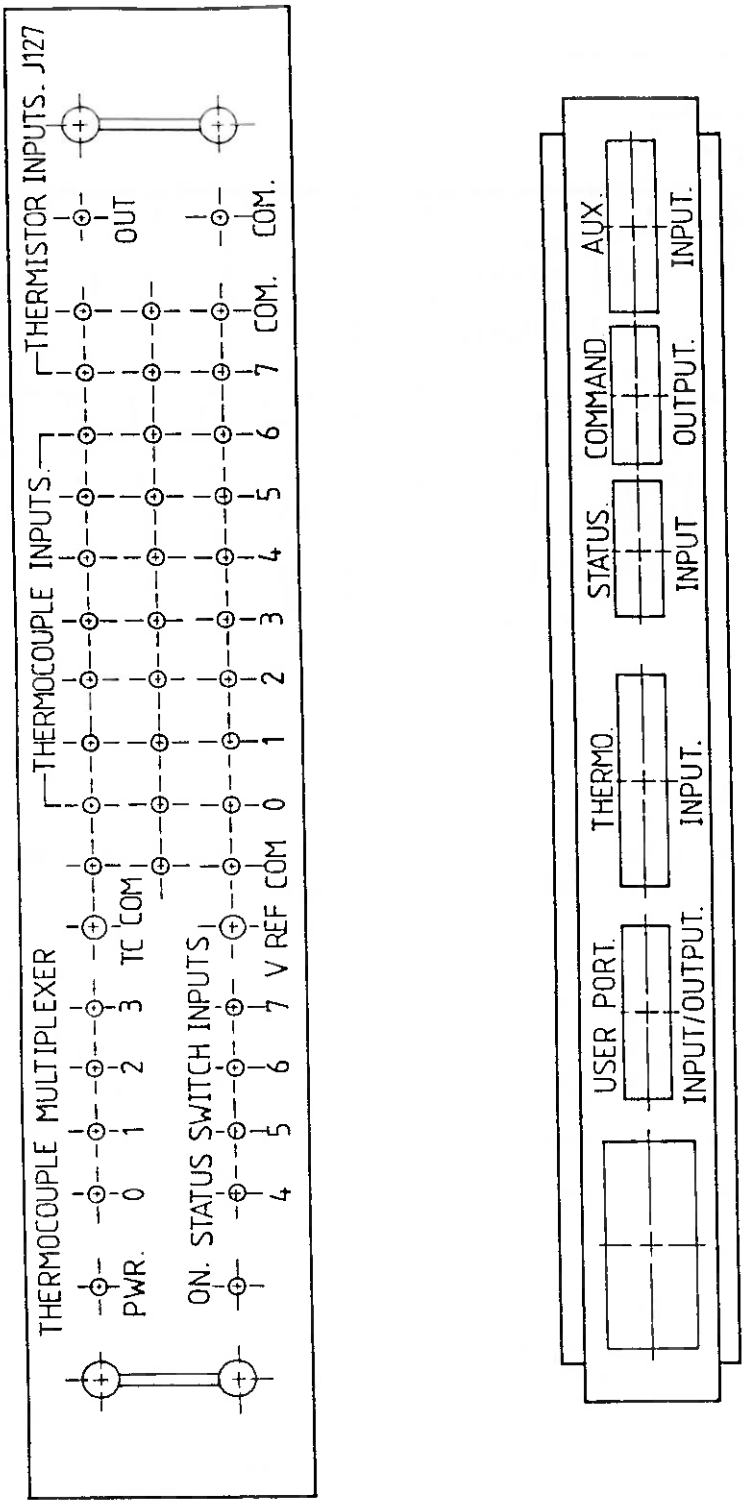


Fig 9a "Thermocouple Multiplexer" Computer Interface (J127, custom designed and made by Research School of Physical Sciences, Australian National University). Front (upper drawing) and back (lower drawing) connections.

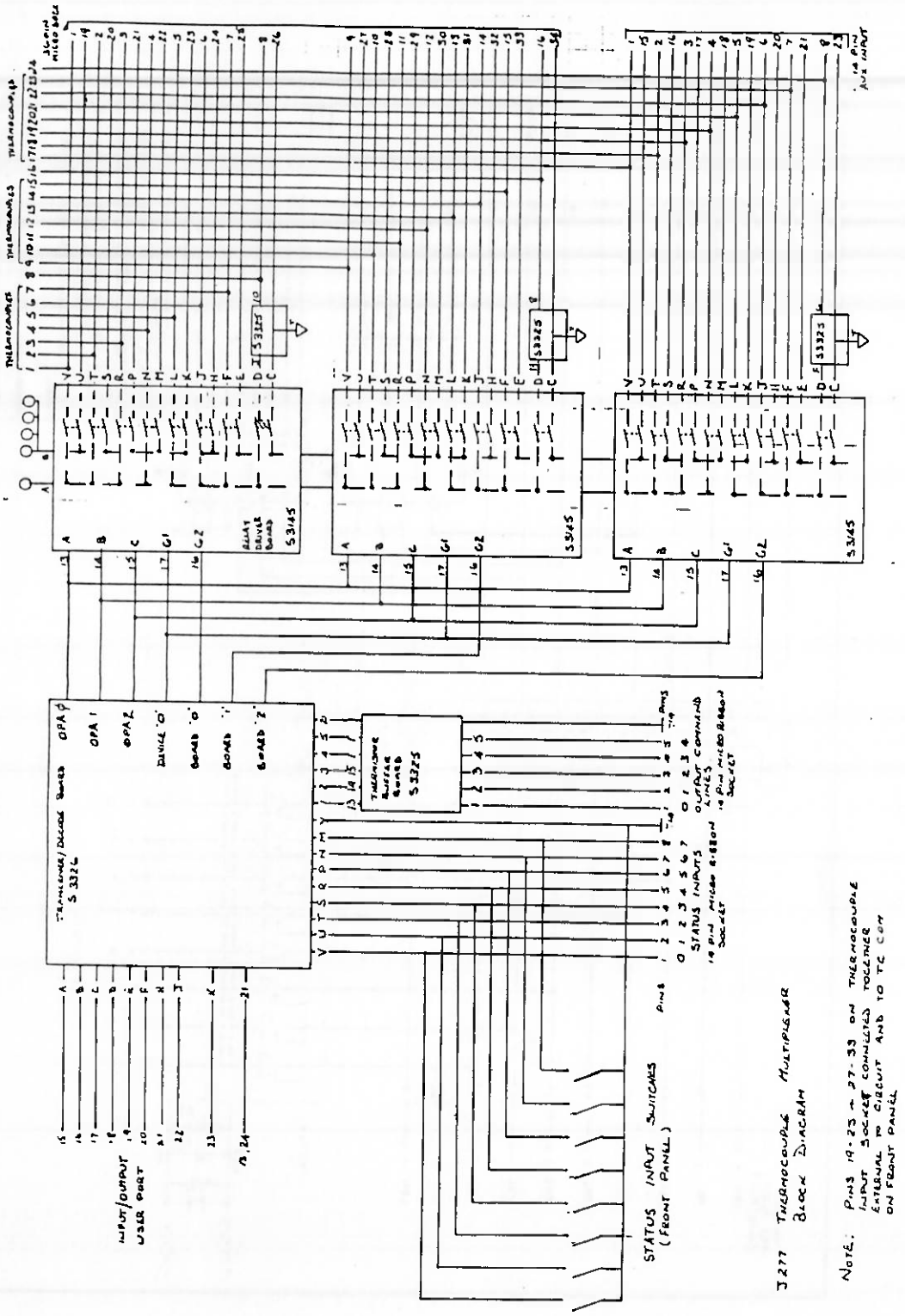


Fig 9b "Thermocouple Multiplexer" (alternatively referred to as "Computer Interface") block diagram.

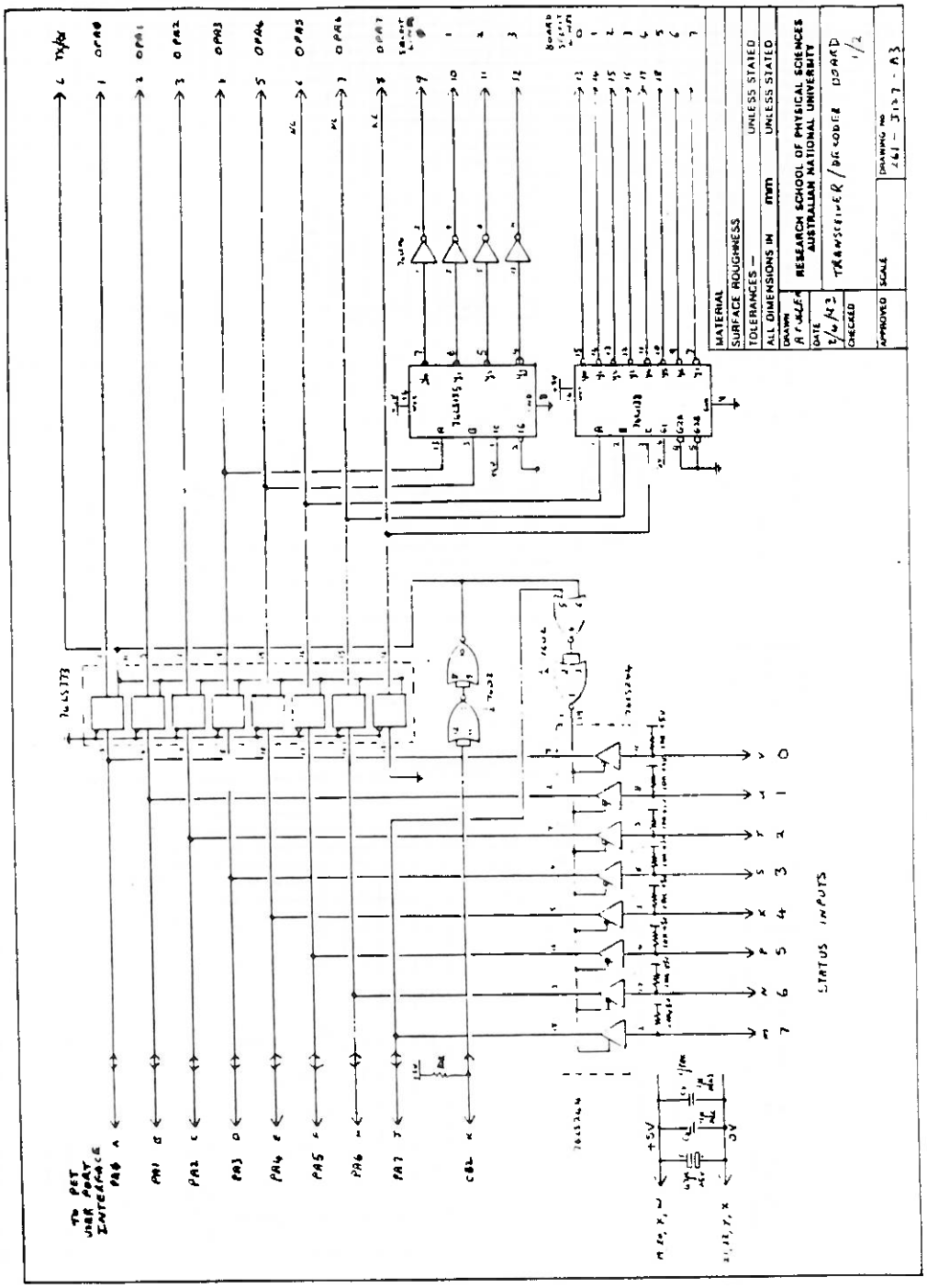


Fig 9c "Thermocouple Multiplexer" Transceiver-Decoder board, with "status input" connections (leading also to "Status input switches", see Figs 9a, b).

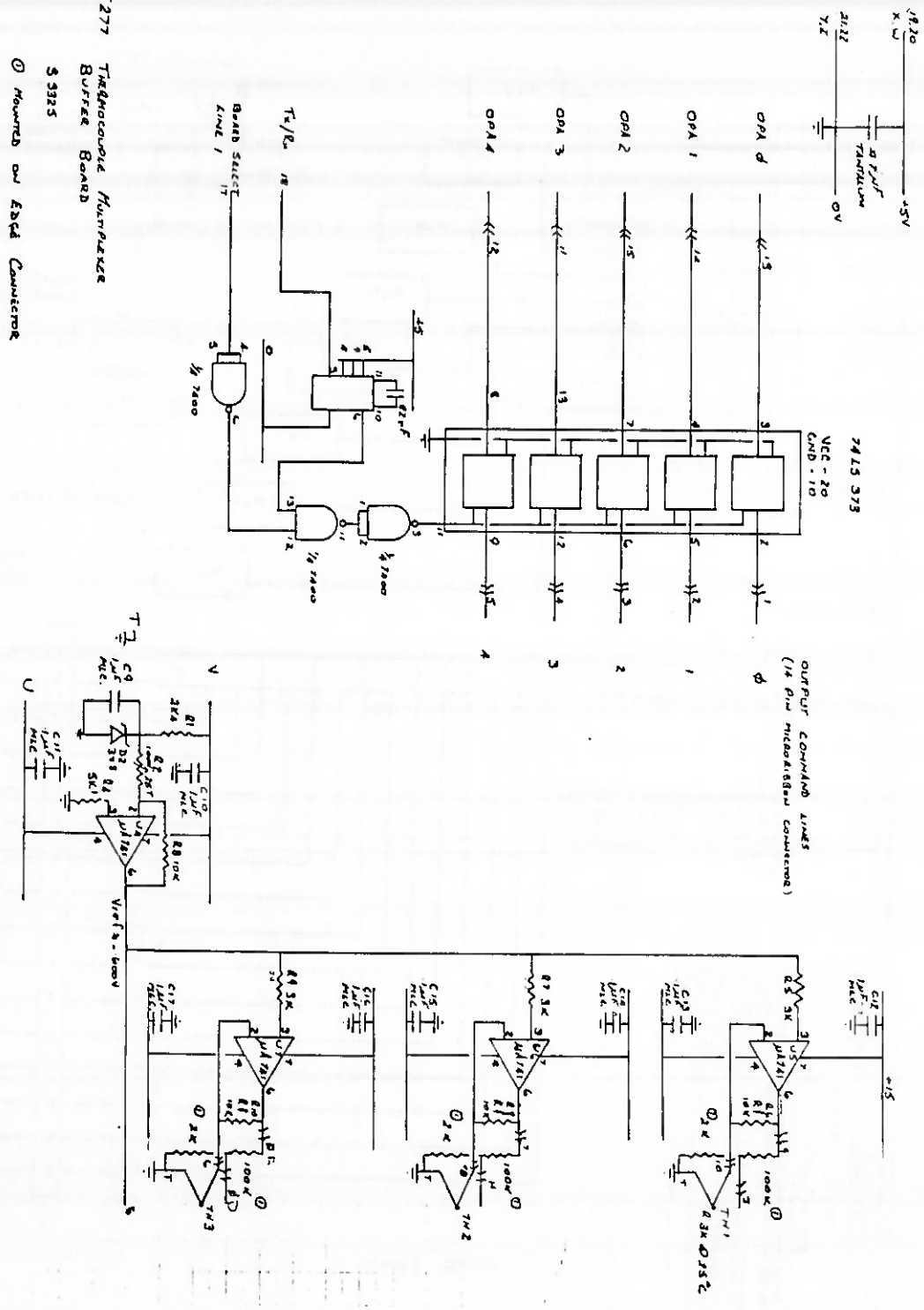


Fig 9d "Computer Interface", showing "Output Command line" circuits (left), and 3 thermistor buffer circuits (right) with common reference voltage generator.

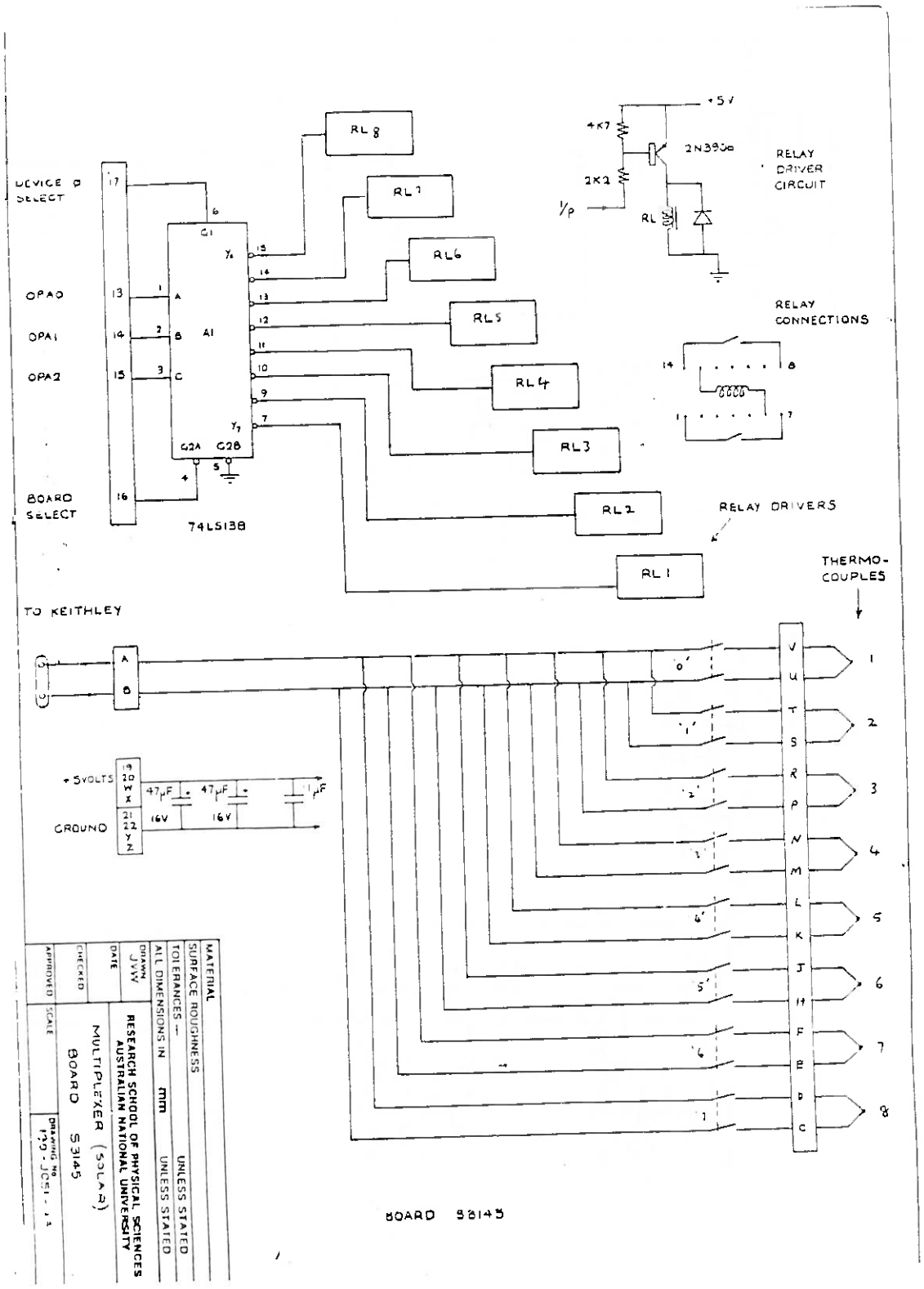


Fig 9e "Thermocouple Multiplexer", showing one of three boards of thermocouple relay circuits (Input 8 servicing a thermistor buffer output voltage, see Fig 9d).

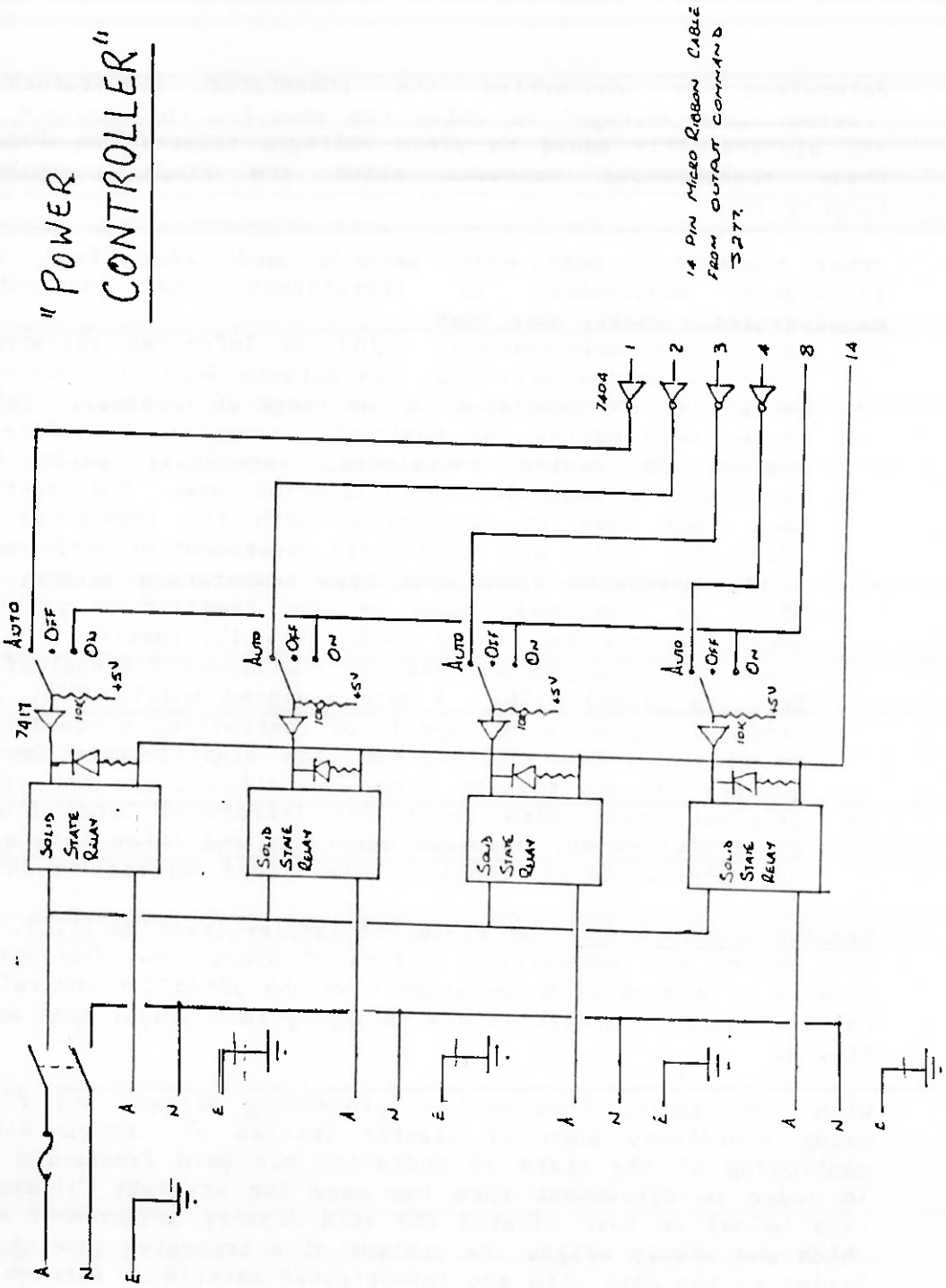


Fig 10 Schematic of "Power Controller", switching power loads (240 V heater, fans, etc.) under computer control via "Computer Interface Command Lines", see Fig 9d.

determined by converting the thermistor temperature to a 'thermocouple voltage' to which the measured thermocouple voltages are algebraically added to yield voltages relative to 0°C. It is these thermocouple voltages which are finally converted to temperatures.

Other temperature measurement methods used, apart from 'straight' resistance measurement of thermistors and conversion via manufacturer's chart, have been

- contactless measurements, using an Infra-red thermometer (by Linear Laboratories, 445S. San Antonio Road, Los Altos, Calif. 94022), of 1°C precision in the range of interest. This method proved very useful for monitoring temperature profiles in PCM samples in sealed containers, especially while following variations through the crystallization zone. The instrument has been used also in conjunction with the greenhouse (section IV.2), its design and preliminary assessment of performance.
- a high-precision transistor type temperature sensor, type LM-35CH, as mentioned, used as the temperature probe of the controller for the 'Grant Bath' (Fg. 12, Section III.3). This controller designed and made at the Research School of Physical Sciences (Model J126; a more advanced model, J276, is now in production), which is capable of controlling a temperature bath to within a few millidegrees, has significantly improved the quality of our results since installed late last year. The original Grant Bath controller introduced large fluctuations (> 0.5°C) which, although monitored and taken into account in the calculation of enthalpy, have flawed our earlier data.

Density measurements, as explained earlier (section II.2), provide a fast method for determining degrees of hydration. One measures the density at a nominal temperature - we use 32-33°C - and relates this to the degree of hydration via an appropriate graph, such as given in Fig. 6.

With PCM samples from various processing stages, and PCM systems using containers such as plastic bottles of various kinds, fast monitoring of the state of hydration has been frequently required. In order to circumvent then the need for straight "thermoanalysis" (see below) we have adopted the said density measurement method, in which one simply weighs the content of a truncated-cone shaped flask filled to the mark with the investigated material. Between weighings the flask is kept dry in an oven at about 45°C (many samples can, however, be weighed in direct succession), and the material is to be assessed at the said nominal temperature, i.e. kept in a "hot box" or the like for several hours before being poured into the flask. Calibration was obtained by weighing distilled water at STP. With our fast-operating, high-capacity (3kg) Precisa-3000 precision scale (10mg), with automatic tare subtraction, this method has been found extremely convenient and sufficiently precise and reproducible. The flask is 250 ml and an alternative in form of a test tube with perforated capping is occasionally used when only smaller amounts of sample material are available.

Thermoanalysis is the term applied to the method of dehydration used to assess the content of water in $CaCl_2$ (or other) aqueous solution. Very high precision work of this type is carried out elsewhere with a Mettler Thermoanalyser (see e.g. Feilchenfeld [1984]), in which the loss of weight of the sample by evaporation can be followed continuously as its temperature is raised through substantial levels such as up to 400°C. A comparatively primitive setup uses an evaporation pan heated over a bunsen flame and before-and-after weighings. Various precautions are necessary to avoid gross errors in the resulting degree of hydration, not least to ensure complete dryness of the evaporation pan at the time of taring. A capability for fast and accurate weighing, to at least 10 mg precision for samples in the 10-20 gram range, is another requisite. Our Precisa-3000 scale (from PAG Oerlikon AG, PO Box 557, Wallisellenstrasse 333, CH-8050 Zurich, Switzerland), of precision 10 mg at capacity up to 3kg, has proven highly adequate for this task, thanks also to its automatic taring feature.

Samples of PCM were poured into the (dried and) tared evaporation pan and immediately weighed. The (covered) pan was then heated over the bunsen flame, at first very carefully to avoid spillage during the burning-off phase, for a total of about 15 minutes, with the $CaCl_2$ residue kept at about 370°C for 10 minutes, and then weighed again. With W the original weight and w the residual weight, the degree of hydration is calculated as

$$H = \frac{110.99}{18.016} \left(W/w - 1\right)$$

assuming pure $CaCl_2$ aqueous solution. With 1% NaCl content for 99% CaCl , i.e. about 0.5% NaCl content for the CCH, this H value is modified by w being replaced by 0.99 w, with the resulting degree of hydration:

$$H = 6.223 \left(W/w - 0.99\right)$$

(W/w = intial weight/final weight).

Note that this 0.99 value is uniquely determined by the solubility of sodium chloride in CCH, assuming the assessed hydration sufficiently close to the hexahydrate composition. The given formula is thus universally valid - for the process considered or whenever sodium chloride is present to saturation, and within the indicated limits of precision - independently of the particular sample investigated.

III.2 PCM Processing

In the laboratory calcium chloride hexahydrate would normally be prepared by dissolving anhydrous calcium chloride in water in the weight proportion 110.99/108.10. For "technical" CCH one would usually dissolve calcium chloride dihydrate "flakes" in tap water, in the weight proportion 147.02/72.06. For PCM these would be completed by adding excess water and other additives in the defined amounts at suitable temperature. The question relating to suitable amounts of excess water were discussed at length in the previous chapter. As to the other additives, generally nucleating and gelling (or

"thixotropic") agents, their precise nature can usually not be detailed due to proprietory limitations. General accounts on nucleating and gelling agents used with hydrated salt PCM's can be found in the PCM literature, including in particular Lane [1983] and [1986], Abhat [1982] and Kimura [1984].

The nominal objective of this project has been, however, to investigate the possibility and ways of processing a certain industrial waste product - Distiller Blow-Off (DBO) from the Osborne (S.A.) soda ash plant of I.C.I. - into a useful PCM for thermal storage. Credit for suggesting this source of abundant and potentially cheap CCH goes to Mr Aert Driessen of the Bureau of Mineral Resources, Canberra. Also, credit for making this material available for pertinent investigation, at first on a small laboratory scale but later at the 1-ton level, goes to Mess. M.V. Melvin and G. Watson of ICI Alkali Group, Melbourne, and to Dr L. Pollard of I.C.I., Osborne.
According to information supplied by I.C.I. this composition of DBO is, approximately, in water

Calcium chloride 100 gpl
Sodium chloride 47 gpl
Calcium hydroxide 6 gpl

with some 1-2% suspended matter, which however, tends to settle leaving "clarified DBO". The Ca, Cℓ and Na contents were essentially confirmed by analysis at the Research School of Chemistry, A.N.U., resulting in 4.8%Ca, 2.3%Na and 12%Cℓ . Processing this clarified DBO into CCH involves these following major steps:

- neutralization of the calcium hydroxide - that is unless one sees it as part of the PCM formulation, e.g. following Carlsson [1979].

- Evaporation of the very large amount of excess water (~ 80%) , coupled with the precipitation of the large excess of sodium chloride above its solubility limit in CCH - which is about 0.5 percent, as mentioned in the previous section.

Neutralization is achieved relatively easily with hydrochloric acid, according to the reaction

$$Ca(OH)_2 + 2HC\ell \rightarrow CaC\ell_2 + 2H_2O$$

which results simply in an increases of the $CaC\ell_2$ concentration and thus is the final yield. The required amount of HCℓ (36%) has been found to be somewhat less than 2cc per litre DBO, which in fact is far from negligible considering that this amounts to 1 litre HCℓ for 100 kg final product, (since 100 gpl $CaC\ell_2$ means about 200 gpl CCH).

As to the large sodium chloride component, its main nuisance effect resides in the problem of its disposal as a solid residue at the

bottom of the evaporation pan following collection of the liquid CCH. That a large part of the sodium chloride would in fact precipitate out of solution in the course of evaporation, due to its negative temperature coefficient of solubility as compared with the positive value for calcium chloride, was pointed out to us by Dr Ben Selinger (Department of Chemistry, A.N.U.) early in this work. One may add parenthetically that within the framework of a large-scale production operation it would presumably be attempted to utilize this sodium chloride residue as well: perhaps in salt gradient solar ponds for electricity production, where very large amounts of very-low-cost salt are required. Very large amounts are required also, of course, in the very "Solway process" producing the DBO effluent.

Processing the DBO to as far as the hexahydrate level proved feasible using natural outdoor evaporation only. The final product could be extracted via a filtering mesh and was pumped into large plastic drums using a peristatic pump. The latest evaporation setup, using 300 litre evaporation pans made of simple wooden frames and plastic sheeting, on the roof of the Cockroft Building, A.N.U., was shown in the photograph, Fig. 2. In Fig. 1 a schematic description of the complete process was given.

The net CCH yield in this latest set-up was approximately 100 litre CCH, i.e. 150 kg, resulting from 800 litre (~ 900 kg) evaporated DBO. The residual salt weighed about 40 kg (not all of it recovered) of which one third, approximately, was found by chemical analysis to be $CaC\ell_2$.

At 100 gpl $CaC\ell_2$ content of DBO, it would follow from these results that a practical yield of nearly 90% of the total CCH is routinely achievable in this process, with the missing 10% admixed to the residual sodium chloride. Results on evaporation rates are given in Table A.1, Annex. In an alternative CCH production set-up for pilot-size applications, we used commercially supplied calcium chloride dihydrate "flakes", essentially as described above in relation to laboratory-prepared "technical" CCH. The material supplied contains 73% $CaC\ell_2$ on average (minimum 70%), 2% sodium chloride, and less than 0.02% other metals. The setup is depicted in Fig. 11, consisting mainly of a stirrer in a 200 litre plastic drum kept at a controlled temperature.

Spectrophotometric measurements

A Model-303 Perkin-Elmer Atomic Absorption Spectrophotometer with a set of hollow-cathode lamps and acetylene-air flame has been used for chemical analysis of samples of DBO or PCM, etc., and also of distilled water suspected contaminated through leakage. The latter was tested for Calcium content and from measured concentrations the amounts of leaked PCM could be assessed. Samples were assessed for Sodium content, at dilution levels corresponding to Na concentrations in the 2-5 ppm range, as well as for Ca and for concentrations of additives.

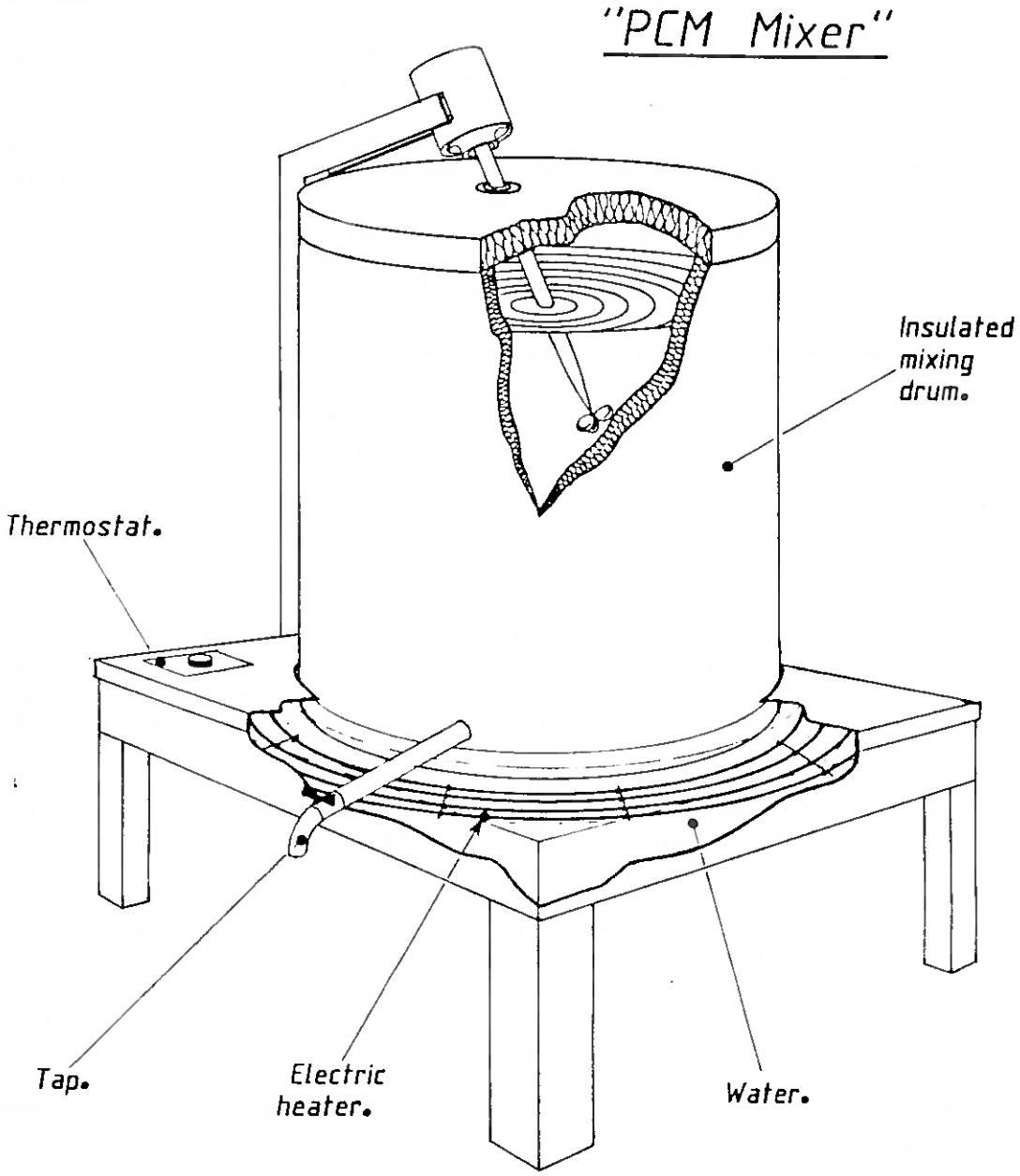


Fig 11 Phase change material processing setup, with stirrer and temperature control.

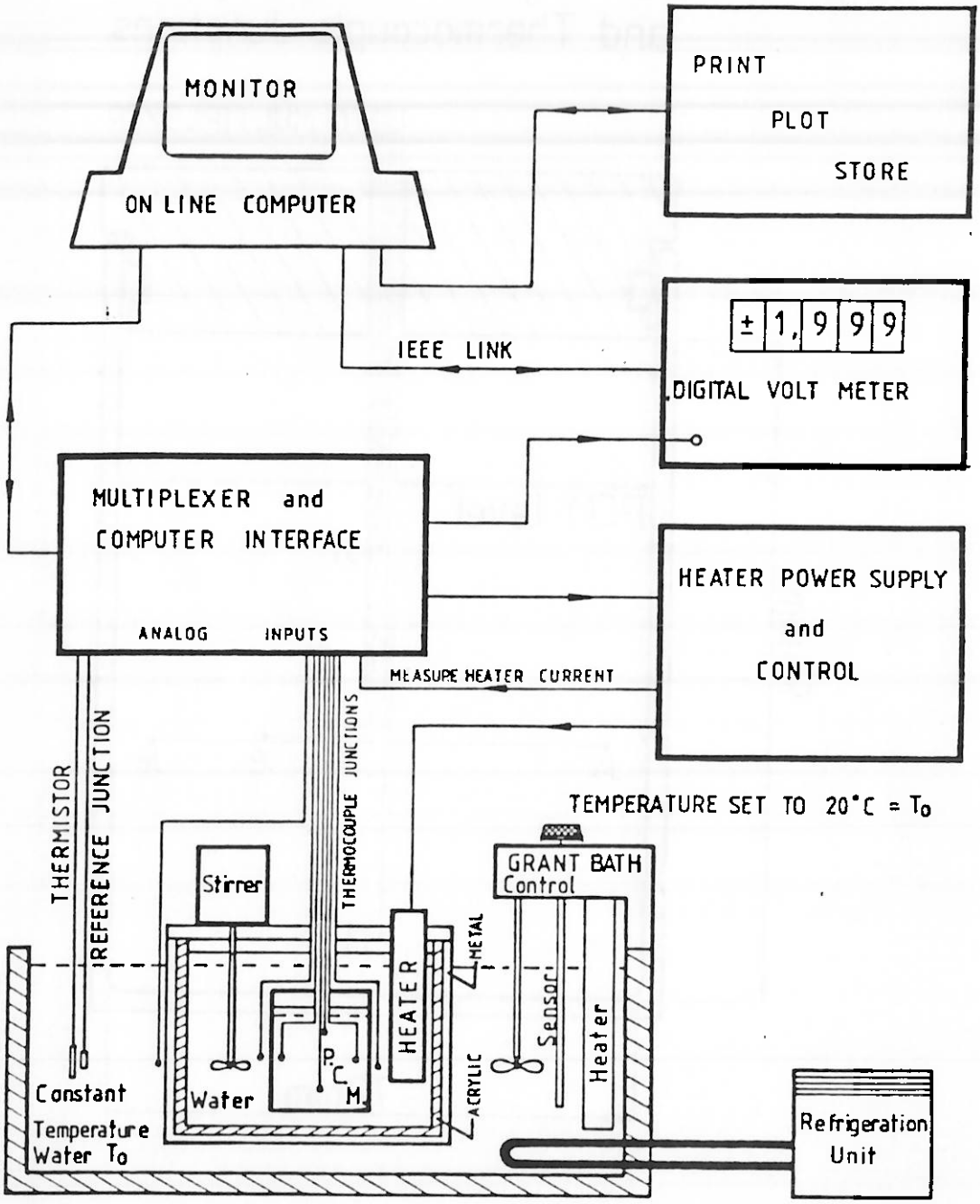


Fig 12 Schematic of "Continuous Thermal Analysis" setup. There actually are 3 thermocouples attached to the inside (acrylic) cladding and two to the metal outside of the water "vessel". See Fig. 13 for the actual arrangement of thermocouples in the PCM capsule. The "Grant Bath" holds approximately 26 litres at the level shown. (Grant Bath "temperature set to 20°C = T_o" is only an example).

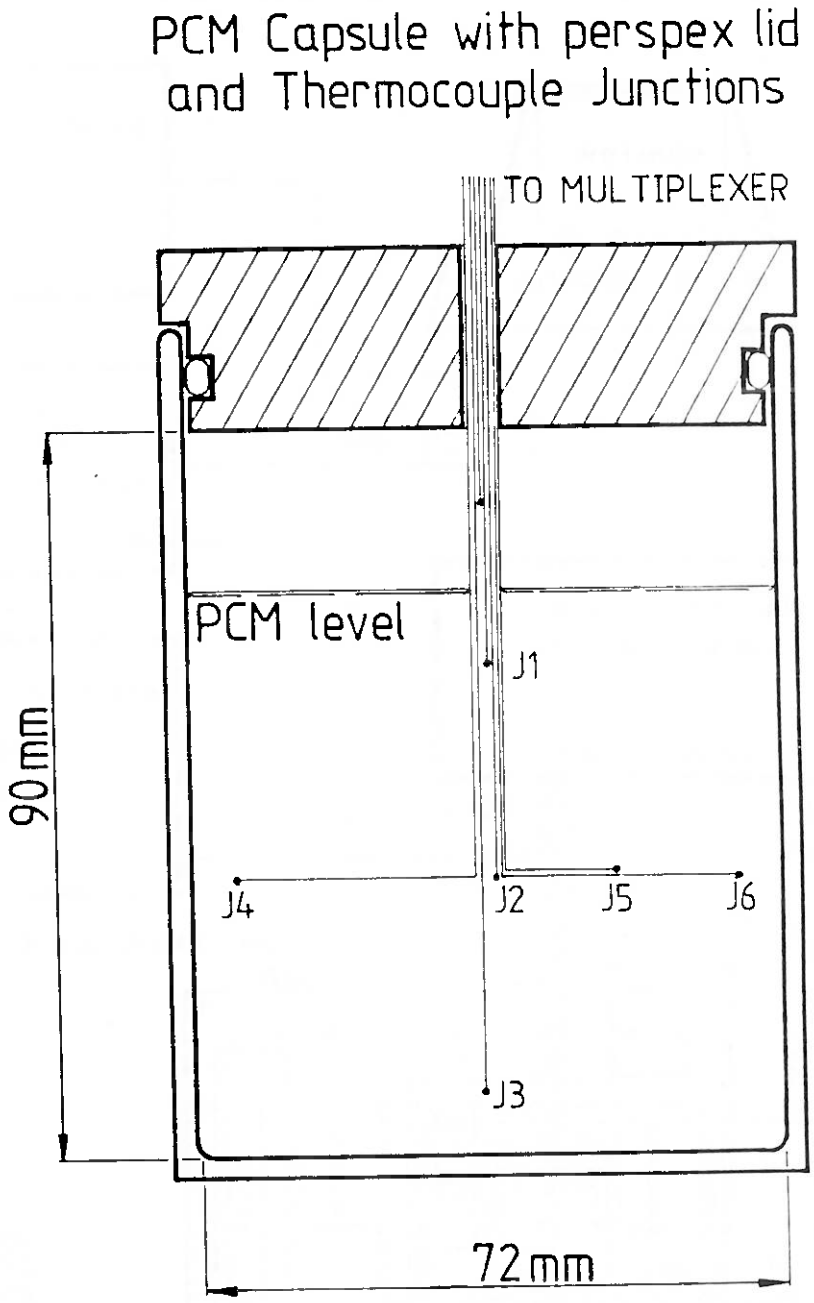


Fig 13 showing the "PCM capsule", with its thick acrylic lid and (hermetic) lead-through of thermocouples (Copper Constantan, 38 SWG, with PVC coating, from Dural Plastics & Engineering, Dural NSW 2158). This capsule was made by cutting the top off a 500 ml "Kartell" polythene bottle. (Thermocouples 1, 2, 3 are doubled by spares, labelled 17, 18, 9, respectively; the latter actually measured, see cycle 172, Fig A.3e).

A computer program, "SPECTRO", is run interactively with these Atomic Absorption Spectrophotometer analyses, mainly in order to convert the measured absorption count into the relevant "absorbance" value, and from there into ppm concentration in relation to standard solutions. A representative printout from such a computer run, obtained with a sample of remnant from the PCM assessed in the calorimetric evaluation experiment (section III.3) is shown in Table A.2, Annex, and further discussed there.

III.3 PCM laboratory assessment - cycled thermal anaylsis

The melt/freeze characteristics of two samples have been assessed in succession, in a specially designed apparatus capable of continuous monitoring of sample's enthalpy. These samples (labeled S3 and S4) were prepared from DBO by the method described using natural ("solar") evaporation.

The first sample (S3) was assessed over a period of 35 days, after which its heat-of-fusion had declined to about 50 percent of its starting (and nominal) value of about 200 kJ/kg.

The second sample (S4), which was formulated differently, has been "running" since August 1985 with ultimately no degradation over 500 daily melt/freeze cycles and beyond.

Fig. 12 shows the apparatus, mainly a constant-temperature bath, in which is immersed a semi-insulated vessel holding the PCM capsule. This water is continuously stirred and its temperature is set by a heater under computer control, usually under a diurnal 8-hour ON, 16-hour OFF cycling routine. Temperatures are monitored by a thermistor and thermocouples arranged as explained Fig. 7, and essentially located as in Fig. 12, providing among others for continuous monitoring of the heat transferred across the vessel enclosure on the basis of prior calibration.

The capsule is cylindrical, with the dimensions and thermocouple arrangement as shown in Fig. 13. It contained 0.382 kg PCM, when filled to a height of approximately 70 mm.

The vessel normally contained 970 ml of water, to a height corresponding to the upper capsule rim, and the total water equivalent (including the PCM capsule etc.) was then found to amount to 1.233 kg.

Denoting this water equivalent by M and the mass of PCM by m the amount of heat δE (for change of enthalpy) received by the PCM during a time interval δt is calculated as $\delta E/m$ Joules per kilogram PCM,

$$\delta E = - MC_w(T_w - T'_w) + [P_h + P_{st} - hA(T_w - T_v)]\delta t \quad ,$$

where c_w = 4185 J/kg°C is the specific heat of water, T_w, T'_w are present, previous temperature of water in vessel, P_h is the heater power (~ 68 watts), assumed constant (or 0) during δt ; this is calculated as I^2R, where I is very precisely measured across a 20 mΩ precision resistor and R = 4.204 Ω is frequently monitored. P_{st} is the rate of heat contributed by the stirrer, which was found to amount to 0.178 watt.

A is an assumed area/thickness constant for the heat transfer across the vessel enclosure, set to 18 metres (0.090 m^2 area of vessel in contact with the constant temperature bath, divided by 0.005 metre insulation thickness), T_v is the exterior vessel temperature, and h is an adjustable heat transfer parameter, equal in first approximation to the heat conductivity of the "semi-insulation" material, i.e. the inner perpex cladding of the vessel, which is about 0.1 Watt/cm°C. the adjusted value of h is found close to 0.12 Watt/cm°C.

T_w and T_v, the vessel's inside and outside wall temperatures, are each measured as an average over a number of thermocouple temperatures: 3 on the inside, 2 on the outside, each also monitored individually.

Finally, δt is the precise time interval over which δE is calculated, this precision being especially critical during "heater-ON" time intervals. It has therefore been very carefully assessed with a stop watch, by checking the computer clock and measuring cycle times. Nominally set to 30 seconds these turned out to be 29.95 seconds instead, caused by the computer internal clock being fast by 6 seconds per hour.

Measurements taken every 30 seconds, as explained, are averaged every 6 (or 12) minutes and the results stored in memory and recorded on magnetic disk every 6 (or 12) hours. When retrieved, each of the 60 "time points" then represent 12 (or 24) measurements for each temperature probe, and the sample's enthalpy value (and the heater current) at the end of that time point. The enthalpy values are relative to an arbitrary reference value to which the δE's are algebraically added in succession every 30 seconds. This reference can be arbitrarily chosen (once) for each enthalpy plot, covering say 24 hours, to fit into a standard interval such as from −50,000 to +250,000 J/kg, the normal enthalpy ordinate drawn by the plotting routine. A number of such plots presented in the Annex will completely clarify this description involving "time points" etc.

The requirement for highest precision in the measurements of electric currents and cycle time arises from the fact that the sought enthalpy value is the result of subtraction of two relatively large numbers, namely the total electrical energy supplied and the total heat

conducted out of the vessel, each of the order of 10^6 joules over 24 hours. This is to be compared with about 80000 joules heat of fusion for the 382 gram PCM sample. Moreover, over a complete charge-discharge cycle, say over 24 hours, the said subtraction should of course yield zero, ideally, for precisely restored conditions.

Such a precise balance is, however, quite difficult to maintain over long times, for a variety of reasons, and allowance must be made for variations, to be accounted for by means of corrections at retrieval time. One of such reasons is the occurrence of small variations in the assumed value of the conduction parameters, h, from causes such as very small variations in the level of water inside and/or outside the vessel, causing changes in the effective heat transfer area.

A different category of error is introduced by variations in the other calibration constant, M, caused for example by small amounts of water leaking into or out of the vessel. Too large M decreases both rising and falling enthalpy variations, δE , and in proportion to the temperature change $T_w - T'_w$. It follows that the calculated rate of sensible heat, when the liquid PCM is cooling down, is particularly affected by this type of error, and thus the calculated specific heat of the liquid PCM is a particularly sensitive measure of this error. We have in fact used this measure to maintain the correct value for this M parameter, following its initial calibration by means of water in lieu of the PCM. The correct specific heat value in a small range above the 29.3 transition temperature was assumed to be 2200 J/kg°C.

Conversely, any departure from this specific heat value seen in the resulting data was used to correct these data, temporarily at retrieval time, in accordance with the algorithm detailed in Appendix A. The other corrections included in this algorithm are to obtain:

a) accurate heat conduction parameter, h, which was determined through the requirement that identical states be associated with equal enthalpy values - e.g. when the PCM is frozen and all temperatures equalized with that of the constant temperature bath;

b) accurate value for the "stirrer power" contributed heat, obtained through the requirement for flat enthalpy registered over an extented period of time, when the stirrer is continuously running with the system in its "ground state": PCM frozen and all temperatures close to the constant temperature bath.

c) accurate value for the heat loss rate through the vessel perspex lid when all temperatures are equalized with the constant bath temperature at a value close to the transition temperature and well above room temperature. Under these conditions the only heat exchange with the vessel exterior is through the lid. The indicated condition applied during slow temperature traverses through the PCM melting or crystallization zones (see section V.2).

These error sources are analysed in Appendix A, and the algorithm for obtaining the corrected δE at retrieval time, from the original data read from the records obtained with incorrect parameter values, is there derived on the basis of this analysis.

Results, both with and without such corrections, are presented in a series of temperature profile and enthalpy curves vs. time plots in the "Annex", following general discussion of these results in section VI. From the corresponding printouts it is relatively easy to construct also plots of enthalpy vs. temperature, similar to those published by Feilchenfeld [1984]; a few plots of this type are also shown in the Annex.

IV. PHASE CHANGE STORAGE APPLICATIONS

Cost-effective solar space heating has traditionally been viewed as a relatively short-term reachable goal of solar energy research. For most applications this then evidently involved some form of energy storage, with phase change storage one of the few practical solutions. Two space heating application options using PCM storage are discussed in section IV.1.

Related applications are in greenhouses, for night-time heating and, in some cases, day-time heat removal. Success with experimental greenhouses using rockpile heat storage has been reported by Blackwell [1981], Jolly [1986] and others, including P. Dart [1986] of the Research School of Biological Sciences on this campus, who has been operating over the last two years a greenhouse of the type developed by Blackwell and Garzoli [1981].

PCM storage in greenhouses has been used successfully by B. Haber [1985] and others. A small experimental greenhouse with PCM storage has been developed here and is being investigated as part of this project. This will be described in section IV.2.

Finally, some aspects of the possible use of PCM storage in conjunction with heat pumps will be discussed in section IV.3.

For this project, only applications based on calcium chloride hexahydrate phase change material were considered. With the particular formulation used the transition temperature considered is 29°C, subcooling averaging 3-4°C; and the heat of fusion, despite higher values observed in our experiments is conservatively estimated at 180 kJ/kg, equivalent to 50 kWh/ton.

IV.1 PCM Space heating

The heating load for an average $100m^2$ home may be estimated at 50 kWH a day. This amount of energy can be stored in 1 ton of PCM (see above), so that 1 cubic metre (1.5 ton) of PCM may be considered as a suitable average for space heating systems. This store is charged either by solar energy - directly, e.g. as a "storage wall" (Fig. 14), or indirectly by means of solar collectors - or by off-peak electricity or other means. With off-peak electricity, charging of the PCM store can always be brought to completion and overcharging avoided without difficulty. With solar charging, cloudiness and the other causes of intensity variation will usually cause variations in the effective ultilization of the store, and overcharging to dangerously high temperatures must be prevented by proper design.

A solar space heating system, using CCH phase change material, which appears to have a proven record of successful appreciation is the Dow Chemical "Enerphase" system (Lane [1986]). "Enerphase" panels are black, approximately 10 by 20 inches in size and 2 inches thick, fitting between standard (US) building studs. Each panel contains some 20 lbs of PCM, two being required to store roughly 1 kWH - or about two panels per square metre of floor area. 200 Enerphase panels installed as a South facing wall (North-facing in the Southern hemisphere) with single glazing provide 25 square metres of collector area, capable of absorbing up to approximately 100 kWH average on a Winter day.

A "storage wall" system using some 250 litre PCM encapsulated in black polyethylene tubes was proposed last year to be installed in a home, next to an existing Trombe wall. This proposal, by Kaneff and Brandstetter [1986], has so far not been implemented for lack of funding. A different proposition, also not directly included in the reported project, was sponsored by a private investor (Mr W. Radford) and has resulted in a space heating system which uses a 200 kg PCM store charged by off-peak electricity. This system has run successfully several months now in our laboratory. Details can however not be disclosed at the present time.

IV.2 Greenhouse heating/stabilization

As part of this project, a fully implemented application of PCM heat storage, utilizing in the vicinity of 100 kg CCH processed from "distiller blow off" has been in operation and under preliminary assessment over recent months. This system provides night heating, and more generally temperature stablization, for a small ($1.8 \times 2.5\ m^2$) experimental greenhouse located on the roof of the Cockroft Building at the Australian National University.

It has been shown by researchers at this campus (P. Dart [1986]) that solar air collectors, such as developed by ALCAN (Alcan Australia Ltd, PO Box 12, Granville, NSW 2142), in collaboration with CSIRO [1980], can provide, in conjuction with a rock-bed storage system, adequate cost-effective heating for a greenhouse in a relatively cold Winter climate such as Canberra's. The greenhouse referred to is at

the Research School of Biological Sciences (RSBS) and is close to identical with the original proto-type developed earlier at the CSIRO Division of Irrigation Research, in Griffith (NSW), by Blackwell and Garzoli [1981].

Rock-bed storage has its drawbacks in terms of cost-effectiveness and, in particular, space requirement. In fact, the usual comparison of hydrated salt PCM storage with rock-bed storage assigns the latter a volume 10 to 15 times larger than required for equal storage capacity in PCM, as quoted for example by Kohler [1983].

A feature common to the RSBS greenhouse and ours is the heat supply by solar "air-collector", supplemented by the normal greenhouse heat, and extraction of heat from the store by use of fans. The concrete-encased rock-bed is replaced by our "bottled PCM", see photograph Fig. 15. The important difference is, of course, that the PCM discharges most of its heat at around the 29°C transition temperature, whereas the rock-bed will discharge its heat at a continuously decreasing temperature starting from, say, 40°C. This allows much simplified heat transfer requirements for the PCM system, providing in particular approximately constant heat supply so long as the fan power stays constant.

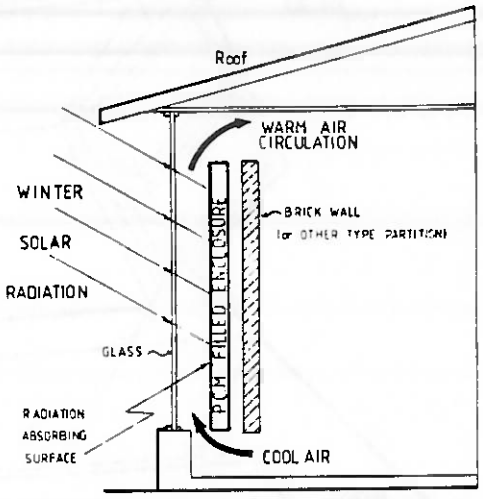
Fig. 16 shows a photograph of the experimental greenhouse, which is built essentially of masonite walls and perspex windows, held together by a wooden frame, and a double-skin polycarbonate roof. The PCM modules are stacked near the North-facing side and air from a solar collector is blown across these modules by a 12-volt fan powered by photovoltaic panels - a convenient, though non-essential, arrangement. A special insulated and separately ventilated compartment has been installed inside this greenhouse to accommodate a PET-Commodore micro-computer with disk storage and measurement and control interface electronics. A schematic drawing showing the greenhouse and PCM store, as well as the measurement and control arrangement is presented in Fig. 17a.

Towards the termination of this project covered by this report only a very crude assessment of the operation of this greenhouse in general, and its PCM store in particular, had been possible, covering visual inspection of the PCM modules and thermometer readings. The relevant results included minimum night temperatures usually some 10 degrees above ambient, and the PCM cycling reversibly between its liquid and solid states, though with exceptions and usually not to completion.

Detailed computer records have become available by the time of writing (i.e beyond termination of this project) and a few are presented here for the sake of completeness. These records, presented in the Annex in the form of temperature plots, Figs. A.7a-b, show clearly the stabilization effect of the PCM modules. These temperatures, represented by thermocouples Nos. 1-6 as sketched out in Figs. 17a,b, show moreover special effects. For example, cutting-in of the PCM exhaust fans, automatically as programmed, when the greenhouse representative central temperature (thermocouple No. 11) starts to exceed 25°C. This is evidenced by a

SOLAR SPACE HEATING based on

TROMBE WALL METHOD



3 to 4 square metres of ABSORBER SURFACE and 100 kilograms of PCM are required per kilowatt HEATING LOAD for a 6hour discharge.

Fig 14 Conceptual design of PCM "collector-storage wall" for passive residential heating. (A small circulating fan is optional and, in practice, highly beneficial.)

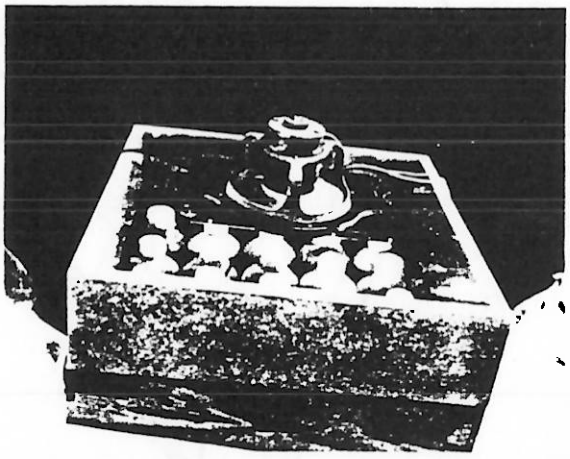


Fig 15 PCM module with 25 one-litre plastic bottles, shown with (solar-powered) hot-air intake fan.

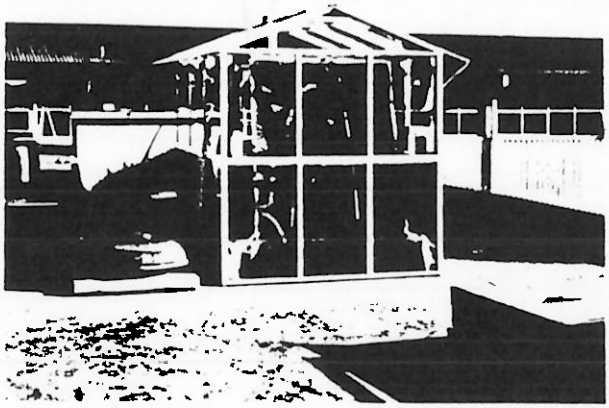


Fig 16 Experimental small (1.8 m by 2.5 m) greenhouse with 3 PCM modules (Fig 15). Inside (facing North): Solar "air collector".

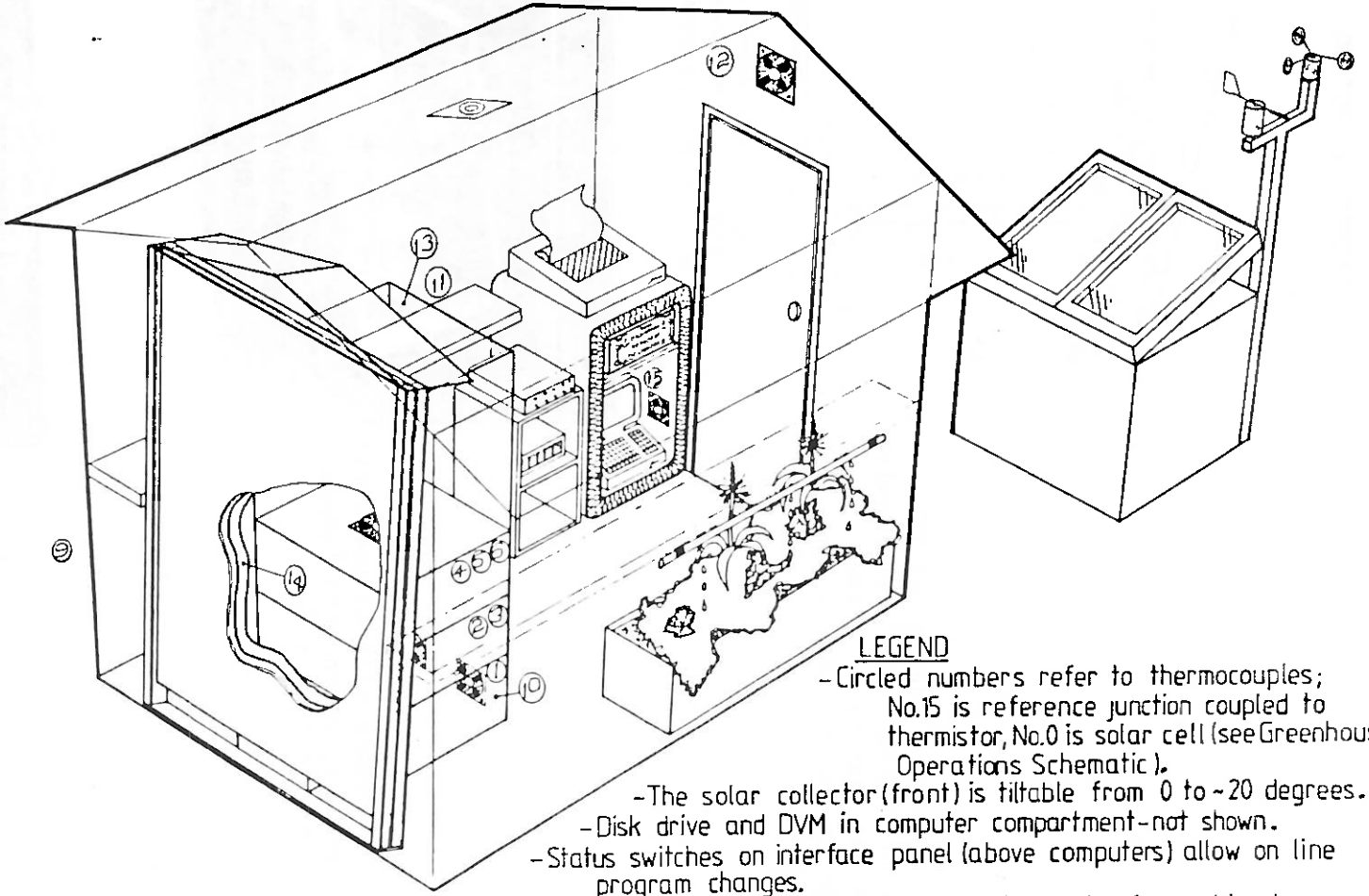
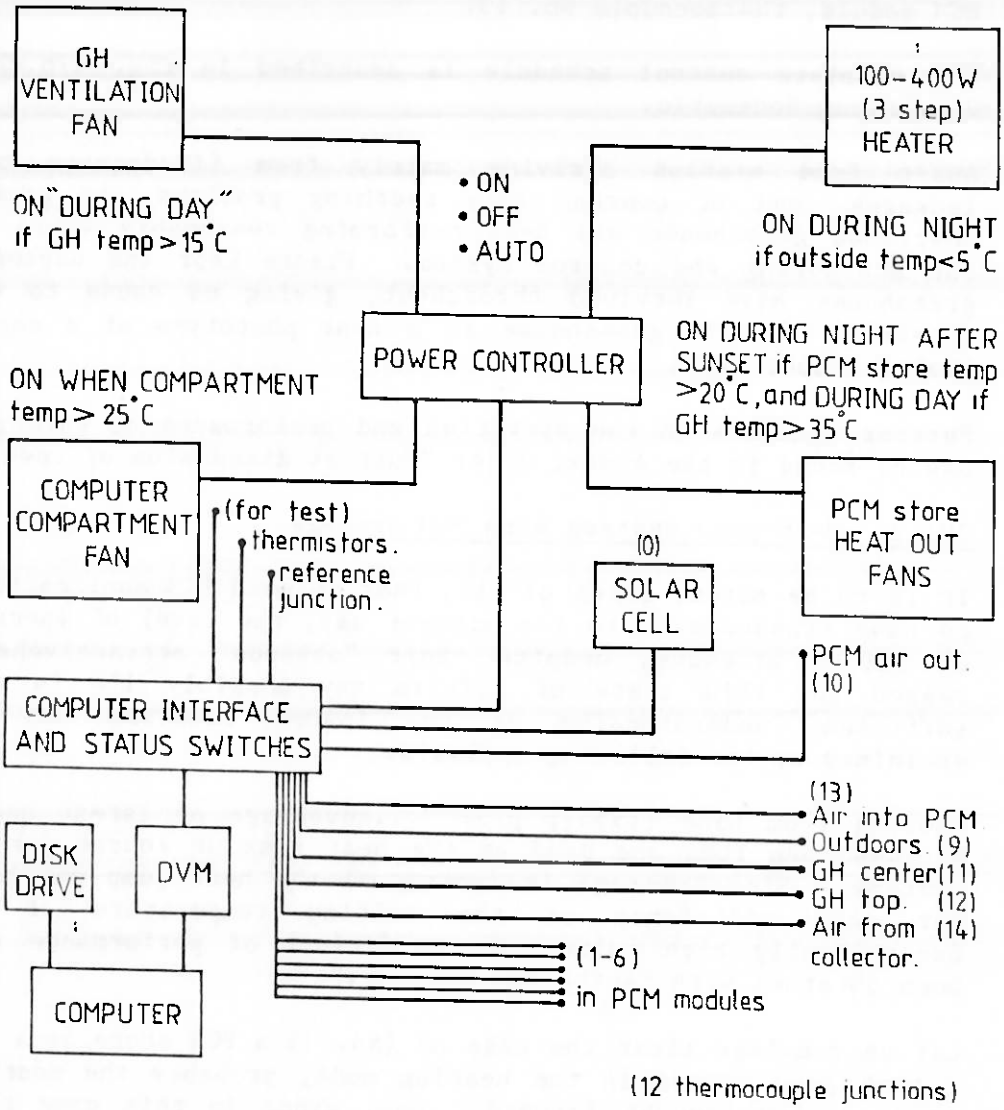


Fig 17a Schematic of experimental greenhouse; all relevant information detailed in "Legend".

GREENHOUSE OPERATION SCHEMATIC.



- STATUS SET:

No.0	Over ride "during day" condition
No.1	Over ride "GH temp > 35°C" condition
No.2	Set day to (7-19.30) from (8.30-17)
No.3	Over ride "during night" condition
No.4	Set night to (21-5.30) from (18-7.30)

Fig 17b Greenhouse Operation schematic details current monitoring and control options for the experimental grenhouse, Figs 16 and 17a.

corresponding fall in the temperature of the air steaming into the PCM module, thermocouple No. 13.

The complete control schedule is described in Fig. 17b, Greenhouse Operations Schematic.

Apart from mishaps deriving mainly from (inadequate container) leakages, and of course early teething problems, in general, the described greenhouse has been performing reasonably well, including the monitoring and control system. Plants kept and nursed in this greenhouse have survived throughout, giving no cause to doubt the potential of this greenhouse as a near phototype of a commercially viable proposition.

Further comments on the operation and performance of this greenhouse can be found in the Annex, under "Further discussion of results".

IV. 3 Heat pump systems with PCM storage

It is to be noted, first of all, that no such PCM applications appear to have transcended, to the present day, the level of speculation or of failed attempts, despite their "obvious" attractiveness. The reason for this state of affairs may possibly lie in a lack of sufficient understanding of the issues involved, as could be explained by the following analysis.

Quoting from Lane [1983], p.9: "...advantage of latent heat storage accrues when PCMs are used as the heat sink or source for heat pump systems. Since storage is isothermal the heat pump can be designed for peak efficiency at the melting temperature of the PCM. Exceptionally high values of coefficient of performance (COP) have been obtained with isothermal sources."

Let us consider first the case of (No. 1) a PCM store as a source for a heat pump system in the heating mode, probably the most prominent case usually brought forward. Now, since in this case the nominal benefit lies exclusively in the COP value's excess above 1.0 (given that for CPO = 1 simple resistance heating would be sufficient) this extra heat should represent the largest part of the heating load commonly around 75%, and come essentially "free" such as from the outdoor (cold) air. Supplying this extra heat from a PCM store, for the sole purpose of achieving "exceptionally high COP values", would thus totally defeat the very purpose of the heat pump. (Of course, a heat pump can also raise temperature, but this is not the sought advantage.)

The case coming to mind next (No. 2) may be a heat store used as a heat sink, at the heat pump's hot output side. This can be considered as a classical case of potential peak load saving, i.e. by replenishing the heat store via the heat pump at off peak hours only and discharging this store mainly during peak hours. The "catch" here, however, is that off-peak hours usually are night hours, when the heat pump performance normally is at its lowest. (Of course, frosty conditions occur also during the day).

The other two cases (Nos. 3 and 4) refer to heat pumps in the cooling mode. Here, firstly, a "coolth" store as a heat sink, i.e. at the cold output side, would conceivably be simply water turned into ice (by the heat pump, during night hours), as for example in an "ice cell" of those offered commercially by Merryful Pty. Ltd. [1985]. Thus no "ordinary PCM" would be required here at all.

The last case, a coolth store as a heat source, is another classical case of potential peak load saving. Here, contrary to "case No. 2", the off-peak night hours would be the most suitable time for recharging the store. Also contrary to "case No. 3", conventional PCM in the 10-20°C transition temperature range and possibly up to 30°C, could function effectively as a "coolth" store enhancing the unit's COP. The problem here is then only one of trading off increased cost and complexity of this air conditioning system and its maintenance against the cost benefit derived from its temporal COP enhancement (which occurs significantly only during harsh outdoor conditions).

It should thus be recognized at first that the issues involved are in fact quite complex and that PCM storage for heat pump systems is not such an "obviously attractive" proposition.

In the authors' opinion, the case in favor of (non water) PCM in heat pump systems reduces to the following two possibilites mainly:

1° PCM store as a heat sink charged by the heat pump hot side as in case No. 2, with the proviso that the heat pump can be run efficiently and over sufficient time during off-peak hours to charge the PCM store. This store must be large enough to provide the bulk of the heating load during peak hours. For example, for 3 peak hours per day a 5 kilowatt heat pump with a COP of 4 in the heating mode would require a store of capacity

$$3 \text{ hours} \times 5 \text{ KW} \times 4 = 60 \text{ kWH}$$

fitting easily into a cubic metre for a PCM (not CCH) of average storage capacity. This type of heat pump operation with PCM storage was advocated by Dr S. Chandra during discussions at a meeting with the project supervisors in Heidelberg West, Victoria, at Siddons Industries [1986] on 17 November 1986.

2° The second possibility views a system combining cases 1 and 4, i.e. a single PCM store functioning both as a heat source in the heating mode and a coolth store in the cooling mode. However, as a heat source it would now be tapped only "on demand", i.e. whenever the COP dropped below a certain limit without the use of the heat store. Under these conditions the bulk of the "extra heat", as discussed under case 1, would still be supplied via the "free" outdoor air. Also, as a simultaneous coolth store, in the cooling mode, this single PCM store would not suffer the cost benefit disadvantage discussed in case 4, provided that a simple "switchover" method was available.

This second possibility was also discussed during the said meeting at Siddons Industries, though on rather hypothetical ground on the part of the project supervisors, and with a good deal of scepticism as to its feasibility on the part of Siddons Industries.

We have in the meantime tentatively concluded that such a dual-function PCM store in conjunction with heat pumps is in fact a possible option, and we are pursuing this idea, for the present based on our calcium chloride hexahydrate PCM. Preliminary details can be found in Annex 2 (In Confidence).

V. LITERATURE SURVEY

It probably will be correct to state tht the existing PCM literature is dominated largely by two recent books edited by G.A. Lane of the Dow Chemical Company: "Solar Heat Storage: Latent Heat Materials", Vol. I (1983), and Vol. II: Technology (1986). In section V.1 we briefly review from these books passages of particular relevance in the present context.

A second important source of information, apart from early material published in Workshop Proceedings etc., comes from articles published since the late seventies in "Solar Energy". In section V.2 we review some relevant findings notably in articles by Carlsson [1979], Lane [1981], Kimura [1984] and Feilchenfeld [1984] published in this journal. Section V.3 briefly mentions a few relevant articles from other sources, including our own as well as material from commercial brochures. Our conclusions in the light of this literature survey are then summarized in Chapter VI, Findings and Conclusions.

V.1 Review of G.A. Lane's books: "Latent Heat Materials" (1983 and 1986)

Volume I of this work "Background and Scientific Principles", ((1983) published by CRC press in the US), reviews the (recent) history of phase change thermal storage, in particular its recurrent failures caused by long-term instability of PCMs (most often referring to Glauber's salt formulations) and encapsulants. It then names an impressive number of researchers and countries - including Canada, Germany, Sweden, Denmark, Japan, France, Italy, the Netherlands, Switzerland, Belgium, the United Kingdom, Yugoslavie, India, New Zealand and more, but somehow not including Australia - pursuing PCM research; and concludes: "the enormous interest in PCM technology around the world is proof of the need for reliable storage, based on efficient, compact, isothermal media".

The following two chapters, entitled "The Science of phase change materials" and "phase equilibria", mainly review general principles of Physical Chemistry applied to PCM situations, with (perhaps exaggerated) emphasis on phase diagram varieties. On the other hand too little, from our point of view, is said on actual methods in relation to Thermal Analysis (p.109). Chapter 4, on Crystallization and Nucleation, which starts by saying "understanding crystallization and melting processes is fundamental to PCM research and technology", has been of very great help to us in our attempts (mostly by Dr P.O. Carden) to model the observed behaviour of our PCM sample, from data obtained using our spectral continuous Thermal Analysis technique.

Of the last chapter in Vol. I (Chapter 5, by R. Viskanta), our direct interest here is mainly in section D, in relation to calculation of solidification times. We notice in particular the absence of a simple analytical solution for the case of inward solidification in a cylindrical tube at a constant exterior temperature. Such a solution, under simplifying assumptions (mainly the neglect of a solid-liquid

difference of specific gravity), is here presented in Appendix B, characterized in particular by a proportionality of the time required for complete freezing to the square of the tube's radius.
Volume II of that work, "Technology" (published 1986), starts with a general review of phase change materials:

- Organics - including paraffin waxes (m.p. 43-56°C), polyethylene glycols (m.p. 7, 23°C), fatty acids (e.g. stearic acid, studied by Arndt [1984] at the Western Australia Institute of Technology), and some further categories. Organics are generally disadvantaged in comparison with salt hydrates by poorer heat transfer, lower density, flammability, and higher cost.

- Salt hydrates - with emphasis largely on $CaCl_2 \cdot 6H_2O$ and on $Na_2 SO_4 \cdot 10H_2O$ (Glauber's salt). Dow Chemical's version of the former is described as "congruent melting", this being achieved by the addition of potassium chloride jointly with sodium chloride to their joint limits of solubility: 4.7 wt% KCℓ and 0.8 wt% NaCℓ. "The combined effect is to reduce the melting point of $CaCl_2 \cdot 6H_2O$ to 26.9°C, making it congruent melting, and making $CaCl_2 \cdot 4H_2O$ metastable, melting at 26.7°C". E. Korin, with Menczel [1980] and others, have investigated a similar system.

Chapter 2 describes the theory, technology and effects of thickening and "gelling" salt hydrates, with the purpose of preventing gravity-induced segregation. Gellants refer in general to more viscous types of "thixotropic additives", of organic (polymer) origin, whereas thickeners usually refer to mineral powders such as sodium silicate, attapulgite clay and silica gel.

In calcium chloride hexahydrate-based PCM a thixotropic additive may be intended to prevent crystallized tetrahydrate from segregating, e.g. towards the container bottom under the influence of gravity, before re-dissolving in more dilute strata. It also may keep nucleating additives at some safe, diffusion-controlled limiting gradient.

Chapter 3, (Lane [1986]) describes encapsulation methods and lists a large number of PCM systems offered by US and European firms. Some of these products are mentioned explicitly in section V.3 below.

Chapter 4 deals with matters related to PCM systems testing, in particular with regard to US National Bureau of Standards requirements and to ASHRAE Standards 94-77. The latter finds in particular that "Theoretical Storage Capacity is Not a Meaningful Parameter" (because, for example, PCM's specific heat in the liquid state usually differ from the solid state). Also mentioned is the "lack of measurement to determine whether the system degrades with cycling".

The last chapter, contributed by John A. Clark, details "Thermal Design Principles", in relation to systems consisting of large numbers of stacked rows of tubes, packed beds of pellets, etc. Air flows, pumping energy, heat transfer and related topics are analysed, along with sizing considerations and insulation factors.

V.2 Review of Articles in "Solar Energy"

- Carlsson [1979], with H. Stymne and G. Wettermark, "An incongruent heat-of-fusion system - $CaC\ell\ 6H_2O$ - made congruent through modification of the chemical composition of the system". This paper "describes means of ensuring that the tetrahydrate never is the stable species, through chemically modifying the system", causing the solubility of the 6-hydrate to decrease and of the 4-hydrate to increase.

  It is of particular interest that this paper specifically refers to stoichiometric calcium chloride hexahydrate, i.e. with no extra water but proposing instead the addition of 2 wt% $SrC\ell_2\ 6H_2O$ to move the peritectic and the hexahydrate melting point closer together.

  Of interest in the context of our findings are also the "heat of crystallization" values of 173 J/g reported for both "puriss grade" and "technical grade" $CaC\ell_2\ 6H_2O$, and lower values, down to 150 J/g, for $CaC\ell_2\ 6H_2O$ with stabilizing additives. These values, determined in a adiabatic calorimeter and "using a ΔC_p correction" are claimed precise to within 5 J/g. Our heat-of-fusion value (equal to the "heat of crystallization", to the best of our understanding our data) is well above 200 J/g and probably as high as 210 J/g (see Fig. A.3b, Annex).

  A third point of interest is Carlsson's conclusion that sodium chloride moves the peritectic point away from the hexahydrate melting point (their Fig. 6(c)) and thus renders the material less congruent-melting. The latter conclusion conflicts directly with Kimura [1984], who found that $NaC\ell$ tends to prevent incongruency. It is also not substantiated by the behaviour of our material, which despite containing $NaC\ell$ to the point of saturation does not form tetrahydrate at water content beyond the nominal peritectic point.

  Lane [1981] criticized the contention by Carlsson et al. that the addition of 2 wt% strontium chloride hexahydrate renders $CaC\ell_2\ 6H_2O$ congruent-melting, in this Technical Note "adding strontium chloride or calcium hydroxide to calcium chloride hexahydrate heat storage material". In this article Lane explained, among other, that the real effect of the added 2 wt% $SrC\ell_2\ 6H_2O$ was the water released by this additive, due to its major part decomposing to the dihydrate, thereby changing the hydration degree rather than moving the peritectic point.

- Junjiro Kai and H. Kimura [1984] found that "a small amount of $NaC\ell$ gave excellent stability" (contrary to Carlsson et al as mentioned), due to a certain "memory effect" which, although not yet clarified is supposed by these authors to cause acceleration of nucleation of $CaC\ell_2\ 6H_2O$ crystals. They conclude by stating that a $NaC\ell$-doped sample at H = 6.11, i.e. containing more water than H = 6.00 but less than the peritectic, which they take

to be at H = 6.14, was found stable over 1000 cycles, yielding no $CaC\ell_2$ $4H_2O$ crystals. In fact they find it difficult to conclude from their experiment whether the excess water should be necessary or not for repeated phase change.

Our experimental results, on the other hand, appear to leave little doubt as to the firm necessity for the extra water and, moreover, its required dosage in excess of at least 0.10 moles of water above the stoichiometric composition.

- S. Sarig, J. Fuchs and H. Feilchenfeld [1984] authored a further important paper in "Solar Energy", which is directly relevant to our work for the following reasons:

  a) it is the only source we know supporting the unusually high heat-of-fusion values observed by us, their Fig. 3 giving in fact a highest observed value (220 J/g), identical with ours as given in Fig. A.3a, Annex, for $CaC\ell_2$ $6H_2O$ with additives (209 J/g without additives).

  b) using an experimental setup in some ways similar to ours (yet more restricted, e.g. incapable of continuous monitoring sample's enthalpy), these researchers investigated the stability of CCH by measuring the heat of melting - as "there are few data available on the heat of melting that can be applied to heat storage devices". We note that these words sound strongly in favour of our own work.

  c) It is clear from their Table 1 that Feilchenfeld [1984], while assuming the peritectic at 6.12 (source not given, but compare with Kimura's 6.14, above), find consistent degradation of CCH at H = 6.1 - 6.2 "without additives". It is less clear, however, in regard to long-term cycling stability, what their findings were with the added 2 wt% strontium chloride hexahydrate, since most of the results are given here for a sample with hydration degree of less than 6.0. They appear to conclude that stratification would be enhanced in any case - resulting in tetrahydrate formation - "by cooling exceedingly slowly while passing through the crystallization zone".

     We have undertaken recently to perform this test. With our sample at daily cycle No. 578, we found no trace of tetrahydrate after more than 50 hours of slow freezing (Fig. A.6), followed by remelting at 34°C.

We mention a few more relevant articles in "Solar Energy":

A. Abhat [1982], in a comprehensive review paper on PCMs, which we found very useful;

M. Nasim and H.P. Garg [1981], who make this interesting comment: "None of the congruent-melting salt hydrates have been judged for use in thermal storage because of cost and safety considerations".

P. Cadier and A. Jaffrin [1982], who describe the La Baronne Solar Greenhouse (France) with PCM stabilization, using $CaC\ell_2\ 6H_2O$.

and a further article by H. Feilchenfeld [1985], with J. Fuchs, F. Kahane and S. Sarig, reporting a failed attempt of melting point adjustment of $CaC\ell_2\ 6H_2O$ by chemical modification, as assessed by their method of slow passage through the crystallization zone (see above).

Y.A. Cengel, M. Toksoy and B.K. Huang [1986], "Transient response of latent heat storage in greenhouse solar system" which describes the successful operation of a large CCH-based heat storage system.

V.3 Literature from Other Sources

No literature survey on PCMs for thermal storage could be complete without mention to the pioneering work by Dr Maria Telkes. Of her many publications, since the early fifties in the form of Patents, Conference and Workshop papers and journal articles, the most relevant in the present context may be "Thermal Storage for Solar Heating and Cooling", (Telkes [1975]), in which the method of stabilizing incongruent melting PCM by the use of thixotropic additives is extensively discussed. Important follow-up work using "habit modifiers" (see e.g. S. Sarig [1975]), was published by S.B. Marks [1983], reporting on long overdue success in stabilizing Telkes' preferred salt hydrate storage medium: sodium sulfate decahydrate (Glauber's salt), against long-term phase separation with which this otherwise useful PCM had been plagued ever since its introduction.

Other "classical" articles on PCM systems are:

"Thermal storage for Solar Heat and Off-peak Air Conditioning", by J.C. Denton, K.W. Kaufman and H.G. Lorsch [1975];

"Thermal Storage Materials for Active and Passive Solar Applications", by C. Wyman and D. Eissenberg [1980];

"Phase Change Products for Passive Homes", by D. Lewis and J. Kohler [1983], who present a descriptive list of PCM products on the U.S. market;

and, most relevantly in the present context, "Heat Storage Units using Salt Hydrate", by S. Furbo [1982], emphasizing the method of "the extra water principle".

Material published (or for publication) on the current subject by the Project supervisors include the following, apart from an early 33-page Internal Report (Brandstetter [1982]) and a more recent Progress Report (to NERDDC, by S. Kaneff and A. Brandstetter [1985]);

"Heat storage in calcium chloride hexahydrate", by A. Brandstetter [1984], a poster paper presented at the 1983 International Solar Energy Society Conference in Perth, published in the Proceedings of Solar World Congress, 1983. This paper presents for the first time publicly our proposed methods for a) processing the Osborne distiller blow off into PCM, using solar evaporation, b) continuous calorimetric evaluation of PCM thermal storage characteristics and c) calculation of heat penetration and PCM freeze time in a cylindrical geometry.

"Phase change storage applications", by A. Brandstetter [1986], Conference paper presented last November at "Solar 86" in Adelaide. This paper is a first in presenting publicly results from our experimental investigations, in the laboratory and with our PCM-stabilized greenhouse.

"On the stability of calcium chloride hexahydrate in thermal storage systems", now under review following which it will be submitted for publication in "Solar Energy".

a draft now in preparation, by P.O. Carden [1987], is tentatively entitled (for current reference) "Modelling the nucleation and subcooling behaviour of calcium chloride hexahydrate phase change material".

Work is in progress for a poster session paper "Phase change storage heating and stabilization in greenhouses", (abstract title) by A. Brandstetter [1987], to be presented at the forthcoming International Solar Energy Society Conference in Hamburg, September 1987.

Finally, a number of commercial brochures or journal advertisements that deserve here special mention:

"Predicted Performance of ENERPHASE (Trademark of the Dow Chemical Company) Thermal Energy Storage Panels", a comprehensive brochure distributed by "Solaroo", Australia agents of ENERPHASE, of 420 Canterbury Road, Surrey Hills, Vic. 3127. The brochure describes the use and expected performance of Dow Chemical's 560mm x 355mm x 55mm louvred panels mounted between standard (US) studs in sun-facing walls. The panels are filled with about 10 kg calcium chloride hexahydrate with additives, melting point 27°C.

"Durability Tests with CALORTHERM Storage Materials", distributed by Calor Alternative Energy, of Appleton Park, Slough SL3 9LG (United Kingdom), which summarize results of tests performed on

their C7, C18, C31 and C70 PCM systems (the numbers indicating the materials transition temperatures). Dr R. Willix [1983] of the Western Australian Institute of Technology has investigated some aspects of these systems, in particular the C31 Glauber salt-based material encapsulated in 1 metre long black polypropylene tubes (36 mm dia for 1 litre, 50 mm for 2 litre PCM), in collaboration with Telecom Australia, we believe.

- Boardman Energy Systems, PO Box 4299, Wilmington DE 19807 (U.S.A.), who advertise PCMs for 15°C, 20°C, 26°C, 31°C (mean transition temperatures) encapsulated in stainless steel tubes. It might be added that the brochure is explicitly shunning the use of calcium chloride hexahydrate in view of its being "very corrosive" (presumably referring to stainless steel) and other reasons.

A large number of PCM products, many using the Dow Chemical Company's TESC-81 CCH-based material, have been advertised over recent years in "Solar Age" (now "Progressive Builder") and elsewhere.

These, apart from the above-mentioned, include a large variety, from "Pennwalt encapsulated pellets" (6-19 mm, made in the US) and Cristopia's "Boulet d'energie (77 mm dia. plastic PCM-filled spheres, made in France), to packaged collector-storage units ready for mounting on sun-facing walls, with names such as "Rodwall", "Enerwall", to mention a few. In addition, "hot box" containers (by Haaland Enterprises, Minn., USA), PCM Greenhouse systems (by Seico Kasai, Osaka, and Sekisui Kasai, Tokyo, Japan), and "Heat Bank" (by Calmac Manuf. Corp of Englewook, N.J. USA), "Heat Battery" (by O.E.M., Inc., Dover, Fla, USA) and "TESI Storage Tank" (by Thermal Energy Storage, Inc., of San Diego, USA) bulk storage systems. The list, largely reproduced from Lane [1986], is far from exhaustive.

VI. FINDINGS AND CONCLUSIONS

It is evident from the above literature survey that not only are $CaCl_2 \cdot 6H_2O$ PCMs likely, and perhaps the most likely, candidates for successful, long-lasting heat storage systems, but also that such systems are already now widely represented on the market.

Exception taken of the Feilchenfeld [1984] paper, all the authors reporting on tests of CCH systems reach the conclusion that this material can be made to behave congruently, which also is our experience as here reported. Contrary to the other authors, the work by Feilchenfeld starts with pure $CaCl_2 \cdot 6H_2O$ and only specific additives - apparently not including NaCl - participate in their tests. Moreover, extra water is not sufficiently accurately dosed: at a peritectic concentration of 6.12, as assumed by these authors (again not clear why, when Mellor [1946] quotes 6.10, Kimura [1984] 6.14 and Lane [1986] 6.255), their usual hydration degree of 6.1 would indeed lead to degradation of the material, according to our findings in chapter 2.

Moreover, we have carried out the stringent test recommended by Feilchenfeld - extremely slow traverse through the crystallization zone - without any deleterious consequences.

Incidentally, their 6.12 peritectic composition may well be correct, according to our findings, although 6.10 would be at least as likely. It is extremely difficult for us, however, to "accommodate" Lane's value of 6.255.

Some of the problems raised in the cited literature that were addressed in our reported work are:

- providing data on the enthalpies of melting and crystallization that can be applied to heat storage devices - on which little data is currently available

- the case of excess calcium chloride, the form of this excess (tetrahydrate?) and its participation in the melting phase. We have mainly addressed the complementary question of excess water.

- On slow cooling while passing through the crystallization zone, is stratification enhanced, and may such information "help to devise accelerated tests for stability, replacing time-consuming cycling"? Our limited experience, based on a single traverse, so far, does not appear to favour this conclusion.

- The effect of dissolved NaCl in the repeated nucleation of $CaCl_2\ 6H_2O$ has been the subject of controversy - should NaCl be removed or, on the contrary, is it beneficial? Our results suggest the former is not the case.

- In how far is the degree of subcooling related to the time until subcooling and to the density (and size) of nucleating particles? These questions have so far been addressed only by experimental observation, but some theoretical work is now also in progress. Generally speaking, our data suggest that nucleation occurs after a certain (variable) time rather than after reaching a certain low of temperature.

Finally, in our attempts towards the design and testing of actual PCM systems - viz. a small PCM-stabilized greenhouse and a small off-peak local space heating system - we unfortunately can claim only partial success. Further work will be required, mainly in regard to reliable and water-tight means of encapsulation. This problem, however, has been experienced only with the greenhouse, where hot dry air controls heat exchange and "store-item" plastic bottles were used (one type prone to bursting and the other to loss of water); whereas the space heating system, which uses a different kind of bottles has been operating totally satisfactorily and reliably ever since starting operation in November 1986.

In fact, we have tentatively concluded that the type of encapsulation used in this heating system may well, together with certain auxiliary arrangements appropriate for different conditions, constitute a valid means of PCM encapsulation.

Some further discussion of results appears at the end of Annex. 1.

VII. TECHNOLOGY TRANSFER ACTIVITIES

- In section IV.3, "Heat pump system with PCM Storage", we have reported on interest expressed by Siddons Industries Limited in PCM Storage in conjunction with heat pumps in general, and in our proposition in particular. No details of the latter have been released to parties other than ANUTECH Pty Ltd. Our memorandum to ANUTECH of 5 January 1987, replying to ANUTECH's "Research, Development and Commercialization Checklist" is attached to this Report as Annex 2 (In Confidence).

- A Secrecy-Option agreement relating to "research and development in the field of phase change materials for heat storage and utilization" ("the Research") was signed on the 27th November 1986 between ANUTECH (which "performs commercial and administrative functions on behalf of the ANU") and Mr Warren Radford of 14 Spring Street, Balmain, New South Wales ("the Investor").

  This agreement states among other matters that: "The Investor is involved in the evaluation of new technology for manufacture and sales in Australia and overseas and wishes to enter into a research, development and licence Agreement to provide support for the Research and its commercialisation in accordance with the terms of such agreement entered into with ANUTECH".

- Other parties having expressed commercial interest in our work are

  - A.E. Merryfull, of ICE-CEL Pty Ltd (PO Box 145, Sydney 2075), with whom latest written exchanges took place in December 1986 concerning possible cooperation on Phase Change systems R & D.

  - A confidential non-disclosure agreement was signed with K.J. Croagh, Managing Director of Vulcan Industries, and Mr Ron Harris, Research and Development Manager, on 18 February 1987, concerning cooperation on "Research and Development of phase change materials for heat storage and utilization, in collaboration with Warren Radford, who "carries out installations of heating systems, hot water systems, space heating in the building industry".

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IX. ANNEX - Detailed Experimental Results

Five categories of detailed experimental results are presented:

- Evaporation rates of the distiller blowoff (DBO), turning into dense calcium chloride solution in the 300-litre evaporation pans on the roof of the Cockroft Building (photograph Fig. 2). Results are summarized in Table A.1.

- Spectrophotometer analyses (Perkin Elmer Model 303) of PCM samples, to obtain concentrations of sodium in PCM samples, and from there the weight percent of sodium chloride. Computer printouts of results are reproduced in Table A.2.

- Continuous calorimetric evaluation of our first sample of 382 gram PCM, labelled S3 (from DBO origin, 'S' for solar-evaporated), which had a tentative low dosage of additives. This test ran from 5 August 1985, to 13 September 1985 when it was aborted. Figs. A.1a, b represent cycles 14 and 32 of this run and show the rapid decline in enthalpy-of-melting experienced with this sample - although no tetrahydrate was detected. Results are shown in the usual form of temperature profiles - thermocouple labels corresponding to locations shown in the inset of Fig. A.3b - and of an enthalpy curve referred to the same time abcissa. Unless otherwise indicated, 'time points' correspond to 6 minute time intervals, averaging over 12 consecutive temperature measurements for each thermocouple.

  Fig. A2 describes the decline of the latent heat storage capacity of sample S3 over the whole run.

- Continuous calorimetric evaluation of our second (and present) sample of 382 gram CCH, labelled S4 and similar in all respects to S3 except for increased dosage of additives

This test started on 15 September 1985 and has been running essentially uninterrupted and with the same sample. The 'history' of this test is sketched out in Table A3.

Figs. A.3a-h represent a variety of daily cycles of sample S4, in the usual form (see above). On a number of these plots we have calculated the heat of fusion values corrected for extra water in accordance with Fig. 5. Although variations in these heat-of-fusion values, as well as in the subcooling temperature differentials and times, can be discerned in Figs. A.3a-h there has been no systematic downward trend in the heat of fusion now over more than 500 daily cycles. The rather large variation in the subcooling characteristics, on the other hand, can probably be traced back to a near-to-critical dosage of nucleator in this sample from the beginning up to cycle No. 425 (see Table A.3) when the dosage was slightly increased. At the rated water excess no tetrahydrate ever formed, as verified by visual inspection.

Fig. A.4a presents a description of the variation of the subcooling temperature differential during the first 300 cycles, not including the 30 first cycles where time allocated for melting was insufficient, obviating subcooling (see Fig. A3a). A further description is given in Fig. A.4b in the form of a histogram.

Figs.A.5a,b present enthalpy vs temperature 'scatter plots' similar to those brought in the Feilchenfeld [1984] paper, from which the heat of fusion supposedly can be directly read off. The lowest part of the plot is unfortunately not accurately enough defined to allow to read off the specific heat in the solid CCH, therefore we have arbitrarily assumed this to be 1.4 J/g according to latest literature (Lane [1986] and drawn a 'fitted line' accordingly. Note that the line measuring the heat-of-fusion is drawn at the point of the alleged transition temperature. Agreement with the values found in Fig. A.3b is remarkably good.

Finally, in Fig. A6 we present a plot of temperature and enthalpy of the sample (S4) as it was made to pass very slowly downward through the crystallization zone, as recommended for a very stringent test of congruency by Feilchenfeld [1984]. After this test the sample was found to have retained its usual characteristics and normal cycling was resumed. [The initiation of freezing was obtained in this test by rubbing the capsule exterior with ice cubes, while the interior temperature stayed at 28.5-29°C].

- The 5th category of detailed experimental results relates to the continuous monitoring and control of our (small) greenhouse with its (≈ 100 kg) PCM heat store. Resulting temperature and insolation profiles retrieved in the form of digital plots, similar to those shown for the cycled PCM sample, are presented in Figs. A.7a-b and briefly discussed in "further discussion of results".

Note: a sixth category of results relates to the space heating system which was generally described in Section IV.1. This system was designed and set up in collaboration with Mr Warren Radford (see Section VII: Technology Transfer activities) and will not be further detailed.

Table A.1

Solar evaporation rates of "distiller blow off" (pan No. 1)

Date (1986)	Time	Depth (mm)	Approx. litres*	Temp. (°C)	Deg. of hydration	Comments
5 Feb	17:30	64	260			Start evaporation
10 Feb	12.30	41	165			
14 Feb	17.15	29	120			till now mild, sunny weather
17 Feb	19.20	20.5	80			weather deteriorating
19 Feb	13.45	19.5	75		10.3	No sunshine
20 Feb						Sunny day
21 Feb	16.30	17	70	36	8.1	Sunny day
24 Feb	13.00	15.5	60		8.4	
26 Feb	16.20	15.5	55	41		NaCℓ precipitating
28 Feb		15.5	50		~7.5	
3 Mar	12.30	14	45	35	~7.5**	pumped to drum (afternoon)
17 Mar			45			back to evap. pan
23 Mar			sol. 10	~25	6.1	frozen CCH
			liq. 30	~25	6.7	"supernatant"
6 Apr			35	~40	<6.0	several hot days collect to drum

* after NaCℓ started precipitating only the final yield is measured, others are roughly interpolated.

** the average from the 3 pans was estimated to be at H = 7.6.

Table A.2

Sodium concentrations in DBO evaporated to 7.6 H_2O (average)
- in printouts from Atomic Absorption Spectrophotometer analyses
(Perkin-Elmer 303, with SJ(England) Hollow Cathode Lamp,
from Activon Scientific Products, No. 4154)

5 March 1986

"Wavelength": 294.5 (589 nm)

Na in solutions of 2 gr "PCM"/liter
Samples 1,2,3 from pans 1,2,3, following
evaporation (of DBO 1,2,3), at time of collection

Element Investigated - Sodium

Standard 1	Conc 2 PPM	%Absorb 40.4	Absorb .2235
Standard 2	Conc 5 PPM	%Absorb 57	Absorb .3653
Sample 1	**Conc. 3.25 PPM**	%Absorbance 44.7	Absorbance .2555
Work Line	Absorbance = .07839 * Concentration		

Element Investigated - Sodium

Standard 1	Conc 2 PPM	%Absorb 39.7	Absorb .2185
Standard 2	Conc 5 PPM	%Absorb 56.7	Absorb .3623
Sample 2	**Conc 2.81 PPM**	%Absorbance 39.7	Absorbance .2185
Work Line	Absorbance = .0775 * Concentration		

Element Investigated - Sodium

Standard 1	Conc 2 PPM	%Absorb 39.7	Absorb .2185
Standard 2	Conc 5 PPM	%Absorb 56.6	Absorb .3612
Sample 3	**Conc 3.54 PPM**	%Absorbance 47	Absorbance .2739
Work Line	Absorbance 0.773 *Concentration		

Note: 2 gr "PCM"/liter is approximately equivalent to
1 gr $CaCl_2$ (anhyd.) per liter.

Table A.3 - Diary for PCM Sample "S4", to 31/12/86

(complements the information from Figs. A.3a-h)

Cycle No(s).	Date(s)	Temp (°C) Lo-Hi	Comments
1-7	15-21/9/85	24-33	heat ON 9:30-16:30;
8	22/9		Crashed, due to faulty DVM;
	28/9		resume - and further crash
11	4/10		resume, following DVM repair;
12-14	5-7/10	24-33	adjusting H-parameters;
15	8/10		change heat ON time to 9:30-17:30;
16-17	9-10/10	24-33	Note: change diskette once in 6 days
18	11/10/85		H-par. to .1179 (from .1205);
19-20	12-13/10	24-33	testing - before going overseas;
31-35	14-28/10	24-33	proceeding smoothly;
36-72	29/10-4/12	24-33	room warmer → melting faster;
73	5/12/85		A.B. resuming supervision, Grant Bath level found low - top up;
74-99	6-31/12/85	24-33	all normal;
100	1/1/86	24-33	starting the new year ...
101	2/1/86		Lo-hi temp to 19-33°C;
102-113	3-14/1/86	19-33	heat-of-fusion value increasing;
114	15/1/86		Lo-hi temp to 23-38°C;
115-121	16-22/1	23-38	
122	23/1/86		"Student hand-on experiments";
	24-25/1		system failures, lost disk records inspect capsule : frozen, less ~ 10 ml;
125	26/1/86		Lo-hi temp to 24-33°C;
126	27/1	24-33	late freezing, 8 hours delay;
127	28/1/86	24-33	Power failure at ~ 13:30 - rebooting
129	30/1/86	24-33	normal freezing (4°C supercooled)
130	31/1		did not freeze;
131-135	1-5/2/86	24-33	back to normal;
136-142	6-12/2		several instances of delayed freezing;
143	13/2		normal;
144	14/2		did not freeze;
145-149	15-18/2	24-33	normal, except water level in vessel low (was topped up on 24/1/86);

150-153	19-23/2	24-33	severe supercooling;
154	24/2/86		lo-hi temp to 22-33°C;
155-161	25/2-3/3	22-33	still severe supercooling;
162	4/3/86		lo-hi temp to 21-33°C;
163-167	5-9/3	21-33	normal;
168	10/3		lo-hi temp back to 22-33°C;
169-182	11-24/3	22-33	generally normal, some delayed freezing;
183	25/3		lo-hi temp to 23-33°C;
184-189	26-31/3/86	23-33	some delayed freezing, cy 184 did not freeze
190-205	1-16/4	23-33	mostly severe supercooling;
206	17/4/86		normal;
207	18/4		lo-hi temp to 22-33°C;
208-214	19-25/4	22-33	normal;
215-218	26-29/4	22-33	most did not freeze;
219	30/4/86		lo-hi temp again down to 21-33°C;
220-222	1-3/5	21-33	normal;
223	4/5/86		did not freeze;
224-225	5-6/5/86	21-33	froze, but heat of fusion only ~ 175 J/g
	7/5/86		Inspect capsule: frozen, less 1-2 cc
227-234	8-15/5	21-33	normal, one (5h) delayed freezing
235-241	16-22/5		did not freeze, 7 cycles in a row
	23/5/86		Inspect (~32^{0}C): totally melted
243-269	24/5-19/6/86	21-33	normal, except low heat of fusion (~170 J/g), and instances of delayed freezing;
270	20/6/86		lo-hi temp. to 22-33°C;
271-273	21-23/6		normal, except one (9h) delayed freezing;
274	24/6/85		lo-hi temp. to 21-38°C;
275-276	25-26/6	21-38	normal freezing;
277-282	27/6-2/7	21-38	Instability of H-par. due to warping of Grant Bath lid;
283	3/7/86	21-38	did not freeze;
	4/7/86		new Grant Bath lid - 25 mm thick (previously 5 mm);
285-309	5-29/7	21-38	continued "criticality";
310	30/7		lo-hi back to 21-33°C;
311-313	31/7-2/8	21-33	"normal" delayed freezing;
314	3/8/86		lo-hi temp down to 19-33°C;
315-342	4-31/8	19-33	normal - some with little supercooling
343-347	1-5/9/86		thermistor "playing up" (replaced 6/1/87);
348-352	6-10/9	19-33	normal, except some deep supercooling;

353	11/9/86		did not freeze;
354-356	12-14/9		mostly deep supercooling
357	15/9/86		lo-hi temp up to 19-38°C;
358-369	16-27/9	19-38	one delayed, two did not freeze;
370	28/9/86		lo-hi temp back to 24-33°C;
371-385	29/9-13/10	24-33	never froze;
	14/10/86		capsule inspection: (supercooled) liquid, and vessel level found raised;
	15-16/10/86		Problem resolved: influx was due to capillary action by thermocouple wires - remedied;
389	17/10/86	24-33	Resume
	18/10/86		capsule inspection: frozen + 12mm supernatant;
391-394	19-22/10/86	24-33	still severe supercooling;
395	23/10/86		lo-hi to 18-42, start 4cy/day routine;
396-397	24-25/10	18-42	4cy/day, only one out of 8 froze;
	26/10		change over to 2cy/day routine;
	27/10		lo-hi to 18-38°C;
400-406	28/10-3/11	18-38	2cy/day, but froze only twice;
	5/11/86		recording interrupted (extra water in PCM).
409	6/11/86		resume with new Grant Bath temp. controller (J126), lo-hi to 22-38°C;
410-417	7-14/11/86	22-38	2cy/day - froze only once;
	19/11/86		Open the PCM capsule (first time);
	20-22/11		evaporate 21.06 gr extra-weight water, AND increase dosage of nucleator;
	23/11/86		lo-hi to 22-33°C and back to 1cy/day;
427-432	24-29/11	22-33	supercooling minimal, but low heat of fusion;
	30/11/86		tetrahydrate formed: dissolve, and add 1 cc water;
434-439	1-6/12/86	22-33	heat of fusion high, then decreasing
	8/12/86		still tetrahydrate: dissolve, and add further cc water;

442-448	10-16/12	22-33	melting now incomplete, needs higher upper temp.;
449	17/12/86		lo-hi temp to 22-38;
450-453	18-21/12	22-38	heat of fusion back to normal
454	22/12/86		lo-hi to 18-42, 2cy/day
455-462	23-30/12	18-42	no abnormal supercooling, but slightly low heat-of-fusion;
	31/12/86		Inspect capsule: has 13mm supernatant liquid. (This is 19 wt% at 25°C, corresponding to 2 wt% excess water
nearing 600	May 1987	21-34	so far nil degradation.

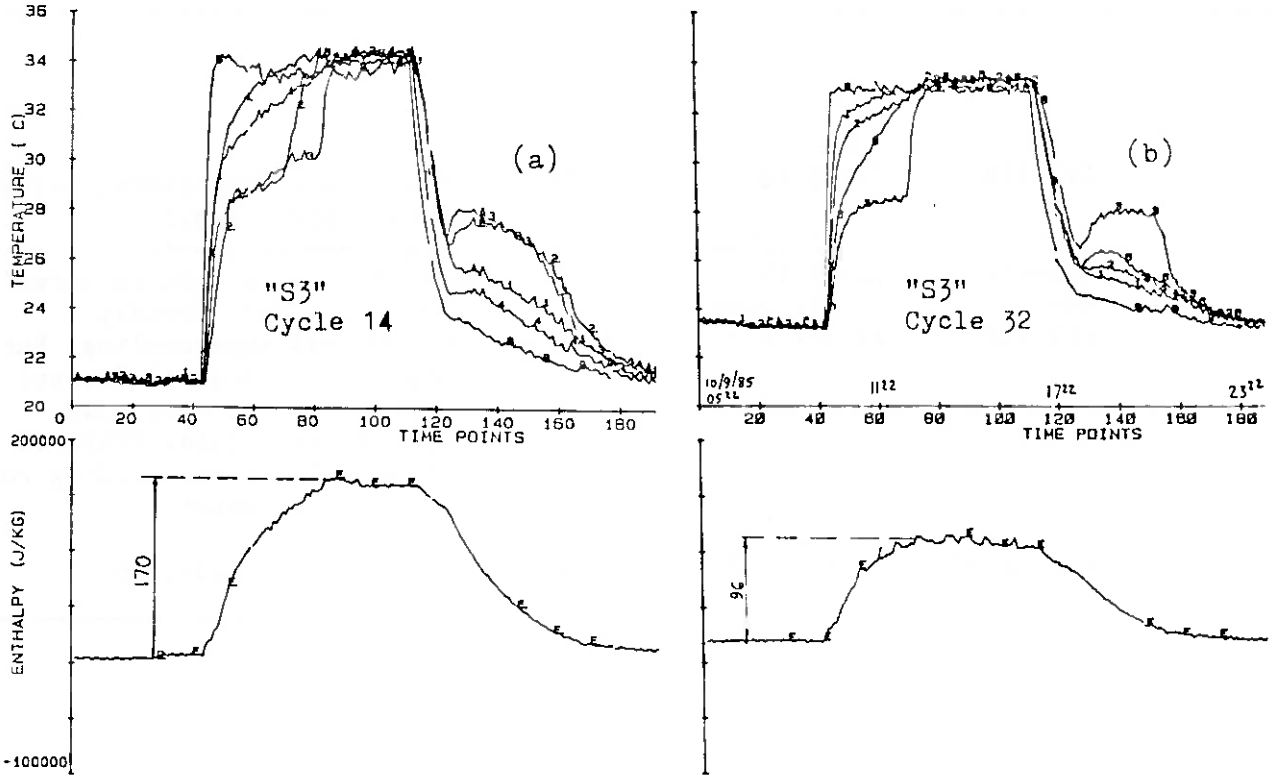


Fig. A.1 showing (a) start of decline of storage capacity of sample 'S3', and (b) terminal decline of this sample (of too low dosage of additives) before experiment was aborted.

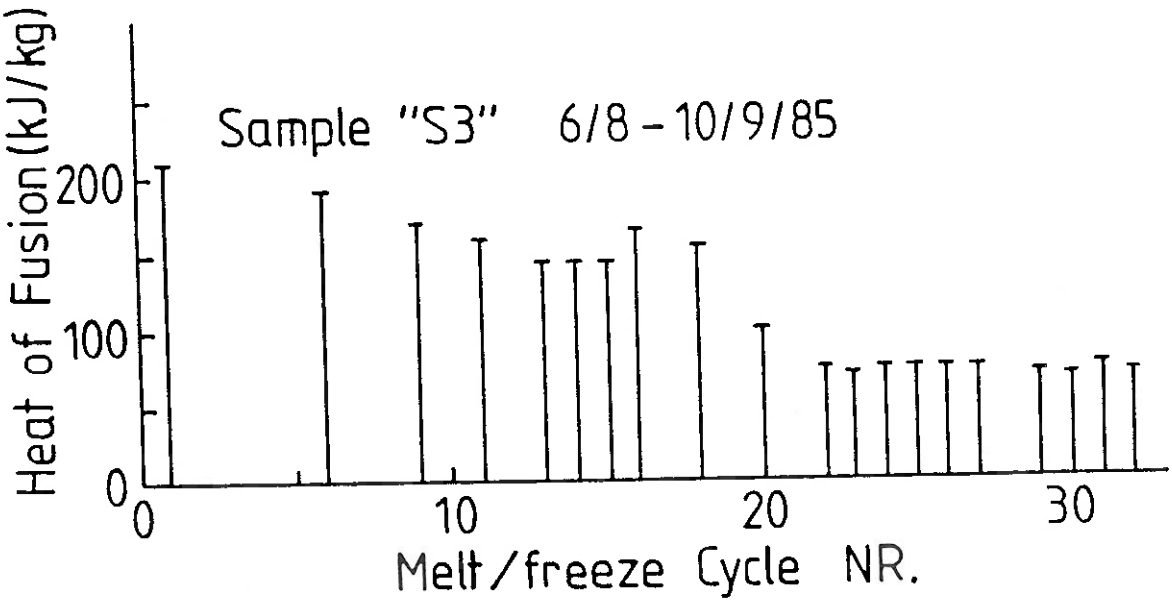
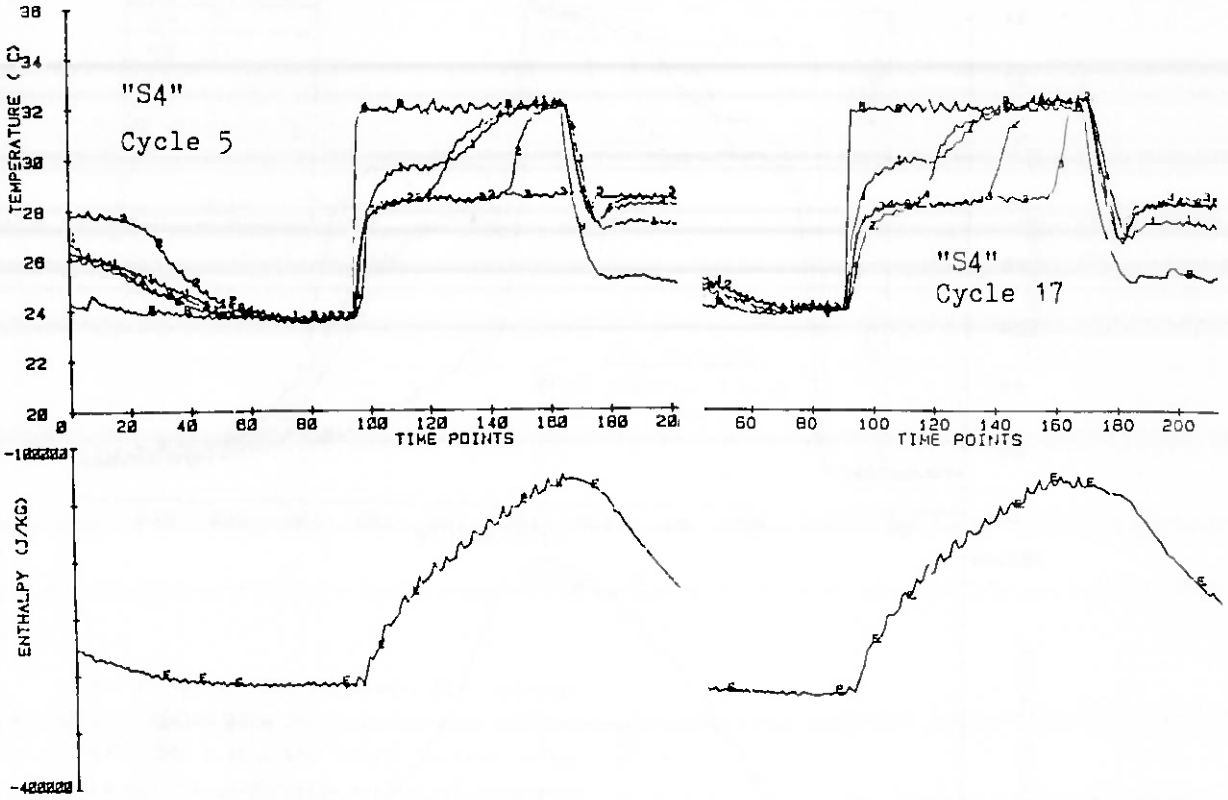


Fig. A.2 describing the total course of decline of sample 'S3'.



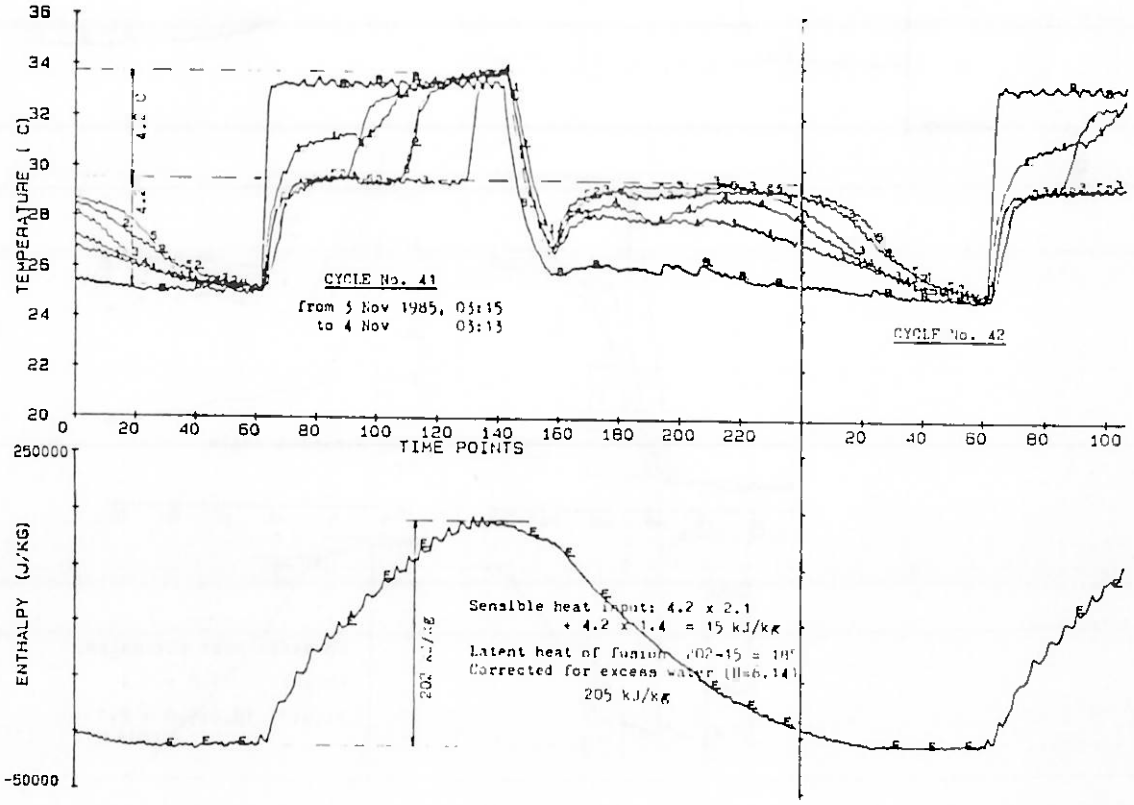


Fig. A.3a Early cycles. Note the insufficient heater-ON time in cycle 5, and the decrease in melting time between cycle 17, of 10 October, and cycle 41 of 4 November, 1985.

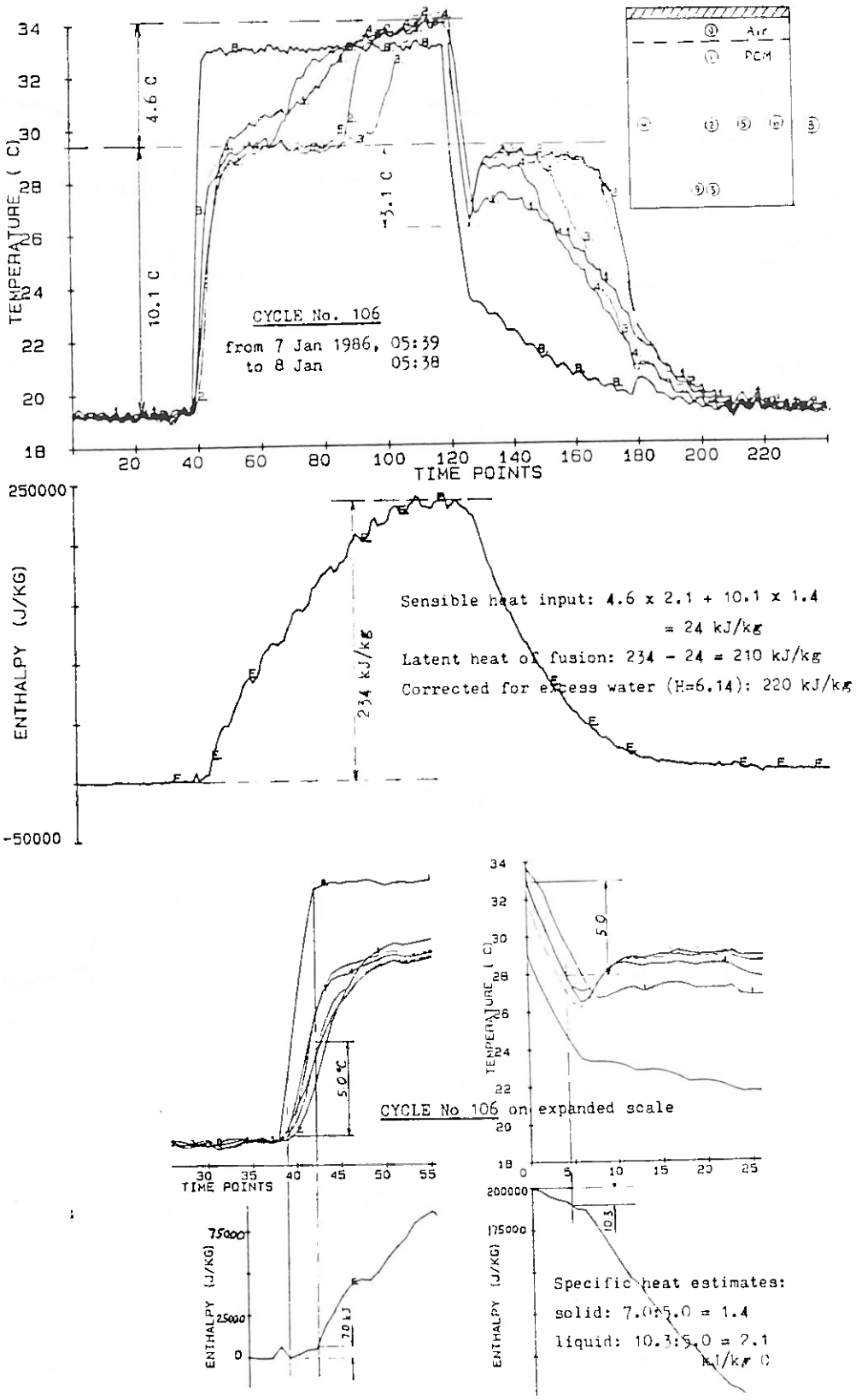


Fig. A.3b Cycle 106, with probably the highest heat-of-fusion observed in this experiment. Below, expanded-scale retrievals provide better, though still not very satisfactory, means for estimating specific heats in the solid and the liquid state.

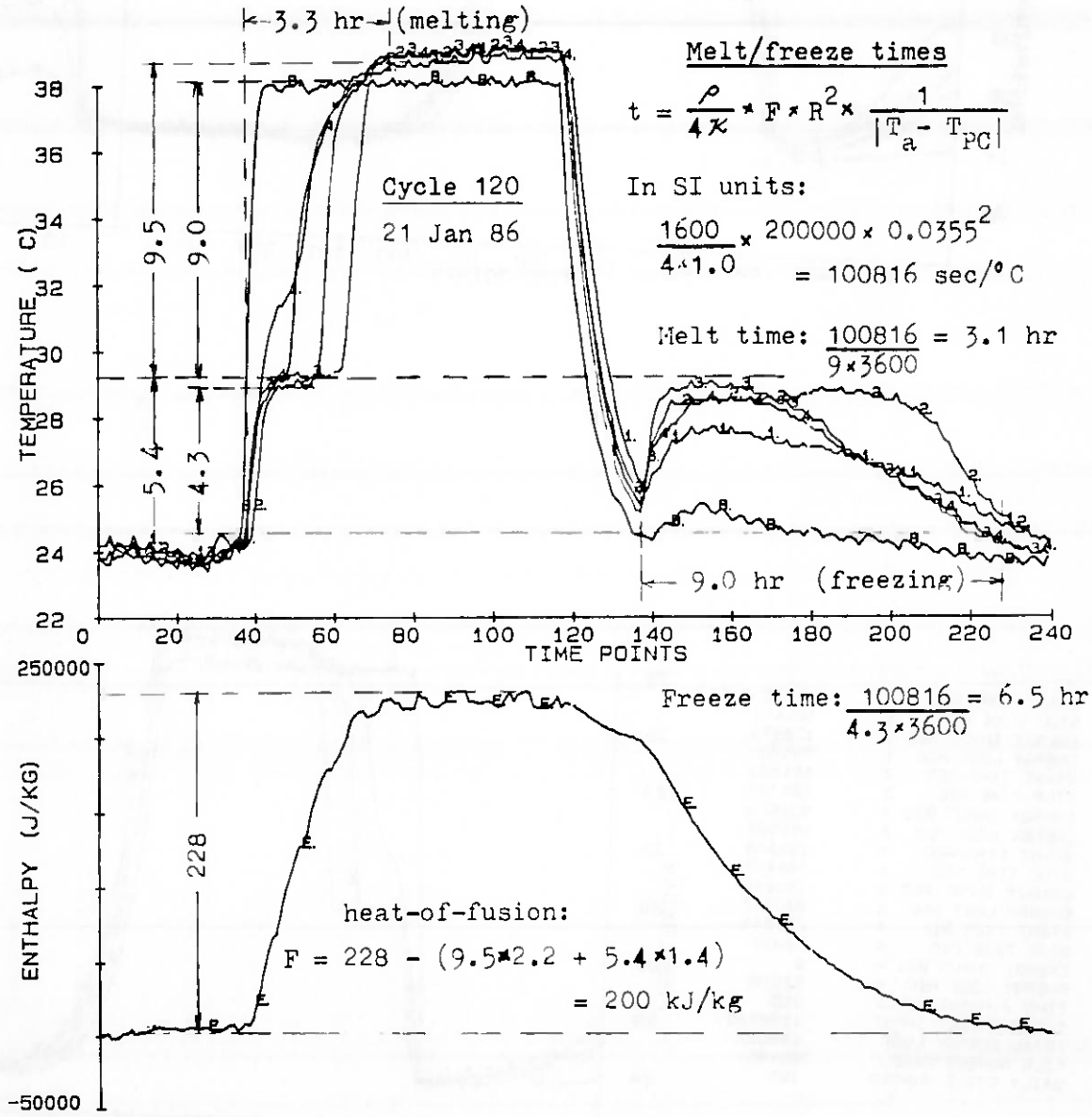
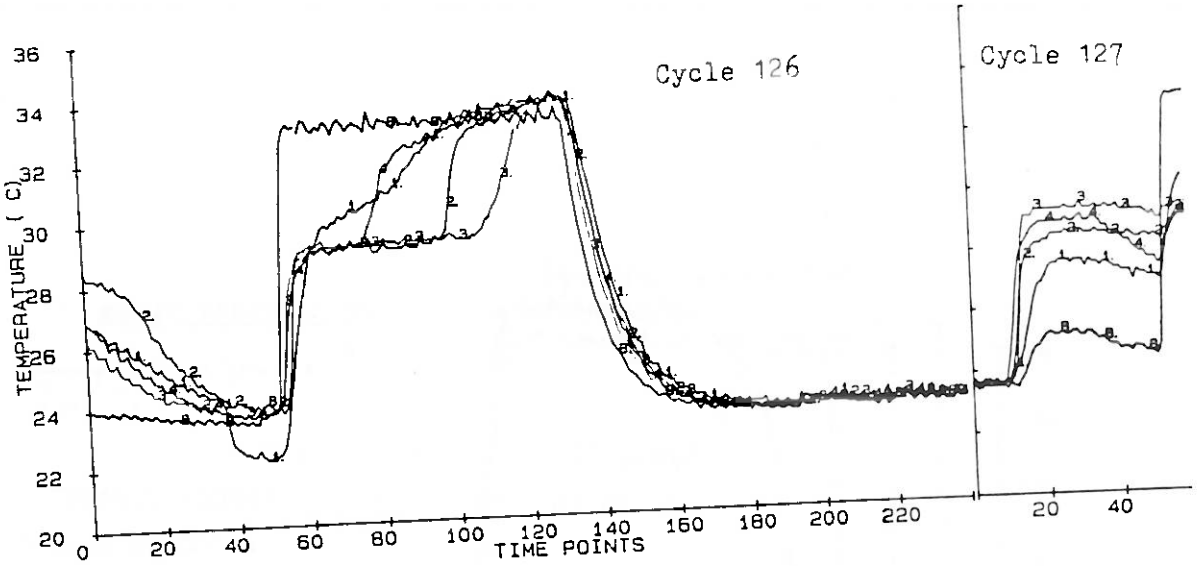


Fig. A.3c Cycle No. 120, in which measured (approximate) melt and freeze times are compared with calculated times, Appendix B. (This plot was used on "Students'Day", National Science Summer School 1986, on 21/1/86, for "hands-on" experiment, see Table A.3).



START TIME REC	1	41553
STOP TIME REC	1	101451
ENERGY INPUT REC	1	173975
ENERGY LOST REC	1	58622
START TIME REC	2	101551
STOP TIME REC	2	161449
ENERGY INPUT REC	2	851026
ENERGY LOST REC	2	656562
START TIME REC	3	161548
STOP TIME REC	3	221446
ENERGY INPUT REC	3	169244
ENERGY LOST REC	3	230747
START TIME REC	4	221545
STOP TIME REC	4	41438
ENERGY INPUT REC	4	0
ENERGY LOST REC	4	52576
TIME / POINT (SEC)		360
TOTAL ENERGY INPUT		1194245
TOTAL ENERGY LOST		998507
FILE NUMBER/DATE		260186
DAILY CYCLE NUMBER		125

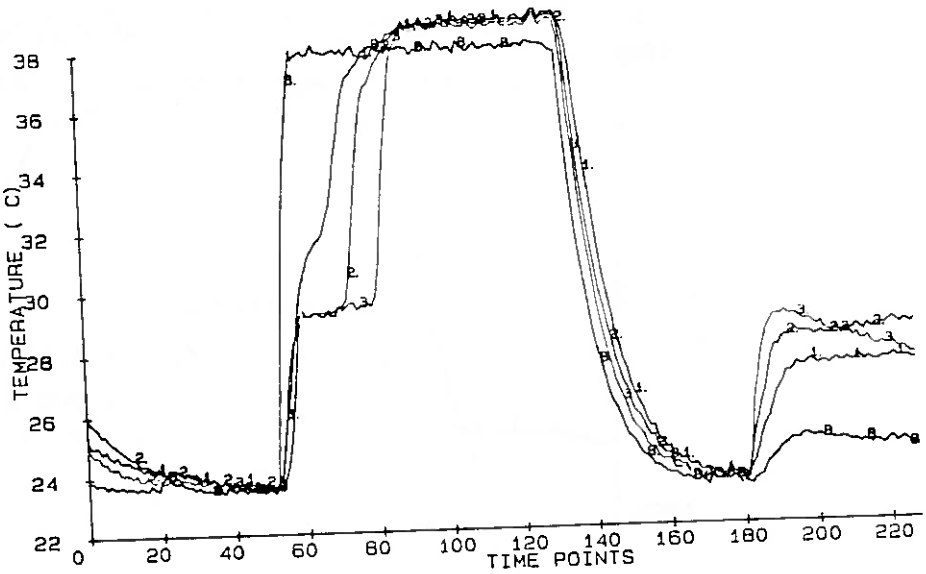
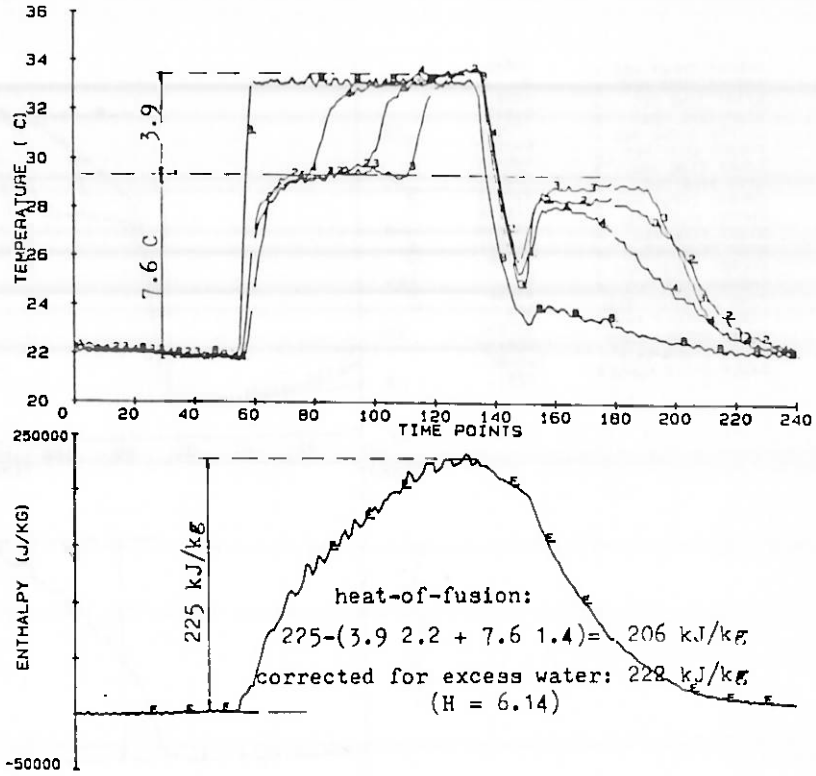
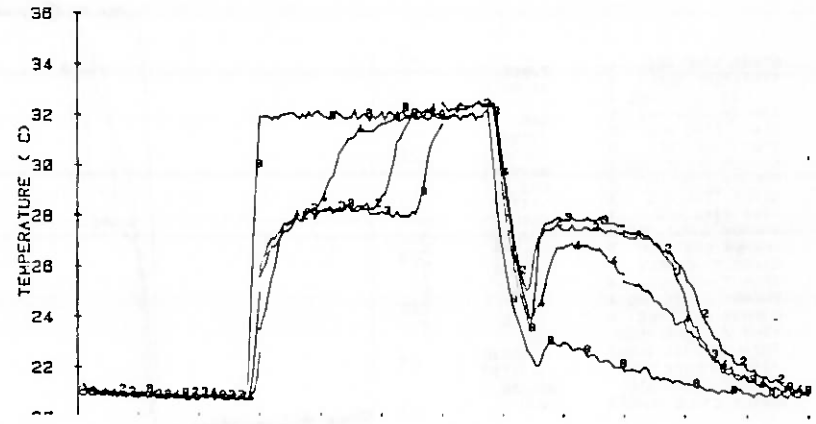


Fig. A.3d Cycle No. 125, with slightly delayed freezing, and No. 126, with extremely delayed freezing.

START TIME REC	1	35854
STOP TIME REC	1	95741
ENERGY INPUT REC	1	102385
ENERGY LOST REC	1	29005
START TIME REC	2	95841
STOP TIME REC	2	155727
ENERGY INPUT REC	2	665529
ENERGY LOST REC	2	588058
START TIME REC	3	155826
STOP TIME REC	3	215730
ENERGY INPUT REC	3	153108
ENERGY LOST REC	3	267112
START TIME REC	4	215829
STOP TIME REC	4	35711
ENERGY INPUT REC	4	0
ENERGY LOST REC	4	30170
TIME / POINT (SEC)		360
TOTAL ENERGY INPUT		921022
TOTAL ENERGY LOST		914345
FILE NUMBER/DATE		130386
DAILY CYCLE NUMBER		171



START TIME REC	1	35810
STOP TIME REC	1	95730
ENERGY INPUT REC	1	102513
ENERGY LOST REC	1	28070
START TIME REC	2	95829
STOP TIME REC	2	155754
ENERGY INPUT REC	2	688223
ENERGY LOST REC	2	582127
START TIME REC	3	155853
STOP TIME REC	3	215758
ENERGY INPUT REC	3	151247
ENERGY LOST REC	3	278403
START TIME REC	4	215857
STOP TIME REC	4	35740
ENERGY INPUT REC	4	0
ENERGY LOST REC	4	31580
TIME / POINT (SEC)		300
TOTAL ENERGY INPUT		921883
TOTAL ENERGY LOST		824097
FILE NUMBER/DATE		140388
DAILY CYCLE NUMBER		172



START TIME REC	1	35839
STOP TIME REC	1	95726
ENERGY INPUT REC	1	102499
ENERGY LOST REC	1	29566
START TIME REC	2	95825
STOP TIME REC	2	155713
ENERGY INPUT REC	2	668041
ENERGY LOST REC	2	596203
START TIME REC	3	155812
STOP TIME REC	3	215700
ENERGY INPUT REC	3	157075
ENERGY LOST REC	3	248272
START TIME REC	4	215759
STOP TIME REC	4	35642
ENERGY INPUT REC	4	0
ENERGY LOST REC	4	54316
TIME / POINT (SEC)		360
TOTAL ENERGY INPUT		927615
TOTAL ENERGY LOST		928357
FILE NUMBER/DATE		150386
DAILY CYCLE NUMBER		173

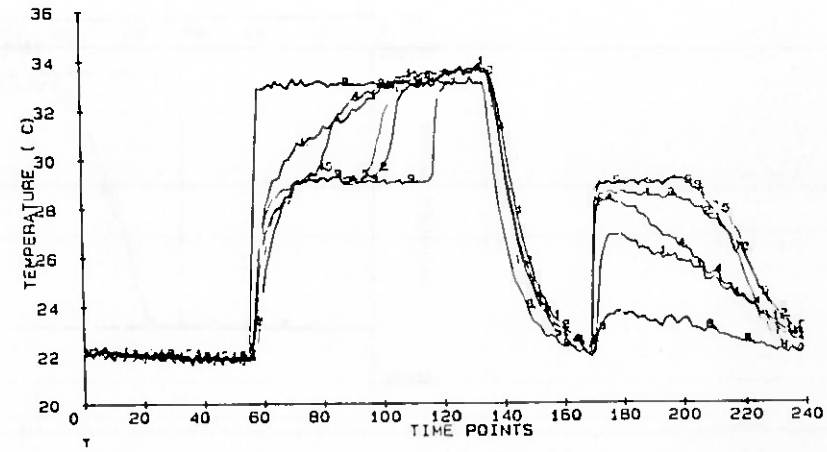
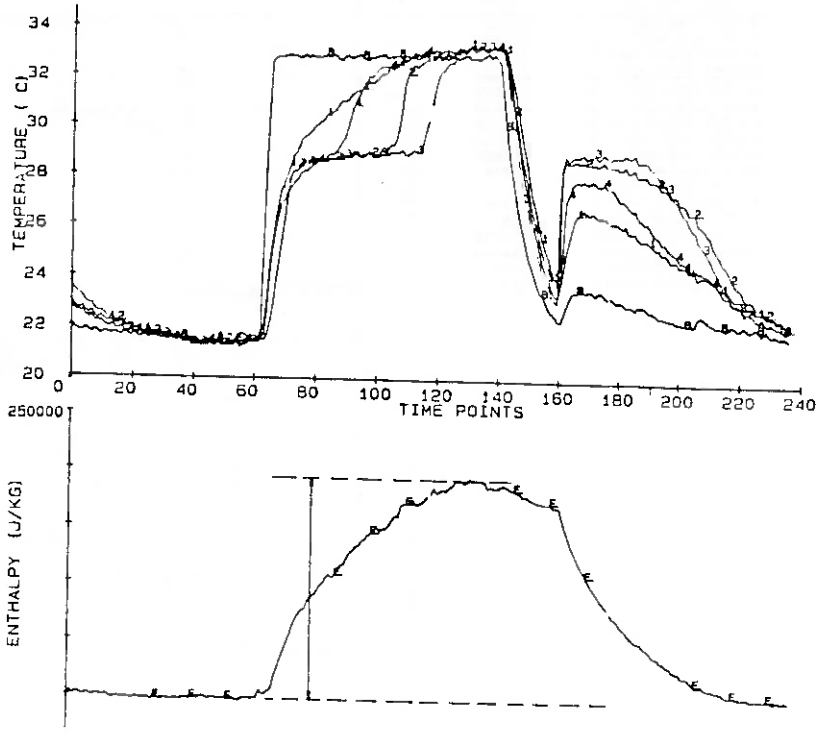


Fig. A.3e "Mid-term" typical series of cycles, No. 171 with enthalpy curve and heat-of-fusion calculations, followed by Nos. 172, 173.

ENERGY INPUT REC 1	90848
ENERGY LOST REC 1	0
START TIME REC 2	4436
STOP TIME REC 2	90947
ENERGY INPUT REC 2	150834
ENERGY LOST REC 2	684297
START TIME REC 3	545446
STOP TIME REC 3	150934
ENERGY INPUT REC 3	210822
ENERGY LOST REC 3	241594
START TIME REC 4	337429
STOP TIME REC 4	210921
ENERGY INPUT REC 4	30808
ENERGY LOST REC 4	0
TIME / POINT (SEC)	41131
TOTAL ENERGY INPUT	360
TOTAL ENERGY LOST	925891
FILE NUMBER/DATE	928442
DAILY CYCLE NUMBER	060586
	225



START TIME REC 1	21813
STOP TIME REC 1	81700
ENERGY INPUT REC 1	0
ENERGY LOST REC 1	688
START TIME REC 2	81759
STOP TIME REC 2	141646
ENERGY INPUT REC 2	823974
ENERGY LOST REC 2	643737
START TIME REC 3	141745
STOP TIME REC 3	201633
ENERGY INPUT REC 3	472056
ENERGY LOST REC 3	591187
START TIME REC 4	201732
STOP TIME REC 4	21614
ENERGY INPUT REC 4	0
ENERGY LOST REC 4	55538
TIME / POINT (SEC)	360
TOTAL ENERGY INPUT	1296030
TOTAL ENERGY LOST	1291150
FILE NUMBER/DATE	260686
DAILY CYCLE NUMBER	276

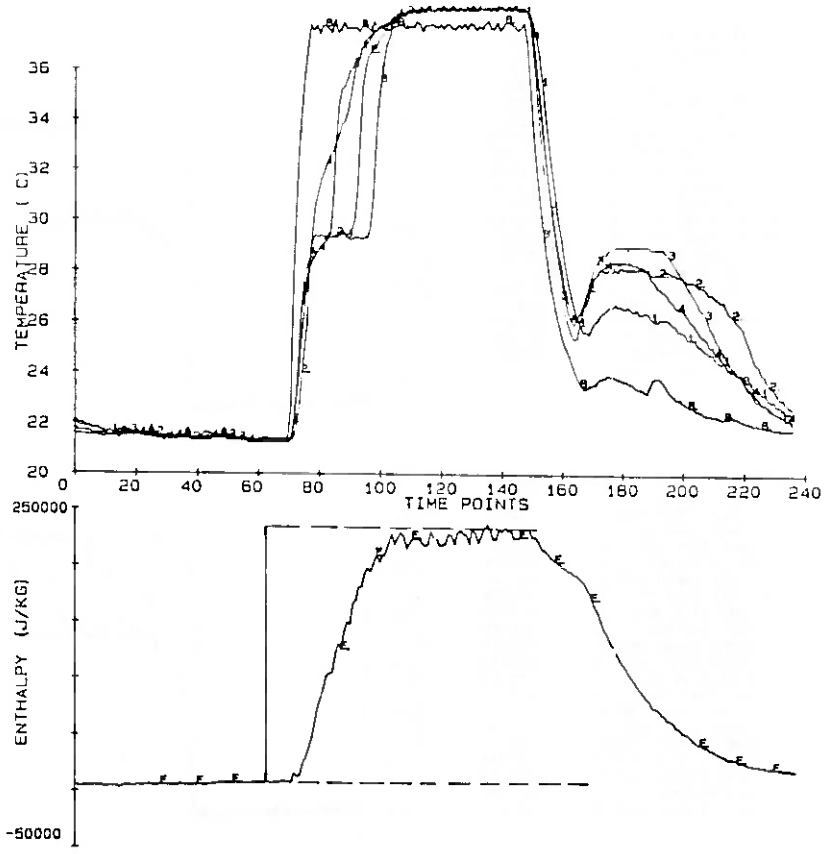
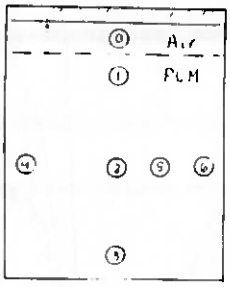
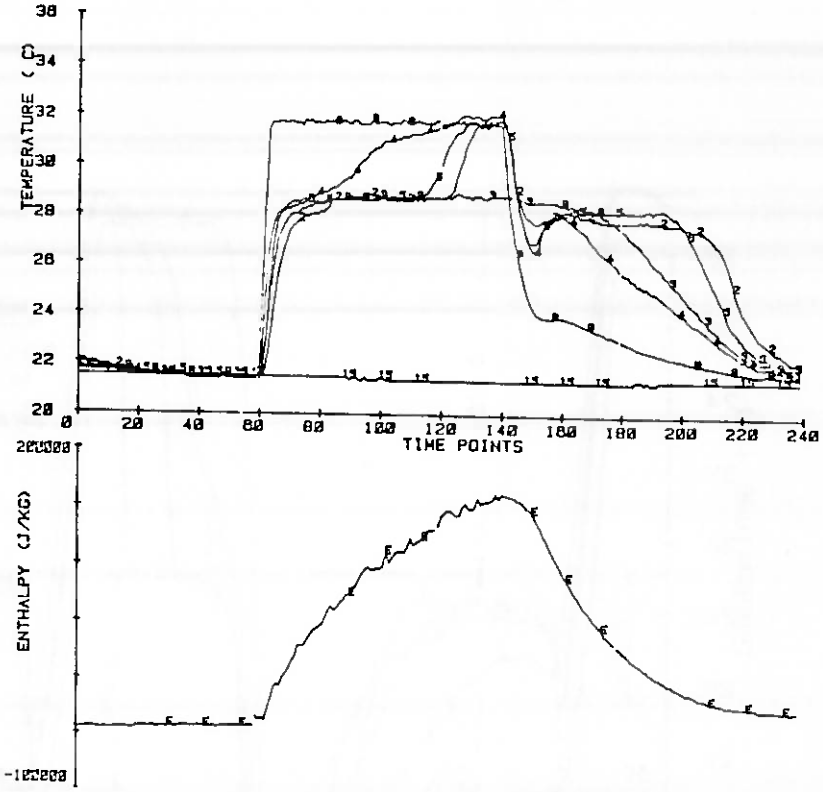


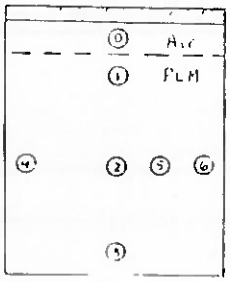
Fig. A.3f Cycles No. 225, of those with unusually low heat-of-fusion (see Table A.3), and No. 276 where it is significantly higher.

START TIME REC	1	
STOP TIME REC	1	32744
ENERGY INPUT REC	1	02832
ENERGY LOST REC	1	3838
START TIME REC	2	3003
STOP TIME REC	2	02731
ENERGY INPUT REC	2	153021
ENERGY LOST REC	2	594041
START TIME REC	3	472020
STOP TIME REC	3	152720
ENERGY INPUT REC	3	212620
ENERGY LOST REC	3	101002
START TIME REC	4	205208
STOP TIME REC	4	212700
ENERGY INPUT REC	4	32552
ENERGY LOST REC	4	3838
TIME / POINT (SEC)		34070
TOTAL ENERGY INPUT		380
TOTAL ENERGY LOST		783619
FILE NUMBER/DATE		775278
DAILY CYCLE NUMBER		191200
		445





START TIME REC	1	
STOP TIME REC	1	32710
ENERGY INPUT REC	1	02557
ENERGY LOST REC	1	5705
START TIME REC	2	6307
STOP TIME REC	2	02050
ENERGY INPUT REC	2	152002
ENERGY LOST REC	2	830050
START TIME REC	3	070020
STOP TIME REC	3	152701
ENERGY INPUT REC	3	212607
ENERGY LOST REC	3	240027
START TIME REC	4	300833
STOP TIME REC	4	212700
ENERGY INPUT REC	4	32552
ENERGY LOST REC	4	3838
TIME / POINT (SEC)		44023
TOTAL ENERGY INPUT		360
TOTAL ENERGY LOST		1094080
FILE NUMBER/DATE		1091040
DAILY CYCLE NUMBER		171200
		449



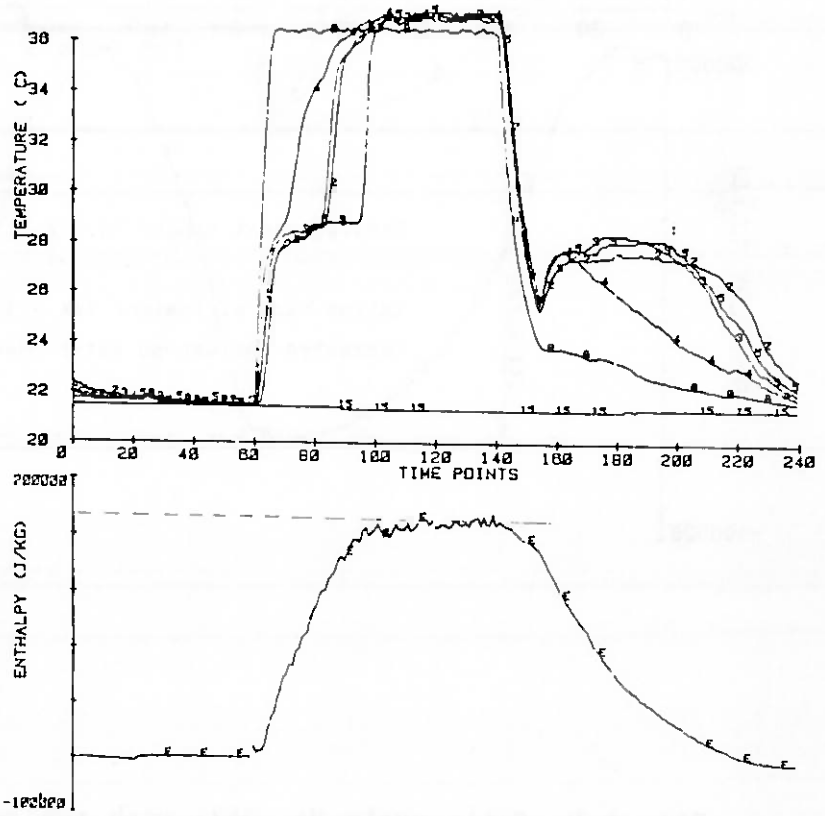


Fig. A.3g Cycle No. 445, of 13 December 1986, where 32°C upper temperature was insufficient for complete melting, and No.449 where melting is complete and heat-of-fusion measurable.

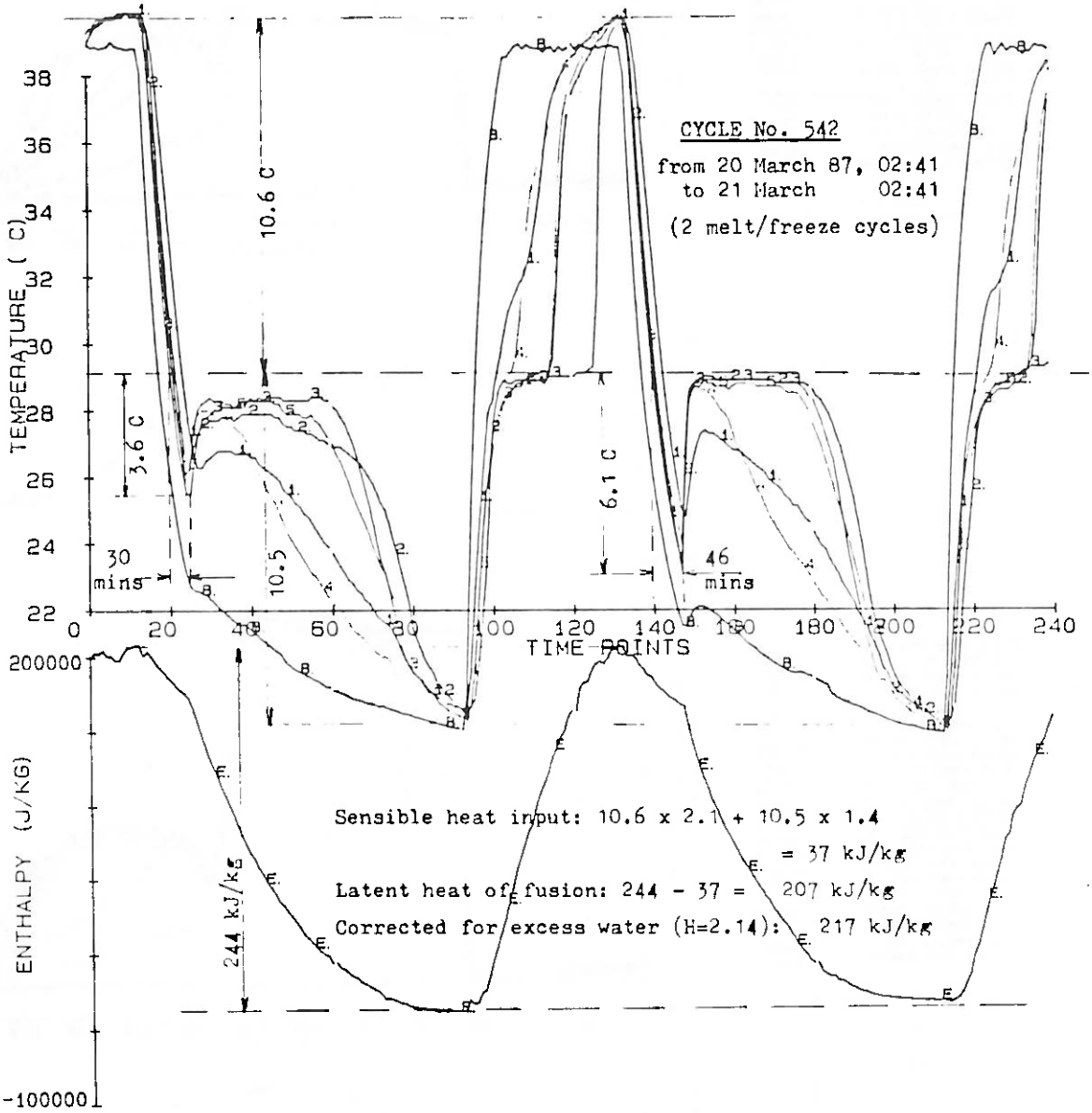


Fig. A.3h Daily cycle No. 542, with two melt/freeze cycles. Note the heat-of-fusion value of 217 kJ/kg (corrected for excess water) comparable to cycle No. 106, Fig. A.3b. ("Two cycles per day" were run also much earlier, see Table A.3). Note also the near-proportionality between time and degree of sub-cooling.

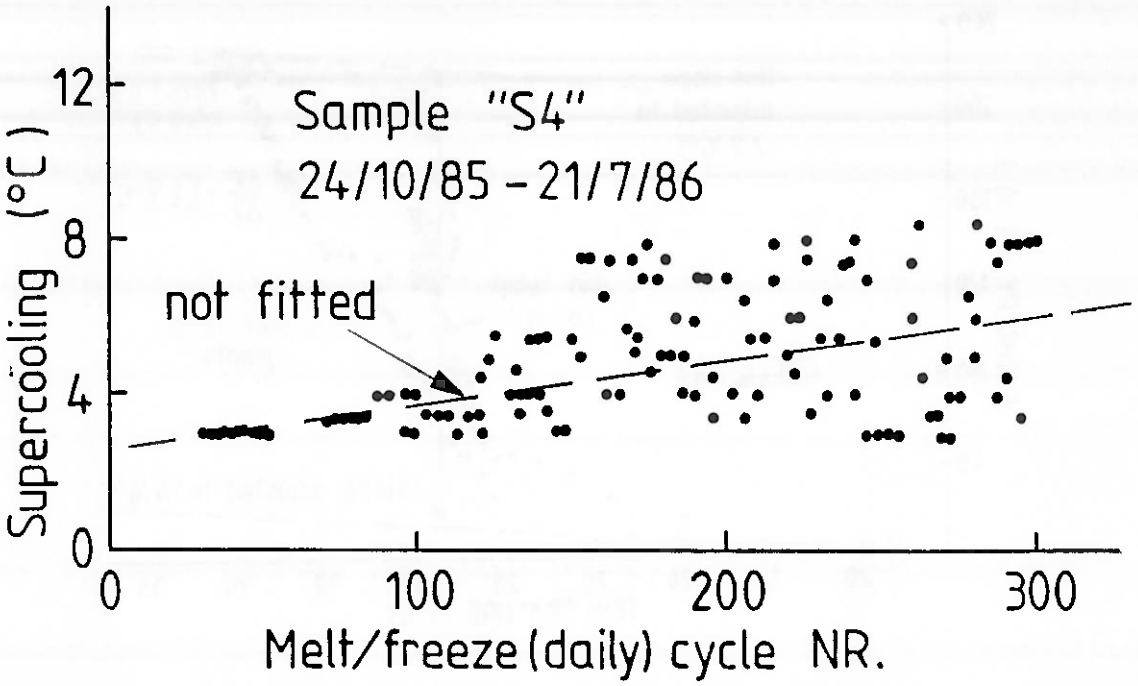


Fig. A.4a describing the time variation of the supercooling behaviour of sample 'S4' over first 300 cycles (1-30 not included).

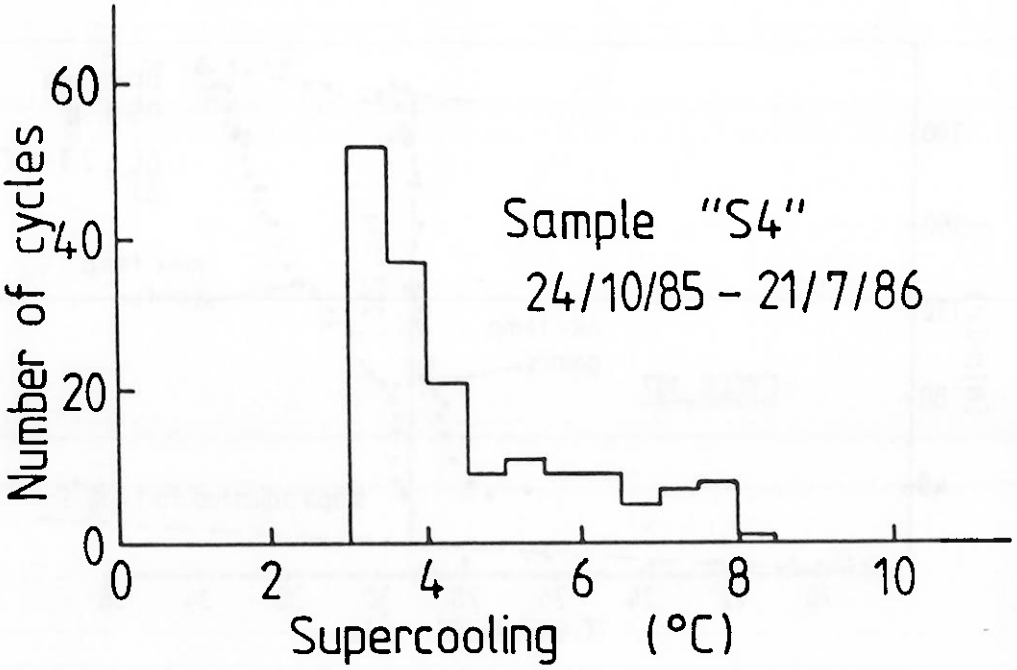


Fig. A.4b Histogram of the degree of supercooling of sample 'S4' over 169 cycles between Nos. 31 and 300.

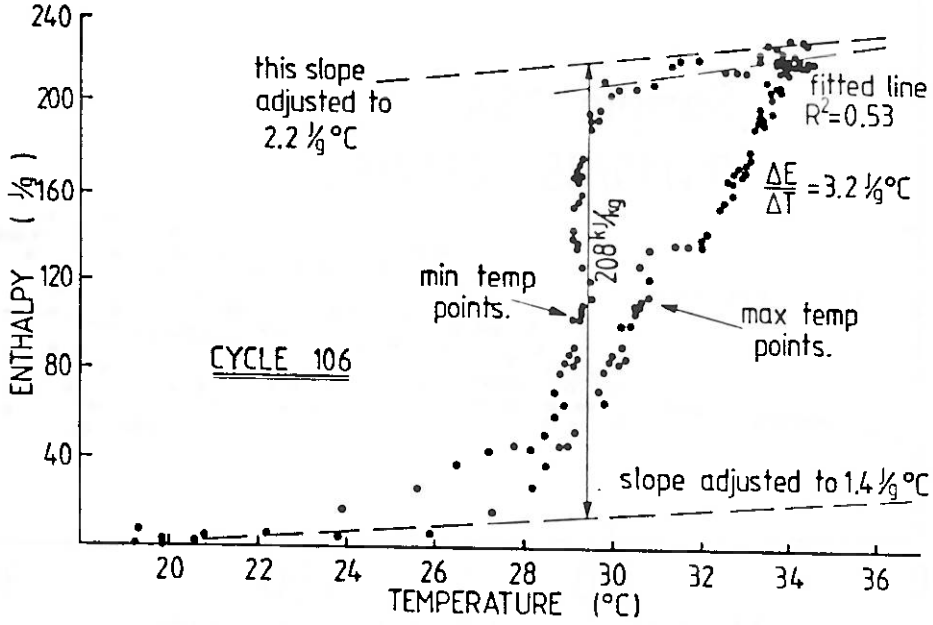


Fig. A.5a Scatter plot of enthalpy vs. temperature for cycle No. 106. Note the agreement of this heat-of-fusion value with Fig. A.3b.

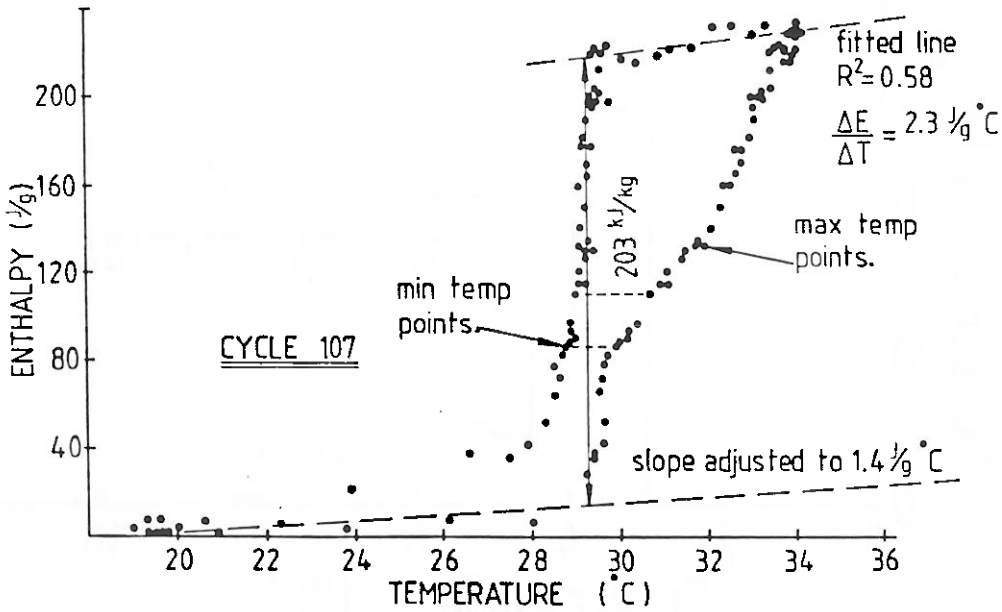


Fig. A.5b Scatter plot of enthalpy vs. temperature for cycle No. 107. Note the inadequacy of these plots for the determination of specific heats.

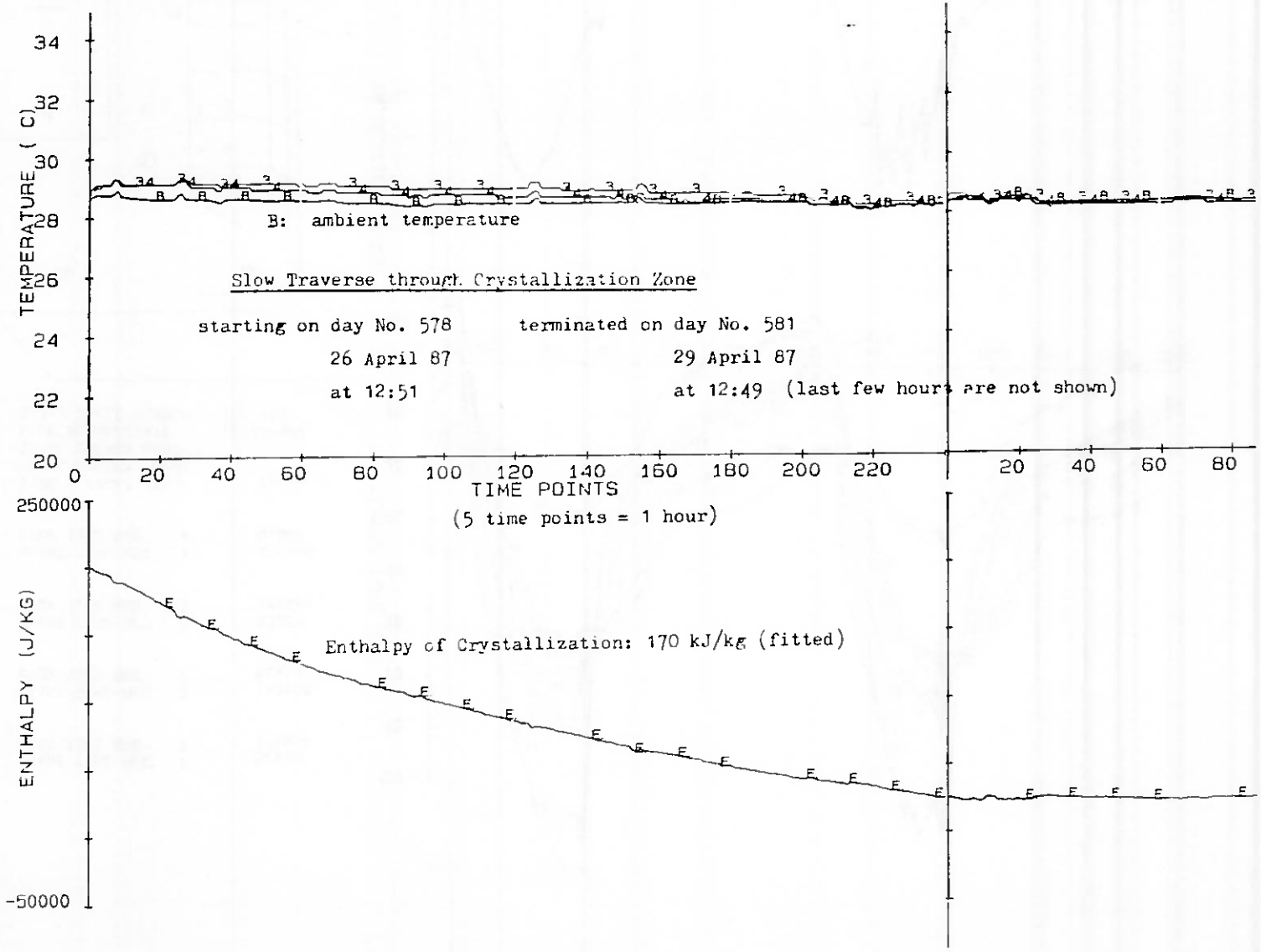


Fig. A.6 Slow traverse through the crystallization zone, sample 'S4' at cycle No. 578.

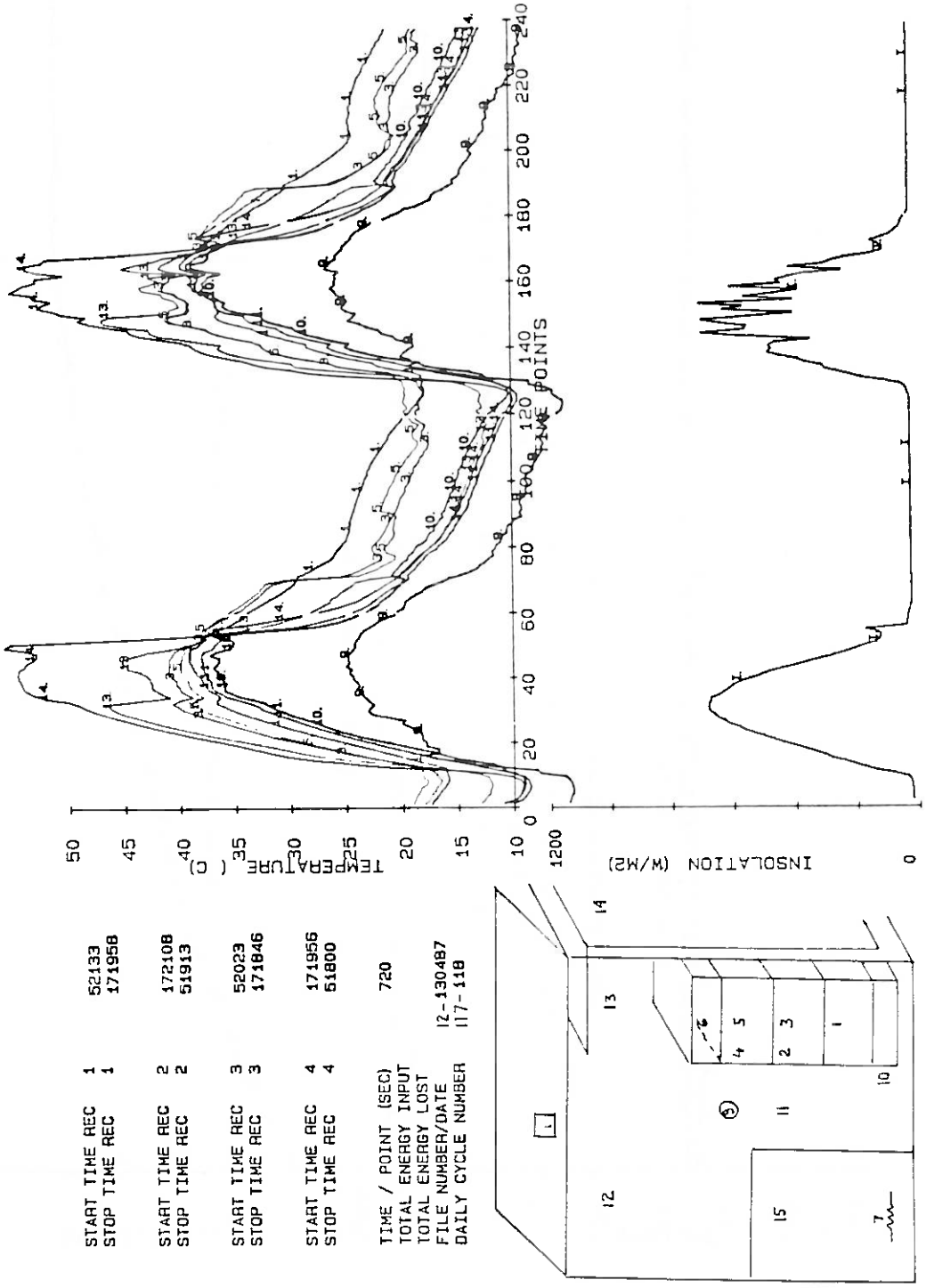
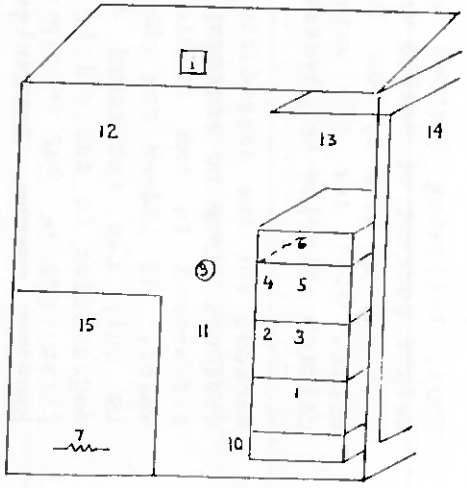


Fig. A.7a Greenhouse temperature profiles (consult Fig. 17a for identification) and insolation (about 30% attenuated by greenhouse roof) on 12-13 April 1987 - on roof of Cockroft Building, Australian National University.

START TIME REC	1	51909
STOP TIME REC	1	171720
START TIME REC	2	171830
STOP TIME REC	2	51635
START TIME REC	3	51744
STOP TIME REC	3	171654
START TIME REC	4	171704
STOP TIME REC	4	51609
TIME / POINT (SEC)		720
TOTAL ENERGY INPUT		
TOTAL ENERGY LOST		
FILE NUMBER/DATE		14-150487
DAILY CYCLE NUMBER		119-120



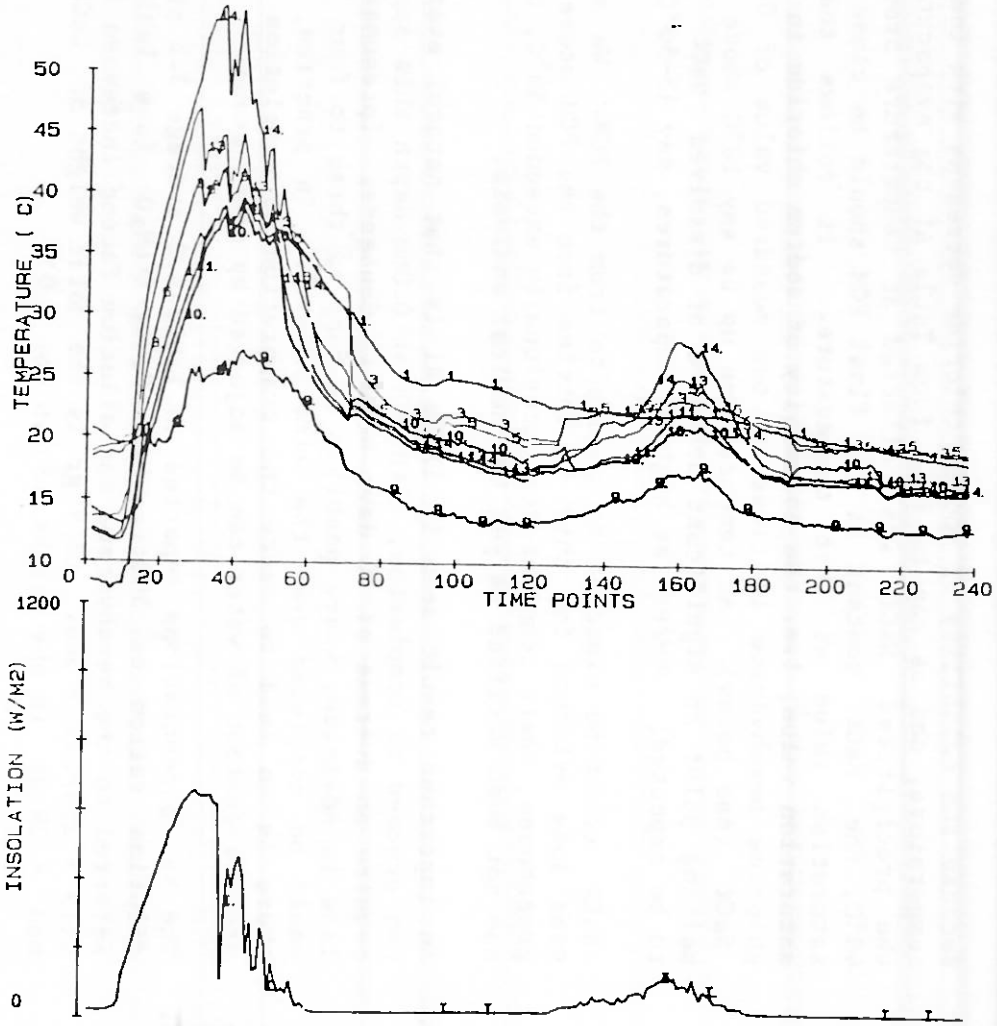


Fig. A.7b as Fig. 7a, for 14-15 April, 1987

Further Discussion of Results

1. Because the solubility of sodium chloride decreases with increasing temperature, and as can be seen from Table A1 the evaporate above the precipitated NaCℓ was collected at temperature around 35-40°C, the NaCℓ content in the final PCM should be close to the saturation value at that temperature. It follows that this saturation value, i.e. the solubility of sodium chloride in calcium chloride hexahydrate is close to our measured value of 0.45 wt% NaCℓ (see below). At temperatures up to say 10°C above the CCH melting point no significant decrease of dissolved NaCℓ is thus to be expected; whereas at higher temperatures, say 45-50°C, some

   NaCℓ could be expected to precipate from the PCM. We may have seen some evidence for this in bottles from the PCM store in the greenhouse, where temperatures occasionally exceeded 50°C, but this has not been verified as yet by chemical analysis.

2. An important result seen in Table A1 is that natural evaporation can proceed to completion, although at 0.06m depth this appears to require an average of 50 days here in Canberra; (presumably much less in Adelaide, where possibly as many as three to four 'passes' could be completed over the warm season). In practice, anyhow, there is no need to carry the evaporation to completion and the precise content of water can be adjusted by other means.

3. The Na concentrations reported in Table A.2 average 3.2 ppm, at a dilution ration of 500:1, for $CaCℓ_2 \cdot 7 \cdot 6H_2O$ (see Table A.1). Referred to the hexahydrate the dilution factor increases to 500 x (219 + 29)/219 = 566. (219 gr is the molar weight of $CaCℓ_2 \cdot 6H_2O$ and ≈ 29 gr is the weight of 1.6 mol H_2O).

   Thus, following further dehydration to 6 molecules of water the weight percent of sodium would become 100/566 = 0.177 wt%. Multiplying this by the NaCℓ/Na weight ratio of 2.54, we finally obtain 0.45 for the weight percent of sodium chloride in our calcium chloride hexahydrate.

4. Reasons for the degradation of our first sample, Fig. A.1, are not obvious, since no segregation was observed, nor are we aware of any difference in the chemical composition such as the content of water. If indeed the change in the following (successful) sample is only the increased dosage of additives, then the observed degradation is due solely to a deficient dose of additives in the first sample. Our interpretation of the data as shown in Fig. A.1, pending further investigation of that sample, is a) that CCH crystals will not necessarily nucleate further material; and b) that the initial rapid degradation - which definitely appears to subsequently taper off (Fig. A.2) - may be due simply to an effective decrease in additives: Fig. A.1b in fact indicates that there occurs freezing only in the bottom part of the PCM sample, and practically none in the top part, consistent with a strong downward gradient in the nucleator additive's density.

5. Comparing the heat-of-fusion values obtained from the time-enthalpy curves, Fig. A.3, with those obtained from temperature-enthalpy curves as in Fig. A.5, one notes that good agreement is obtained only after the $\Delta E/\Delta T$ slope, in the latter, at the initial temperature rise is taken equal to the (solid) specific heat value. This deficiency in the second method may be due to insufficient time resolution (or too fast temperature rise) in our data, but it also could turn out to be an intrinsic limitation. The description by Feilchenfeld [1984] using this method tends to substantiate this, in our view. Our "straightforward" derivation of the heat-of-fusion from the total rise in enthalpy between two well defined temperatures and over a time interval more than sufficient for complete melting appears plainly superior despite its unsophisticated simplicity.

   A more smoothly defined maximum than shown by our enthalpy data would clearly be desirable, to improve the precision, and could possibly be achieved by a better method of "keeping" the temperature in the bath surrounding the sample capsule. On the other hand it is not at all certain that the fluctuations in the enthalpy curve only reflect fluctuations caused by the on/off switchings of the electric heating element. It may in fact appear from Fig. A.6, which was obtained with this heater switched off, that such fluctuations genuinely originate in the PCM while traversing the crystallization zone or the melting zone. This question may appear at first sight an interesting object for investigation. The point of practical interest remains of course the magnitude of the heat-of-fusion measured. We have found no reason to doubt the results obtained here, as represented by Fig. A.3b, showing that this latent heat storage capacity may easily exceed 200 kilojoules per kilogram for low-side temperature even as high as 20°C. We have shown, on the other hand (section III.2) that this capacity declines with rising low-side temperature.

6. The supercooling behaviour as exhibited in Fig. A.4a undisputably shows a certain upward trend in the supercooling temperature differential with time. It is not clear, at present, whether this is not entirely due to the near-critical (or rather "just beyond critical") dosage of additives that in our estimate characterized this sample until recently. In fact, following the slight increase in nucleator dosage on 19 April 1987 the supercooling temperature differential has completely reverted to normal. More cycling is thus required to resolve this question.

7. Much time and effort have gone into the greenhouse setup and, in particular, its relatively advanced and powerful monitoring and control system, which enabled us to produce such plots as shown in Fig. A.7. The various temperature profiles (actually in different colours, originally) tell a good part of the story of this greenhouse, over the last four months or so, and its PCM store in particular. Such as, for example, in Fig. A.7a, the "strange" fall in the store inlet air temperature (No. 13) as the collector air-out temperature feeding it actually is rising. The riddle is

solved by reference to Fig. 17b, "greenhouse operation schematic", which tells us that the PCM store exhaust fan started operating as the greenhouse central temperature (No. 11) started to exceed 35°C. Various other examples can be found by careful examination of these plots.

Unfortunately this PCM store has been "plagued" by inadequacies of the containers used, as already mentioned in section IV.2 - two types of "store-item" plastic 1-litre bottles, which either tended to develop leaks or to lose water in the hot, dry environment experienced during the Summer months, causing segregation (section II.3). However, numbers of individual bottles performed correctly, altogether, as was verified by visual inspection, and the whole store performed essentially as required, as is evident from the plots shown in Fig. A.7.

APPENDIX A - Enthalpy Correction Procedures

In section III.3 the change of Enthalpy, ΔE, during a small time interval Δt (say 30 seconds) has been expressed as

$$\Delta E = -Mc_w(T_w - T'_w) + [P_h + P_{st} - hA(T_w - T_v)]\Delta t \qquad (A.1)$$

with the notation defined there.

For any given value E_o, of the Enthalpy at time t_o, the enthalpy E at any later time $t_o + n\Delta t$ is given as $E_o + \Sigma\Delta E$, and thus, evidently, even small systematic errors in any of the terms multiplied by Δt can accumulate over time into a very large error on E.

The object here is to calculate the error on E, some part of which may also be caused by the first term through an error on M. Note that an error induced by M, though not cumulative, can severely affect the "size" of the enthalpy curve, since M represents the calorimeter's "water equivalent".

We first discard the heater power P_h as a possible source of error by assuming, and ensuring so far as possible, that $P_h = I^2R$ is measured accurately (see section III.3 for details on this question). The same cannot be said of the stirrer power, P_{st}, which, though quite small compared to P_h, is a priori a parameter of unknown value.

We assume moreover that T_v and T_w, being temperatures measured by thermocouples with a common reference junction, are differentially accurate. There then remain only M and h to be accounted for, since C_w is a universal constant and A is a parameter made redundant through h.

Under stated assumptions it is easily seen that the error on ΔE is given by (disregarding for the time being the stirrer power):

$$-\delta(\Delta E) = (T_w - T'_w)\, c_w \times \delta M + (T_w - T_v)\Delta t \times A \times \delta h \qquad (A.2)$$

with Δt now referring to a "time point interval", e.g. 12 x 30 sec. δM and δh can be obtained to first approximation from the uncorrected enthalpy plot as follows:

$$\delta M = -\frac{m}{c_w}\,\delta c\ , \qquad (A.3)$$

where c is the PCM specific heat (liquid).

$\delta h = \frac{\delta h}{h} \times h$, where $\frac{\delta h}{h}$ equals the change in enthalpy over a

complete cycle divided by the total heat loss over this cycle.

"To first approximation" means by assuming for each of these errors that the other is small, and repeating the procedure if necessary - that is until the enthalpy curve levels out and the specific heat is as required (we assume it to be 2210 kJ/kg °C). By "complete cycle" we mean a return to the initial "quiescent" state.

Assume now that data obtained was calculated with incorrect M, h and P_{st} values, and that a corrected plot or printout is required.

To obtain this, at retrieval time, enter first an arbitrary starting value E_o, say $E_o = 0$. Then every successive corrected value can be calculated as

$$E_{n+1}^{corr} = E_n^{corr} + \Delta E_n^{corr}$$

$$= E_n^{corr} + E_{n+1} - E_n - \delta(\Delta E_{n+1}) \qquad (A.4)$$

with the last term given by eq. A.2, and E_n being the uncorrected nth Enthalpy value.

Thus, evaluating sequentially

$E_o^{corr} = 0$ (or any other desired starting value, e.g. E_o)

$$E_1^{corr} = E_o^{corr} + E_1 - E_o - \delta(\Delta E_1)$$

etc., each Enthalpy value can be evaluated in turn and plotted or printed out.

Where a stirrer power correction, P_{st}, is required - as with early data where this was not yet accounted for - the δh correction must be re-evaluated:

$$\delta h \rightarrow \delta h - \frac{P_{st} \times \text{total time of plot (seconds)}}{\text{total energy lost (joules)}} \times h \qquad (A.5)$$

For example, in a 24 hour plot where the 0.178 watt stirrer power was not accounted for, and supposing the plot "level" ($\delta h = 0$, originally) we obtain

$$\delta h \rightarrow \delta h - \frac{0.178 \times 3600 \times 24}{\text{total energy lost}} \times h$$

Note that "total energy lost" is the incorrected value for this quantity, which is the accumulated heat loss $\Sigma\, hA(T_w - T_v)$ normally calculated by the program and recorded.

And finally, under "slow traverse" and similar conditions (see Fig.A.6, Annex) where the vessel water temperature T_w is very close to the exterior bath temperature, T_v, and is much above the air temperature, T_a, to which explicit heat transfer is normally neglected, a further correction to ΔE is required. Since also, under these conditions, the heater and stirrer can both be assumed to be turned off, we have then here for the heat flow balance

$$\Delta E = -Mc_w(T_w - T_w') + [P_{st} - hA(T_w - T_v)]\Delta t \qquad \text{(A.1b)}$$

where P_{st} now stands for an assumed constant heat flow across the vessel's lid, equivalent to a "negative stirrer power" contribution. For example, at $T_w \sim 28^0C$ we found that by entering -0.483 (watt) for "stirrer power" a flat enthalpy resulted at steady conditions - i.e. at steady temperature, with the sample completely melted (in a supercooled state) or completely frozen. Conversely, without this correction entered a rise in the enthalpy curve would result, over 24 hours say, equal to

$$\frac{0.483 \times (24 \times 3600)}{0.3823 \times 1000} = 109 \text{ kJ/kg} \quad \text{(0.3823 being the PCM mass).}$$

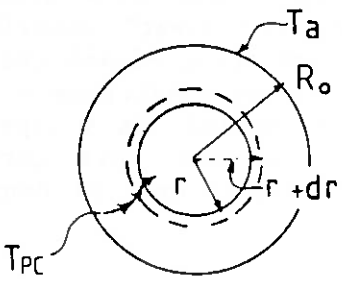
It is of course from this observed rise in the enthalpy curve that the 0.483 watt correction can be calculated.

Obviously, and partly in hindsight, a better apparatus could be designed where corrections such as described here would not be necessary, or would be required to only a much lesser degree.

APPENDIX B - reproduced nearly verbatim from Brandstetter [1982], and self-contained apart from references

Melt-freeze Time of a PCM Body under Cylindrical Symmetry

This problem, which assumedly applies to the situation envisioned in this project, has been the object of a detailed and rather complicated analysis by Solomon [1979] . A much simpler and more amenable analysis is presented here, and tested against results in Solomon [1979] , with reasonable agreement. Useful predictions as to the freeze time of our PCM-filled tubes are obtained, based on the thermal conductivity measurement results presented above, hereafter denoted κ (for solid). We consider a cylindrical segment of PCM of transition temperature T_{PC}, exposed to a uniform ambient temperature $T_a < T_{PC}$ which will cause it gradually to freeze. Consider a thin shell, thickness dr, whose turn has just come to freeze. Its mass is, for length ℓ, $\rho\ell \times 2\pi r\, dr$, with ρ being taken as some mean density, such as 1.6, ignoring the minor problem raised by the change of density with phase-change. (This problem, however, affects the symmetry assumption, due to stratification). Let F denote heat of fusion. Then the amount of heat lost radially outwards by this shell upon freezing is given by $dQ = F\rho.2\pi r\ell\, dr$; and, with the temperature gradient $\partial T/\partial r$ at the solid (outer) boundary of this shell determined by the equation of heat conduction, the above equation can be put in the form - starting with the equation of heat conduction



$$dQ = 2\pi\ell\kappa r\,(\partial T/\partial r)\,dt, \quad \text{i.e.} \quad dt = \frac{F\,\rho\,dr}{\kappa(\partial T/\partial r)}$$

(dt is the infinitesimal time interval for the shell of radius r, thickness dr, to freeze). The required temperature gradient, at a certain point r_o, will now be determined as follows: using again the equation of heat conduction, we can write

$$\Delta T = \int_{r_o}^{R_o} \frac{\partial T}{\partial r}\,dr = \frac{\dot{Q}(r_o)}{2\pi\ell\kappa}\int_{r_o}^{R_o}\frac{dr}{r} \quad \text{(phase boundary at } r_o\text{)},$$

whence

$$\Delta T = T_{PC} - T_a = \frac{\dot{Q}(r_o)}{2\pi\ell\kappa}\log\left(\frac{R_o}{r_o}\right) \quad (\dot{Q} = \text{radial outward heatflux}).$$

Thus, for every r_o between 0 and R_o the temperature gradient (in the solid phase, at the liquid solid boundary) will be given by

$$\frac{\partial T}{\partial r}\,r_o = \frac{\dot{Q}(r_o)}{2\pi\ell\kappa}\,\frac{1}{r_o} = \frac{T_{PC} - T_a}{\log(R_o/r_o)}\,\frac{1}{r_o}.$$

Substituting in the above expression for dt, and integrating, the freeze time t for our PCM cylinder of radius R_o, supposing initial temperature just above T_{PC} throughout (because of convection in the liquid phase cooldown should be relatively fast, therefore this approximation sounds valid), is found to be as follows:

$$t = \int_0^{R_o} \frac{F\rho r \log(R_o/r)}{\kappa(T_{PC} - T_a)}\, dr = \frac{F\rho}{4\kappa(T_{PC} - T_a)} R_o^2$$

Here F is heat of fusion (calories per gram)

ρ is specific gravity (gram/cm) - liquid-solid average

κ is thermal conductivity of solid phase (calories per cm °C per second)

R_o is outer radius of cylindrical PCM slab

T_{PC} is characteristic phase change temperature

T_a is "ambient" temperature, more exactly temperature at R_o.

As an immediately relevant example, let F = 40, ρ = 1.6, κ = 0.0025, R_o = 1.25, and $T_{PC} - T_a$ = 2°C (corresponding to, perhaps, over 4 degrees actual temperature differential referred to heat transfer medium); the freeze time according to the above formula is then 5000 seconds. In practice, however, the temperature differential may be found considerably smaller due to heat transfer limitations, which may constrain the required amount of heat to be transferred during a much longer period of time, such as 5-6 hours (which usually is the desired situation).

The correctness of the above formula has been assessed by applying it to the examples from Solomon , p.252, where a close-to-cylindrical geometry is considered.

With F = 241.2 kJoule/kg, ρ = ½(865 + 785) kg/m³, R_o = 0.05m, κ = 0.19 x 10^{-3} kJoule/m-°C/sec and T_{PC} = 27.67°C, it is found there that the freeze time for T_a = 20°C would be 23.7 hours. Precisely this same result happens to come out with the above formula as well. For other T_a values tabulated the agreement is less precise, although acceptable for most practical purposes. In particular is worth noting that the times calculated for melting agree quite well with those resulting with the above formula with $T_a - T_{PC}$ in the denominator, except for a systematic upward 10-15% shift caused probably mainly by the heatup time neglected in our analysis.

X. LIST OF ABBREVIATIONS/DEFINITIONS

A	area/thickness, in metres
c, c_w	specific heat, s.h. of water (4185 joules/kg°C)
cc	cubic centimetre (= millilitre)
CCH	calcium chloride hexahydrate
COP	coefficient of performance, the ratio between quantity of heat energy "pumped" to electrical energy input.
DBO	distiller blowoff, the waste effluent from the Solway process producing soda ash
DVM	Digital Voltmeter
E	Enthalpy, often referred to one kilogram of material, e.g. "enthalpy of fusion"
g	gram, for instance j/g, i.e. joule per gram, equal to "kilojoule per kilogram"
h	heat conductivity, in Watt per metre per degree C (W/m°C), here used as an adjusted parameter
h.o.f.	heat-of-fusion, in kilojoules per kilogram
H	degree of hydration, in mol water per mol calcium chloride
I	electric current, Amperes
j,J	joule
kJ	kilojoule
kg	kilogram
(ℓ)	weight fraction of liquid phase
mℓ	milli-litre
mV	millivolt
m	mass of phase change material (in kg) in calorimetric evaluation experiment
M	(Mass of) "water equivalent" in calorimeter, here used as adjusted parameter
P_h	heater electric power (~ 68 watts)

P_{st}	stirrer power (~ 0.178 watt) contributed in heat to the calorimeter
R	heater resistance (4.204 ohm), used to calculate $P_h = I^2R$
RSBS	Research School of Biological Sciences, at the A.N.U.
s	solubility - usually in gram $CaCl_2$ per 100 ml water.
(s)	weight fraction of solid phase
t	time, usually in seconds
time point	time over which measurements (usually 12 or 24) are averaged
T	temperature in degree Celcius
T_{ref}	temperature of thermocouple reference junction
T_w, T'_w	present, previous water temperature inside the "vessel"
T_v	the temperature at the vessel's metallic exterior
V	volts, voltage
w	residual weight (in grams) of calcium chloride sample after complete dehydration (also used as subscript denoting "water")
W	initial weight of (hydrated) calcium chloride sample
wt%	weight percent (i.e. percentile by weight)
X	(overall) weight fraction of calcium chloride
X_s, X_ℓ	weight fraction of calcium chloride in the solid, liquid phase
$\delta t, \Delta t$	time increment per measurement, per "time point" (12 or 24 measurements)
$\delta E, \Delta E$	Enthalpy increment over time δt, Δt
ΔT_{tc}	thermocouple temperature differential relative to reference junction
δh	error in the h-parameter
δM	error in the M-parameter
$\delta(\Delta E)$	resulting error on ΔE.

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