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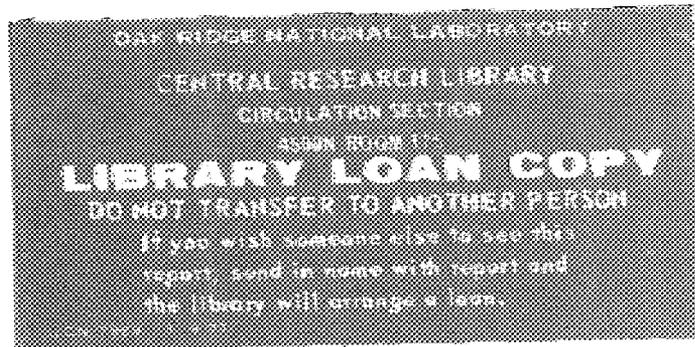


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Thermal Energy Storage Technical Progress Report April 1985–March 1986

J. F. Martin



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THERMAL ENERGY STORAGE TECHNICAL PROGRESS REPORT
APRIL 1985—MARCH 1986

J. F. Martin

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ABSTRACT

Progress in the development of Thermal Energy Storage (TES) technology under the Oak Ridge National Laboratory TES Program for the period April 1985—March 1986 is reported. Program goals and project structure are presented. Each of the projects active during this report period is discussed, and technology transfer activities are also reported.

1. PROGRAM OVERVIEW

This report presents the status of projects active under the Oak Ridge National Laboratory (ORNL) Thermal Energy Storage (TES) Program during the 1-year period ending March 31, 1986. ORNL is the principal research laboratory for the development of diurnal TES technologies, acting as field manager for the Department of Energy (DOE), Office of Energy Storage and Distribution. The application areas of the program are those of industrial reject heat conservation, electric utility load leveling, and passive and active solar energy storage. The ORNL program is conducted in consultation with, and with the concurrence of, DOE.

The purpose of the TES program is to perform research and development (R&D) in critical, high-risk technology areas and to transfer the results to the private sector so that advanced, high-performance TES systems may be developed and marketed for specific applications. This purpose is expressed by the overall goals of the TES program: to (1) create the technology base required for development of efficient, cost-effective TES concepts in diurnal heating and cooling and industrial applications and (2) work with industry, universities, technical societies, and trade associations to transfer the technologies to the private sector.

In pursuit of this goal, the following five program objectives have been identified as representing the critical areas for resource allocation. Each objective is associated with a benefit to the technology of

TES, and the necessary targets with which to measure progress toward achieving the objectives have been established. The strategy followed is to initiate projects that address generic technical problems that must be overcome to meet these targets.

1. Develop TES concepts and media that provide both heat (winter) and cool (summer) storage for heat pump systems.

Benefit: Improve heat pump applicability for utility load control through performance that equals or exceeds nonstorage heat pump performance.

Targets: economic — \$21.5/kWh (\$6500/10⁶ Btu) installed cost (1984 dollars).

technical — Heat exchange effectiveness of 0.95 cool storage temperature: 7 to 12°C (45 to 53°F) cool; 38 to 49°C (100 to 120°F) hot; round-trip efficiency of 90%.

2. Develop TES concepts for capture, storage, and reuse of high-temperature energy that significantly increase the utilization of industrial reject heat.

Benefit: Make economically feasible the conservation of the significant energy available from industrial waste heat.

Targets: economic — \$27/kWh (\$8100/10⁶ Btu) installed cost (1984 dollars).

technical — Storage temperatures of 175 to 1100°C (350 to 2000°F); round-trip efficiency of 85%.

3. Develop TES with ideal thermal response for passive solar building heating.

Benefit: Enable passive solar systems to provide building temperatures in the ideal thermal comfort range.

Targets: economic — \$12/kWh (\$3500/10⁶ Btu) installed cost (1984 dollars).

technical — Raise level of stored energy utilized in the thermal comfort range by a factor of 10 over existing storage technology.

4. Perform research to advance the understanding of new TES materials and processes.

Benefit: Identify advanced concepts with improved technical and economic characteristics.

Targets: economic — Assess projected system costs.

technical — Determine physical and thermal properties and conceptual system descriptions.

5. Interact with commercial/industrial sector directly (workshops) or through technical societies and trade associations to evaluate research needs and to effect transfer of the technologies developed.

Benefit: Fulfill TES program goals through transfer of developed technologies to industry for implementation.

Targets: Wider recognition of the value of thermal storage by the private sector.

That the value of TES is becoming more widely recognized is apparent from the recent introduction of commercial systems into the market place. However, it is also apparent that the simple storage systems initially envisioned for TES are not adequate to provide the reliability or performance required of a commercial system. Thus, the need in application areas for high-performance TES systems is better defined than in the past; the present program is sharply focused to address specific problems.

TES media that undergo a change of state (e.g., phase, structure, or chemical composition) at a desired storage temperature are required for improvement of present storage systems. The economics of storage must be considered because the ultimate goal of the TES program is successful technology transfer. Further, the elements that make up the reliability of a workable system must be addressed. The results of previous years' R&D in this program are seen in the identification of these materials that have good prospects for meeting the requirements of a viable TES system:

1. clathrates, double clathrates, semiclathrates, and related compounds that show two transition temperatures, thereby providing cool storage for air conditioning and heat storage for heating;

2. salt hydrates and their containment materials that allow integration into a passive solar structure, thereby allowing lightweight, practical building components to replace massive passive solar walls; and
3. multicomponent, high-temperature phase-change materials (PCM) that allow direct contact heat exchange for industrial applications.

Within this context, the ORNL TES Program is focused on the identification and solution of the problems of TES for both building heating and cooling and industrial applications. Specific program activities are designed to extend the technology for TES systems by

1. developing advanced high-temperature storage media for industrial applications,
2. demonstrating gas hydrates for use in cold storage/heat pump applications,
3. investigating doubly complexing systems suitable for dual-temperature (cold storage/heat storage) TES systems for heat pump applications,
4. defining physical and thermal characteristics required for PCM storage materials for direct gain passive solar applications,
5. conducting laboratory materials testing to identify appropriate TES media materials, and
6. performing technical and economic evaluations to identify TES developmental requirements and R&D objectives.

The total scope of the program is shown in Fig. 1, which is the work breakdown structure (WBS) of the ORNL program. From this comprehensive structure, and by a process of prioritization, budget considerations, and a consideration of the capabilities of the research community, certain projects were funded. These research activities are presented in the following sections of the report.

1.1 Basic Materials Research

1.1.1 Heat transfer

Work package 1.1.1.1 consists of experimental studies of the properties of clathrates of fluorocarbon refrigerants used as a cool storage media. The objective of this research, which was done in-house, was to

(a) BASIC SCIENCES

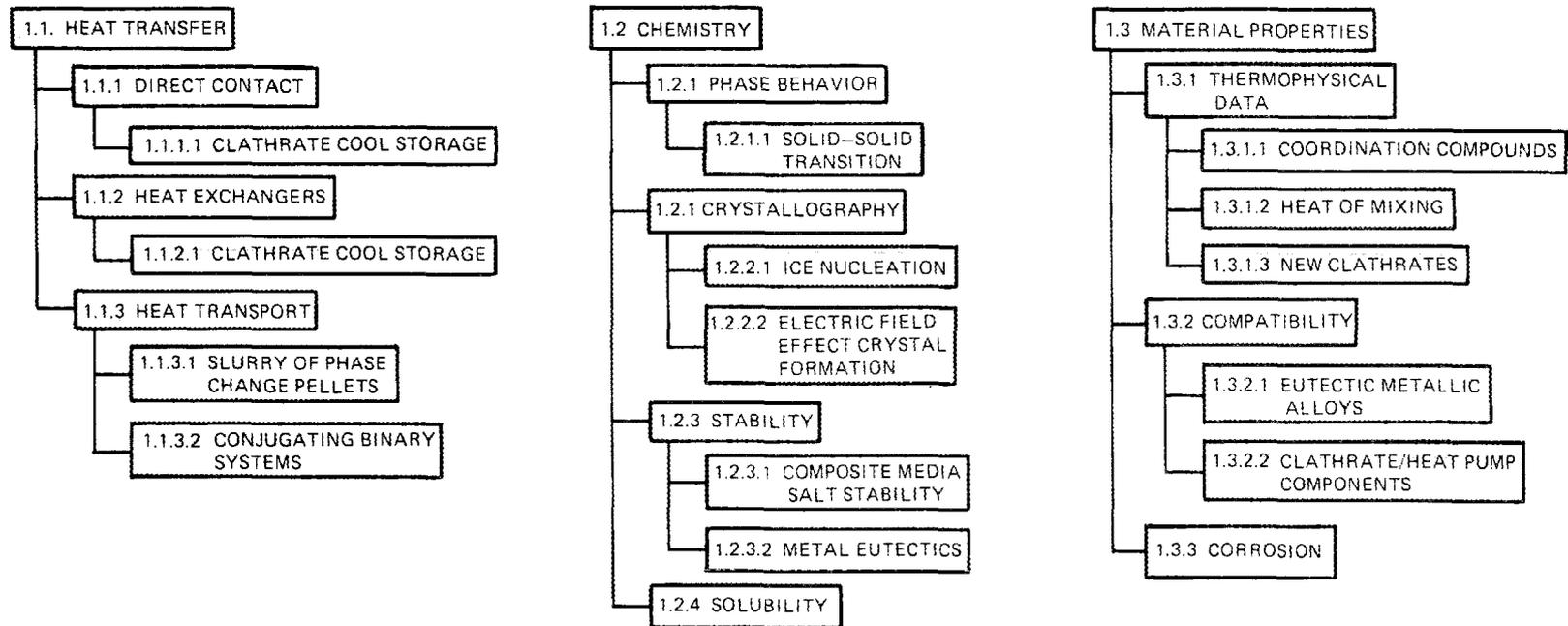


Fig. 1. Program work breakdown structure: (a) basic sciences and (b) applied research.

(b) APPLIED RESEARCH

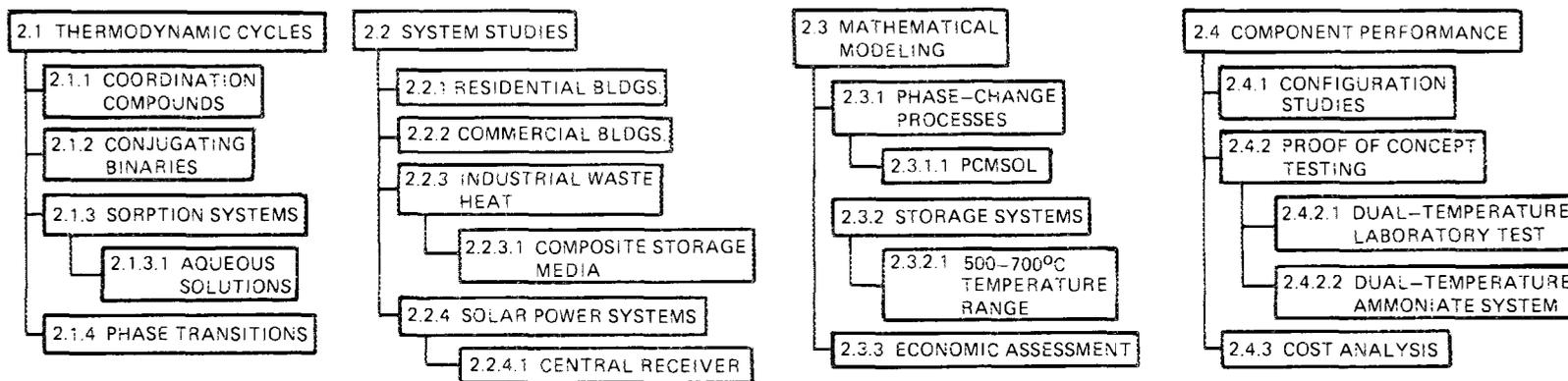


Fig. 1 (continued)

confirm the pressures and temperatures at which clathrates of mixtures of refrigerants formed. Mixing two refrigerants, which form clathrates at different pressures and temperatures, allows tailoring the pressure and temperature of clathrate formation and, therefore, the storage charging/discharging temperature.

Previous research has confirmed the technical feasibility of forming a clathrate or ice-like solid to provide latent heat storage of cool at temperatures higher than ice formation (0°C) and, therefore, more favorable for a heat pump cool storage system. Theoretically, direct contact heat exchange to charge and/or discharge the storage medium is possible because the gas component of the clathrate can be one of several common fluorocarbon refrigerants. Thus, such clathrates have many characteristics favorable to cool storage in heat pump systems. The subject experiments were designed to confirm the theoretical performance of mixtures of refrigerants.

Work package 1.1.3.1 consists of research in the enhanced heat-carrying capability of fluids slurried with solids that can undergo solid-solid phase change. The objective of the project is to establish proof-of-principle for improved TES performance by utilizing combined mechanisms of enhanced heat transfer, heat transport, and TES associated with a phase-change slurry used as the system working fluid. Preliminary concept and background development work already completed and reported shows that using a phase-change slurry as the thermal system working fluid (i.e., to remove thermal energy from the heat source and to transport it to, and reject it at, the heat sink) can potentially yield considerable reduction in system heat transfer surface area and/or pumping power while increasing TES efficiency and end-use temperature.

Specifically, combined utilization of the phenomenon of increased energy transport caused by phase transition of a change-of-phase additive to a carrier fluid, with the recently recognized phenomenon of enhanced heat transfer at a surface as a result of particle/fluid and particle/boundary layer interaction, will be used to demonstrate enhanced performance of thermal energy systems.

1.1.2 Chemistry

Project 1.2.1.1 of the program WBS consists of a reinvestigation of techniques for producing pellets of cross-linked high-density polyethylene by electron beam or gamma radiation. It was necessary to determine proper processing to preclude pellet-to-pellet adhesion, establish upper limits of temperature and pressure that allow satisfactory performance in a packed-bed thermal storage system, and determine the economics of large-scale production of the material.

Previously prepared samples of this solid-solid transition TES material, although deemed satisfactory from laboratory-scale tests, experienced problems of adhesion under large-scale field testing. Because of the seriousness of this deficiency in material performance, a follow-on project was implemented to determine if a satisfactory processing procedure possibly could be developed.

WBS project 1.2.3.1 consists of laboratory experiments aimed at demonstrating the stability of the composite salt/ceramic TES material under development as part of the TES program. This material, which has been under development over the past several years, allows energy storage at high temperature by utilizing the latent heat of the salt phase change.

The composite material allows the latent heat of fusion of carbonate salts to be utilized by immobilizing the salt in a matrix of a nonmelting ceramic. Thus, a pseudo-solid storage medium is formed, and pellets of this material are suitable for packed-bed storage systems with the resulting efficiency of direct contact heat exchange with the storage charging/discharging fluid. Long-term cycling of a laboratory-scale bed of pellets with detailed mass balance data on individual cycled pellets has allowed determination of the degree of carbonate loss with time. Analytical studies are aimed at a description of the chemistry involved in salt loss and redistribution in the bed.

The objective of WBS project 1.2.3.2 is to develop a TES medium consisting of an integral outer shell with a high melting temperature and an internal core of latent heat storage material with a lower melting temperature. The outer shell is to be inert and act as an encapsulation of, and corrosion protection from, the latent heat storage material.

Metallic eutectic alloys have long been of interest for use as TES media. Their high thermal conductivity (on the order of $200 \text{ J/m-s-}^\circ\text{C}$) and heat of fusion (300 to 500 J/g) make them excellent candidates. However, commercial use of alloy systems requires expensive containment in corrosion-resistant tubing. A solution to this problem is to develop a means of achieving an impermeable coating of the metallic eutectics so that a packed bed of spherical shot of the storage medium can be used in direct contact with the heat transfer fluid. Using silicon-based alloys, it is possible to achieve a heat storage shot with a relatively high-temperature, corrosion-resistant outer shell and a lower-temperature eutectic alloy inner core.

1.1.3 Material properties

WBS project 1.3.1.1 seeks to utilize the complexing of ammonia/salt for dual (winter/summer) temperature thermal storage. The concept is a monovalent system that utilizes the heat of sorption of a gaseous ammonia on a solid sodium bromide to provide a heat pump storage system that can store heat in the winter and store cool in the summer.

Analogous to the hydration reaction, a number of inorganic salts undergo ammoniation reactions with gaseous or liquid ammonia. These reactions may be suitable for latent TES at temperatures and pressures at which the ammine of the salt can be formed and decomposed. Suitability of an ammoniation reaction (or reactions) for TES depends on, among other things, the thermochemistry and phase equilibria of the salt-ammonia systems. Both liquid and solid ligand/solid absorbent systems were examined. Thermodynamic, physical, and chemical properties of many possible substances were determined. The most promising concept, sodium bromide-ammonia, was studied in detail.

Under WBS project 1.3.1.2, promising liquid-liquid and liquid-solid systems suitable for TES are being studied. Available experimental data on phase equilibria, heats of mixing, and heats of solution are being utilized to predict the potential heat storage capabilities of promising systems. Accurate models for the activity coefficients of the mixtures are being used to represent the phase behavior. Several systems will be selected for the measurement of heats of mixing.

Many systems based on heats of mixing can be considered for thermal storage. Some complex at two temperatures, thus presenting the possibility of dual-temperature, winter/summer storage for buildings in a single system to provide greater seasonal efficiency. Others exhibit an apparent enhanced specific heat over the temperature range of mixing with the possibility of higher storage density over sensible heat storage systems.

The experimental determination of the rate of diffusion of silicon into an aluminum-silicon alloy is the subject of in-house research conducted under WBS 1.3.2.1. The objectives of this research are to determine the silicon shell thickness required to retain a liquid aluminum-silicon alloy and to determine shell stability in the presence of phase redistributions occurring during melting and recrystallization.

Silicon-encapsulated shot of aluminum-silicon or other similar eutectics offers an extremely attractive possibility for direct-contact, high-temperature, latent heat storage. Successful development of pellets of one or more of these materials would make available storage media with a high latent heat of fusion, high heat conductivity, and corrosion resistance. However, the question of stability of the silicon shell to redistribution during repeated melting and recrystallization must be addressed to ensure that a practical material will result from such development efforts. This project provides experimental data on the nature of the material interface so that a determination of media stability can be made.

1.2 Applied Research

1.2.1 Thermodynamic cycles

WBS project 2.1.1 concerns the design of heat pump cycles that utilize complex compounds for TES. Existing thermal storage equipment for heat pumps is not adequate for light commercial or residential building applications. Combining a heat pump with ice or water TES results in low coefficients of performance. The first cost of separate storage systems for winter and summer cannot be justified by existing utility rate incentives.

The heat pump/dual-temperature storage concept investigated in this project has the advantage of combining the heat pump and both heat and cool storage in one hardware design. The direct coupling of the refrigerant and the storage medium results in much-higher thermodynamic efficiencies than possible with conventional heat-coupled equipment. The high energy densities of complex compounds yield compact heat pump/storage packages but use ~50% of the space of a conventional chiller/cool storage package.

1.2.2 System studies

WBS project 2.2.3.1 is a study of the economic and technical feasibility of heat recovery in a periodic kiln brick plant through the use of latent heat storage. Laboratory testing has demonstrated that the concept of using sodium-barium carbonate/magnesium oxide composite material is viable. A system design and benefit analysis provide an intermediate stage between laboratory proof-of-concept and technology transfer. The participation of a commercial firm with extensive experience in periodic kiln and heat recovery technology is an asset to this study. Laboratory data provide input characteristics of the storage medium to computer simulation of a brick plant kiln sequencing operation. This technique allows the real advantage of latent heat storage in plant energy recovery to be determined.

1.2.3 Mathematical modeling

WBS project 2.3.1.1 is a combined analytical and experimental project to validate the computer code PCMSOL, which was developed in-house to model the response of a direct-gain room containing latent heat thermal storage. A second objective of this project is to determine the level of modeling detail needed to predict adequately the temperature response of a room with various configurations of TES.

Conventional TES components for passive applications consist of mass storage systems (concrete, brick, or water walls), which absorb or release sensible heat. These systems usually require large temperature differences to be effective, thus leading to room overheating. A computer simulation, PCMSOL, has been developed by ORNL to predict the

thermal response, interior surface temperatures, and comfort levels of a direct-gain room fitted with thin wall panels containing a latent heat storage medium in place of conventional wall sheathing. The code employs detailed finite-difference techniques to predict the thermodynamic state of any latent/sensible heat storage wall material subjected to radiation, conduction, or convection. The validated code may be used to determine confidence levels for predictions of simpler, less sophisticated codes.

2. TECHNICAL PROGRAMS

There was a good balance between more basic research in TES materials and applications studies this report year. Six of the seven categories representative of the program were represented by active projects. Eight of 12 projects are expected to be ongoing next year as the program concentrates on supporting the most promising advanced concepts. Although there is a lack of extensive economic studies because this is a technology-oriented program, the economic practicality of each concept is one of the important criteria for continuing program support.

2.1 Mixed Fluorocarbon Clathrates (WBS 1.1.1.1)

Several heat pump refrigerants form gas hydrates (clathrates) that have good potential as cool storage media for heat pump systems.¹⁻³ These icelike materials have several characteristics that give them an advantage over chilled water or ice storage. Like ice, a clathrate stores energy as latent heat, thus giving it an advantage of lower storage volume over sensible heat storage in chilled water. Latent heat storage also presents a much reduced temperature range to the evaporator coil. Additionally, fluorocarbon clathrates freeze at higher temperatures (10 to 12°C) than ice, providing an advantage in heat pump capacity over that achieved when freezing ice for storage. These advantages may be amplified by the possibility of direct-contact heat transfer into and out of storage because the fluorocarbon is both the refrigerant and, with water, the storage medium. Thus, the heat transfer penalty from heat exchanger surface temperature drops may be avoided. Finally, storage at higher-than-ice temperature can reduce heat gain of the storage vessel.

The phase diagram for R-12/H₂O mixtures is shown in Fig. 2. R-12, like many refrigerants, is only slightly soluble in water; thus, curve A-Q₂-D very closely approximates the vapor pressure curve of R-12 alone. Points Q₁ and Q₂ are invariant quadruple points where four-phase equilibria exist, and the line Q₁-Q₂ defines a transition from H₂O(l) and R-12(g) to the R-12 gas hydrate, releasing a heat of formation of 76 kcal/kg of hydrate.

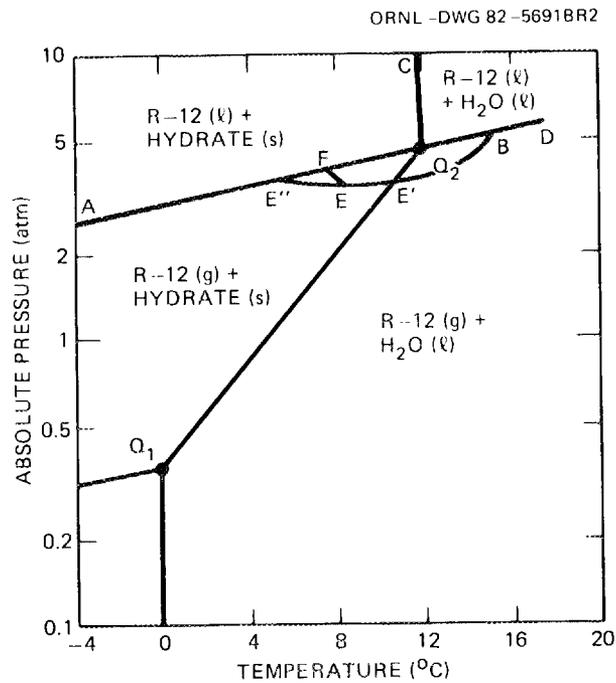


Fig. 2. Phase diagram for R-12/H₂O mixtures.

A conceptual cool storage system based on the R-12 gas hydrate is shown in Fig. 3. The system consists of a vapor-compression refrigeration cycle with the conventional evaporator replaced by a storage tank crystallizer in which the gas hydrate is formed and dissolved. A completely discharged storage tank consists of R-12(g), R-12(l), and H₂O(l) in equilibrium, as shown at point B in Fig. 2. At the initiation of the charging period, the compressor will reduce the pressure in the storage tank, causing R-12(l) to vaporize. This, in turn, reduces the temperature in the storage tank. The pressure and temperature will continue to decrease in such a manner until the Q₁-Q₂ curve is crossed and gas hydrate begins to form. The heat released by the formation of the gas hydrate vaporizes the R-12(l). When the rate at which R-12(g) produced in this manner is sufficient to maintain a constant pressure in the storage tank, an equilibrium (point E) will be reached. The position of point E depends on the thermal driving force required to produce the gas hydrate ($T_{E'} - T_{E''}$). Gas hydrate continues to form until all the H₂O(l) in the storage tank is consumed, at which time the charging process is

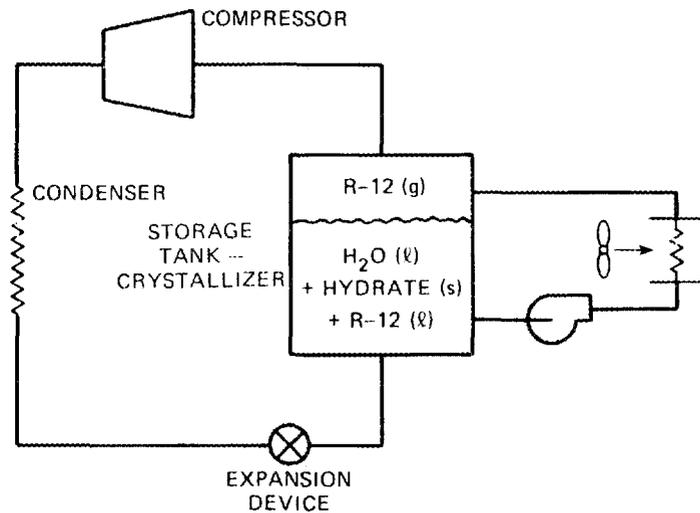
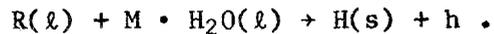


Fig. 3. Conceptual gas hydrate cool storage system.

complete. The completely charged storage tank will consist of R-12(g), R-12(l), and R-12 gas hydrate in equilibrium, as shown at point F. A small amount of R-12(l) should remain in the storage tank to be used later to initiate discharge of the storage system via a pump, fan, and evaporator coil in the building supply duct.

Clathrates of mixed fluorocarbon refrigerants were investigated.⁴ The R-12/water-phase diagram upper-invariant point of 449 kPa requires a pressure vessel to contain the clathrate, an economically unattractive fact for commercialization.

The characteristics of three refrigerants — Trichloromonofluoromethane (R-11), Dichlorodifluoromethane (R-12), and Dichloromonofluoromethane (R-21) — that form clathrates at temperatures suitable for cool storage are shown in Table 1. These refrigerants combine with water to form a clathrate according to the reaction



The number of molecules of water n needed to form the hydrate per molecule of each of these refrigerants is given in Table 1. Also shown are the heat of formation h per unit mass of the clathrate and the upper-invariant point (Q_2) or pressure and temperature at which the clathrate forms.

Table 1. Characteristics of refrigerants considered in this study

Refrigerant	Q_2		Molecular weight	Water (mol)	Latent heat of fusion [J/g (Btu/lb)]
	Temperature [°C (°F)]	Pressure [kPa (psia)]			
R-11 (CCl ₃ F)	8.7 (47.6)	59 (8.6)	137	16.6	281.7 (121.2)
R-12 (CCl ₂ F ₂)	12.1 (53.8)	449 (65.4)	121	15.6	170.4 (116.6)
R-21 (CHCl ₂ F)	8.6 (47.5)	101 (14.7)	103	16.9	276.6 (118.9)
R-114 (C ₂ Cl ₂ F ₄)	No hydrate		171		

Refrigerant R-21 forms a clathrate at atmospheric pressure; however, this refrigerant is very chemically active and would only be appropriate for a closed system (i.e., separated from the heat pump refrigerant by a heat exchanger). Refrigerant R-11 forms a clathrate at <1 atm. Thus, the possibility of forming a clathrate at 1 atm by mixing R-12 and R-11 exists.

When a single refrigerant such as R-12 is used in a gas hydrate, cool storage system, the gas hydrate is formed at point Q_2 of the phase diagram of the refrigerant/water system (Fig. 2). The pressure and temperature of this point correspond to that shown in Table 1. In a cool storage system, gas hydrate (solid) will coexist with some water (liquid), some refrigerant (liquid), and a gaseous portion containing the refrigerant saturated with water vapor. The system, when in equilibrium, has to operate at the invariant point Q_2 (Fig. 2), where R-12(l), R-12(g), H₂O(l), and gas hydrate can coexist.

If two completely miscible refrigerants are used to form a mixed clathrate, the system has three components (water and two refrigerants) but the same four phases as in the previous case. Mixed-hydrate formation should occur at a point between the two Q_2 points of the single refrigerants in the mixture, a fact confirmed by previous experiments.⁵ If, however, only one refrigerant is used, the hydrate will form at the end of this line corresponding to the Q_2 point of the refrigerant used.

In a mixture of two refrigerants — one that does not form a hydrate [like Refrigerant-114 (R-114)] and the other one entering into the hydrate — three components and four phases will be present, and, therefore, one degree of freedom will be available. Hydrate will be formed at

different pressures and temperatures, depending on the composition of the mixture, with only the hydrate-forming refrigerant entering into the hydrate. Inactive R-114 and the remaining water, if any, will not combine and will remain as liquid coexisting with the solid hydrate.

Mixtures of R-11 and R-12 were tested. The results are shown in Fig. 4, which is a phase diagram showing the locus of Q_2 points for

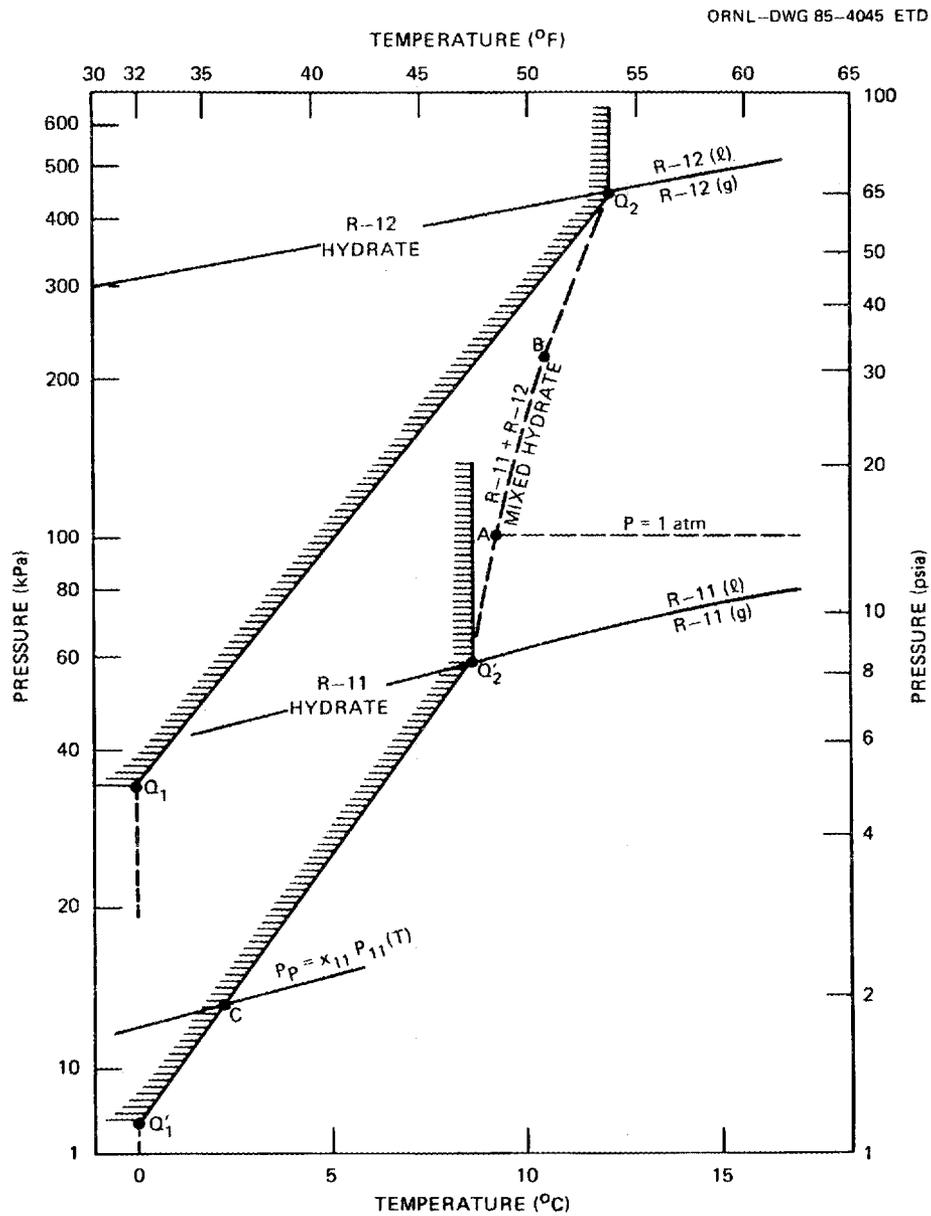


Fig. 4. Phase diagram for R-12 + R-11 + H₂O.

various ratios of refrigerants. The mixture composition of 0.88 mole fraction of R-11 and 0.12 mole fraction of R-12 forms a mixed hydrate at 1-atm pressure and 9.2°C (48.6°F).

Clathrates of mixtures of R-11 and R-14 (dichlorotetrafluoromethane) were also formed. Only R-12 entered into the clathrate. By varying the composition of the mixture, clathrates over a range of temperatures and pressures were obtained. All of the hydrates formed at pressures below atmospheric and temperatures <8.7°C (47.6°F).

Finally, clathrates from mixtures of R-12 and R-114 were also produced. Only R-12 entered into the clathrate structure, as in the case of R-11/R-114. For temperatures >0°C (32°F), all of these clathrates were at pressures above atmospheric.

Tests to simulate heat pump storage were successfully completed in the experimental crystallizer. Mixtures of R-11/R-12 formed clathrates in the closed system (required because of the different vapor pressures of the two refrigerants) by cooling the refrigerant-water mixture. Discharge tests in which excess refrigerant was circulated through an external heat transfer loop were accomplished without problems.

2.2 Chemistry

2.2.1 Radiation cross-linked polyethylene (WBS 1.2.1.1)

Previous research at the University of Dayton Research Institute (UDRI) developed cross-linked, high-density polyethylene (HDPE) as a thermal storage material.^{6,7} The HDPE was cross-linked by electron-beam radiation to obtain a thermally form-stable material that melted at 130°C and had a latent heat of fusion of 40 to 50 cal/g. At its melting point, the cross-linked material changes from a white, opaque solid to a transparent, viscoplastic liquid. Repeated cycling through the melting point showed that the material melts and freezes congruently and has the basic properties required for TES.

The thermally form-stable property of HDPE depends on the extent of cross-linking. In their uncross-linked condition, polyethylene pellets will melt and fuse together. After being cross-linked, however, they

retain their shape when heated above the melting point and do not fuse together.

Under the initial program, the material was irradiated with total doses of 2 to 12 mrad by electron beam. Tests of these materials showed that total doses of 6 to 8 mrad were sufficient to ensure that the pellets would retain their solid property above the melting temperature. Therefore, a radiation dose of 6 mrad was selected as sufficient to provide a form-stable material with an attractive heat of fusion, and a relatively large batch of material was prepared for prototype storage-system testing. However, subsequent tests by other investigators showed that the material fused to a single mass in larger batch thermal cycling tests; thus, it was declared unsuitable for use in packed-bed systems.

UDRI conducted a follow-on program⁸ to reexamine the effect of radiation dose on material melting characteristics. Because the end results of electron-beam and gamma irradiation provide the same cross-linking of polyethylene (cross-linking by free radicals), both procedures were included in the program.

Small-scale laboratory screening tests were conducted to determine the final processing desired for packed-bed tests. Two commercially available HDPE materials, one selected under the initial program and a second program with higher uncross-linked heats of fusion and crystallization, were included. Initial tests uncovered another important processing variable for the gamma-irradiated material. The relatively long irradiation exposure times resulted in excess oxygen diffusion into the material with the result that pellet-to-pellet adhesion increased. Therefore, irradiation under an inert atmosphere, N₂, and under vacuum were added to the investigation.

The HDPE with the higher heats of fusion and crystallization was chosen from the screening process. An optimum dose of 10 mrad under a nitrogen atmosphere was selected. Under an air atmosphere, no satisfactory form stability from either gamma irradiation or electron-beam results was achieved. However, in a nitrogen atmosphere and at the same doses, the gamma radiation process gave superior results. Likewise, gamma irradiation in a vacuum was superior to electron-beam results at similar doses, although slightly less effective than under a nitrogen

atmosphere. Both materials experienced a reduction in heats of fusion and crystallization from the cross-linking process, but the effect did not continue to increase at higher levels of radiation as was expected. This effect is not yet fully understood.

A large sample of cross-linked pellets was produced and tested further in the UDRI thermal test unit. This packed-bed unit held 250 lb of material. The heat transfer fluid was an ethylene-glycol-based fluid. Thermal cycling was between 140 and 40°C. A series of 111 cycles of charging and discharging was conducted.

Counterflow charge/discharge was employed in a 40-run series. Good bed utilization was experienced with this mode of operation. The polyethylene material is less dense than the ethylene glycol heat transfer fluid (0.96 vs 1.13 specific gravity). Therefore, a fluidized-bed flow cannot be achieved except at impractically low flow rate. Thus, all flow modes were with an immobilized bed of pellets. Interpellet adhesion was experienced under the first-run series conditions. In an attempt to reduce this effect, bed material support screens were installed at 1-ft intervals in the bed. This modification failed to alleviate the problem although the pellets were easily broken apart and, when in a solid mass, showed little or no pressure drop over the free pellet bed.

Seventy-one runs were made with top-to-bottom flow for both heating and cooling (charging/discharging) the bed. The heat storage performance was again satisfactory. Although the pellets stuck together, a significant increase in bed pressure drop was not encountered.

Thus, further improvements, where indicated by this research, could be made in the medium. However, the initial objectives were met, and the program was complete at this stage.

2.2.2 High-temperature composite storage media (WBS 1.2.3.1)

Studies of a novel high-temperature latent heat storage medium were continued. The material consists of a composite mixture of a metallic salt, the latent heat storage component, and a higher melting temperature ceramic. The two components are mixed as finely divided powders, formed into convenient-sized pellets, and sintered to provide a storage material that can, by reason of its solid form, be used as storage media in a

packed bed while storing energy as the latent heat of the salt. The salt, when molten, is retained in the ceramic matrix by surface tension forces. The concept has been demonstrated in laboratory-scale experiments.

This material has three important advantages for combined sensible/latent heat storage. The first is the efficiency of heat transfer into and out of storage, which results from direct heat transfer between the storage material and the heat transfer fluid. The second advantage is avoidance of buildup of solid salt on heat exchanger surfaces during storage discharge. This problem often dictates the number of heat transfer tubes in a storage system. Finally, by retaining its solid properties when the salt is molten, this storage medium avoids the requirements of containing a liquid salt in a corrosion resistant vessel.

The previous year's research⁹ identified ten congruent melting compositions spanning a temperature range of 397 to 898°C and investigated five of these and three ceramic support materials. A final system consisting of 47.8 (wt %) Na_2CO_3 -52.8 (wt %) BaCO_3 with an MgO matrix was chosen for development. Various methods of fabricating pellets suitable for packed-bed, direct-contact heat exchange storage media were investigated: laboratory cold-pressing, automatic die pressing, extrusion, molten salt impregnation, and pelletizing.

An effective spray-drying process producing powders with controlled particle size and surface area was developed, and the fabrication of the chosen sodium/barium medium was optimized. Long-term pellet sensitivities to powder characteristics, pressing method, drying/densification heat duty cycle, volume fraction of salt, and heat transfer fluid chemical composition were determined. The loss mechanisms of carbonates from the composite were determined, and long-term bed stability experiments of 50 lb of laboratory-scale pellets were completed.

Thermogravimetric measurements were performed on a single 5.0-g pellet to determine its vapor loss in air. The measurements consisted of continuous weight monitoring of the sample at the test temperature under constant gas flow rate for 75 h. Gas flow rates of 100 and 200 cm^3/min and nominal temperatures of 800, 850, and 900°C were used. Weight loss rates became constant after 25 h. Results showing that the vaporization

rate of carbonate is independent of gas flow rate but dependent on the exposed pellet area are consistent with those previously observed from Na_2CO_3 melt and $\text{Na}_2\text{CO}_3/\text{MgO}$ composite. Vaporization rates determined for the pellets were 0.06 mg/h-cm^2 at 900°C and 0.002 and 0.006 mg/h-cm^2 at 800 and 850°C , respectively.

To understand better the process of salt redistribution within a storage bed, a laboratory-scale packed-bed test series was conducted. The pellet bed size was 3 in. in diameter and 180 in. high. One-inch-diam by 1-in.-high pellets were tested. The bed temperature was kept constant independent of the gas flow by a three-zone external heating system. Thus, the bed was artificially kept above the salt melt temperature at the entrance, below the salt melt temperature at the exit, and at an intermediate temperature in the middle of the bed. Five runs were made. The conditions of the tests and the bed weight loss that resulted are shown in Table 2.

Table 2. Comparison of accounted weight loss of pellets vs that estimated from chemical analysis^a

Pellet	MgO (g)	BaCO ₃ (g)	Na ₂ CO ₃ (g)	Total (g)	Loss estimated (%)	Loss accounted (%)
Pretest	46.7	25.5	27.8	100.0	0	0
116 ^b	46.7	32.8	28.7	108.2	8.2 (gain)	8.9 (gain)
218 ^b	46.7	30.4	27.0	105.8	5.8 (gain)	9.3 (gain)
225 ^c	46.7	24.5	18.5	89.7	10.3 (loss)	10.2 (loss)
245 ^c	46.7	25.4	16.0	88.1	11.9 (loss)	12.7 (loss)

^aBasis: 100 g of initial pellet, no MgO loss or migration.

^bFrom coolest or condensation zone.

^cFrom hottest or vaporization zone.

The bed weight change recorded for runs 3 through 5 are considered insignificant. The greater weight changes of the first two runs result from the reaction of the salt with the bed Inconel liner rather than from vapor carryout of the bed. After sufficient time for the carbonates to

equalibrate with the Inconel, low overall weight changes were recorded as shown.

However, there is a salt redistribution in the bed. Salt migration is continuous from the bed zone, which ranged from above melt temperature to the zone that was kept below melt temperature. The longer test time of run 4 produced a greater redistribution than that of the shorter run 3. The former showed 33.84 g lost from the vaporization zone and 29.27 g gained by the condensation zone; the latter showed a corresponding 18.88-g loss and 20.71-g gain. Run 5, a uniform-bed temperature test with no flow through the bed, resulted in a slow redistribution of the salt toward the initial uniform pellet condition. Such a redistribution would also be expected from an actual bed designed for counterflow charge/discharge.

Recognizing that more flexibility in storage temperature range is desirable while retaining the advantage of the latent heat contribution, preliminary work toward a second lower-temperature series of composites was initiated. A lower temperature range (500°C) allows the advantage of mild steel ductwork over the higher-temperature storage system. Table 3 lists the characteristics of some candidate salts that were considered. Two, NaNO_3 and NaOH , show material-cost and storage-density advantages over the others. The nitrate was selected for initial testing because it

Table 3. Salts for low-temperature TES

Salt	Melting point (°C)	ΔH_f (cal/g)	Cost (\$/kg)	Density (g/cm ³)	Cost (\$/Mcal)	Storage density (cal/cm ³)
LiNO_3						
NaNO_3	306	41	0.17	2.26	4.10	92.7
KNO_3	334	12	0.53	2.11	44.20	25
LiOH	471	208	7.45	1.46	35.79	304
NaOH	299 ^a 323	43 40	0.82	2.13	18.96	91.6
KOH	243 ^a 306	28 37	1.04	2.04	36.99	57.12

^aSolid phase transition.

was more stable and had the lower cost. Pellets of NaNO_3/MgO were formed by using techniques developed for the carbonates. Tests of stability in 350 and 450°C air were conducted. The results of these preliminary tests indicate good stability at 350°C (Fig. 5). The weight loss at 450°C is suspected to result from conversion of nitrate to nitrite with a loss of weight in oxygen. The results, however, are promising, and further development and testing of this material will be included in the program.

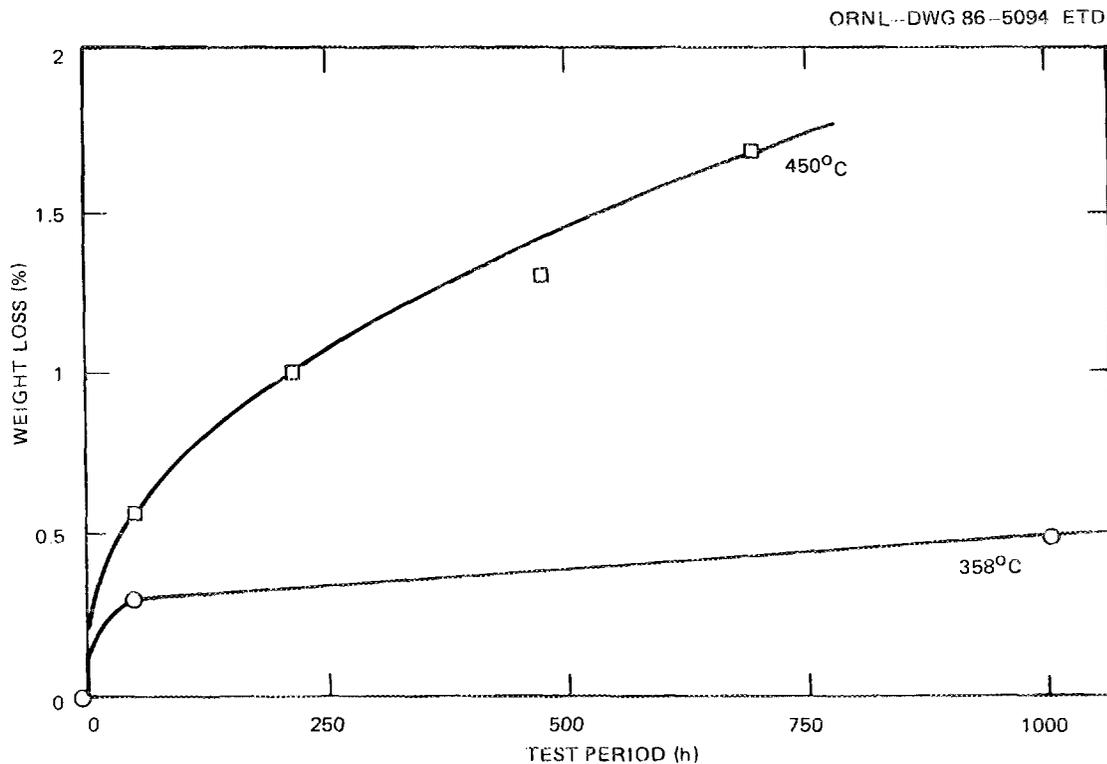


Fig. 5. Weight loss of NaNO_3/MgO pellets.

2.2.3 Encapsulation of metallic eutectics (WPS 1.2.3.2)

Energy storage in the latent heat of fusion of metals would provide a favorably high storage density in high-temperature applications.¹⁰⁻¹³ The heat storage density of a eutectic alloy of silicon/aluminum is 517 kJ/kg. Salts have storage densities based on latent heat of ~200 kJ/kg, where sensible storage densities of high-temperature materials are on the

order of 1 to 2 kJ/kg-°C. Compositions, melt temperature, and storage density of silicon eutectic alloys are shown in Table 4.

Containment of a molten metal, however, poses severe requirements on the strength and corrosion resistance of containment materials. This project was aimed at alleviating most of those requirements through encapsulation of the alloy in a nonmelting, corrosion-resistant shell.¹⁴⁻¹⁷ Such a storage medium would allow a packed-bed, direct-contact heat exchange storage system. The aluminum-silicon alloy was chosen by these studies.

A pure silicon shell encapsulating the alloy would provide an ideal storage medium because of the high melting temperature and corrosion resistivity of the silicon. The initial effort in producing such a shell was a scheme of "self-encapsulation." It was hypothesized that a shot-making process, in which the alloy in the initial molten state was silicon rich, might result in the required product. Controlled cooling of spherical drops of the hypereutectic in a salt column would allow

Table 4. Properties of some eutectic systems

Alloy	Eutectic reaction	Eutectic temperature (°C)	Eutectic composition (wt % Si)	Heat storage capacity (kJ/kg) (calculated)
V-Si	VSi ₂ /Si	1400	95	1921
Be-Si		1090	61	1812
Zr-Si	ZrSi ₂ /Si	1360	75	1685
Ti-Si	TiSi ₂ /Si	1330	78	1570
Cr-Si	CrSi ₂ /Si	1320	75	1515
Mg-Si	Mg ₂ Si/Si	950	57	1212
Ca-Si	CaSi ₂ /Si	1023	61.4	1111
Mn-Si	MnSi ₂ /Si	1142	50.5	1090
Ni-Si	NiSi/NiSi ₂	966	38	609
Cu-Si	Cu ₃ Si/Si	802	15.8	422
Al-Si		577	12	571

precipitation of silicon at the cooling drop surface as the alloy composition followed the aluminum-silicon phase diagram liquidus line. Work with ternary alloys, such as the aluminum-magnesium-silicon system, has demonstrated that encapsulating shells of other primary products, such as Mg_2Si , can be achieved via solidification processing.

Two other methods for producing silicon-encapsulated aluminum-silicon alloy shot were considered and developed as part of this project: (1) aluminothermic reaction coating and (2) packed-bed cementation siliconizing. In the aluminothermic reaction coating method, the liquid aluminum-silicon alloy is reacted with solid silica (SiO_2) to form reaction products consisting of solid alumina (Al_2O_3) and silicon. This technique has been used to produce solid shells up to 3 mm thick.

Pack cementation siliconizing is a deposition process, similar to pack cementation carburization, in which silicon is transferred via vapor transport from the bed components to the product to be coated. Appropriate pack compositions, reaction times, and temperatures have been defined for the pack cementation siliconizing method to obtain encapsulating silicon shells with thicknesses up to 0.1 mm on eutectic and hypereutectic aluminum-silicon alloys. The best pack cementation siliconization practice developed to date utilizes a pack consisting of SiO_2 (73%), Si (25%), and a mixed chloride salt ($NH_4Cl/AlCl_3 = 2/1$) (2%) in a flowing stream of forming gas (95% N_2 -5% H_2) at 600°C for 8 h with a rotating bed arrangement.

The thermal properties (i.e., specific heat; latent heat of fusion; and ability to withstand thermal cycling about the eutectic temperature, 577°C) of shot produced with the various techniques described above were investigated. In general, the thermal properties of the aluminum-silicon alloys prepared in the program were in keeping with those presented in the technical literature.¹ Most of the silicon-encapsulated shot that were subjected to thermal cycling at about the eutectic temperature exhibited exudations (i.e., cracking of the silicon shell and bleeding of the eutectic liquid) during the first several thermal cycles. Pack cementation siliconized shot produced during the latter part of this program withstood thermal cycling without exudations.

Of the techniques evaluated to produce silicon-encapsulated Al-Si shot (solidification in fused salts, aluminothermic reduction, and pack cementation siliconization), pack cementation siliconization holds the most promise for producing integral silicon coatings on these binary alloys. Pack cementation siliconized-aluminum-30% silicon shot have an experimentally determined heat of fusion value of 81 cal/g and an effective specific heat capacity of 0.58 cal/g K, which makes them attractive phase-change heat storage materials. Although the pack cementation siliconized shot have fragile silicon shells, they withstood several thermal cycles near the eutectic temperature of 577°C without fracturing. Modeling of heat storage systems using such shot clearly indicates that such systems offer a combination of fast thermal response and near isothermal heat exchanger capability.

Although the concept of a corrosion-resistant encapsulated shot containing a large energy storage metallic phase-change material continues to hold promise, further work is required to fully develop this technology.

2.3 Material Properties

2.3.1 Dual-temperature storage in complex compounds (WBS 1.3.1.1)

Complex compounds, as well as dual-temperature heat and cool storage, are being studied for cool storage.¹⁸ These compounds consist of a metal-inorganic salt as the central atom and a ligand — such as NH₃, H₂O, or methanol — that is coordinated around the salt atom. The most common complexes are hydrates and ammoniates with water and ammonia as the ligand(s). The thermochemical reaction between the solid salt and the gaseous ligand cycles from an endothermic phase to an exothermic phase. Exothermically, the heat evolution during the adsorption of the ligand gas is used for heating purposes. The endothermic desorption reaction yields the heat rejection means or cooling cycle.

A computerized data base was generated to provide preliminary complex characteristics for selection of systems for detailed study. Several promising salts selected were experimentally investigated with

ammonia as the ligand. Coordination steps were characterized with temperature, vapor pressure, and reaction rates; energy storage density, chemical stability, and the physical condition of the absorbent were also determined.

2.3.2 Heats of solution for TES (WBS 1.3.1.2)

A two-phase program was initiated to study the application of heats of mixing to dual-temperature storage.^{19,20} The first phase was aimed at the identification of potential liquid-liquid and liquid-solid systems. Appropriate systems are those that exhibit large differences in the heat of mixing over a narrow temperature range. A second phase will consist of experimental measurements of thermodynamic properties of several selected systems and the improvement of analytical procedures developed in the first phase from the experimental results.

Efforts have concentrated on systems with upper critical solution temperatures in the range of 40 to 70°C for heat storage with heat pump systems. Mixtures for which both phase equilibrium and heats of mixing data are available have been investigated to establish procedures for the estimation of heats of mixing and energy storage capabilities of the systems. A reliable analytical procedure that utilizes the van Laar model for activity coefficients, with the temperature dependence of the activity coefficients established from phase data at temperatures removed from the critical region, has been developed.

Initial aqueous systems considered, including propylene carbonate-water and succinonitrile-water, indicate moderate changes in the heat of mixing in the critical region. Several nonaqueous systems have been determined that have large changes in the equilibrium phase compositions, and corresponding large potential aqueous systems with these properties, including three-component mixtures, are being identified for further experimental study. Analytical procedures are also being extended to aqueous systems with components, such as amines and substituted pyridines, with lower critical solution temperatures in the required range.

2.3.3 Silicon/aluminum-silicon diffusion studies (WBS 1.3.2.1)

In evaluating the potential of silicon encapsulated shot of Al-Si eutectic for use in direct-contact phase-change heat storage, a key question is: "Will an integral silicon shell remain structurally stable during repeated cycling of the shot through the eutectic temperature?" The Al-Si phase diagram indicates that, provided the upper temperature of the cycle is sufficiently far from the liquidus temperature, the equilibrium ratio of solid silicon to liquid alloy is high enough so that the average shell thickness could retain the liquid alloy. However, the question of stability arises from several factors. One is the mechanical strength of the shell subjected to the stress imposed by volume expansion of the alloy on melting. It may be possible to compensate for this by increasing the shell thickness or by incorporation of the voids. Perhaps a more fundamental factor is the stability of the silicon shell to redistribution during repeated melting and crystallization, which could lead to disintegration. A number of mechanisms could provide the driving force for such redistribution:

1. A temperature gradient in a fixed direction across a shot, which, even though small, could lead to preferential deposition of silicon crystals on the cool side, with thinning of the shell on the hot side.
2. Dendritic growth of primary silicon crystals from supercooled liquid, which could lead to entrapment of alloy and migration of aluminum from the interior of the shot to the surface.
3. The relatively high diffusion coefficient of silicon in aluminum, which provides a path, even isothermally in the solid state, for interdiffusion of silicon and aluminum, with gradual redistribution.

Thus, although the equilibrium phase relationships show the possibility of an integral silicon shell, the equilibrium is dynamic, not static, and the distribution of the silicon and aluminum phases must be considered.

An experiment has been initiated to test the integrity of silicon shells as containers for Al-Si eutectic. It is intended to be independent of methods used to fabricate self-encapsulated shot and to provide

basic information on the inherent stability of silicon in contact with Al-Si eutectic to migration under conditions of temperature cycling through the eutectic temperature but below the hypereutectic liquidus temperature.

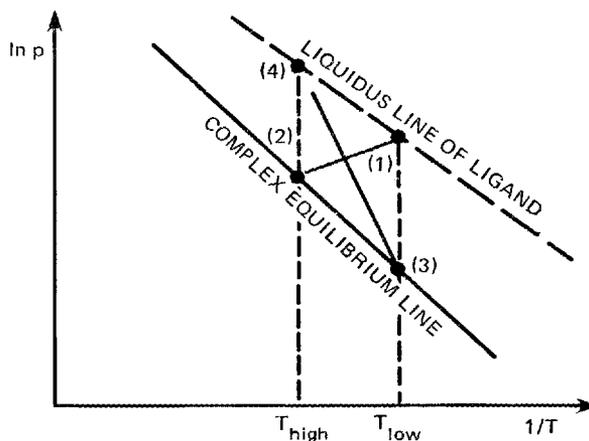
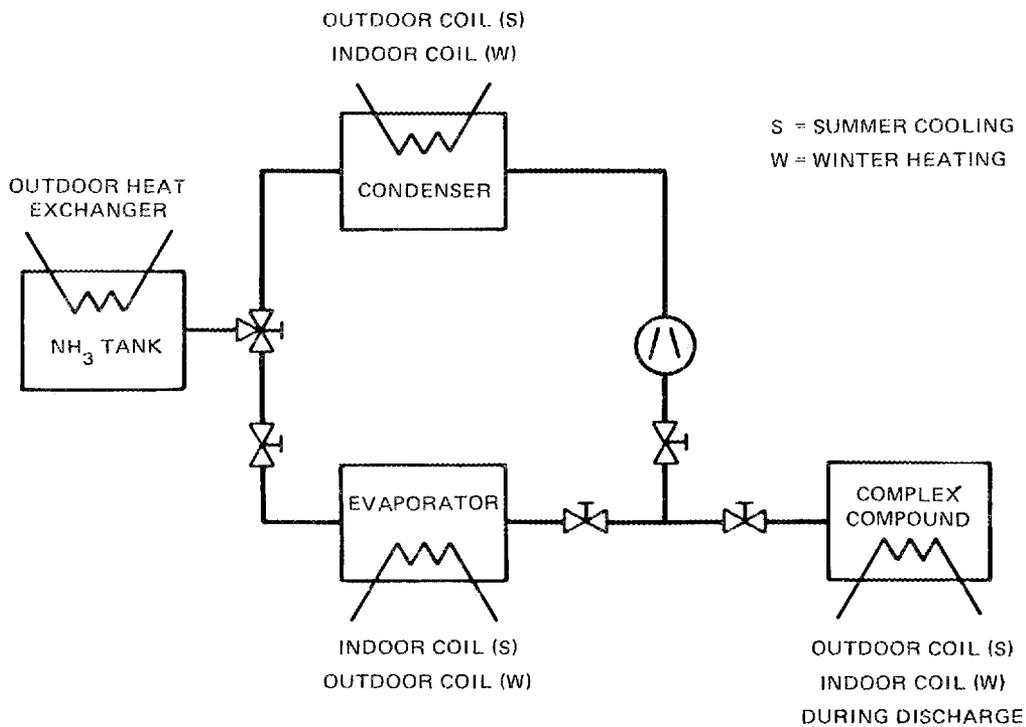
Polycrystalline shapes, such as plates and rods (or cups), will be immersed in (or filled with) Al-Si eutectic, maintained at temperatures between 550 and 650°C, and subjected to physical and metallographic examination for dimensional stability. Two sets of cycling conditions are planned: one is the temperature cycling of the samples between 550 and 650°C; in the second, the samples will be maintained at various nearly constant temperatures between the eutectic temperature (577°C) and 650°C before examination. The latter isothermal experiments would measure the inherent rate of redistribution of silicon and alloy resulting from the dynamic equilibrium even in the absence of a significant temperature gradient. The former temperature cycling experiments are more complex because some of the solid silicon must dissolve in the liquid alloy during the heating part of the cycle and then recrystallize on the silicon surface during the cooling part of the cycle. These conditions simulate more closely the behavior of a silicon shell during cycling of encapsulated shot, although the stresses induced by volume expansion may be smaller than in spherical shot.

For analysis, the cooled samples will be sectioned, polished, and examined optically and by energy-dispersive X-ray fluorescence in a scanning electron microscope (SEM-EDX). Electron dot maps of a section will be used to determine the distribution of silicon and aluminum crystallites and the extent of degradation that has occurred.

Equipment and materials have been assembled, and the experimental program has been initiated.

2.4 Heat Pump Complex Compound Storage (WBS 2.1.1)

From the experimental data generated under WBS 1.3.1.1, the most promising complexing reaction was chosen for cycle study. The storage/heat pump system chosen for further development is a monovalent sodium bromide-ammonia system. Its operation is depicted in Fig. 6. During the heating season, off-peak charging of storage is by desorption of NH_3



(1) → (2) DISCHARGING = HEATING WITH COMPLEX COMPOUND AND COOLING WITH LIGAND
 (3) → (4) OFF-PEAK CHARGING

Fig. 6. Monovalent storage system.

through compressor operation. The building is heated by the condenser coil as in a conventional heat pump system. Ammonia flows from the storage vessel through the evaporator coil to the salt storage vessel. Summer off-peak charging is similar to building cooling by the desorption process with heat rejection by the condenser coil. On-peak cooling is by the discharge of storage through the evaporator coil.

The design goals are an energy flow of 100 W/kg of salt and a storage capacity of 6 h at 8 to 10 kW. Results show the desorption process fulfills this requirement, and the adsorption process fulfills 80% of the requirement. Further optimization of the adsorption rates may be possible with rate-enhancing additives to the salt and/or more efficient complex heat exchanger design.

Ammonia sorption rates as a function of differential pressure (ligand pressure minus complex equilibrium pressure) were determined for salt layer thicknesses of 1, 5, and 8 mm. The desorption temperature was held between 2 and 3°C; the adsorption temperature was held between 40 and 41°C. The thinnest layer is highly sensitive to pressure. Figure 7 shows the desorption data, and Fig. 8 shows the adsorption data. These data were fit by the Elovich equation:

$$d\theta/dt = a \exp(-b\theta) ,$$

where θ is the degree of absorption and a and b are constants. The resulting expressions were then available to the computer for simulation of the process.

Desorption rates were found to be sensitive to differential pressure and adequate for heat pump applications. Absorption rates were shown to be lower and not greatly influenced by differential pressure. Two additives, LiNO_3 and CaCl_2 , which were expected to promote increased diffusion into the salt, were investigated. Both additives showed promise. Addition of 7 to 10% mass fracture of LiNO_3 resulted in an increase in adsorption reactions of 25% after 30 min. The reduced desorption rates found can be compensated by increased pressure. Partial liquifaction of the complex compound was observed, and this must be addressed in heat exchanger design.

The addition of CaCl_2 , which has a high swell factor, produced a porous complex favorable to high diffusion rates. However, the salt

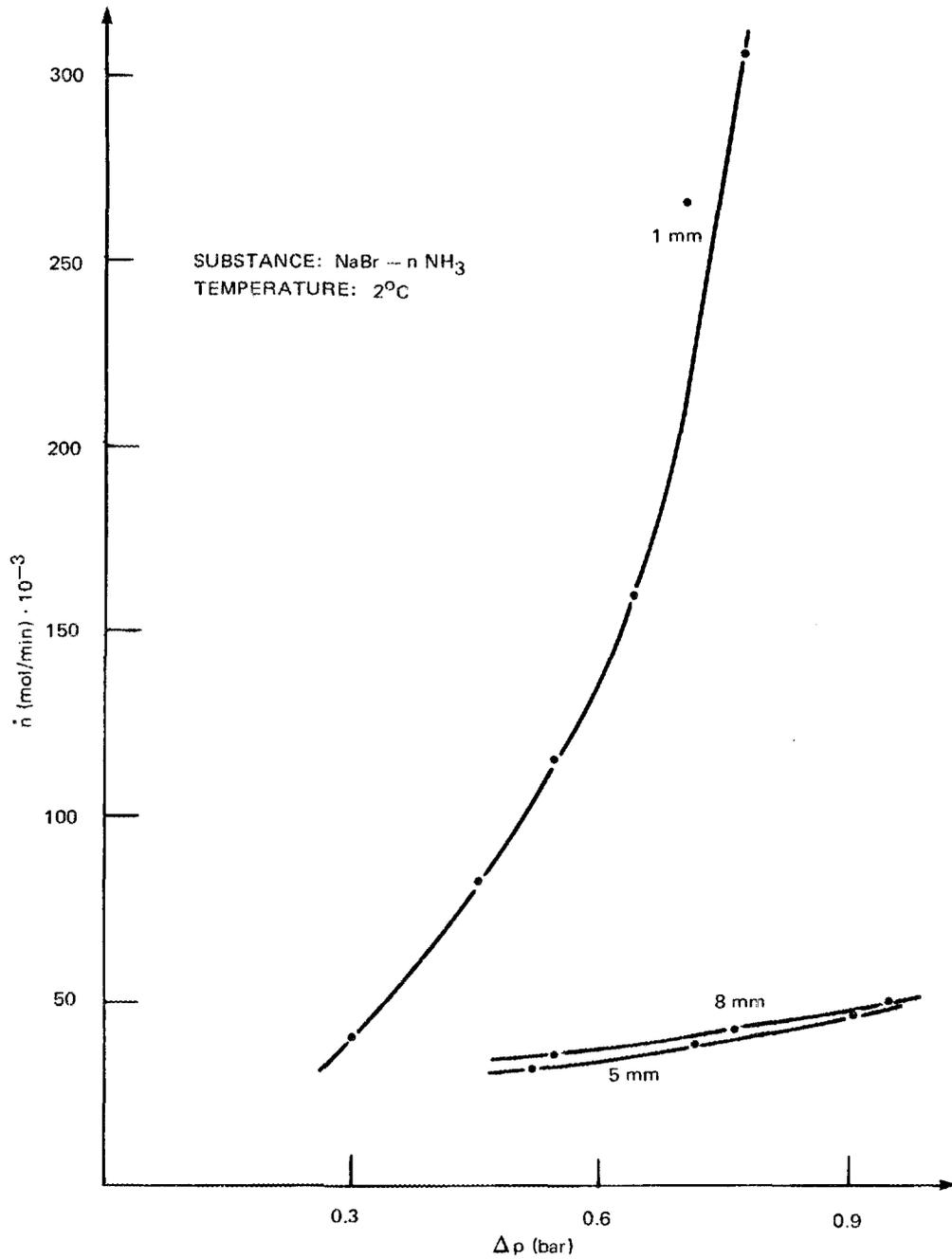


Fig. 7. Desorption rate vs differential pressure.

layer tested with this additive was too thin to show a significant improvement in performance.

Laboratory tests of input/output heat and power were made in the subscale prototype unit depicted in Fig. 9. The solid salt is retained

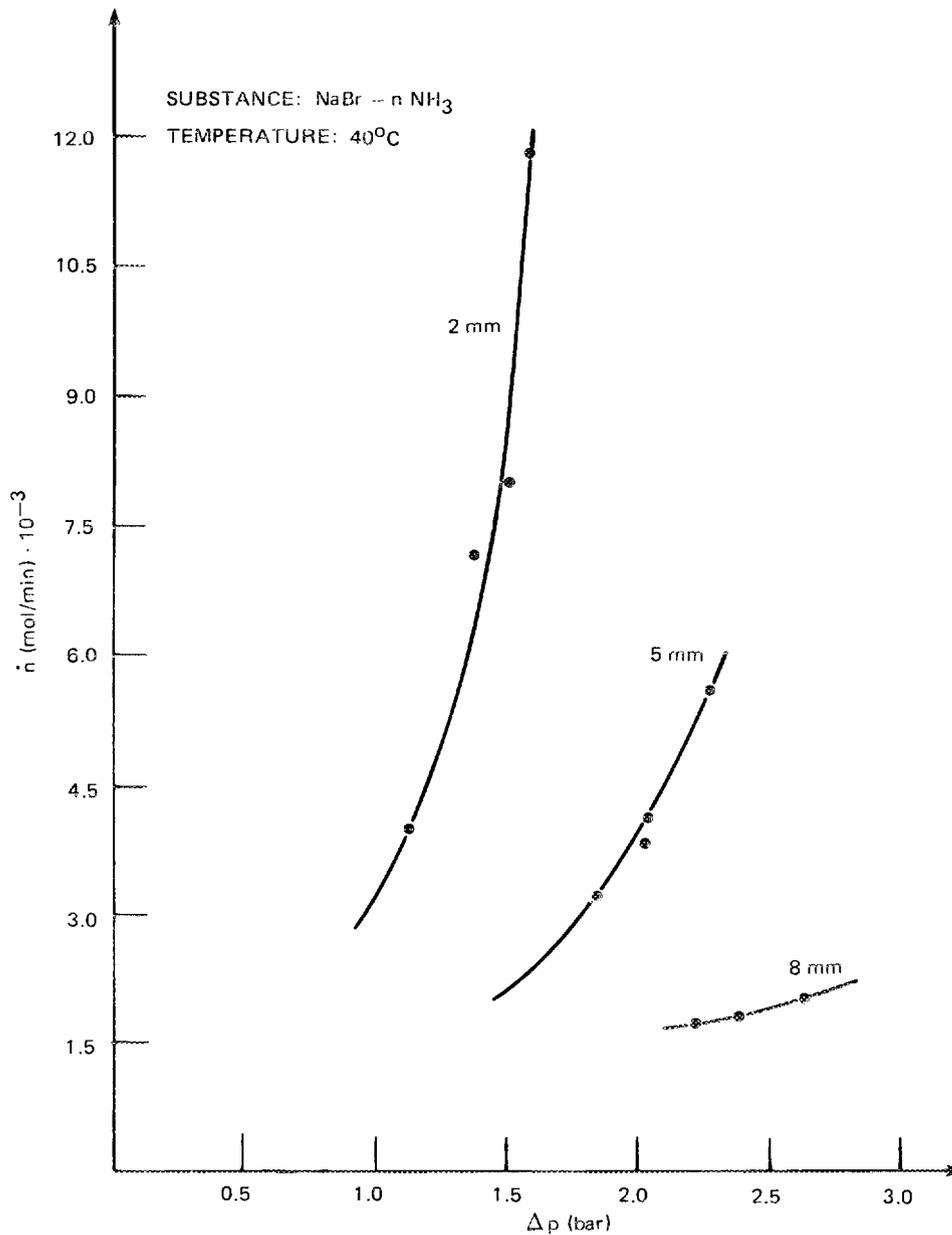


Fig. 8. Adsorption rate vs differential pressure.

on a tray-type heat exchanger (Fig. 10). A final heat exchanger configuration included perforated pipes into the salt layer to improve ammonia distribution into the salt and fins to enhance heat transfer in the solid salt.

Tests were conducted at loads from 40 to 70 W/kg and with various salt layer thicknesses. Although the modifications of the heat exchanger

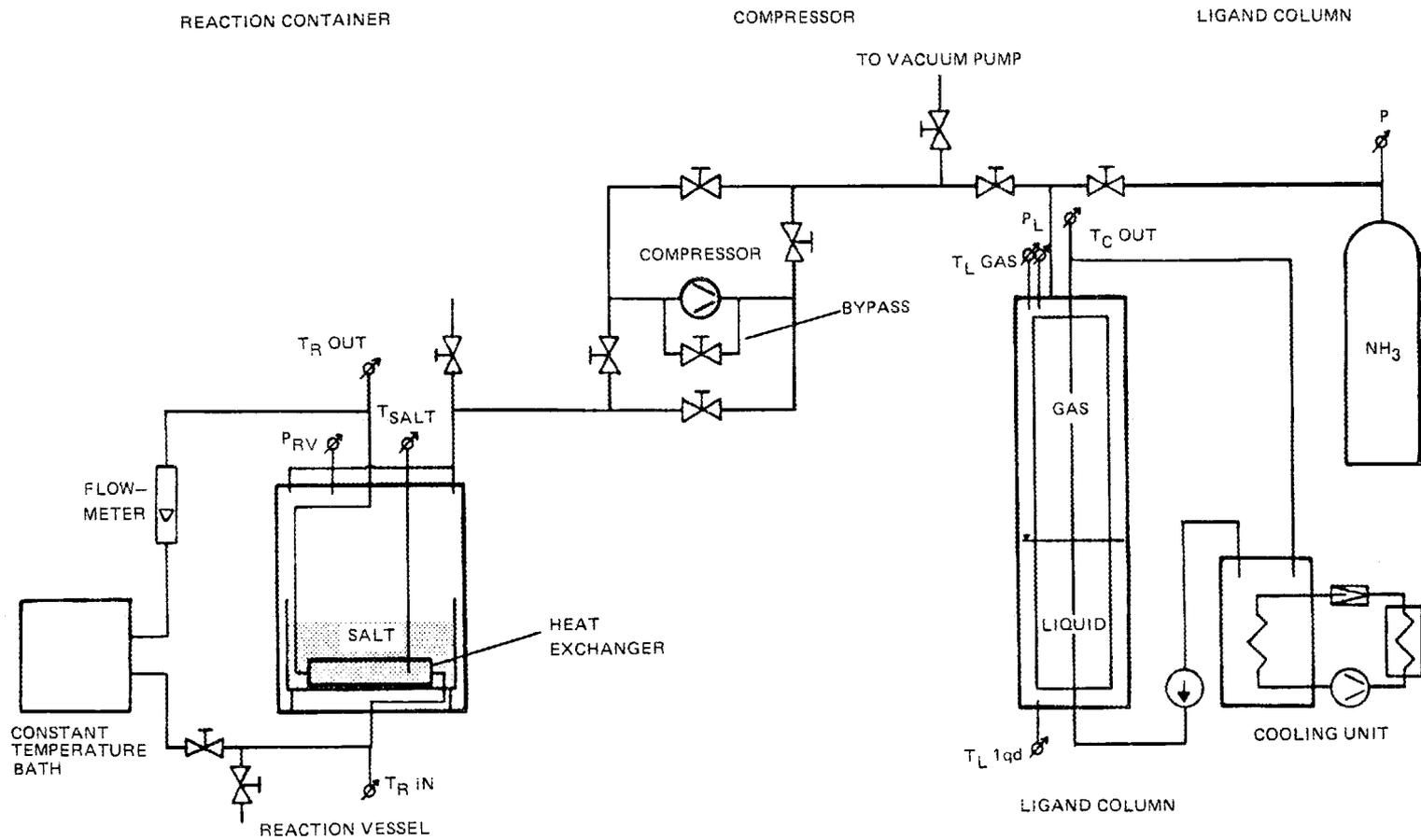


Fig. 9. Schematic of subscale prototype.

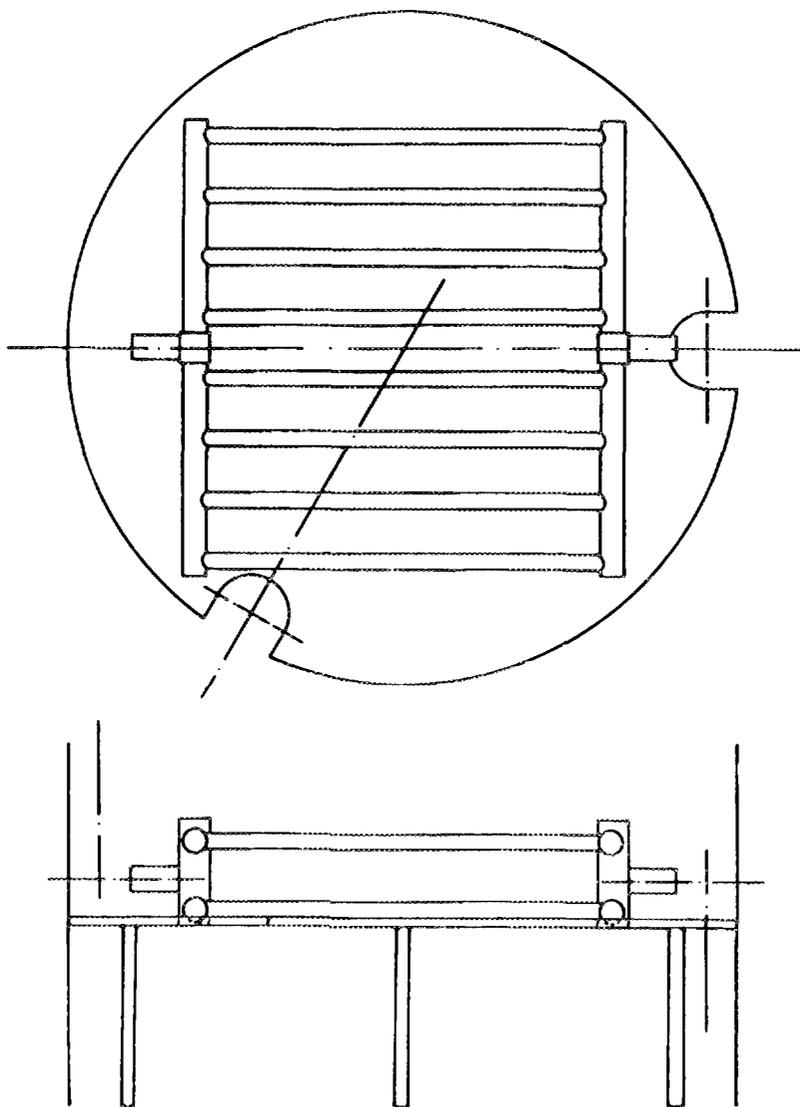


Fig. 10. Heat exchanger array.

increased the energy densities achieved in test by 50% over the original configuration, the design goal for adsorption has not yet been achieved. Further heat exchanger modifications will be required to produce the required adsorption performance.

Three systems were modeled by means of computer simulation: (1) a conventional compression heat pump operating with R-22, (2) a heat pump/storage system with one complex compound, and (3) a system studied in the initial phase of the program consisting of a dual complex compound heat pump.

Calculations were made for summer and winter operation. Eight outdoor temperatures from 28 to 42°C and an indoor coil temperature of 5°C were assumed for the summer cycle. The winter cycle calculations were of eight outdoor temperatures ranging from 0 to 14°C with an indoor coil temperature of 42°C. The cooling and heating demands were set at 10 kW, and the mass flow was calculated according to the heat exchanger characteristics, that is, evaporation, condensation, or reaction. A single-stage compressor was used for the R-22 cycle because the compression ratio did not exceed 4.5. The complex compound concepts used a two-stage compressor.

Figure 11 shows the heat pump operating efficiency of the NaBr-NH₃ system in comparison with the R-22 cycle for the heating cycle. Summer

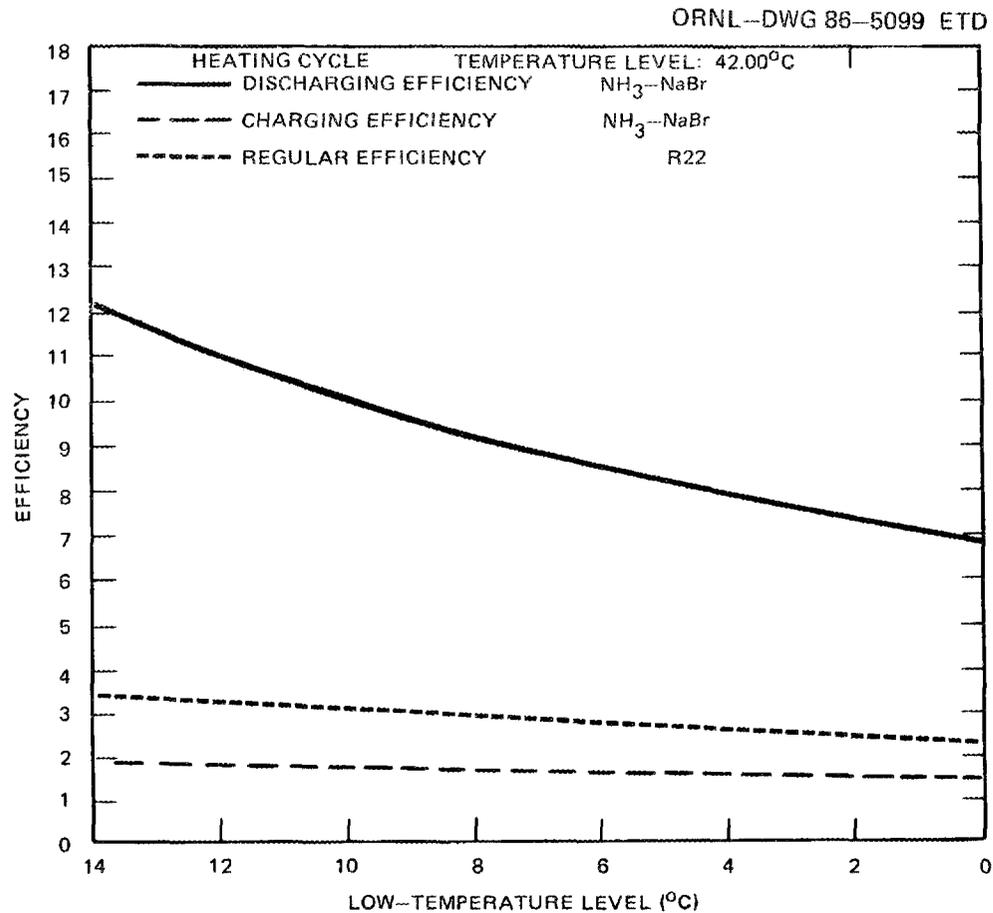


Fig. 11. Comparison of efficiencies for NaBr and R-22 in the heating cycle.

cooling results are shown in Fig. 12. Above 42°C, even the charging process is seen to be more efficient for the complexing storage system.

The technical performance of the heat pump system with storage in a complex compound has been found to be favorable compared with a conventional heat pump without storage. Initial economic studies are also favorable. Several technical issues, for example, the requirement for an oil-free compressor, need to be addressed. A 10-kW prototype system is required to further study this concept and to develop the necessary system components.

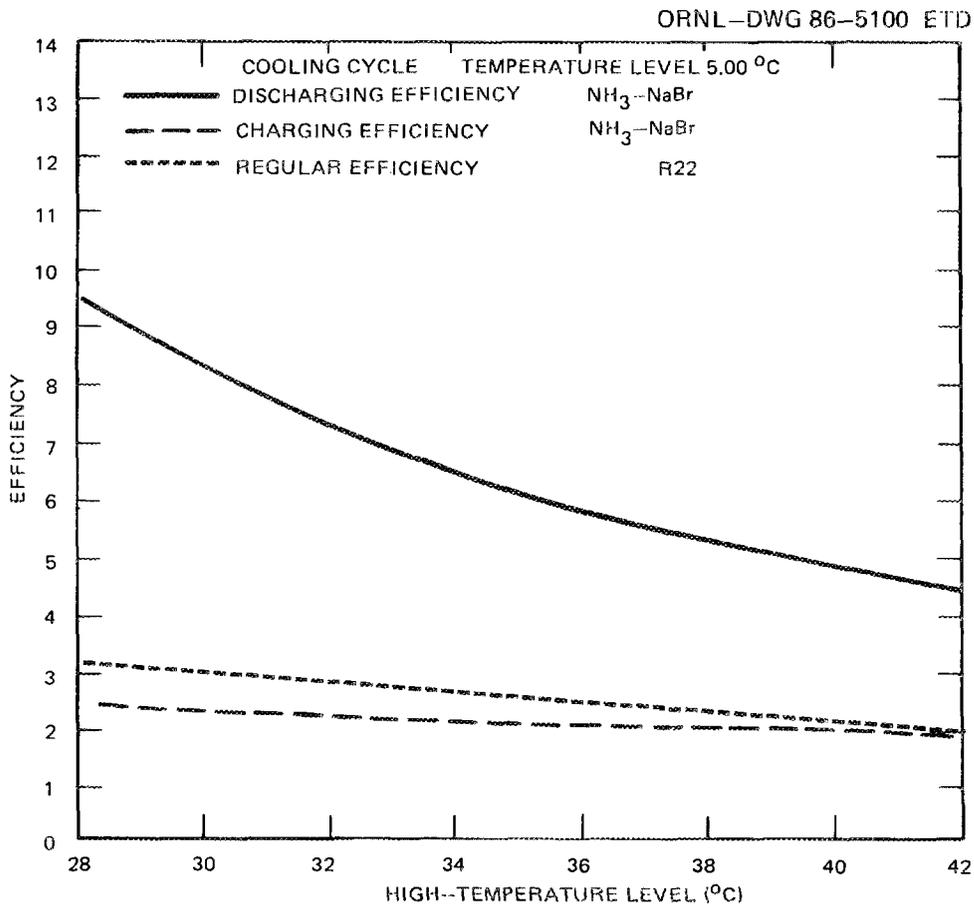


Fig. 12. Comparison of efficiencies for NaBr and R-22 in the cooling cycle.

2.5 Application of Composite Latent Heat Storage (WBS 2.2.3.1)

The economics of a TES waste heat recovery system utilizing composite storage media for periodic kiln were investigated. The industry initially chosen under this program for application of TES to energy recovery was SIC-32, the brick and ceramic industry. Therefore, the present analysis was based on a representative periodic kiln brick plant. The study was of a five-kiln, four-TES unit operation with a startup of one 72-h kiln every 24 h. Thus, quasi-continuous plant operation was simulated.

The individual kiln cycle is represented by the kiln gas outlet temperature variation with time (Fig. 13). During heatup (28 h) and soak (20 h), the kiln exhaust is combustion gas that cannot be utilized directly but must either yield its energy to clean air through a heat exchanger for on-line use or to charging a heat storage unit for later discharge by clean air. The cooling part of the cycle (24 h) discharges clean air that can be either stored or used directly for drying. Heat recovered from the heatup and soak part of the cycle is used for combustion air preheat with the excess used for drying.

The study was based on the use of 200×10^9 Btu/year-kiln and a fuel cost of \$5/million Btu. Composite materials for two salt melt temperatures are presently under development. Therefore, two each of the TES units in the plant studied are high- and low-temperature storage units. Specifically, the high-temperature units are 830°C, and the low-temperature units are 630°C. To generalize the results of the study, a series of composite media with different melting temperatures were assumed. The values used are shown in Table 5.

Storage in sensible heat only, representing use of MgO, was also modeled. Thus, the advantage of sensible heat storage can be determined separately from the additional advantage of latent heat storage media represented by the composite material under development.

Two TES unit cycle times, 20 and 60 min, were simulated. The plant operation time simulated was 24 h, the heat load repetition rate. Heat supplied directly from kiln cooldown, that is, without being stored and

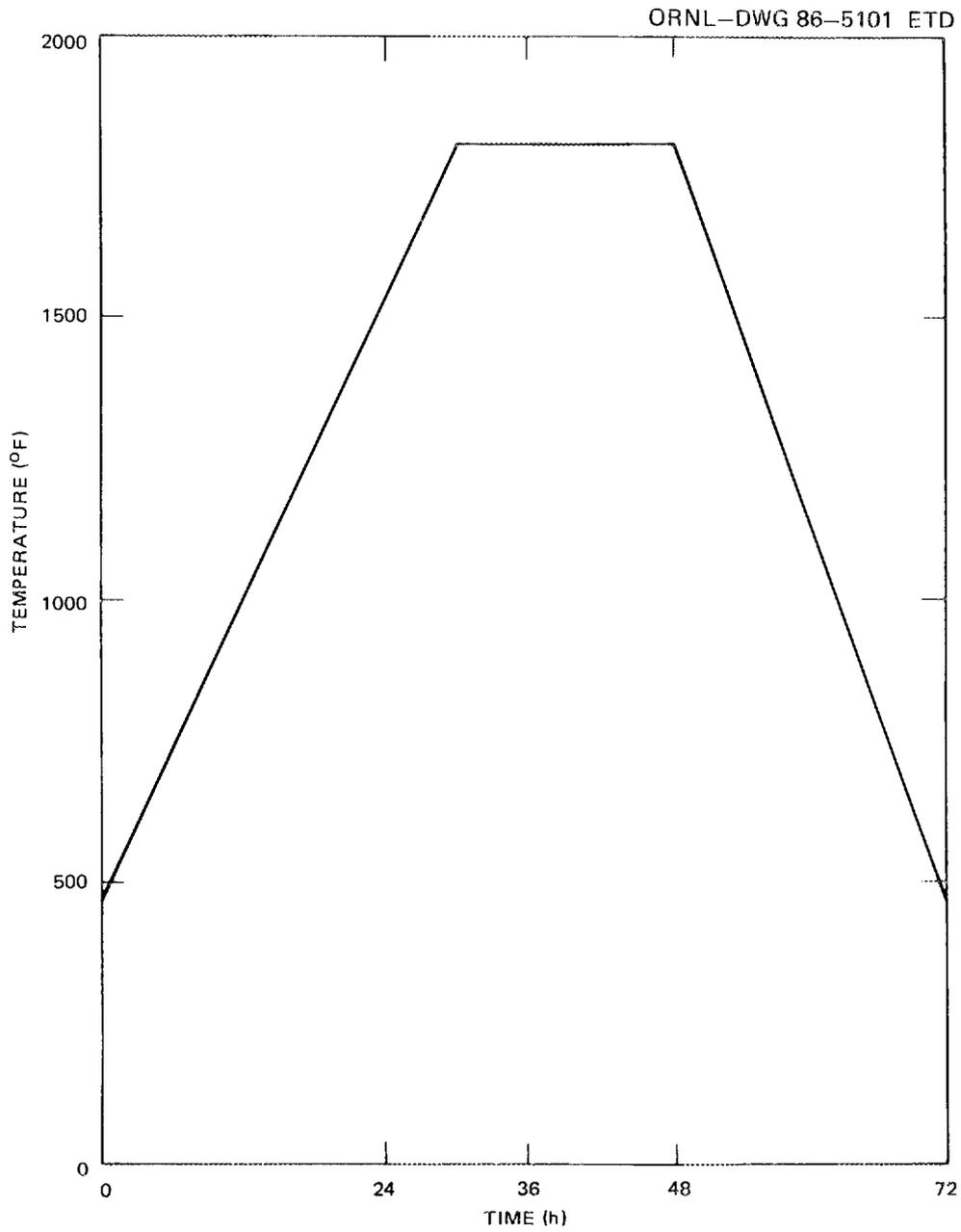


Fig. 13. Kiln gas outlet temperature.

Table 5. Multiple media melting temperatures

TES unit	Melting temperature (°C)		
	Zone A	Zone B	Zone C
High-temperature bed	815	704	576
Low-temperature bed	593	537	482

through storage from kiln heatup and soak, was calculated as a function of storage system size. The effectiveness of storage, the ratio of heat delivered through storage to that which is theoretically available, was determined, and a comparison of storage volume between MgO and a composite was made at 99% effectiveness. The results for full-day simulation, as well as the final storage cycle, are shown in Table 6 for both TES cycle times.

The advantage of TES in heat recovery and representative results from the study are shown in Table 7. All of the drying and combustion air preheat requirements are supplied by recovered kiln exhaust heat.

Table 6. Reduction in material required by using composite material at 99% storage effectiveness

Media	Cycle time (min)	Storage volume (ft ³)		Savings (%)
		Full day	Final cycle	
MgO	20	663		
	20		787	
	60	1320		
	60		2340	
Composite	20	586		11.6
	20		696	11.6
	60	1064		19.4
	60		1260	46.2

Table 7. Storage material required for maximum heat recovery full-day performance, 20-min cycle

Media	Heat recovered ^a directly	MBtu/% from storage	Storage value (ft ³)	Total savings at \$4/MBtu
MgO	182.1/69.5	79.7/30.4	2340	1047
Composite	182.1/69.5	79.9/30.5	1440	1048

^aHeat required 262.0 MBtu.

The amounts directly used from cooldown and through storage and reuse are shown. At 99% storage effectiveness, the advantage of the composite over sensible media is seen by the 40% reduction in storage volume or storage material.

2.6 Validation of Computer Code PCMSOL

The development of a passive solar TES concept of a heat storage wallboard was continued with tests of representative panels and comparison of test results with computer modeling of the system.²¹ Plastic wall panels filled with latent heat storage material can conceptually replace conventional wallboard, thus spreading the heat storage function over a large area in a passive solar room. Previous tests of several plastic containment materials and several storage media indicated the feasibility of the concept.²² Therefore, tests of full-scale panels in a solar test chamber were conducted, and, to allow extrapolation of experimental results to a wide range of climates and allow seasonal performance determinations, the ORNL computer code that simulates passive solar latent heat storage was validated.

Validation of PCMSOL²³ was accomplished both by analytical and experimental means. The model was divided into the following submodels for this purpose.

Exterior flux on building. This is a computer code grouping that calculates solar geometry, as well as beam and diffuse solar fluxes incident on the outside of the passive solar building. It predicts beam and

diffuse flux incident on the window from the solar azimuth and elevation. The effect of ambient air temperature is also part of this grouping.

Because the code is to be used for seasonal simulations, the incident flux model is designed to use either measured or typical meteorological year (TMY) data containing direct and diffuse fluxes on the south-facing wall. The ambient temperature is also assumed to be measured or available from TMY data.

Flux incident on interior walls. This model predicts how much of the flux on the window is transmitted, determines where it strikes the interior surfaces, and computes how much is absorbed or reflected.

The transmission through the window material is calculated by using the characteristic glazing transmission or the transmissivity at normal incidence and a factor that accounts for the effect of incidence angle. The total direct flux entering the chamber is calculated from the total direct beam on the south-facing wall, the window transmissivity, the window area, and the azimuth and elevation. Each interior wall of the chamber is divided into smaller elements. The direct entering flux is allocated between the elements of each wall upon which the flux impinges, assuming the elements to be small enough that the flux at the element center is constant over the entire element.

The total diffuse flux entering the chamber is calculated from the diffuse flux incident on the south-facing wall, the window area, and the glazing transmission. The total diffuse flux entering the chamber also must be partitioned between each of the wall elements. This is done by assuming a uniform emitting sky and no reflection from the ground.

Assuming no PCM or thermal mass storage in the floor, a reflective floor is assumed. To account for this, the floor is allowed to be reflective with the degree of specularly an input.

The reflective diffuse flux from the wall is distributed to all other internal surfaces in direct proportion to the ratio of surface area of each element to the total surface area of all walls, floor, or ceiling, except the surface where the reflection originated. This results in only a single diffuse reflection after which all reflected energy is absorbed. Any reflected energy that strikes the window is assumed to pass through.

The total energy absorbed by each interior surface element is the sum of directly impinging beam and diffuse fluxes, the specularly reflected beam, the diffusely reflected beam and the diffuse fluxes, and the portion of specularly reflected beam flux not absorbed by the first wall it strikes.

Comparisons of solar flux measurements in a test chamber with the flux model were used to validate this submodel before incorporation in the code. Figure 14 is a view of the test cell looking down on the floor. It shows the location of calorimeters used in the flux model validation tests. A set of tests was run with all interior surfaces coated with 95% absorbing paint to negate the effects of reflection. Thus, the flux at any point can be assumed to be from that passed by the glazing. Typical clear-day data where direct flux dominates is shown in Fig. 15. Numbers above the data points correspond to the calorimeters at the center of the elements of the same number in Fig. 14. Good agreement is seen between the measured data and model generated fluxes.

Typical cloudy-day data where diffuse flux dominates are shown in Fig. 16. Again, the comparison between prediction and test data is good.

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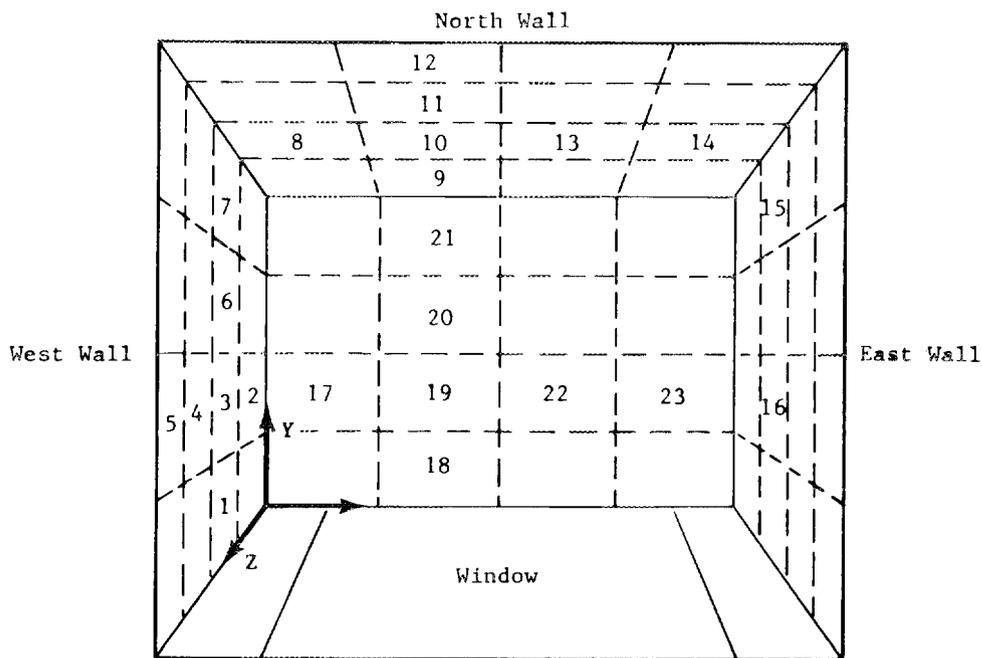


Fig. 14. Instrumentation matrix for interior surfaces.

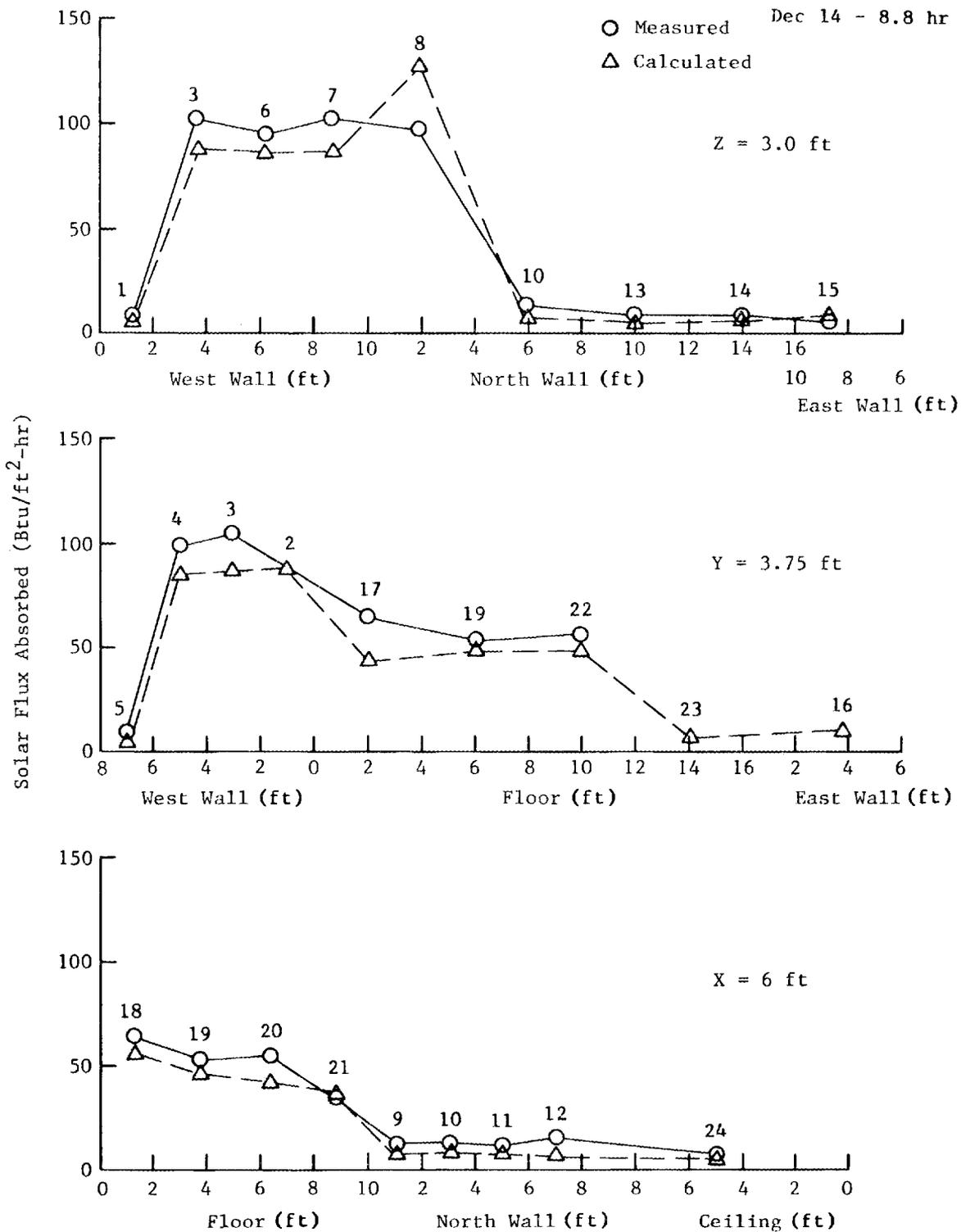


Fig. 15. Interior wall fluxes dominated by direct incident beam radiation.

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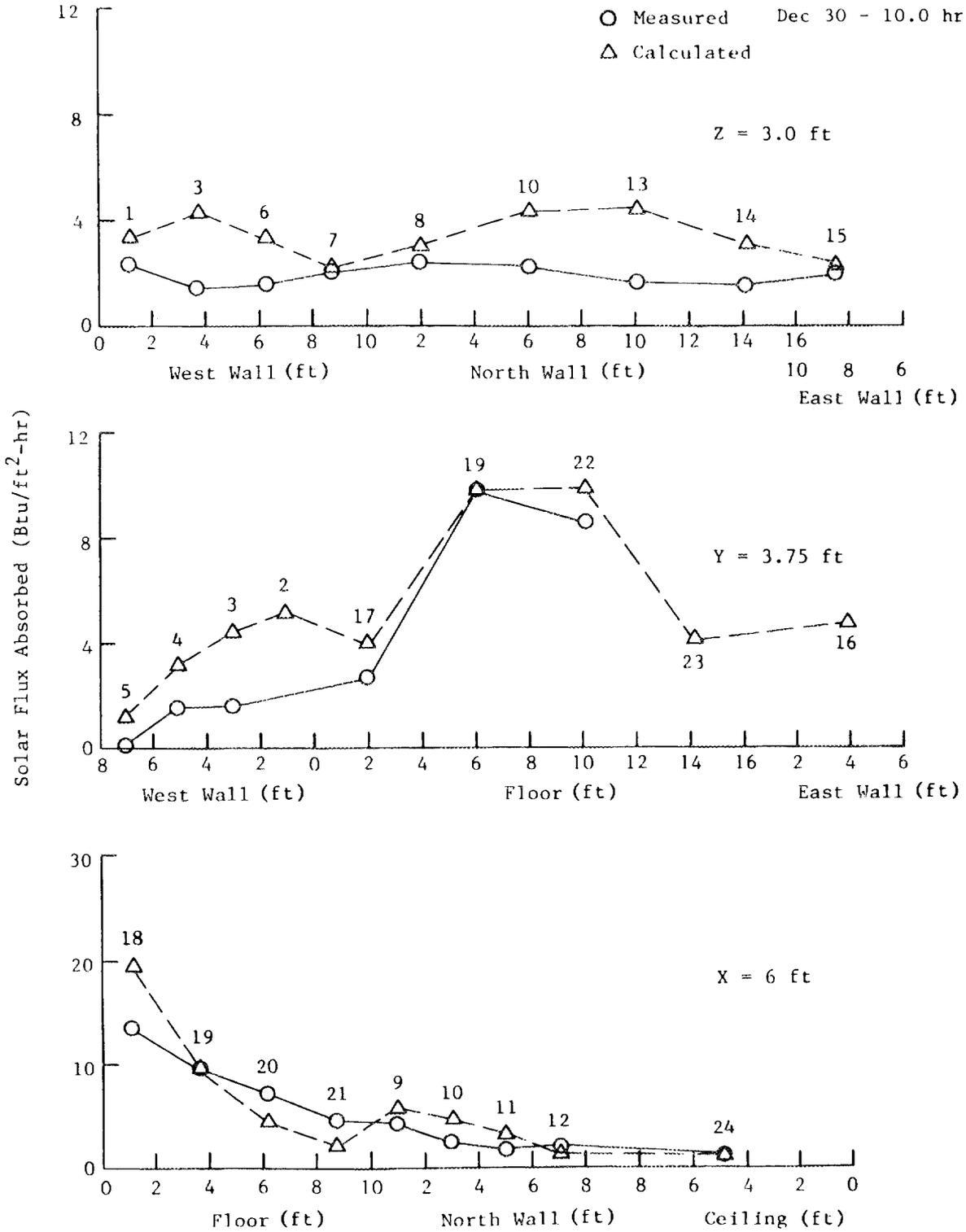


Fig. 16. Interior floors dominated by direct incident diffuse radiation.

Results of a second set of tests in which the floor reflectivity was 0.60 and its specularity was 0.2 are also shown. These tests include, therefore, the effects of reflection from the floor. Clear-day results are shown in Fig. 17. The correlations between measured and calculated fluxes for both direct and diffuse reflected solar flux are seen to be quite good.

PCM model. This code is specifically for the analysis of direct gain solar buildings that employ PCM wall panels to moderate interior temperatures. The response of the PCM is evaluated separate of any other effect. Experimental data were taken to validate this part of the code. Two storage panel thermal models — PCMSOL and a thermal analyzer model — were compared with data from several PCM panel combinations.

A test rack, capable of exposing up to eight panels to solar radiation simultaneously, was used to measure PCM surface temperature and heat flux during realistic freezing/melting cycles. Figure 18 is a photograph of the test rack with eight panels in place. The panels measured 2 by 2 ft. Openings at the top and bottom of the rack allowed free convection cooling of the front side of the panel.

The results of tests of a 1/2-in.-thick panel containing a 27°C melting salt hydrate are shown in Fig. 19. The measured front and back temperatures, along with results of the two simulations, are plotted. Both the predictive models reasonably characterize the PCM for both melting and freezing. The phase change-temperature of the salt is shown not to be the 27°C used in the simulation but, rather, about 21°C. Neither computer simulation handles supercooling, which this, as well as other salt hydrates, exhibits.

Non-PCM thermal interchange. Whereas the solar flux model and the PCM model were validated with experimental data, the convection and radiation interchange between interior nodes and between exterior nodes and the environment were validated by analysis only.

System response. Proper interconnection of the submodels was validated by comparison of PCMSOL results for the test building with measured data. The system test was to determine if all the submodels were working together properly and also to establish confidence that the thermal interchange models were adequate.

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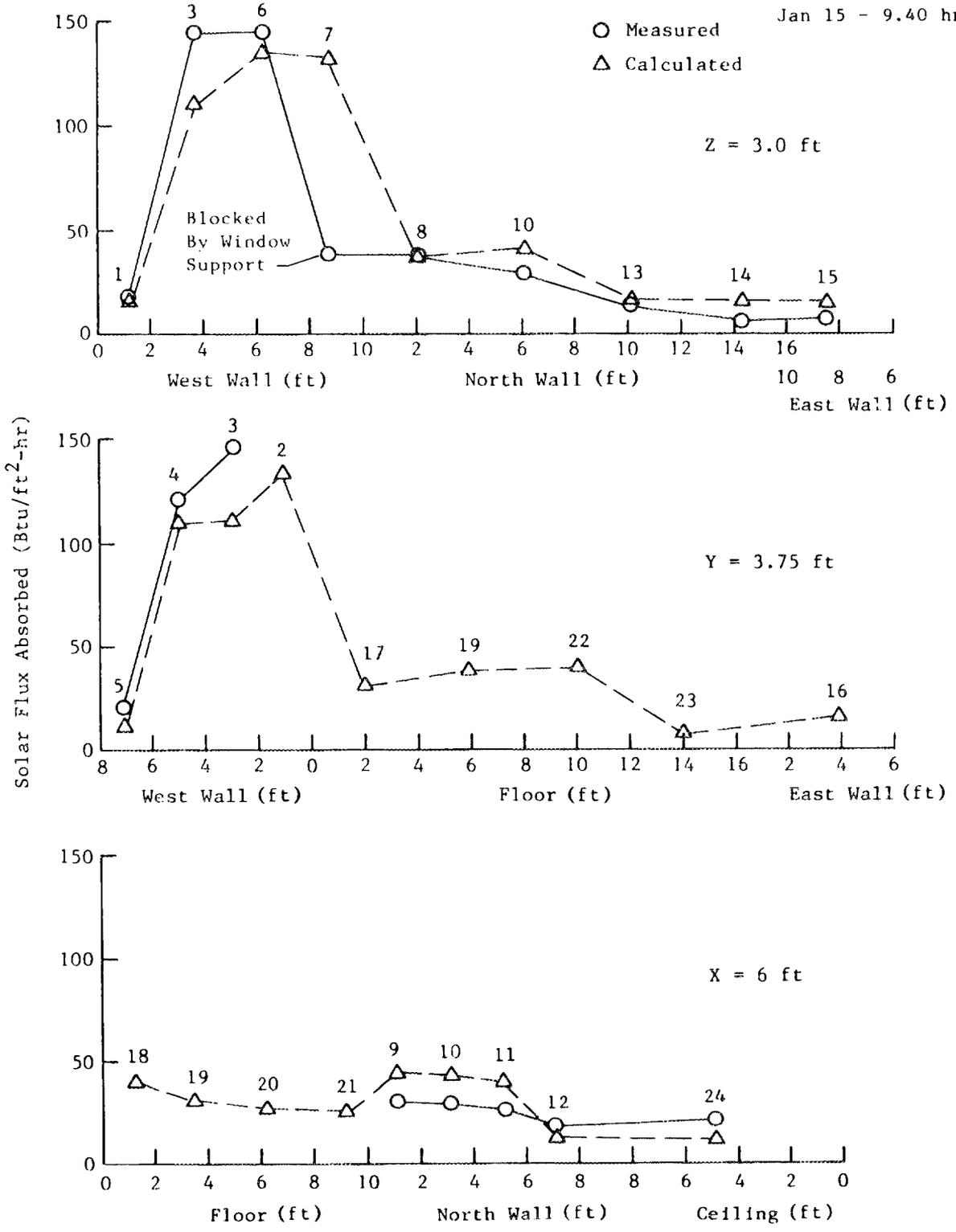


Fig. 17. Interior flux distribution with reflective floor.

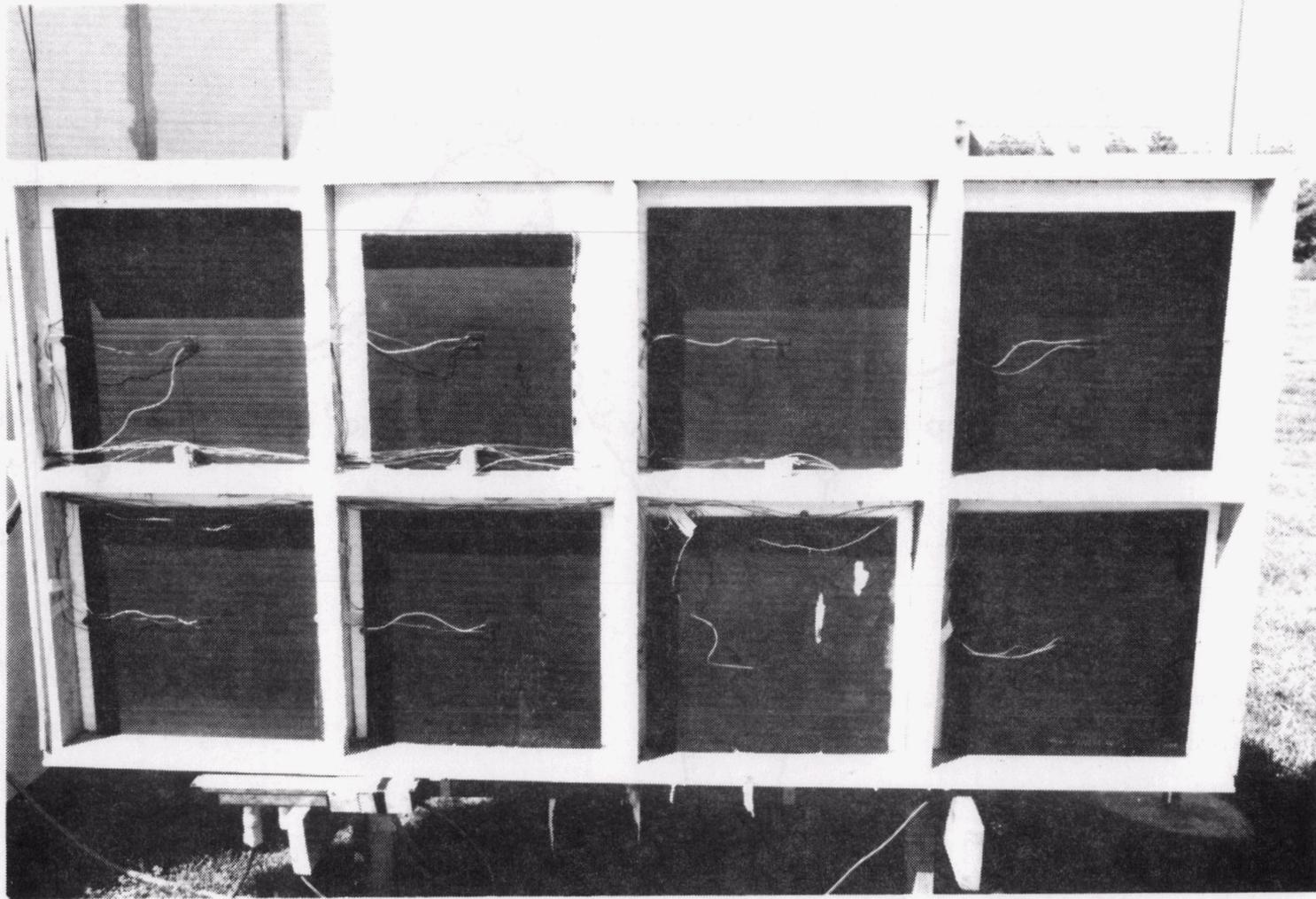


Fig. 18. PCM test rack showing test panels in place (glazing removed for clarity).

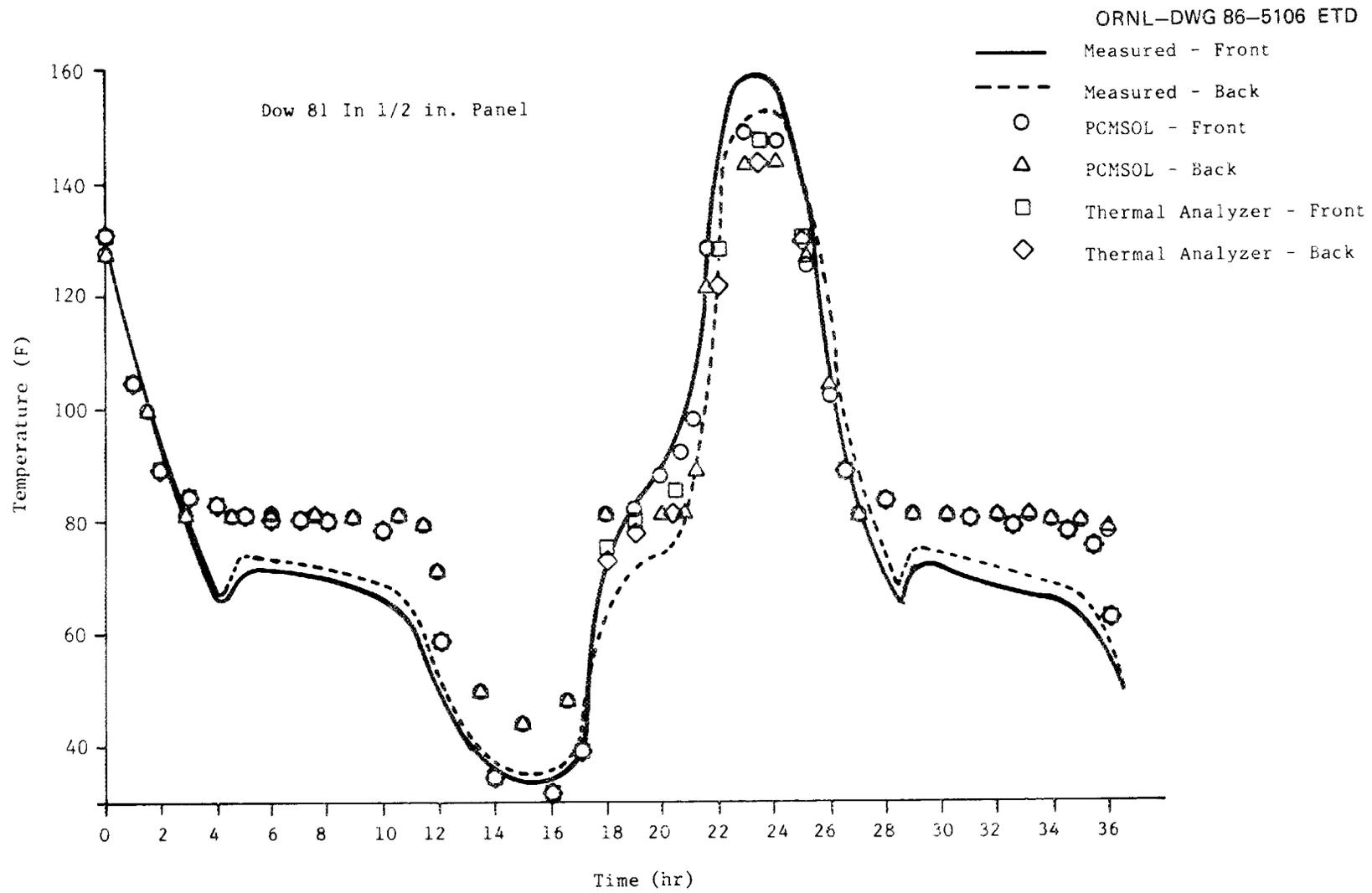


Fig. 19. DOW 81 in 1/2-in. acrylic panel.

The tests were conducted in the direct gain chamber in which the solar flux validation tests were run. Eight 4- by 8-ft panels 1/2 in. thick containing a 27°C melting temperature PCM were attached to the test cell walls as shown in Fig. 20. In addition to the temperature and flux measurements on the panels, solar fluxes were measured as beam and total (on horizontal surfaces and the plane of the window). Ambient air temperature, wind velocity, interior air temperature, and mean radiant temperature were also measured.

Average room air and mean radiant temperature were selected to compare PCM with the test data. The room air is normally used as the control parameter for heating and cooling equipment, and the two temperatures combined give a good indication of the comfort level in the room. If these two parameters match between TES and model, there is a high degree of confidence that the auxiliary energy use and the predicted comfort levels are accurate. Results are shown for two continuous 1-week periods in Figs. 21 and 22. The PCMSOL temperatures track the experimental data very well. No long-term bias is evident in either set of

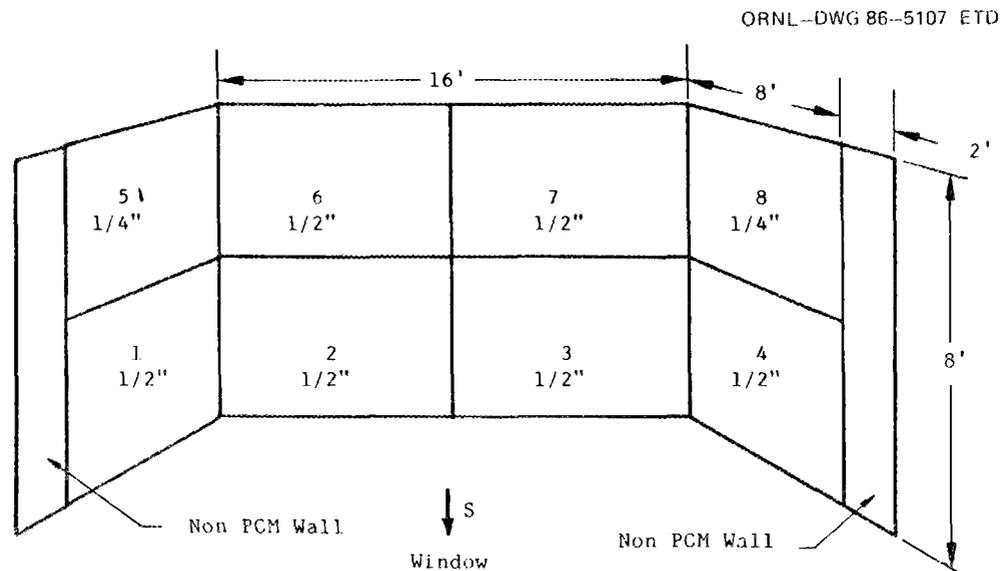


Fig. 20. Placement of panels filled with DOW TESC-81 on interior walls (fractional inch numbers indicate inside thickness of panels. Thermocouples were attached to the center backsides of all panels. Panels 1, 2, 5, and 6 also had thermocouples attached to the center fronts).

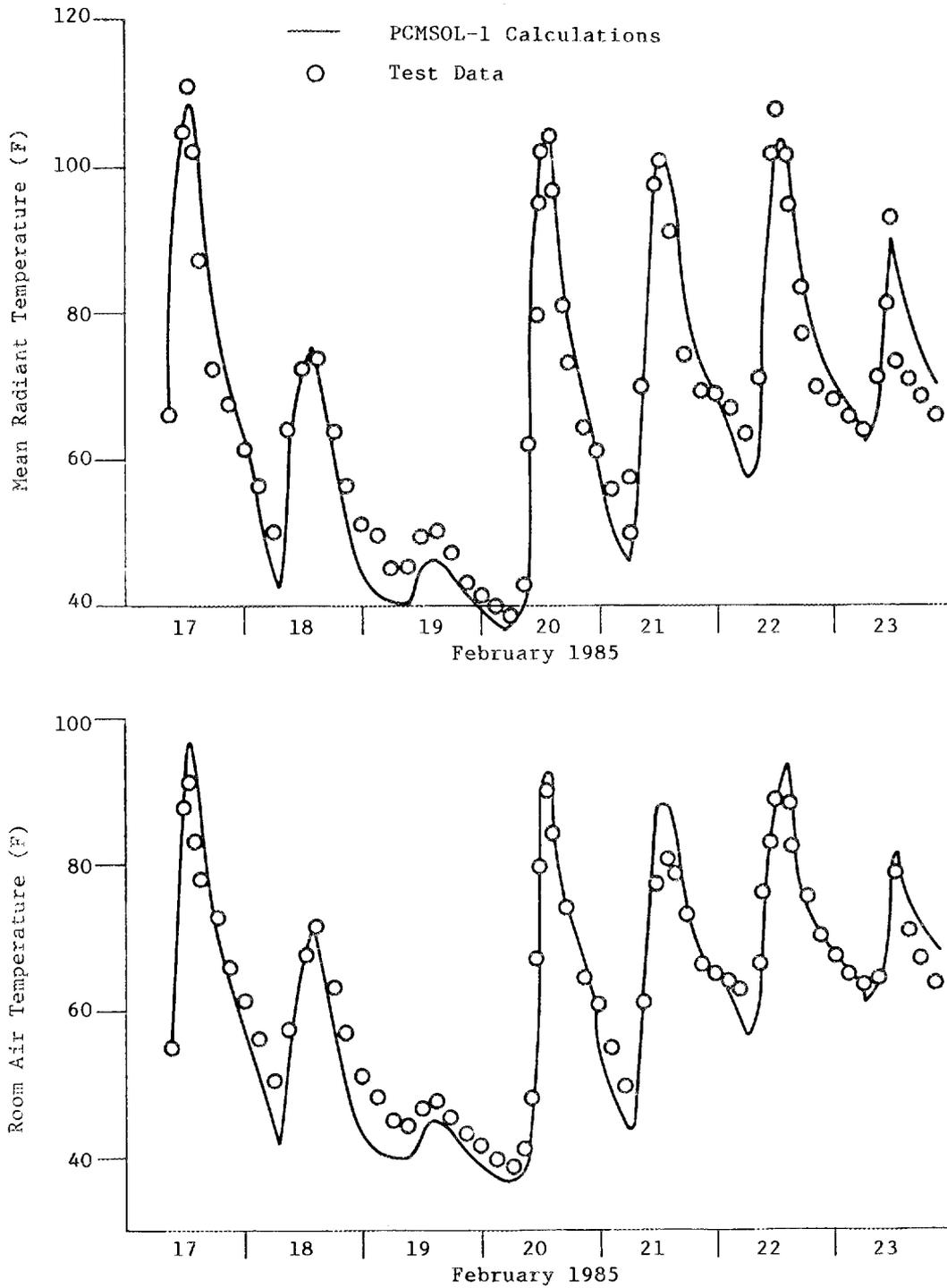


Fig. 21. Comparison of PCMSOL-1 with passive solar test chamber with PCM on walls - February test.

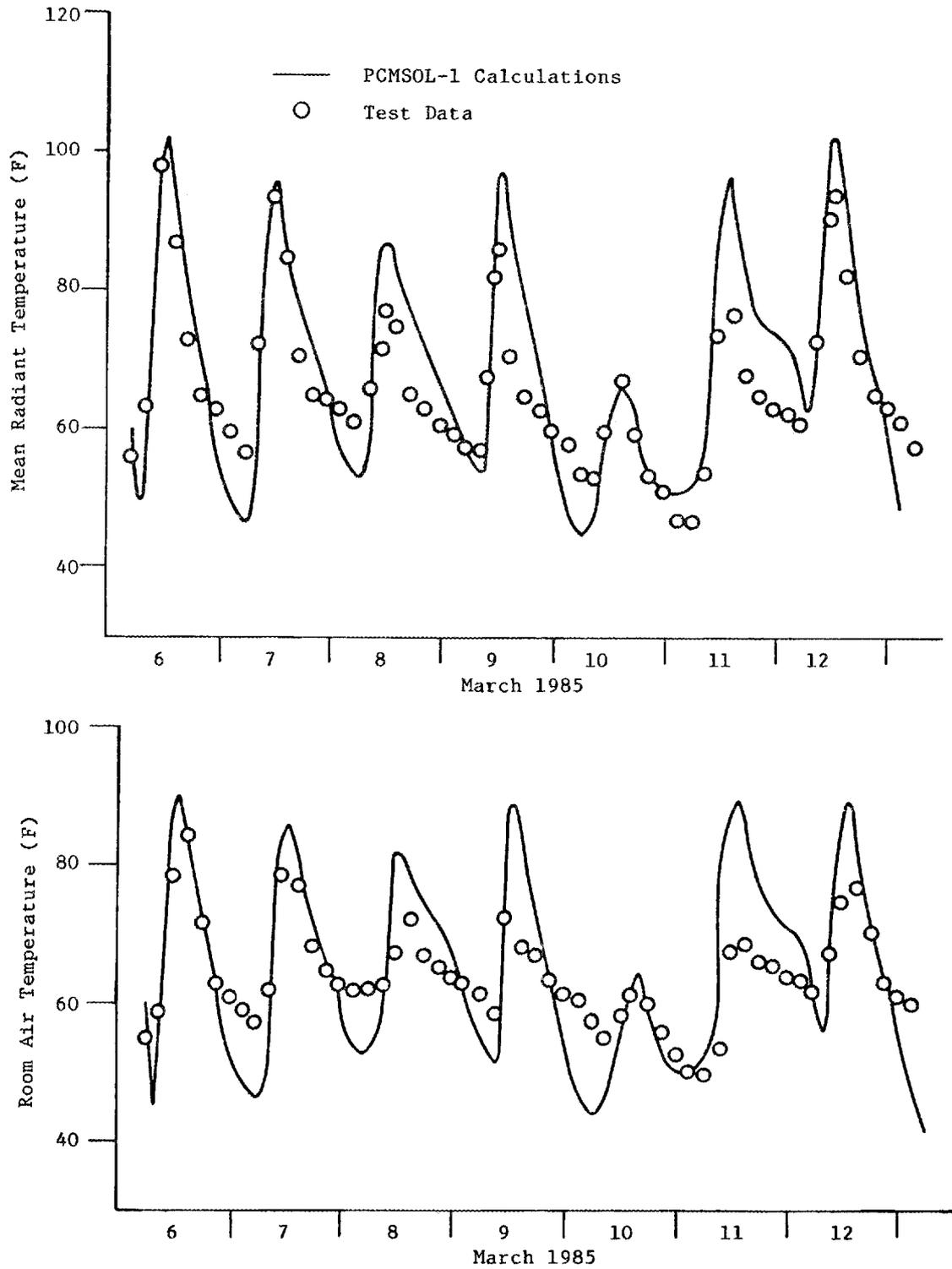


Fig. 22. Comparison of PCMSOL-1 with passive solar test chamber with PCM on walls - March test.

data. The model does predict a greater daily temperature variation than is observed in the test data, probably because of the assumption in the simulation of a constant PCM melt temperature when, in fact, the salt hydrate used is known to exhibit melting (dehydration) over a significant temperature range.

The program was successful in validating the computer code PCMSOL. A computer model of a complex series of physical interactions, such as the passive solar room represents, cannot practically simulate all of the processes and interactions perfectly. It represents, therefore, a compromise and must be subject to revision and improvement as its usefulness is validated. Thus, this program indicated several improvements that will be incorporated in PCMSOL in future studies.

3. SUMMARY AND CONCLUSIONS

Progress in the development of advanced TES technologies for the period of April 1984--March 1985 has been presented. Each of the ORNL/TES program activities during this period has been summarized, and references to detailed reports of specific projects have been given. In accordance with DOE guidelines, the program has continued during this eighth year of ORNL participation as long-range and generic technology development.

Investigation of clathrates of the commonly used heat pump refrigerants was concluded. The concept of forming an icelike crystal with a higher melting temperature than water was demonstrated. Such a cool storage medium has the advantages of freezing temperatures that allow more-efficient heat pump operation and the possibility of eliminating heat transfer coils by direct contact freezing and/or melting, thereby also increasing the efficiency of the air conditioning system. The phase behavior of the clathration process both for single refrigerants and mixtures of refrigerants, which gives an additional degree of freedom in tailoring the temperature and pressure of freezing, was determined. The economics of commercialization of cool storage based on clathrates is currently under investigation. No further DOE-sponsored development is required at this time.

A project to verify enhanced energy transport capability of fluids slurried with solids that can undergo solid-solid phase change was initiated in 1983 and deleted from the program for budgetary considerations in 1984. It was to be resumed in this report period but was not active because of the lateness of program funding. The objective of the project is to establish proof-of-principle for improved TES performance by combining enhanced heat transport and latent storage in a single system. Preliminary concept and background development work has indicated potential savings in system heat transfer and pumping power.

The techniques for producing pellets of cross-linked high-density polyethylene by electron-beam radiation were reexamined because of less-than-predicted performance in a field test of earlier produced material. The alternate irradiation process of gamma radiation was also tested. A revised radiation dose that produced improved solid-solid storage media

was determined. However, the economics of processing large batches of material were found to be higher than predicted in the original development program.

Development of one formulation of salt/ceramic composite storage material has been essentially completed. Pellets of sodium/barium carbonate-magnesium oxide have been cycled for over 6000 h, and the material performance over multiple melt/freeze cycles was determined. This same technology can now be applied to the development of several other salts, thereby allowing a range of transition temperatures to be available to store high-temperature industrial waste heat.

Modest progress was made in developing an encapsulation technique for metal eutectics. A process of forming an inert shell consisting of silicon over a silicon/aluminum eutectic alloy by a self-encapsulation process was not completely successful. Several alternative methods, as well as experimental studies of the stability of the alloy/shell interface, are under investigation.

A promising new storage technology has been found in the complexing of metallic salts with ammonia, water, or some other suitable ligand. The adsorption of a ligand gas in a solid salt avoids many of the problems found in existing phase-change storage processes. A wide number of sorption systems were examined, and experimental data on the thermodynamic properties of several salt/ammonia complexes were measured. A dual-temperature (winter heat and summer cool) storage system of sodium bromide and ammonia was defined. A prototype stage is under consideration if sufficient industrial interest and support are found.

University research in the field of liquid-liquid and liquid-solid systems for TES was supported. The change in heat of mixing is the mechanism sought for storing thermal energy. If one or more promising systems are found, the present theoretical study will be combined with an experimental program to determine accurately the phase diagrams and the values of heats of mixing.

The ORNL computer code PCMSOL, which simulates latent heat storage and its effect on a solar room, was validated by experimental data. Several modifications to the program, which will increase its utility for solar design, were suggested by this project.

A mix of completed projects and expanding and ongoing projects is to be found in the year's program. As in the past, the future research directions will be guided by these results. TES is increasingly recognized as an engineering technique for energy management, especially in the area of cool storage. The DOE program provides the long-range research from which the storage industry can draw for improvements in storage technology.

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