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THERMAL ENERGY STORAGE TECHNICAL PROGRESS REPORT

April 1987-March 1988

J. J. Tomlinson
R. J. Kedl

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R. J. Kedl

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THERMAL ENERGY STORAGE TECHNICAL PROGRESS REPORT
APRIL 1987-MARCH 1988

J. J. Tomlinson
R. J. Kedl

ABSTRACT

Progress in the development of thermal energy storage (TES) technology under Oak Ridge National Laboratory's TES Program for the period April 1987 to March 1988 is reported. Program goals and project structure are presented. Each of the projects active during this report period is discussed, and the contribution of specific projects to major technology transfer activities is described.

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1. PROGRAM OVERVIEW

This report presents the status of projects active under Oak Ridge National Laboratory's (ORNL's) Thermal Energy Storage (TES) Program during the 1-year period ending March 31, 1988. ORNL is the principal research laboratory for the development of diurnal and industrial TES technologies, acting as field manager for the Department of Energy's (DOE's) Office of Energy Storage and Distribution. The application areas of the program are industrial reject heat utilization, energy conservation through demand-side electric utility load leveling, and passive 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 efficient, cost-effective TES systems may be developed and successfully marketed for specific applications. This purpose is expressed by the overall goals of the TES Program: (1) to create the technology base required for development of TES concepts in diurnal heating and cooling and industrial applications and (2) to work with industry, universities, technical societies, and trade associations to transfer the technologies to the private sector.

The use of TES is growing in those areas where the economic benefit is obvious. Because of vigorous TES incentive programs and high on-peak electrical demand tariffs implemented by electrical utilities, the use of cool (ice or chilled water) storage systems is growing rapidly. However, data from these installations indicate that the performance (efficiency) of these systems is lacking. The results indicate that the systems use appreciably more energy than conventional cooling systems. Since electric utility regulatory bodies are quite sensitive to energy penalties associated with implementation of new technologies, the benefits of commercial cool storage could be short-lived unless efficiencies are increased. Thus, there is need for R&D on TES media and systems, with the goal of enabling TES systems to perform the required functions more efficiently.

Recognizing the need for efficiency improvements in cool TES systems, the ORNL TES Program is continuing development of technologies that improve heat transfer between a working fluid and the storage medium. Of particular interest is a new concept of defrosting evaporators used to make ice. In this process, water additives and surface coatings are used to reduce ice adhesion. Other systems in which a component of the TES medium is the heat transfer fluid are being studied as a means of maximizing the utility of system components. Two efforts in which this principle is used are currently under way: (1) development of ammoniated complex compounds with ammonia as the working fluid and (2) a study of conjugating liquid systems.

Because of the high energy storage capacity of latent heat over small temperature ranges, TES media that undergo a state change (phase, structure, or chemical composition) are of prime interest to the program. Generically classified as phase-change materials (PCMs), these chemical systems are volumetrically advantageous; however, since a state change occurs across the transition temperature, effective containment of the PCM can be a challenge. The program has continued the development of several concepts for containing PCMs via simple, cost-effective techniques and for providing heat transfer systems that are enhanced through the use of PCMs.

The total project scope for the program during the reporting period is shown in Fig. 1. The thrust of each diurnal and industrial project falls into one of four application elements shown in the first column of Fig. 1.

ORNL-DWG 89C-4442 ETD

APPLICATION ELEMENT	TES SUBPROGRAM	
	DIURNAL	INDUSTRIAL
HEAT TRANSFER ENHANCEMENT	DEVELOPMENT OF ICE SELF-RELEASE MECHANISMS SLURRY HEAT TRANSFER	
MATHEMATICAL MODELING	EVAPORATIVE HEAT TRANSFER	PACKED-BED THERMAL MODEL
MEDIA DEVELOPMENT	HEAT OF MIXING WITH CONJUGATING LIQUIDS	COMPOSITE MEDIA DEVELOPMENT COMPOSITE MEDIA FIELD TESTING
SYSTEM DEVELOPMENT	DEVELOPMENT OF AMMONIATED COMPLEX COMPOUNDS	

Fig. 1. ORNL TES Program structure.

1.1 HEAT TRANSFER ENHANCEMENT

Heat transfer is a critical issue in all TES applications since it limits the rate at which thermal energy can be provided to or withdrawn from a source and delivered to an end use. Heat transfer can be enhanced by increasing the surface areas exposed to a heat flux, by techniques that introduce additional heat transfer mechanisms into the heating or cooling process, or by techniques to reduce fouling of the heat exchanger.

Heat transfer is of particular concern in systems in which thermal storage is effected through freezing and melting. In this case, heat transfer through the solid material is conduction limited and is controlled by the TES medium's surface area exposed to the working fluid. Insufficient surface areas either limit the heat transfer or meet the heat transfer requirement at the expense of large temperature gradients between the TES material and the working fluid.

An example of the need for heat transfer enhancement can be found in conventional ice storage systems in which large evaporators are used to form ice for off-peak building cooling. During a typical charging cycle for a static ice builder, ice is grown to a thickness of 3–6 cm on evaporator tubing (~2.5 cm OD) that is submerged in a tank of water. Based on a typical 6-cm-thick ice build, the length of coil required for a commercial ice storage system can be very large. For example, a 3500-kWh (1000 ton-h) system for a typical commercial building would require more than 3 miles of evaporator tubing. In addition to being a major cost item in an ice storage system, this tubing occupies an appreciable volume, which would otherwise be used for ice storage. Development of an ice self-release system whereby ice formed on a submerged flat-plate evaporator surface is periodically freed from the surface because of buoyant forces could be a major advance in latent storage technology.

During the reporting period, a project to study ice self-release was initiated. Objectives of the project are to define the physical and chemical mechanisms involved in self-release of ice from submerged evaporator surfaces in open tanks, to determine the parametric limits of the self-release process, and to determine the suitability of the self-release approach for cool storage closed-refrigeration-cycle systems.

A second approach for heat transfer enhancement involved the investigation of a slurry of form-stable PCMs in pipe flow for increased heat transport due to latent heat and increased turbulence at the pipe wall. Experiments to confirm these ideas using sensible heat only were completed.

1.2 MATHEMATICAL MODELING

The thermodynamics of thermal storage systems based on sensible heat are generally described through equations that can be solved analytically. Solutions to many interesting problems involving latent heat storage are found only through mathematical modeling using iterative techniques. Progress has been made in two modeling efforts currently under way. The objective of the first effort is the development

of a thermodynamic description of a packed bed of PCM immersed in a boiling or condensing heat transfer fluid. Experiments are under way to verify the model with an evaporating fluid; the verified model will be used for technical evaluation of storage heat pump systems with PCMs in packed beds used as evaporators or condensers. The second project is the development of a packed-bed TES system model for use in TES design optimization studies for brick plants. The packed bed being modeled consists of pellets of a composite phase-change heat storage material (CPCM).

1.3 MEDIA DEVELOPMENT

Because PCMs have higher thermodynamic efficiency, smaller size, and the ability to store and deliver heat over a small temperature interval, they are viewed as attractive as thermal storage media for building heating and cooling and industrial applications. Thus, development of TES media in which one or more components undergoes a phase transition remained a central element of the program. The first of four projects is an experimental study of multicomponent liquid systems that have large miscibility changes over a small temperature range. The heat of mixing associated with these miscibility changes can be tailored to produce a liquid-based latent heat TES system for building heating and/or cooling applications.

In a second project, efforts to develop an advanced TES material for industrial applications were continued. This material consists of a sintered magnesium oxide (MgO) pellet, with porosity suited to contain a eutectic of carbonate salts. Capillary forces retain the carbonate PCM in the MgO interstices, so the pellet remains solid during thermal charging and discharging. Two additional projects to evaluate the performance of this composite material will be continued during FY 1988: (1) Packed-bed configurations of this medium will undergo field testing in a brick plant to examine performance and lifetime issues when the medium is used to extract thermal energy from the kiln flue gas. (2) A detailed test program will be conducted to measure and evaluate thermochemical and thermophysical properties of the medium periodically during the field test.

1.4 SYSTEM DEVELOPMENT

System development is composed of those projects for which TES media and systems are known, are available, or have been developed but require further work to reduce cost or improve performance. Although TES systems based on sorption are not new, development of a cost-effective system is challenging, particularly because of low adsorption rates. Storage of energy in salts that have been complexed with ammonia is being studied as a means for implementing thermal storage in an ammonia vapor compression cycle, and practical issues such as contamination of the complex with refrigerant oil and evaluation of solid-vapor reactor/heat exchangers are being studied.

2. TECHNICAL PROGRAMS — DIURNAL THERMAL ENERGY STORAGE

2.1 DEVELOPMENT OF ICE SELF-RELEASE MECHANISMS

A number of ice-making concepts are based on the periodic removal of ice from the surface on which it is formed. Commonly, ice is melted off the surface, although it can be removed by other means. In any case, ice removal requires energy, and the efficiency of the ice maker is decreased accordingly. In the past, a number of researchers[1] have proposed the possibility of developing a surface/water (ice) system where the adhesion of ice to the surface is very low. Thus, ice can self-release and fall off the surface under the influence of gravity or can float off the surface under the influence of buoyancy. Previous research[2] has identified certain conditions necessary to achieve low adhesion. The surface should be glossy smooth, and it must be hydrophobic, or nonwettable by water. It has been found[3] that small concentrations of electrolytes in the water will decrease the adhesion. A commercially acceptable ice self-release system has not yet been developed, but the search continues because the benefits would be considerable.

W. E. Stewart of the University of Missouri, during a separate study,[4] experimentally evaluated a number of techniques that render ice self-releasing from the surface on which it was formed. One technique involved a surface coated with Rilsan, with one of several electrolytes dissolved in the water. This combination resulted in ice repeatedly self-releasing from a submerged evaporator surface. This study was exploratory in nature, and only the fact of self-release was determined.

The University of Missouri is being funded by the ORNL TES Program to continue development of this concept. The objectives of this research are to define the physical-chemical mechanisms involved, to address the parametric limits of the self-release process, and to determine the suitability of the concept for application in a large-scale engineered system. To reach these objectives, experiments are being conducted in a 4-ft-high column of water (with additive) with a plate evaporator located at the bottom.

Ice self-release was verified on vertical plates in the test fixture, and the phenomenon was recorded on video tape. The ice was noted to release in single sheets as well as semicontinuous pieces. As the ice was growing and releasing regularly from the vertical plate, small differences between measured electrolyte conductivities (concentrations) at the top and bottom of the water column were noted. For an original concentration of 0.220 *M* of $Ca(NO_3)_2$ – the first electrolyte studied – the concentration at the top of the column was measured to be 0.219 *M*, and the bottom concentration was measured to be 0.225 *M*. This observation indicates that as ice is formed, the solution concentration at the ice/plate surface interface increases and lowers the freezing temperature of the surrounding water so that ice cannot freeze rigidly to the plate.

Efforts to obtain self-release of ice from a horizontal plate have been unsuccessful. A finite difference program to evaluate data from 24 thermocouples embedded in the plates is being used to approximate the actual heat being removed through the plate to produce ice.

Further experiments with the coated plates have shown that scratches in the coating do not noticeably affect the ice's "stickiness." The project is continuing.

2.2 SLURRY HEAT TRANSFER

The slurry heat transfer project, conducted by Argonne National Laboratory, consists of research in the enhanced heat-carrying capability of fluids slurried with solids that are form stable or can undergo a 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 as the system working fluid.

Flow experiments using pellets of cross-linked high-density polyethylene (HDPE) slurried in water were conducted in a loop containing an electrically heated pipe section.

The principal findings from experiments using HDPE as sensible heat storage elements are as follows:

1. The pressure drop associated with the slurry-flow 1/8-in.-diam HDPE particles is not greatly increased over that for pure water at the same mass flow rate at particle loadings of up to 25% by volume. The experimentally determined apparent slurry viscosity was found to agree fairly well with existing empirical correlations for the narrow range of conditions explored.
2. A sharp increase of slurry viscosity was found to occur at a high particle volumetric loading (35%). This is an especially interesting observation that was generated in the current study. Under these conditions, existing viscosity correlations became invalid. There appeared to be a mechanistic change of flow regime that occurred under high loadings.
3. The slurry Nusselt number (when plotted vs a modified Reynolds number based on an effective viscosity) was larger than that for pure water and increased significantly with increasing particle loading, indicating heat transfer enhancement. A factor of 2 to 3 increase in slurry Nusselt number over that of pure water was observed.
4. The heat transfer enhancement is also observed when the data are interpreted in terms of the heat transfer Stanton number. The slurry Stanton number was higher than that for pure water and increased with increased flow rate or particle loading.

In addition to a reduction in TES Program resources, temperature and pressure limitations in the existing loop prevented further examination of the slurry concept during phase change.

2.3 EVAPORATIVE HEAT TRANSFER

To allow evaluation of a packed-bed cool storage system used as the evaporator of an air-conditioning system, a thermodynamic model of a packed bed of PCM with a two-phase working fluid is under development and experimental validation by The University of Tennessee. The principal part of the test facility, shown in Fig. 2, consists of a packed

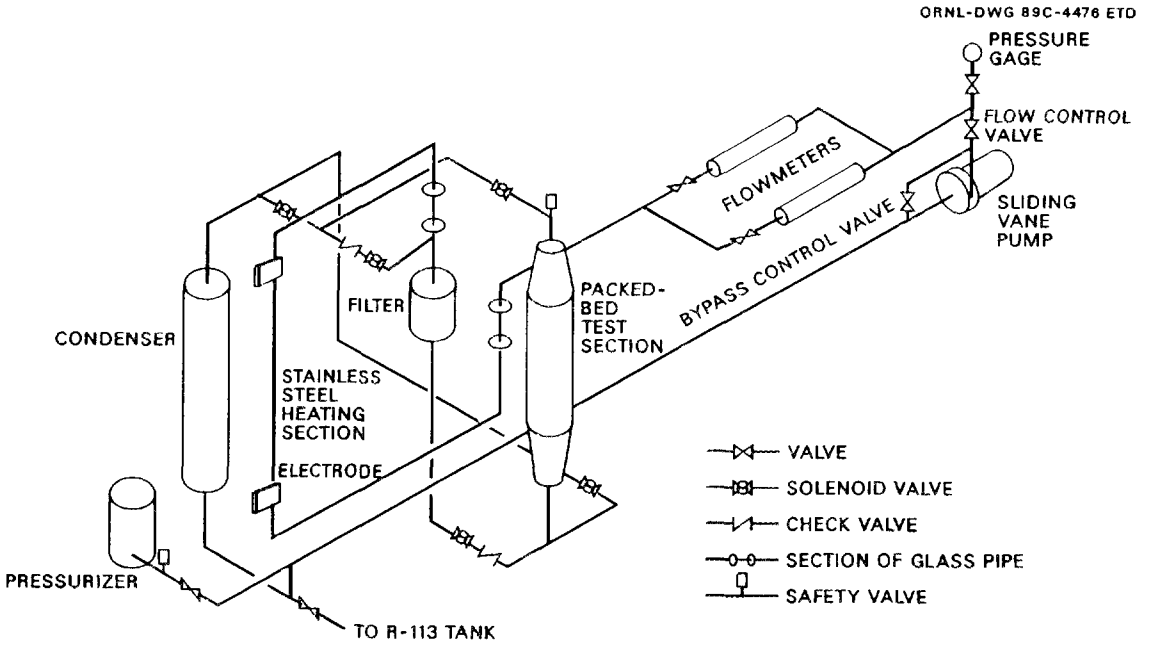

Fig. 2. Schematic layout of packed-bed evaporator test facility.

bed (approximately 5 in. in diameter) that can be heated or cooled using R-113 as the heat transfer fluid. Test runs are made with subcooled R-113 entering the bed at the bottom and leaving as vapor at the top of the packed bed. Measurement of the heat transfer coefficient between the pellets and fluid was accomplished with probes consisting of aluminum spheres instrumented with a heater system and surface thermocouples. The instrumented spheres were the same diameter as the packed-bed spheres.

The total energy input to the instrumented aluminum sphere is balanced with the total energy output by convection heat transfer to the two-phase working fluid and by heat losses through the instrumented spheres lead wires. This relation was used to determine the heat transfer coefficient from each sphere individually. The energy balance was performed after the instrumented aluminum spheres had reached steady state.

The boiling heat transfer coefficient for each sphere was calculated by equating the electrical power expended in the heater element

with the heat removed from the pellet by convection. It follows that

$$h_{2\phi} = \frac{I^2R - Q_{losses}}{A(T_w - T_{sat})} ,$$

where

$h_{2\phi}$ = two-phase heat transfer coefficient ($W/m^2 \cdot °C$),
I = electrical current (A),
R = heater resistance (Ω),
Q_{losses} = conduction heat loss through lead wires (W),
A = sphere surface area (m^2),
T_w = sphere surface temperature (°C),
T_{sat} = fluid saturation temperature (°C).

Natural convection and forced convection tests were conducted in a packed bed of spheres to validate the sphere heat transfer measurement system. For the natural convection tests, water and refrigerant R-113 were used as fluid media. Aluminum spheres of 1.59 and 2.54 cm in diameter were used in separate tests covering a Rayleigh number range of 1×10^5 to 1×10^7. Results shown in Fig. 3 were found to be within 10% of the published correlation of Incropera and Dewitt.[5]

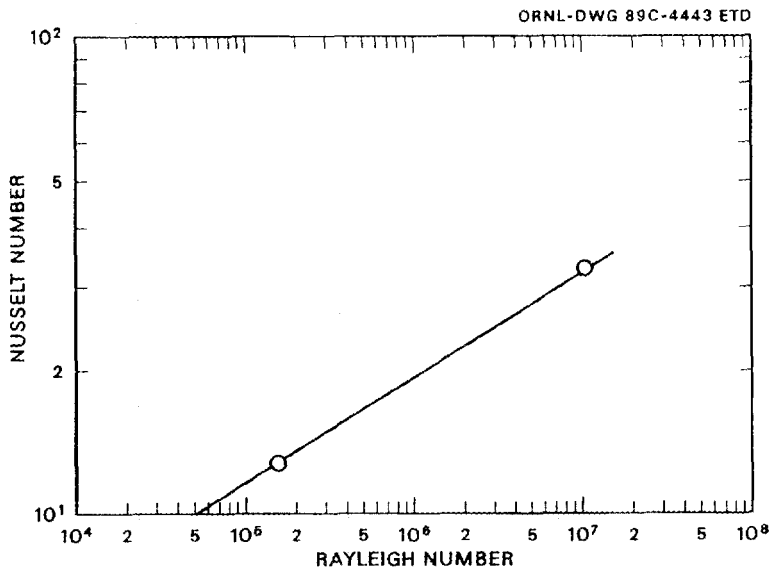

Fig. 3. Natural convection validation of sphere heat transfer measurement system in water and liquid R-113.

A test for forced convection validation using unheated R-113 flow was conducted with the 1.59-cm instrumented spheres located in the randomly packed bed. For each particle Reynolds number Re_p, more than one input power to the instrumented spheres was used to confirm that the Nusselt number correlation in single-phase flow would be independent of the difference in temperature between the surface of the sphere and the ambient fluid. The measurements shown in Fig. 4 clearly confirm this. The results are also compared with the general correlation of Baumeister and Bennett;[6] the agreement is good.

It can be concluded from these validation tests that the heat transfer probes used in the present investigation are dependable sensors for the measurement of heat transfer coefficients under natural and forced convection conditions.

A series of tests with constant mass flow rate was conducted using 1.59-cm spheres and R-113 under liquid-vapor flow conditions. For each mass flow rate, the inlet quality (q) was adjusted to a desired value;

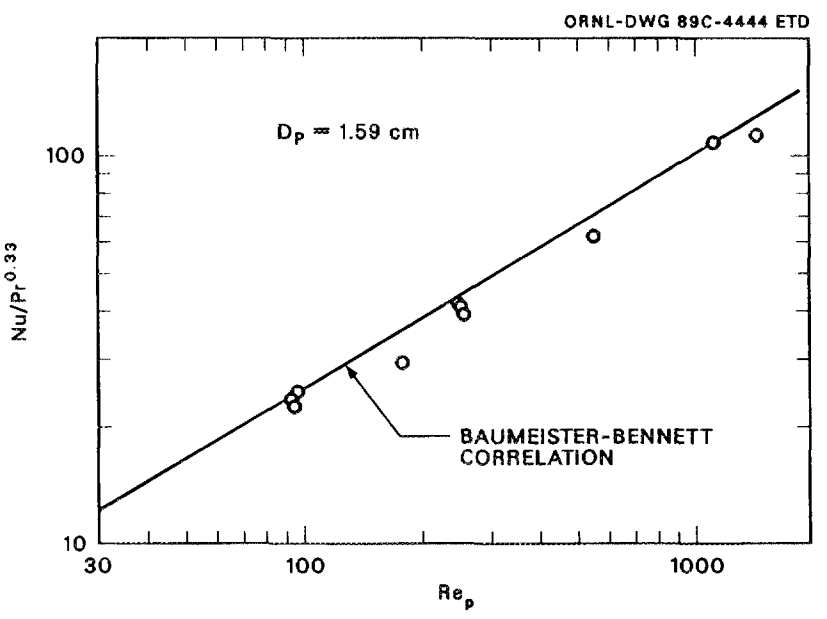

Fig. 4. Forced convection validation of heat transfer measurement system; 1.59-cm instrumented spheres in packed bed with liquid R-113. Nu, Pr, and Re_p are Nusselt, Prandtl, and Reynolds numbers, respectively, and D_p is the pellet diameter.

and the influence of the surface superheat on the heat transfer coefficient was investigated. Here, surface superheat is defined as the temperature difference between the two-phase fluid and the surface of the heated, instrumented aluminum spheres. The heat transfer coefficient was determined at each inlet quality setting by changing the power input to the spheres and allowing the indicated temperatures to reach steady-state values. This procedure was followed for three inlet flow rates over a range of inlet qualities, q, between zero and one. A preliminary correlation of heat transfer coefficient as a function of inlet quality and surface superheat was developed for each flow rate. Work is under way to incorporate the mass flow rate to arrive at a single correlation for two-phase evaporative heat transfer.

2.4 HEATS OF MIXING WITH CONJUGATING LIQUIDS

Several investigators[7] have suggested the use of liquid-liquid systems of limited miscibility to store thermal energy. As the fluid system cycles in temperature from a two-phase region to a single-phase region (near its critical solution temperature), the heat capacity of the fluids is enhanced by the heat of solution. Thus the effective heat capacity of the fluid system may be abnormally high. This concept is under investigation by the New York Polytechnic Institute. The initial phase of this effort consisted of identifying appropriate liquids for storage of heat and cold and predicting the effective heat capacity from theoretical considerations. The results of this effort were reported in the last progress report.[8] During this reporting period, the effective heat capacity for the most attractive liquid-liquid systems was measured. A Hart Scientific Model 501 flow calorimeter was used for these determinations.

The propylene carbonate-water system [upper critical solution temperature (UCST) = 60-70°C] was recommended for heat storage during the initial phase of this investigation. Heats of mixing, H_E, were measured for this system in the range of 50-70°C, and the results are presented in Fig. 5. The measured heats of mixing are consistent with values calculated by analytical procedures. Possible dissociation of propylene

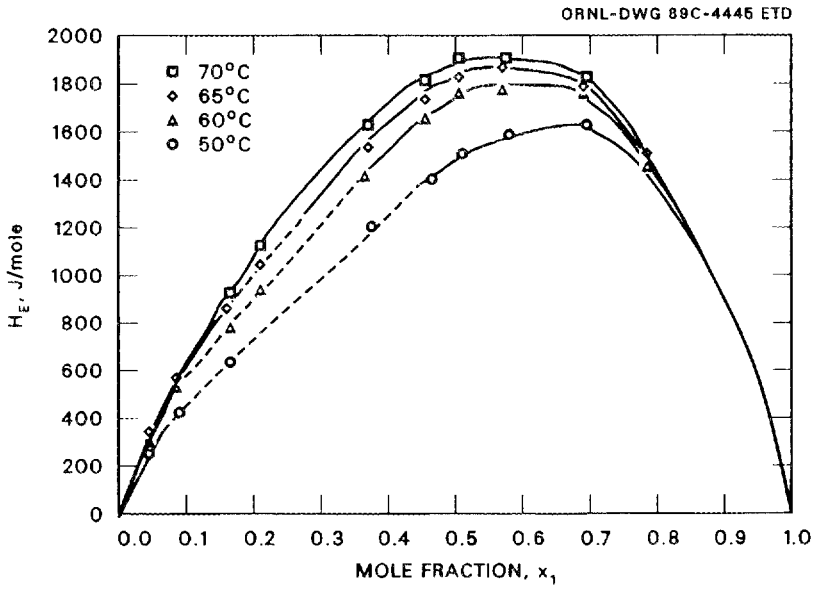

Fig. 5. Heats of mixing for propylene carbonate (1) and water (2) mixture.

carbonate was indicated at 70°C, which is close to the critical region of the system. The heat of mixing of the propylene carbonate system is unusually high for aqueous mixtures with upper critical solution temperatures. However, the TES capabilities of this system at low propylene carbonate compositions appear to be limited because of the high percentage of water in the propylene carbonate phase. These experimental results are consistent with one of the conclusions of the first phase of this investigation, that aqueous systems with UCSTs are unlikely to exhibit large increases in the heat of mixing in the critical region. Therefore, systems with lower critical solution temperatures (LCSTs) have been emphasized in subsequent experimental studies.

In Fig. 6, experimental heats of mixing are presented for methyldiethylamine-water in the range 45-55°C. This system has an LCST approximately equal to 49°C and is thus suitable for heat storage applications. At mole fraction $x_1 = 0.1$ over the temperature range 48-55°C, the H_E for this system varies by about 340 J/mole, corresponding to an effective heat capacity about 30% higher than that of pure water. The experimental heats of mixing for this system are consistent with those predicted by analytical procedures.

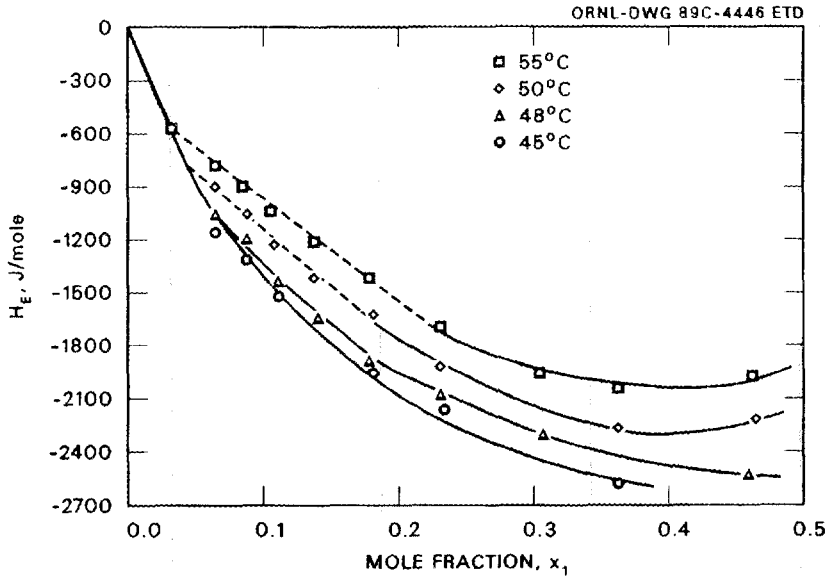

Fig. 6. Heats of mixing for methyldiethylamine (1) and water (2) mixture.

Considerable effort was devoted to identifying liquid-liquid systems and measuring their heats of mixing for the cool storage application. For this application, aqueous mixtures containing glycol and glycol derivatives were of primary consideration because of their low toxicity, compared to other organic fluids with appropriate physical properties. Table 1 lists the glycol compounds considered. The LCST values were obtained either from the literature or from laboratory experiments.

Heat-of-mixing isotherms in the range 5-25°C are presented in Fig. 7 for ethylene glycol diethyl ether-water. This system has an LCST less than -5°C. At a glycol mole fraction of about 0.074, an increase in the heat of mixing of 185 J/mole was obtained between 5 and 10°C. This increase represents an enhancement of about 15% over the heat capacity of water in the same temperature interval.

Heat-of-mixing measurements were made for the diethylene glycol diethyl ether-water system and are shown in Fig. 8. The lower critical solution temperature for this system was found to be about 25°C. Nakayama and Shinoda[9] measured heats of mixing for this system at 25°C and indicated liquid-liquid behavior for compositions $0.01 < x_1 < 0.1$.

Table 1. Potential glycols for cool storage applications

Substance	Molecular weight	LCST (°C)
Ethylene glycol methyl ether	76.1	>>25
Ethylene glycol dimethyl ether	90.1	<20
Ethylene glycol ethyl ether	90.1	>25
Ethylene glycol diethyl ether	118.2	<-5
Ethylene glycol methyl-tert-butyl ether	132.2	<25
Ethylene glycol butyl ether	118.0	49
Ethylene glycol isobutyl ether	109.0	25
Diethylene glycol monomethyl ether	120.2	>25
Diethylene glycol dimethyl ether	134.2	>25
Diethylene glycol methyl-tert-butyl ether	176.3	<25
Diethylene glycol monoethyl ether	134.2	>25
Diethylene glycol diethyl ether	162.2	25
Diethylene glycol monobutyl ether	162.2	>20
Diethylene glycol dibutyl ether	218.3	0
Propylene glycol monomethyl ether	90.1	>32
Propylene glycol dimethyl ether	104.2	<0
Propylene glycol monoethyl ether	104.0	>32
Propylene glycol diethyl ether	118.0	>0
Propylene glycol dipropyl ether	160.0	<<25
Dipropylene glycol methyl ether	148.2	>20
Dipropylene glycol dimethyl ether	162.2	<0
Tripropylene glycol *n*-propyl ether	160.0	<25
Tripropylene glycol methyl ether	190.2	<25
Tripropylene glycol dimethyl ether	204.2	<0
Tripropylene glycol *n*-propyl ether	201.1	<<25

In the present study, at 35°C a narrow two-liquid phase region was observed in the composition range $0.06 < x_1 < 0.11$. The new data for this system are in general agreement with those from the previous study, as shown in Fig. 8.

A polypropylene glycol with a higher molecular weight (MW) is required for cool storage applications. Therefore, heats of mixing were measured for the polypropylene glycol (MW = 725) and water system, which has an LCST in the range of 5 to 10°C. In Fig. 9, values of the heat of mixing for this system are presented for temperatures from 5 to 25°C. It can be seen that for a weight fraction of the glycol $x_1 = 0.4$, the heat of mixing increases about 10 J/g in the range of 10 to 15°C. This

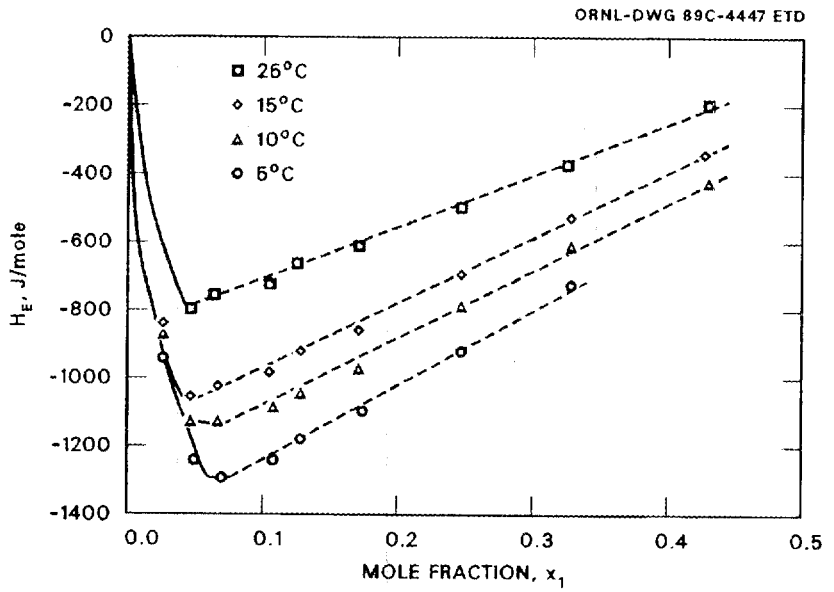

Fig. 7. Heats of mixing for ethylene glycol diethyl ether (1) and water (2) mixture.

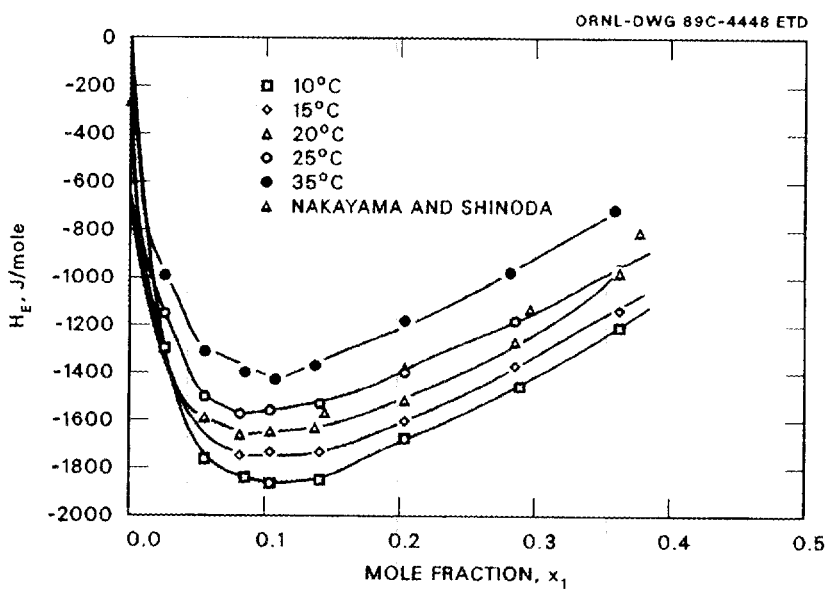

Fig. 8. Heats of mixing for diethylene glycol diethyl ether (1) and water (2) mixture.

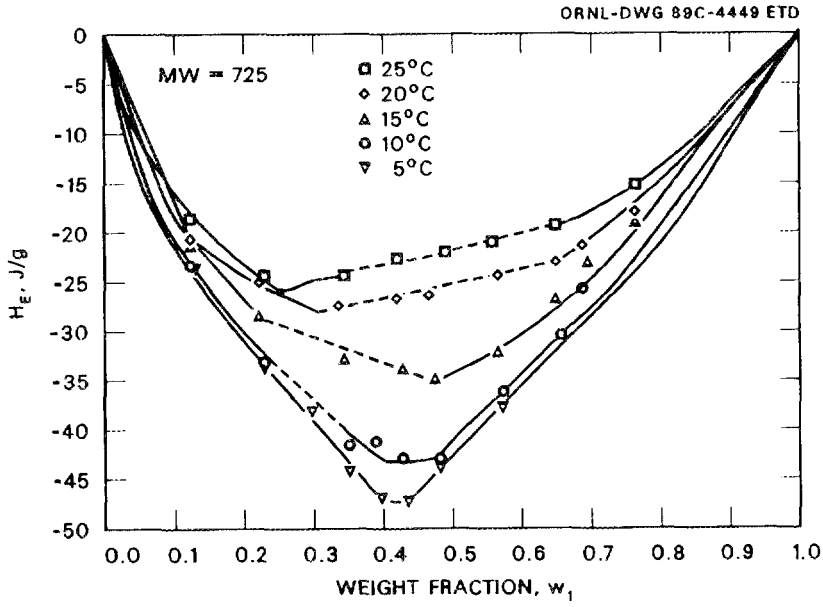

Fig. 9. Heats of mixing for polypropylene glycol (1) and water (2) mixture.

corresponds to an increase in the heat capacity of about 20% over that of water in this temperature interval.

Some three-component (ternary) systems were investigated. It has been found that the addition of a third component to a mixture can increase or decrease the phase separation temperatures. Third components that are soluble in both the other components increase the separation temperatures, while third components that are soluble only in one of the mixture components decrease the separation temperatures.

Since the triethylamine-water system (LCST, 18°C) exhibits large increases in the effective heat capacity in the critical region, the effect of adding small amounts of dipropylamine, sodium chloride, and urea to this system was investigated. It was found that the largest decreases in the phase separation temperatures were obtained by the addition of sodium chloride, but the shape of the resulting phase curve was not similar to that of the triethylamine-water system. However, it was also found from these experiments that the addition of urea resulted in a phase curve close to the desired shape shown by triethylamine-water. Based on these analyses, heats of mixing were measured for the ternary triethylamine-urea-water system.

It was found through equilibrium experiments that optimum results were obtained for initial mole fractions of urea in water in the range 0.077–0.1. The value of the LCST for this system is about 5°C. Experimental heats of mixing for the ternary system with a mole fraction of urea $x_u' = 0.077$ are shown in Fig. 10. It can be seen that the heats of mixing of this system decrease dramatically in the range of 5 to 25°C, with the largest decrease occurring between 10 and 15°C. At a mole fraction of triethylamine $x_T = 0.122$, the experimental heats of mixing show an increase of 602 J/mole (19.4 J/g) between 10 and 15°C. The increase corresponds to an effective heat capacity of 7.2 J/g·°C and represents an enhancement of about 70% over the heat capacity of water in this temperature range.

A result of this study is that heat-of-mixing data will enable the evaluation of potential systems for heat or cool storage applications. The magnitudes and temperature trends of the experimental values were consistent with those predicted in the first phase of this investigation through analytical procedures.[10] Highly accurate liquid-liquid phase equilibrium data are required to obtain reliable predictions of heats of mixing by these methods.

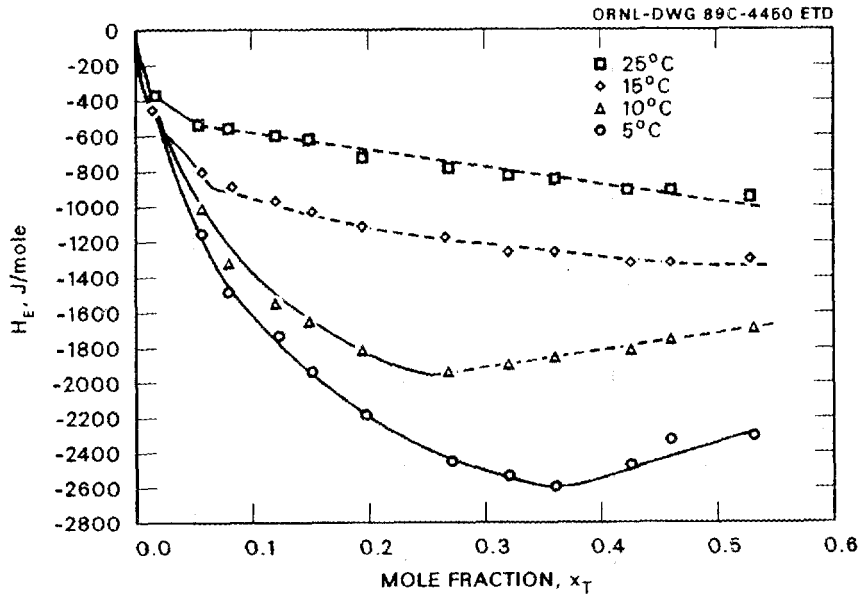

Fig. 10. Heats of mixing for triethylamine-urea-water; $x_u' = 0.077$.

For heat storage, several systems with LCSTs of about 50°C exhibited moderate changes of the heats of mixing in the critical region, including methyldiethylamine-water and polypropylene glycol (MW = 425) and water. Of the systems containing glycols or glycol derivatives which were considered for cool storage applications, the largest variations in the heats of mixing at low temperatures resulted for aqueous mixtures with ethylene glycol diethyl ether and polypropylene glycol (MW = 725). Although the experiments were conducted with commercially available materials, other glycol derivatives could possibly be synthesized which would have improved phase behavior with water for cool storage. Although aqueous systems containing blends of glycol derivatives resulted in reduced molecular weights and altered phase behavior, the ternary systems of the type considered did not exhibit higher effective heat capacities at low temperatures than the optimum binary glycol systems.

The addition of small quantities of a salt or similar compound to binary liquid-liquid systems appears to be a promising area for further study. It was found that the ternary triethylamine-urea-water system exhibited phase behavior similar to that of the nearly optimum triethylamine-water binary system, with LCSTs and effective heat capacities suitable for cool storage applications. It has also been found that the addition of a salt to a binary mixture with nonoptimum phase behavior can decrease the LCST and improve the TES capabilities of the system.

2.5 DEVELOPMENT OF AMMONIATED COMPLEX COMPOUNDS

The use of ammoniated complex compounds for TES and transport systems is a new technology and involves physical processes not previously encountered in conventional heating and cooling operations. Some of these processes may require operating conditions that would impose limitations on the concept for its intended applications. Of greatest concern are the generic problems associated with the solid-vapor reactor/heat exchanger and its attendant equipment requirements. Thus, it was appropriate that a generic study of the process and equipment design requirements be conducted. To give focus to the study, it

was directed toward the cooling application. The study was conducted by Rocky Research.

Several inorganic compounds were identified as candidate ammoniated complexes for low-temperature TES systems: $CoCl_2$, $CrCl_3$, $MnCl_2$, $SrCl_2$, $CdBr_2$, $SrBr_2$, $Sr(ClO_4)_2$, and K_2ZnCl_4. The storage density ranges from 135 to 180 Btu per pound of total storage material, depending on the temperature range, cycle configuration, and material composition.

The most unconventional equipment item for this concept is the solid-bed reactor/heat exchanger where ammoniates are formed. In this vessel, ammonia vapor must come in intimate contact with exposed solids; simultaneously, heat must be added to or removed from the system. Commercial equipment specifically designed for this task is unavailable. A number of laboratory studies have been conducted on this and similar concepts. The equipment used in these studies has been reviewed and evaluated. It was found that most laboratory equipment was small and highly specialized to accomplish a specific task and thus not amendable to scale-up. The most interesting reactor-heat exchanger concepts were developed under the metal-hydride program, although they are probably too costly for the intended application of this study. Commercially available finned tubes and plate heat exchangers were identified as suitable items around which a reactor-heat exchanger could be designed.

Tests were conducted to determine the effect of lubricant contamination on the absorption/desorption rate using the $NaBr \cdot nNH_3$ ammoniate system. Sunisco 3GS oil was sprayed as a fine mist on the salt surface such that a uniform distribution was achieved. Several oil concentrations up to 9.5% (by weight) were tested. It was discovered that the influence of oil on the desorption rate is negligible, even at high oil concentrations. This is shown in Fig. 11, where the desorption time for the ammonia/absorbent range shown is plotted against the oil contamination level. The influence of oil on the adsorption rate is much more significant, as illustrated in Fig. 12. The conclusion is that oil cleanup equipment is required and must be based on the absorption tests. It was found that a well-designed two-stage coalescing cleanup system can reduce the oil concentration in the compressor discharge to about 20 ppb. If a contamination level of 1% is permissible, then a

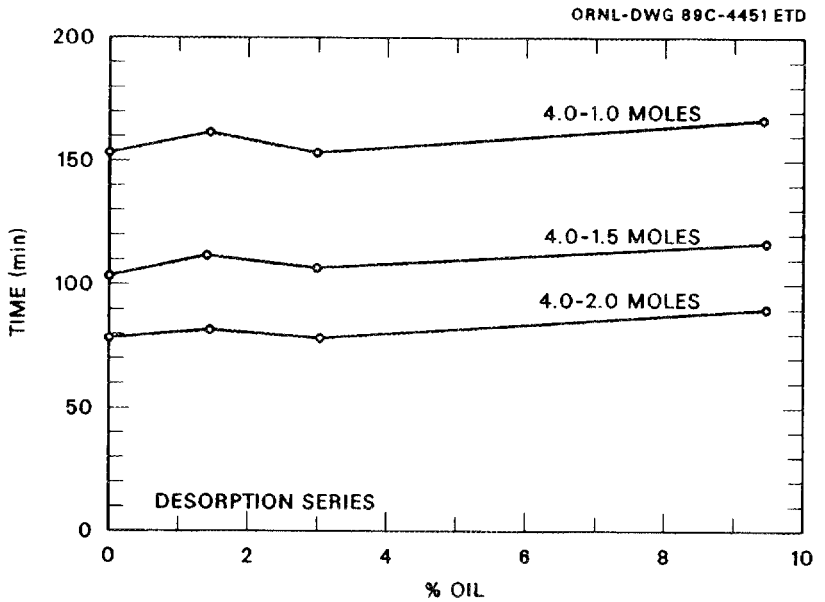

Fig. 11. Desorption periods for $NaBr \cdot nNH_3$ and Sunisco at 5°C.

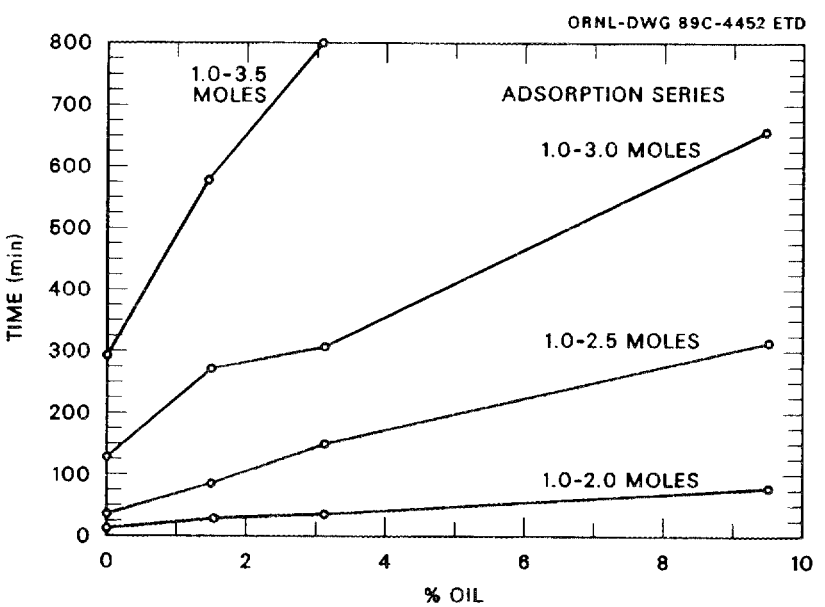

Fig. 12. Adsorption periods for $NaBr \cdot nNH_3$ and Sunisco at 40°C.

12-year life (4380 cycles) would lead to a permissible concentration level of 2.4-2.9 ppm in the ammonia. Thus the suggested cleanup system is more than adequate to sustain the complex reaction over a reasonable lifetime.

3. TECHNICAL PROGRAM – INDUSTRIAL THERMAL ENERGY STORAGE

3.1 PACKED-BED THERMAL MODEL

There is considerable interest in the use of packed beds for TES as a cost-saving measure in a variety of industrial operations. The current objective of a project by Mississippi State University (MSU) is the development of a comprehensive thermal model for the behavior of packed-bed TES systems in general, although the specific application in view is for the brick industry. The ultimate use for this model is development of an optimum, cost-effective TES system for brick manufacture.

A typical brick kiln industry requires heat transfer between air and the bricks in three processes, which may be described as "warm-up," "soaking," and "cool-down." In the warm-up and soaking stages, hot gas must be supplied in order to raise the temperature of the bricks to a high level and to maintain the high temperature for a period of several hours. The cool-down stage involves passing cool air over the bricks to return the temperature of the bricks down to ambient in a controlled manner. Throughout these three operations, the flue gas leaving the brick kiln is hot. A typical temperature-time profile is shown in Fig. 13. The hot air for the warm-up and soaking processes is composed of the hot combustion products obtained by burning natural gas in an ambient air stream. If the thermal energy of the flue gas leaving the brick kiln could be used rather than simply exhausted, the gas requirement for producing hot air would be significantly reduced. For periodic kilns, the demand for heat needed for drying or preheating may not coincide (in time) with the supply from the flue gas leaving the kiln; thus, there is need for a TES system to match the demand for heat with the supply.

A packed-bed TES system may employ a sensible heat storage material or a PCM. It is widely believed that the use of a PCM should result in improved thermal effectiveness relative to a system in which a sensible heat storage material is used. There is a need for a comparative evaluation of sensible vs latent thermal storage, based on the principles of thermodynamics, to determine whether the assumed technical

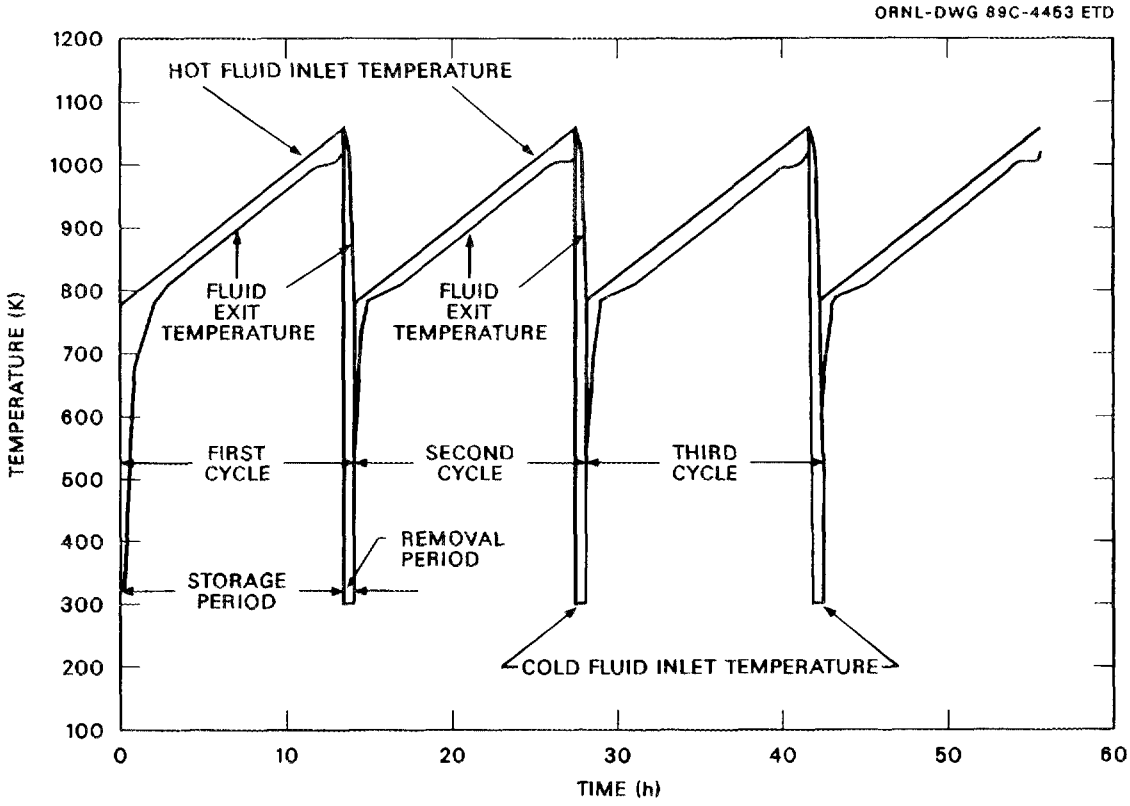

Fig. 13. Typical temperature-time profile for a periodic kiln.

superiority of a storage system utilizing a PCM is significant enough to offset the additional costs involved in the development of such materials.

The geometry of the packed bed is another important design variable. The optimum geometry of the bed and pellets should enhance the heat transfer to and from the storage material without incurring significant pressure drop penalties. Pellet geometrical shapes of practical interest include spheres, cylinders, and rectangular blocks.

An exact theory for the transient behavior of a packed bed requires the solution of the complete set of governing equations comprising the following:

Fluid phase:

1. Mass conservation equation.
2. Momentum conservation equations – the Navier-Stokes equations (or the Reynolds equations if the flow is turbulent).

3. Energy conservation equation (transient, three-dimensional form), based on the first law of thermodynamics.

Bed particles:

Transient, three-dimensional conduction equation (with phase change if PCM is employed).

Container wall:

Transient, three-dimensional conduction equation.

The development of realistic thermal models, therefore, requires reasonable simplifying assumptions that will result in a tractable set of fundamental equations. In its most comprehensive form, the energy balance equations for the fluid phase and the bed particles are as follows:

Fluid stream:

Thermal energy storage	+	Thermal energy convection	=	Particle-fluid thermal energy transfer	+	Thermal energy dispersion in the axial direction
		+ Thermal energy dispersion in the radial direction.				

Bed particles:

For the elements in the interior of each particle in the bed,

Thermal energy storage	=	Thermal energy diffusion.

Particle surface element:

Thermal energy storage	=	Fluid-particle thermal energy transfer	+	Interparticle thermal energy transfer	+	Intraparticle thermal energy transfer.

The differences among the various approximate models are with respect to the simplifying assumptions made. Typical assumptions include the following:

1. Fluid flow through the packed bed approximates plug flow through the voids.
2. The bed particles behave effectively as lumped masses so that the precise geometry of the bed particles is immaterial.

3. A negligible amount of thermal energy is stored in the heat transfer fluid.
4. There is negligible dispersion in the fluid and/or TES material.
5. There is an absence of phase change in either the fluid or the solid medium.

Of the models that have been proposed, those allowing for intraparticle conduction are for spherical particles only, whereas the present work is specifically for cylindrical pellets. Recent work by Arimilli and Graves[11] at The University of Tennessee, allowing for intraparticle conduction, considered the case of spherical PCM bed particles. The MSU model assumes that the particles are cylindrical and constructed of PCM. The MSU model assumes essentially plug fluid flow through the voids in the bed while allowing for two-dimensional effects resulting from nonuniform void fraction in the bed. The transient conduction in each cylindrical particle was modeled as a pseudo-one-dimensional case, as is explained later. From a consideration of second-order terms in the fundamental equations, the thermal energy accumulation and dispersion terms were assumed negligible in the energy balance equation for the fluid stream during both the storage and removal periods. However, the axial dispersion term can be significant during the soak period in a complete cycle.

To extend models to particles of nonspherical shape, MSU employed the concept of an equivalent sphere with a properly defined effective diameter, D_e. In packed beds utilizing spherical particles (with diameter D_s), the unit cell frequently defined is a cube of side D_s which contains a single particle. In the present system using cylindrical particles, a unit cell for the particles with a side equal to D_e, the diameter of the equivalent sphere, was defined.

For the case when the bed cylindrical particles behave approximately in a lumped fashion, the effective diameter, $D_{e,c}$, of the equivalent sphere was defined as

$$D_{e,c} = 6(V_p/A_p)$$

or

$$D_{e,c} = 3(H/D_p) \cdot D_p/[1 + 2(H/D_p)] \ , \tag{1}$$

where

H = length of cylinder,
D_p = pellet diameter,
A_p = pellet area,
V_p = pellet volume.

It was shown that a heat transfer correlation for cylindrical pellets given by Bird, Stewart, and Lightfoot[12] could be reduced to that for spheres via a judicious choice of an equivalent sphere diameter, D_e. For cylindrical particles, MSU showed that D_e could be defined as

$$D_e = 1.32\ D_{e,c} \qquad (Re_m < 50) \tag{2}$$

and

$$D_e = 1.38\ D_{e,c} \qquad (Re_m > 50) \ , \tag{3}$$

where Re_m is a modified Reynolds number defined by

$$Re_m = \frac{\rho_f\ u_o\ D_e}{6\mu_f(1 - e)} \ , \tag{4}$$

where

ρ_f = fluid density,
u_o = superficial fluid velocity,
μ_f = fluid dynamic viscosity,
e = void fraction.

To model transient conduction in a cylindrical PCM pellet, MSU made certain reasonable simplifying assumptions to develop an approximate quasi-one-dimensional, transient conduction model. The spatial coordinate, y, in this approximate model is the radial or axial coordinate, depending on whether the aspect ratio of the cylinder is greater than or less than unity. In either case, y will vary from zero (an adiabatic

surface) to b (the cylinder surface in contact with the fluid) such that

$$\frac{(A_p)(b)}{V_p} = 1 + w \ , \tag{5}$$

where w is a dimensionless parameter whose value is determined by the shape and dimensions of the pellet.

It is easily seen from Eq. (5) that w = 2 for a cylindrical pellet having an aspect ratio of 1. For a very long cylinder, w approaches 1.

The nondimensional term, w, then appears in the transient conduction energy equation for the cylindrical pellets:

$$\rho \frac{\partial \varepsilon}{\partial T} = \frac{1}{y^w} \cdot \frac{\partial}{\partial y} \left[y^w \cdot K\left(\frac{\partial T_p}{\partial y}\right)\right] \ .$$

This equation is written with enthalpy, ε, as the independent variable.

An energy equation for the fluid stream was written and simplified by ignoring radial and axial dispersion terms; the result is

$$\mu_o \frac{\partial T_f}{\partial x} = \frac{ha}{\rho_f \ c_{pf}} (T_{p,s} - T_f) \ .$$

It was further assumed that the densities of the solid and liquid phases of the PCM were approximately equal, as well as the thermal conductivities of liquid and solid PCM. Equations defining energy balances at the surface of the pellet and at the center of the pellet were used to satisfy localized boundary conditions.

The resulting set of fundamental equations for the PCM packed bed was discretized and used to develop a code that predicts the transient response of a packed bed of PCM over a number of complete (storage and retrieval) cycles.

The computer model was used to conduct a preliminary first law study of a PCM packed bed in one of the likely operational modes. The hot fluid entry temperature during the storage period follows the ramp profile shown in Fig. 14. The charging process continues to the stage when all the PCM has melted. The retrieval process uses ambient air and

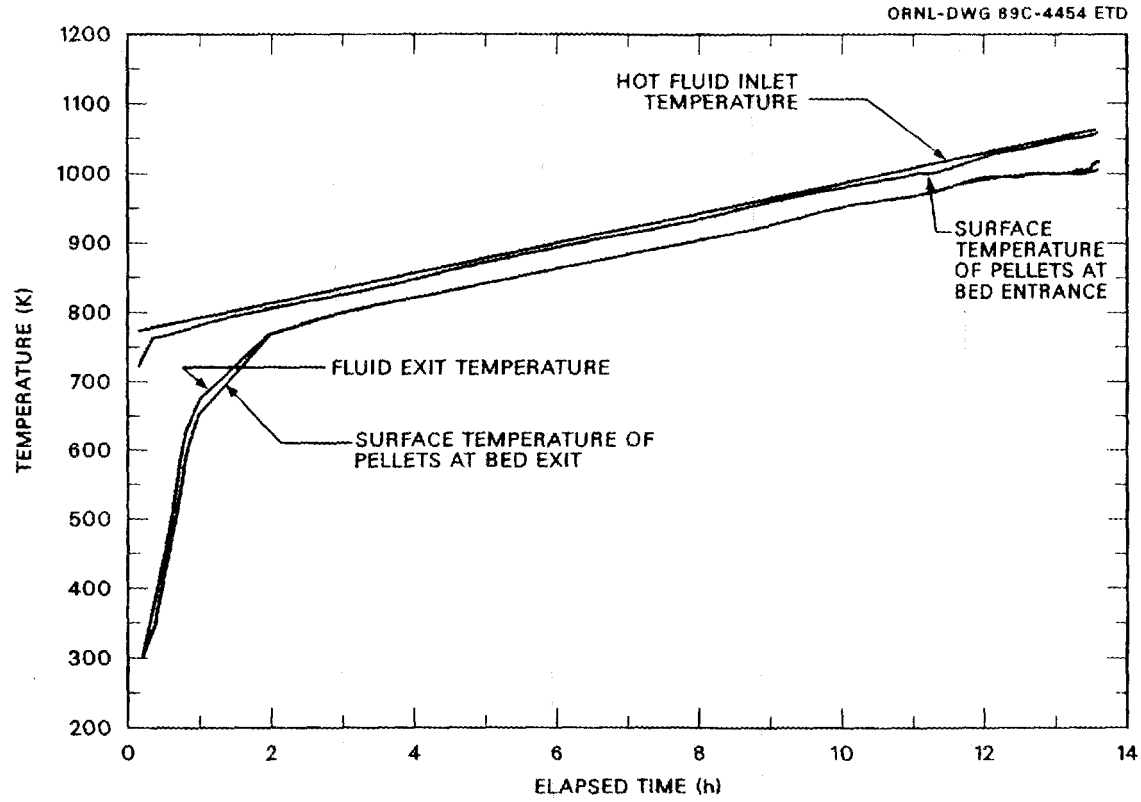

Fig. 14. Typical global performance of packed PCM bed over multiple cycles.

lasts just long enough for all the PCM to freeze. Subsequent cycles follow essentially the same pattern.

Figure 14 shows that the fluid exit temperature during the first charging cycle is lower than during subsequent cycles since the bed is initially at ambient temperature. Further, it can be seen that the fluid exit temperature becomes almost constant at the end of charging because of the presence of PCM pellets (CPCM) with a melt temperature of 973°K. Additional temperatures during the first charge period of the packed bed are shown in Fig. 15. It is apparent that for most of the charge period, the temperature difference between the pellet surface and flue gas is small, as would be expected because of the large heat transfer area of the packed bed. However, this temperature difference can be large early in the charge period, as shown in Fig. 16, where a bed length of 20 pellet diameters was assumed.

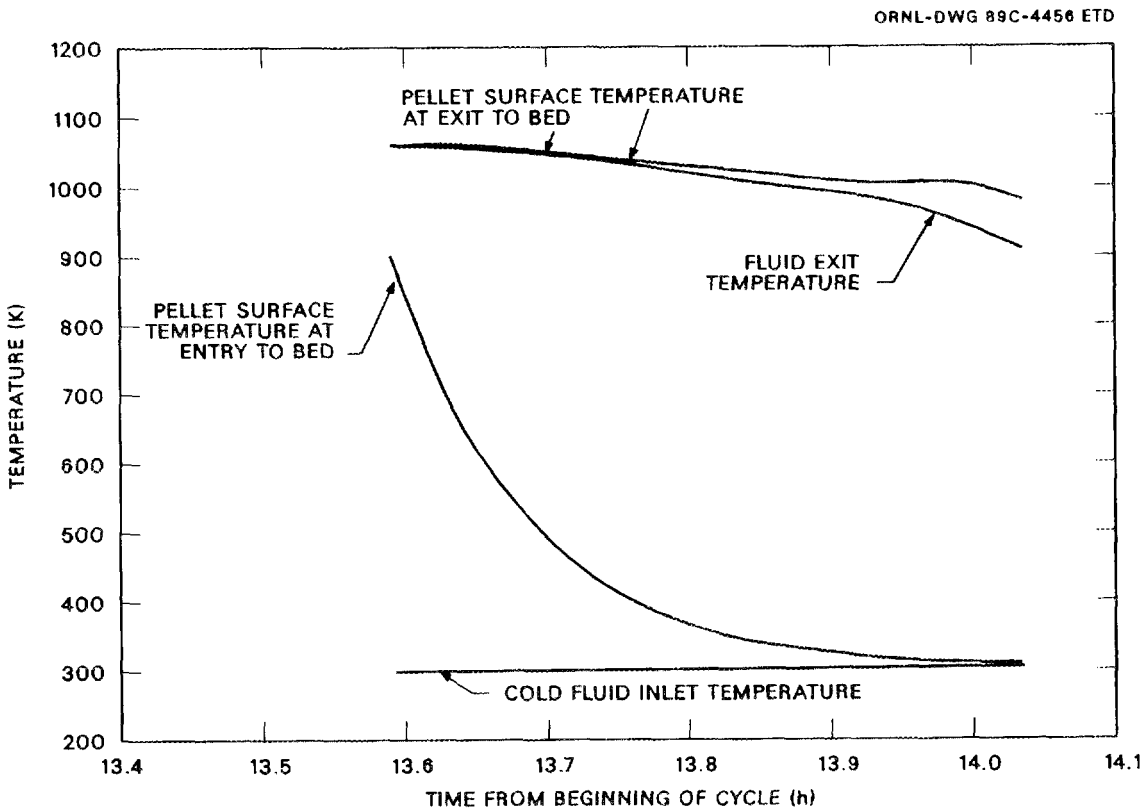

Fig. 15. Packed-bed temperature response – initial charge.

It was noted that temperature gradients are expected to be quite small in view of the prevailing low Biot numbers (less than 0.2 in the runs). The results show this to be generally the case except during phase change, when a significant temperature difference of between 10°C and nearly 100°C may exist between the pellet surface and the core.

The discharge period, defined as that time interval required for all PCM in the bed to become frozen, is quite short in comparison with the charging period, as shown in Fig. 17. Temperatures at various axial locations and at three times during discharge are shown in Fig. 18.

The MSU model was used to generate preliminary second law results for the PCM packed bed charged with flue gas. Entropy generation characteristics are summarized in Figs. 19 and 20 and show availability and energy balances through two cycles for a nominal (not optimized) packed bed with a bed-length-to-pellet-diameter ratio of 50. The difference

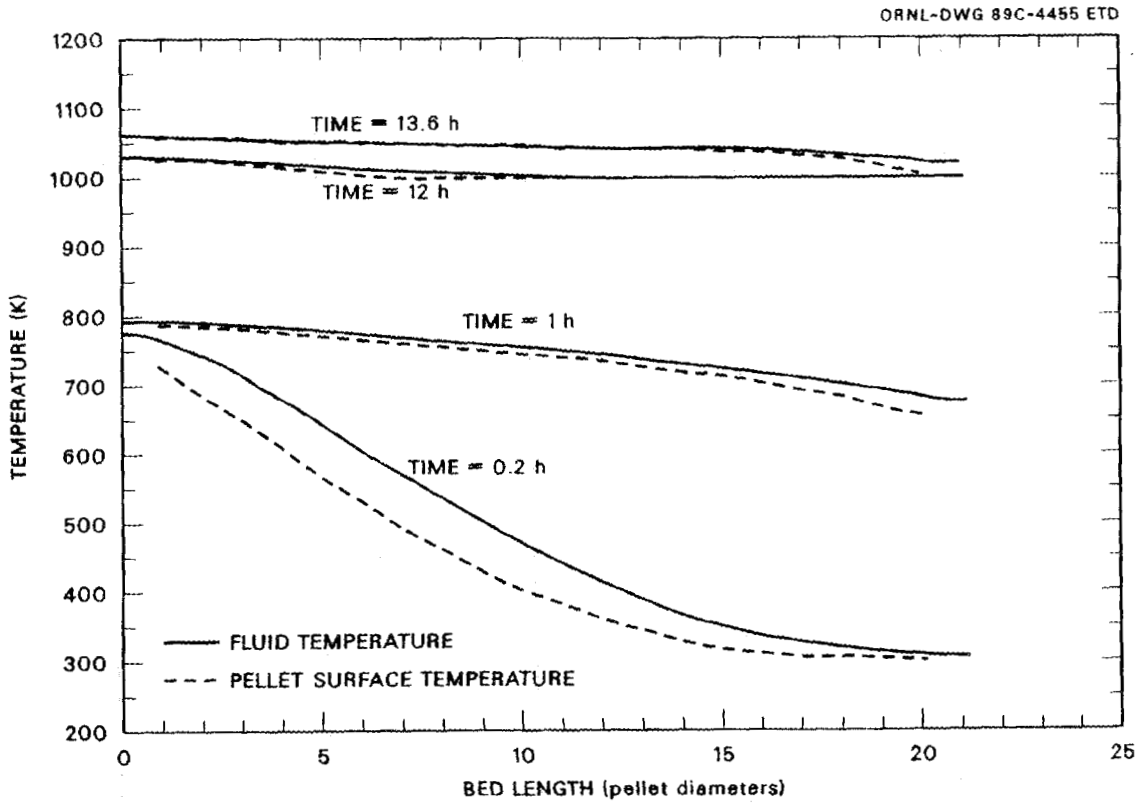

Fig. 16. Axial temperature variation in packed bed – charging.

between the first and second cycles is that the first begins a storage period with a uniform temperature distribution in the packed bed and the second begins with a nonuniform temperature distribution (most representative of cyclic operation). These results indicate that the first cycle is much less efficient in storing and removing both availability and energy and that cycle efficiencies approximate 10%.

These second law results clearly indicate that a major availability loss is through the exiting hot fluid stream at the latter stages of the storage process. This situation could be remedied or improved somewhat by increasing the bed length or by using a range of PCMs in series such that the PCM with the highest melting point is at the hot fluid entry to the bed while that with the lowest melting point is positioned toward the exit to the bed. This idea may be pursued analytically.

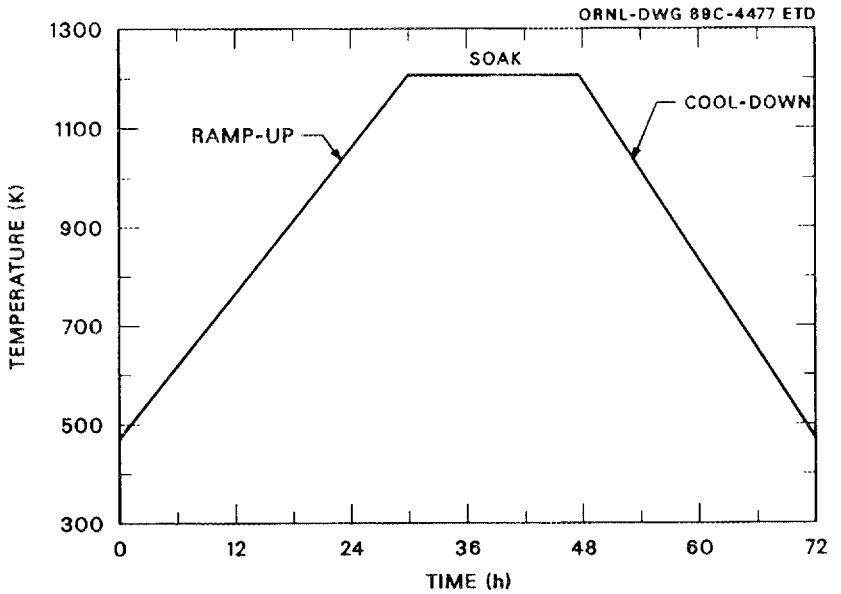

Fig. 17. Packed-bed temperature response – discharge cycle.

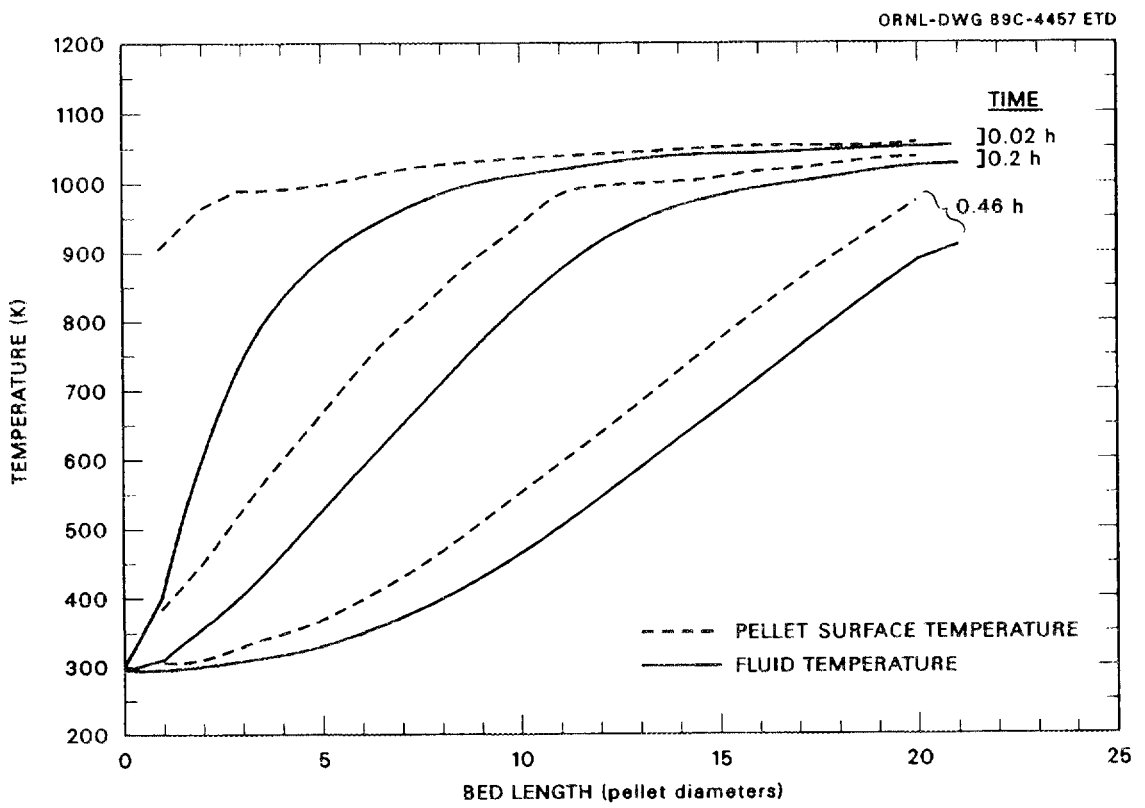

Fig. 18. Axial temperature variation in packed bed – discharging.

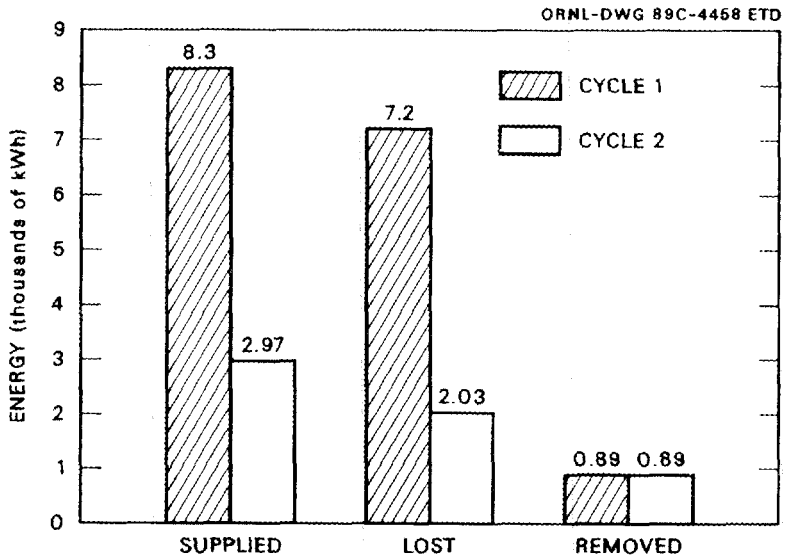

Fig. 19. Energy distribution for packed bed with L/D = 50.

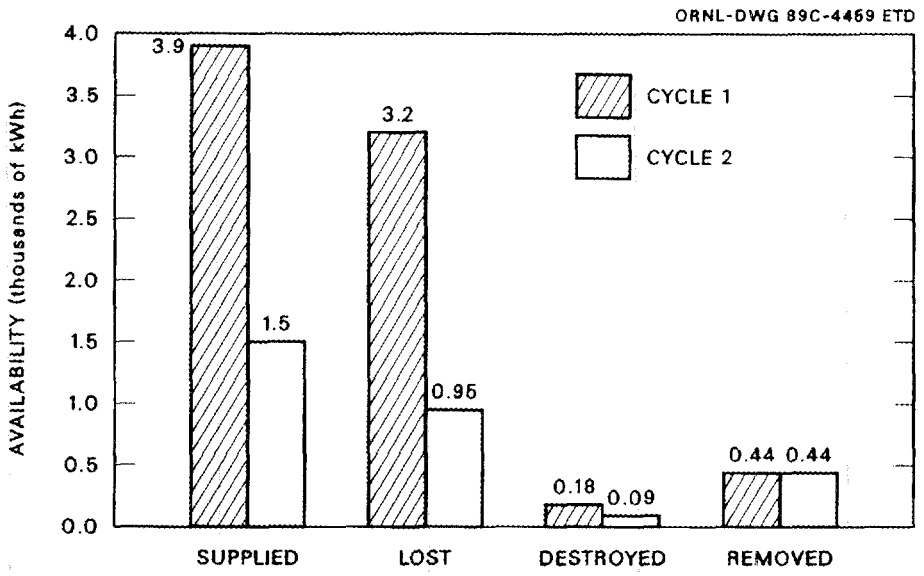

Fig. 20. Availability distribution for packed bed with L/D = 50.

3.2 COMPOSITE MEDIA DEVELOPMENT

Laboratory development of the high-temperature CPCM was completed and described in an earlier TES Annual Technical Report.[13] This material consists of a sodium/barium carbonate eutectic contained in an MgO ceramic. The porosity of the MgO is such that the eutectic can be

retained within the MgO interstices during the solid-liquid transformation of the eutectic. The system results in a form-stable composite that stores latent as well as sensible heat. This material in pellet form has been tested in the laboratory using air as the heat transfer fluid with good results; tests with actual flue gas as the working fluid are the next step.

As part of the process to develop the CPCM, work to identify manufacturing procedures and potential manufacturers of the CPCM and assessments of the media cost continued. This information is useful for ultimate technology transfer efforts as well as the near-term objective of fabrication of a supply of CPCM necessary for execution of the field test. The Institute of Gas Technology (IGT), as inventor of the CPCM technology, was the logical choice for conducting the manufacturer survey. A total of 30 companies was contacted to determine their interest in supplying ~25,000 lb of test media comprised of cylindrical pellets up to 2 in. in diameter and length. It was found that in most cases, a single company did not possess the facilities and capabilities required for spray drying, extrusion, and firing of the pellets; rather, cooperative arrangements between at least two companies were proposed. This indicates that, at this stage of the technology, CPCM manufacture probably requires a dedicated manufacturing facility. From these contacts, five companies were identified as potential suppliers:

1. Ipsen Ceramics (Pecatonica, Illinois) was interested in extruding and firing the pellets; no spray drying facilities are available.
2. United Catalyst (Knoxville, Tennessee), although very interested in the work, would have to contract with a second company for most of the required equipment.
3. Glass Beads Company (Latrobe, Pennsylvania), who spray dried the Na_2CO_3-$BaCo_3$/MgO powder for the earlier bench-scale tests performed by IGT, has no extrusion capabilities; yet they offered to cold press pellets in sizes up to 0.8 in. in diameter.
4. American Matrix (Knoxville, Tennessee), through outside contracts for various operations, could deliver the pellets, although at a premium price.

5. AGROB (West Germany) was found to possess all the facilities necessary to complete the job. Because of differences in cost of raw materials between West Germany and the United States, shipment of MgO from the United States to Germany would result in a worthwhile cost savings.

From the above capabilities, IGT produced four possible options for pellet fabrication:

1. Glass Beads Co. spray dries and Ipsen Ceramics extrudes and fires, delivering 1- and 2-in. pellets.
2. Glass Beads Co. performs the entire job: spray dries the powder, die presses up to 0.8-in.-diam pellets (because of limited press sizes), and fires.
3. Glass Beads Co. performs the entire job: spray dries the powder, extruding in a used extruder purchased by IGT, and fires.
4. AGROB performs the entire job: IGT purchases MgO and ships MgO to West Germany; AGROB purchases all other materials needed, spray dries the composite powder, extrudes 1- and 2-in. pellets, fires, and ships to the United States.

These options and their estimated cost breakdowns are summarized in Table 2. Option 2, with the Glass Beads Company producing only 0.8-in.-diam pellets, was the least expensive U.S. manufacturing option. This yielded a total task cost of $210,954. However, this alternative did not provide the 1-in.-diam × 1-in.-high and 2-in.-diam × 2-in.-high pellets originally specified. The least expensive U.S. approach that delivers both 1-in. and 2-in. pellets is option 3. The Glass Beads Company would perform the job with IGT/DOE purchasing and providing a used extruder. This option yields a total task cost of $276,920. The least expensive alternative that delivers both 1- and 2-in. pellets is option 4; the total task cost for this option is $106,408. In spite of the increased labor, travel, and transportation expenses, AGROB's bid, when combined with the related supervision and materials costs, yielded a final cost that is 73% less than option 1, 62% less than option 3, and 50% less than option 2. Moreover, AGROB has indicated interest in commercializing the technology.

Table 2. Summary of four options for CPCM fabrication

	Option 1	Option 2	Option 3	Option 4
Pellets delivered	1 and 2 in.	0.8 in. diam	1 and 2 in.	1 and 2 in.
Description	Glass Beads Co. spray dries; Ipsen Ceramics extrudes and fires	Glass Beads Co. spray dries, die presses, and fires	Glass Beads Co. spray dries, extrudes and fires; IGT buys and provides a used extruder to Glass Beads Co.	IGT purchases MgO; AGROB ships MgO to West Germany; AGROB produces 1- and 2-in. media and ships to USA
Subcontract for production of 26,000 lb of CPCM, $	361,145	171,936	237,902	44,566
Additional materials supplied, $	0	0	0	8,295
IGT labor, travel, per diem, supervision, G&A, and fee, $	37,341	39,018	39,018	53,547
Total price, $	398,486	210,954	276,920	106,408
Unit price, $/lb	15.37	8.14	10.68	4.10
Relative cost (approximate)	3.8	2.0	2.6	1

3.3 COMPOSITE MEDIA FIELD TESTING

Laboratory development of the high-temperature CPCM has been completed and reported.[14] These tests indicated that, with air as the working fluid, a packed bed of CPCM successfully survived more than

6000 h of testing through 206 freeze-melt cycles with less than a 2% weight loss, although some redistribution of the PCM components was found axially along the test bed. To determine the performance of the CPCM with actual flue gas as the working fluid and to determine the thermal/hydraulic performance of a packed bed of cylindrically shaped pellets, a field test at a periodic brick plant was proposed. To provide information necessary for subcontracting the field test, (1) a conceptual design of the test facility was completed, (2) a packed-bed simulation was completed to determine the influence of bed design on pressure drop through the bed, and (3) the flue gas from an operating periodic kiln was characterized. These activities were completed to provide background information necessary for an outside vendor to estimate the cost of design, fabrication, installation, and operation of a field test facility.

3.3.1 Flue Gas Characterization

A major unknown in the design of a brick plant TES system is the effect of flue gas particulates and composition on the thermal and metallurgical performance of the storage material. Particulates are known to exist in brick plant flue gases in considerable amounts. The concern is that these hot particulates will adhere to the storage material and gradually degrade its thermal/hydraulic performance. There are ways of dealing with this problem (e.g., a "scrubber" section of easily removable pellets), but the extent of the particulates must be determined before a solution can be defined.

A sampling crew from the Oak Ridge Gaseous Diffusion Plant traveled to the Schneider Brick Company (SBC) to sample the flue gas for particulate and chemical composition. The sampling was conducted during that part of the kiln firing cycle where particulates were expected to be the most common, that is, the initial heatup just prior to "soak." The individual sampling consisted of the following:

1. Five samples for total particulates.
2. Three samples for particulate size distribution.
3. Eight samples for oxygen, CO_2, and moisture.
4. Two samples for NO_x and fluorine.

The total particulate results are summarized in Fig. 21, which shows total particulates in grams per hour as a function of time into the kiln cycle. Five data points, at 3.0, 9.0, 11.5, 29.5, and 31.5 h into the kiln cycle, are shown. These data confirm the commonly held belief that particulates are a problem in the early portion of the burn cycle.

The data summarizing particle size distribution are shown in Table 3. The primary conclusions reached from these data is that the particle size distribution varies considerably with time. Early in the cycle, the majority (71.5%) of the particles have a size less than 0.5 μm. Late in the cycle, 82% of the particles have sizes that exceed 7.0 μm.

The data summarizing the flue gas composition are shown in Fig. 22, which shows oxygen, CO_2, and moisture as a function of time into the kiln cycle. These results generally agree with an earlier sampling exercise conducted by IGT. An interesting result is the moisture content. The data show the expected trend of high levels early in the cycle but low levels late in the cycle as the bricks "cure."

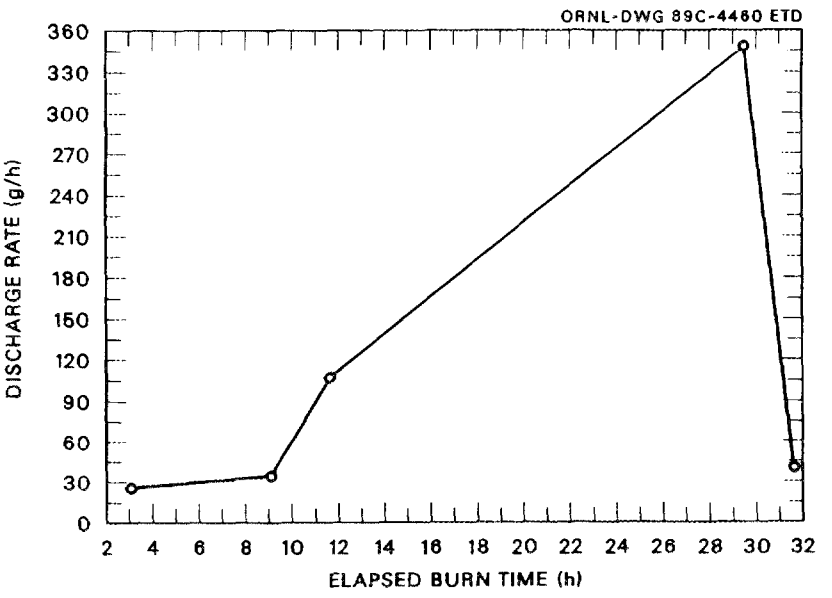

Fig. 21. Total particulates as a function of elapsed burn time (SBC).

Table 3. Summary of flue gas particle size distribution

For the sample taken 15 h into the cycle		For the sample taken 33 h into the cycle	
Size range (μm)	Percent in size range	Size range (μm)	Percent in size range
>12.1	18.1	>16.5	58.3
7.6–12.1	0.8	10.0–16.5	13.4
5.2–7.6	0.0	6.8–10.0	10.1
3.5–5.2	0.0	4.5–6.8	2.3
2.2–3.5	0.5	2.9–4.5	2.9
1.2–2.2	0.0	1.4–2.9	2.2
0.7–1.2	1.9	0.9–1.4	4.0
0.5–0.7	7.2	0.6–0.9	3.6
>0.5	71.5	<0.6	3.2

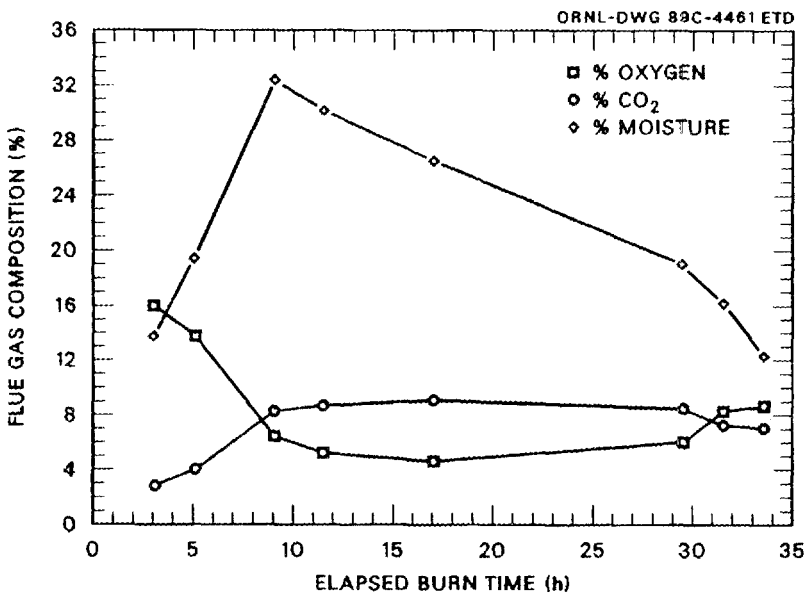

Fig. 22. Flue gas composition as a function of elapsed kiln burn time.

Only a limited amount of data on NO_x and fluorine concentrations was obtained. These samples were taken approximately 9.0 and 11.5 h into the kiln cycle. The data showed no measurable concentrations of NO_x but a considerable increase in the concentration of fluorine. At 9.5 h into the kiln cycle, the fluorine concentration was ~15.6 g/h; at 11.5 h into the cycle, it had increased to 38.9 g/h.

These data will be included in the test facility Request for Proposals so that contractors can consider this information in their designs.

4. SUMMARY AND CONCLUSIONS

The TES Program has made good progress in advancing TES technologies in both the diurnal and industrial areas. In the diurnal area, work to identify and characterize liquid-liquid systems revealed chemical systems that possess heats of mixing almost twice those of water and ternary systems that provide adjustment in the critical solution temperature. These systems, in addition to the PCM slurry concept, may be useful as thermal buffers in heat transport systems. Work was initiated in the area of ice "stickiness," with a goal of developing technologies that would reduce the first costs and improve the efficiency of ice storage by reducing the adhesion of ice to a cold substrate and allowing the ice to fall or float from the surface once it is formed. Basic heat transfer studies in a packed bed with a vaporizing working fluid were continued in an effort to develop a heat transfer correlation useful for future heat pump/TES system studies. The heat transfer effectiveness of this system promises to be quite high because of the large surface area of the packed bed and convective two-phase heat transfer from the bed. Finally, work was continued on the unique solid-vapor adsorption system. This system is attractive for use in vapor compression systems in which ammonia is used.

Based on the prior year's emphasis and success in preliminary development of the CPCM, work was continued on implementating a field test of the media using flue gas from a kiln. Progress was made in several areas that directly support the field test: The flue gas from a periodic kiln was characterized to provide data useful for design of a subscale test facility, and preliminary development of a high-temperature PCM packed-bed model was completed. A search of potential vendors for the CPCM was successful in locating a supplier who will provide the material at $4.00/lb. The program is now in a good position to carry the field test forward.

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