

IMMISCIBLE FLUID - HEAT OF FUSION HEAT STORAGE SYSTEM

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PROJECT OUTLINE

Project Title: Immiscible Fluid - Heat of Fusion Heat Storage System

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Project Goals: The primary objective is to evaluate the feasibility of direct contact heat transfer in phase change energy storage using aqueous salt systems. A secondary objective is to improve knowledge and understanding of heat and mass transfer in direct contact aqueous crystallizing systems.

Project Status: In order to facilitate research into this energy storage device, the project was divided into four major research areas:

- (1) crystal growth velocity study on selected salts
- (2) selection of salt solutions
- (3) selection of immiscible fluids
- (4) studies of heat transfer and system geometry
- (5) system demonstration.

The project status is as follows:

- (1) This study is complete. Crystal growth data was previously obtained for $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (1). During the past year data on $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ were also obtained.
- (2) This study is complete. Sodium carbonate and calcium nitrate were found unacceptable for this storage system but sodium thiosulfate, disodium hydrogen phosphate, sodium sulfate and calcium chloride were found to be acceptable (1).
- (3) The two most promising candidates of over 160 potential immiscible fluids were tested in a bench scale direct contact energy storage device.
- (4) This study is complete. It was found that while the number of immiscible fluid diffusers did not change the storage efficiency, increasing the storage container height did increase the storage efficiency (1).

Contract Number: EY-76-S-05-5190

Contract Period: 6/1/76 - 5/31/79

Funding Level: \$139,000

Funding Source: Department of Energy, Division of Energy Storage Systems

Background:

Thermal energy storage is clearly an essential component of a solar energy system. Indeed, in optimizing the overall performance of virtually any conventional or nonconventional energy system, the storage of thermal energy is required. Heat of fusion systems clearly offer a great potential for high density storage of thermal energy, but this potential has been difficult to realize in practice due to phase segregation, slow rates of energy transport, long term degradation, nucleation problems and the corrosive nature of the systems. Direct contact heat transfer between the aqueous crystallizing solution and an immiscible heat transfer fluid has been proposed as a solution to these difficulties (2,3, 4,5). A feasibility study of this technique has been in progress at Clemson since 1975.

The essence of the technique is that a fluid, (lower in density and immiscible with the aqueous salt solution) is introduced at the bottom of the storage vessel as a dispersed phase. As bubbles of this fluid rise through the vessel, they transfer heat to or from the salt solution, and also agitate the vessel contents. The heat transfer fluid is pumped through the remainder of the primary heat transfer loop (e.g., solar collectors or heat pump exchanger and the air heating units of a residential heating system.) Figure 1 is a schematic of the immiscible fluid-heat of fusion storage system.

Results and Discussion:

1. Crystal Growth Velocity Studies

This fundamental area of study was reported on at the third annual thermal energy storage contractor's information exchange meeting (1). The same apparatus previously detailed was used to collect crystal growth data for $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. This growth data is shown in Figure 2. For a given undercooling only $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ grew significantly faster. $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ all had slower growth rates. Commercially available CaCl_2 was so impure that reliable growth data could not be obtained for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

2. Selection of Salt Solutions:

This study was completed in 1978 and was previously reported (1).

3. Selection of Immiscible Fluids:

A list of over 160 potential immiscible fluids was compiled at the beginning of this study. Excessively high cost, toxicity or high density ruled out many fluids. Bench scale tests showed that fluid viscosities greater than 4-5 cp resulted in excessive carry-over of salt solution during cycling of the storage system. Properly placed and sized screens within the immiscible fluid extended the viscosity range to about 10cp. Various separator designs were investigated including beads floating at the interface. Two of these fluids, Marcol 72 and Therminol 60, were selected for testing in the bench scale apparatus. The fluids were evaluated for solution carry-over, and for system energy storage efficiency, using disodium hydrogen phosphate as the storage medium.

Solution carry-over was determined by measuring the aqueous liquid volume collected in a separator downstream of the storage vessel exit, and by monitoring the salt concentration in the heat transfer fluid by means of atomic absorption spectroscopy. The system was cycled through a series of consecutive runs (15 with Marcol, 13 with Therminol), and periodic measurements made. The total aqueous volume collected was 20 ml in the case of Marcol 72, and 7 ml for Therminol 60. This represents under 2% of the system volume in the former case, and well under 1% in the latter. The salt concentration (as dodecahydrate) in the fluid reached a maximum of 120 $\mu\text{g/ml}$ in the case of Marcol, and 32 $\mu\text{g/ml}$ with Therminol, both well under 0.01% by mass.

The aqueous solution entrained in the heat transfer fluid was quite finely dispersed, and it seems quite likely that the separator did not collect all of it. Upon shutdown after the 15 cycle Marcol run, no observable salt deposition was found in the system, nor were deposits observed in the case of the Therminol run. While this did not represent conclusive proof of the absence of carry-over problems in operation of the direct contact system with these fluids, it certainly was promising.

The system thermal efficiency was also monitored during the consecutive cycles described above to ascertain any effect of heat transfer fluid on system thermal storage performance. The average storage efficiency for 12 cycles of Marcol 72 was 77.6% and for 12 cycles of Therminol 60 was 74.3%. Thus the choice of fluid did not appear to change the storage efficiency.

It was observed that the average storage efficiencies obtained compare well with the value obtained earlier for disodium hydrogen phosphate and Varsol (1). Significantly, there was no trend of efficiency with extent of cycling with Marcol 72. That is, no degradation of performance was evident. With Therminol, only two cycles were monitored for efficiency. One aspect of the system operation that did improve significantly with time was the degree of under-cooling, which decreased appreciably as operation of the storage system continued. With Therminol 60 the undercooling (subcooling below the phase transition temperature before the onset of crystallization) was 8° on the first cycle, and less than 1°C on the eighth and subsequent cycles.

Based on these results, and consideration of the physical properties of the fluids, Therminol 44 also appeared to be an especially attractive candidate for use in direct contact storage units. Its flash point is higher than that of Marcol 72, yet its viscosity is appreciably lower, implying lower carry-over. No operational data are available at present, however.

4. Studies of Heat Transfer and System Geometry:

This study was completed in 1978 and was previously reported (1).

5. System Demonstration:

Using the results of these four preliminary studies a pilot scale system was constructed and tested over a one month period. An overall

schematic diagram of the apparatus is shown in Figure 3. The storage vessel was constructed from mild steel plate coated with epoxy paint to prevent corrosion. The tank was 80 cm high by 60.6 cm in diameter, flanged on top to allow insertion of the immiscible fluid feed manifold. The tank was insulated with 8.9 cm of fiberglass to reduce heat loss to the environment.

The immiscible fluid diffusers used in this experiment were made from one inch (2.54 cm) plexiglass rod. The six diffusers were connected to a feed manifold which hung from the tank lid and was inserted into the tank as a unit.

A phase separator was placed into the system below the immiscible fluid exit. The basket for the phase separator was constructed from one-quarter inch mesh screen. The basket had a depth of five inches (12.72 cm) and a width of fourteen inches (35.56 cm). The packing material for the phase separator was approximately one inch thick fiberglass. In addition, a layer of polyethylene beads approximately 5 cm thick was floated at the solution-fluid interface.

A separator tank was placed on the exit of the storage tank to collect any remaining salt solution carry-over by the immiscible fluid.

In order to have approximately constant flow rates, a positive displacement gear pump was used. To prevent over-pressurization of the system during crystallization, a pressure switch was installed on the tank inlet. This switch, set at thirty-five psig, tripped an alarm input to the data-logging and control computer which switched the system to heating for a timed period to "defrost" the diffuser exit area.

The tank temperature was monitored with several thermocouples and a three junction thermopile was used to determine the temperature difference between the inlet and outlet immiscible fluid temperatures. Immiscible fluid flow rates were continuously monitored. Further details on the apparatus and experimental procedure are given by Mills (6).

Calorimetric Studies

Thermal storage efficiency was measured to detect any salt degradation with continuous cycling. Thermal storage efficiency is defined as the amount of energy added to or withdrawn from the salt solution divided by that which could be obtained if thermodynamic equilibrium was achieved. An efficiency of 100% would indicate that equilibrium has been reached.

Several calorimetric runs were made with water as the storage medium in order to calibrate the apparatus. In these runs the "efficiency" should always be 100% with deviations from this value indicative of experimental error. The overall average efficiency for both heating and cooling was 97.1%. Possible sources of error include inaccuracies in measuring the flow rate and the ΔT across the thermopile and an error in the overall heat transfer coefficient for the tank. The 2.9% error in closure was judged to be adequate to proceed with the salt studies.

For the Marcol-disodium phosphate system cycled for 22 days the average cooling and heating efficiencies were 72.0% and 66.4%, respectively. The cooling efficiency was lower than the average cooling efficiencies (77.3%)

obtained in earlier bench scale work by Marra (7), Costello (8), and Kizer (9). The earlier researchers used an $\sim 2^{\circ}\text{C}$ (3.6°F) approach (between inlet and outlet streams to indicate when the cycle was complete, while in this work it was felt that 5°F (2.77°C) approach was the closest approach the system would probably achieve in practical operation. Since at this point some crystallization was still occurring in the tank, extending the cycle should give increased efficiencies. A cooling run performed subsequently with a ΔT approach of 2.25°C (4.05°F) gave an efficiency 76.0%, only 1.3% lower than the average cooling efficiencies obtained by the other researchers. No undercooling was observed.

Effects of Carry-Over on System Performance

The main thrust of this research was to test the performance of the proposed direct contact-latent energy storage system on a pilot scale. The single most important question was the effect that carry-over of the salt solution by the immiscible fluid would have on the performance of the system.

Polyethylene beads floating at the Marcol-salt solution interface served as a primary phase separator. A second phase separator was then placed in the tank in the immiscible fluid above the floating bead layer. This phase separator was made from fiberglass filter material attached to a quarter inch screen mesh basket below the Marcol exit.

To monitor the apparent salt concentration buildup, atomic absorption analysis (the analytical procedure is given by Marra (7)) was used.

Table I shows the results of the atomic absorption analysis for days 13 through 22 of the extended cycle tests. Note that the cooling runs had a much lower salt concentration than the heating runs, thus indicating that salt was depositing from the Marcol somewhere in the system. The overall level of salt concentration in the Marcol rose on successive runs, thus indicating greater potentials for salt deposition. The amount of carry-over collected in the separation tank also increased with time as can be seen in Table II. On the nineteenth day of the extended cycle tests, 2.85 gallons (10.8 liters) carried over into the separator tanks, over a hundred times the normal amount. Evidently the separator beads must have been agglomerated by crystallizing salt. The Marcol would then collect below the bead layer, lift the beads to the top of the tank and pass large quantities of the salt solution. Such behavior had been observed in the bench scale apparatus [Marra (7)]. Table II also shows the number of "defrost" cycles per cooling run for this set of salt runs. The number of "defrost" cycles decreased significantly after the 2.85 gallons of salt solution was carried over on the nineteenth day. Subsequently, the number of cycles started to increase again with each succeeding run.

In his studies of Marcol 72 and Therminol 60 Marra found that the concentration of salt hydrate increased in the immiscible fluid with time.

The same behavior was found in this study and suggests that the salt hydrate concentration will build up to a level resulting in salt deposition from the immiscible fluid irrespective of the immiscible fluid used.

On day twenty-four of the run the inlet pressure during a cooling cycle failed to drop below twenty-five psig after the "defrost" cycle. Since the system was evidently again getting plugged with salt deposits, the system was again cleaned out and Varsol used to replace the Marcol as the immiscible fluid to investigate the effect of fluid on the fouling problem. Unfortunately, after one day a mechanical failure of the pump forced shut-down. Upon opening the storage tank, it was found that the salt had backed up partially into the diffusers, and then crystallized.

As no suitable replacement pump was available, the study was terminated to allow evaluation and redesign of the system before resumption of the investigation.

A simple experiment verified that the salt in the Marcol was crystallizing onto cool heat exchange surfaces. Three gallons of hot Marcol that had been drained from the surge tank were placed in a bucket with a cooling coil immersed in it. Upon examination of the coil after two days salt crystallized from the Marcol was observable on the coil.

CONCLUSIONS

1. The thermal storage efficiencies obtained in this pilot scale study are consistent with efficiencies obtained in bench scale studies.
2. The disodium phosphate showed no signs of degradation during the run.
3. Salt solution carry-over presents a significant problem to system operability, with salt deposition from the immiscible fluid occurring in the heat exchanger during the cooling runs.
4. Modifications to the system design to counteract the detrimental effects of salt carry-over and of diffuser plugging must be devised to achieve a viable direct contact phase change unit.

RECOMMENDATIONS

It is quite clear from this and previous studies that significant salt solution carry-over in the immiscible fluid is inevitable, and a successful system design must allow for the inevitable salt deposition. In this regard, three key principles are evident. First, the surge tank external to the storage vessel must be eliminated by allowing expansion volume in the storage vessel itself. Second, the heat exchanger design must allow for salt deposition during cooling cycles. By using sufficiently large tubes an external forced convection heat exchanger system should be feasible. This clearly should be closely coupled to the storage tank, and located downstream of the pump. Finally, the immiscible fluid feed manifold should be designed to allow introduction of the fluid at various levels in the tank depending on pressure drop. Thus, as crystallization proceeds and blocks diffusers low in the tank, outlets higher in the tank would become active. On heating cycles the tank would then be melted from the top down.

One scheme for dealing with the heat exchange problem, proposed by Barlow (10) and by Helshoj (11), is to locate it within the heat transfer fluid layer at the top of the storage vessel. Both also proposed means for varying the point of fluid introduction with state of crystallization. However, the internal heat exchanger, while very attractive from the point of view of minimizing the effect of deposition, may present severe heat transfer rate limitations due to the limited heat transfer area and the natural convection mechanism.

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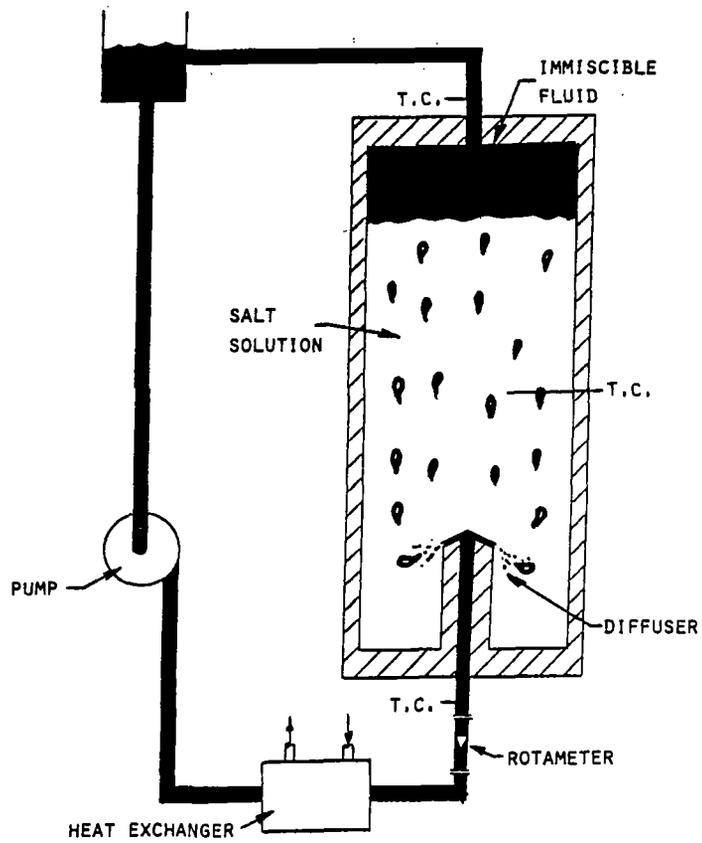


Figure 1. Immiscible Fluid - Heat of Fusion Storage System.

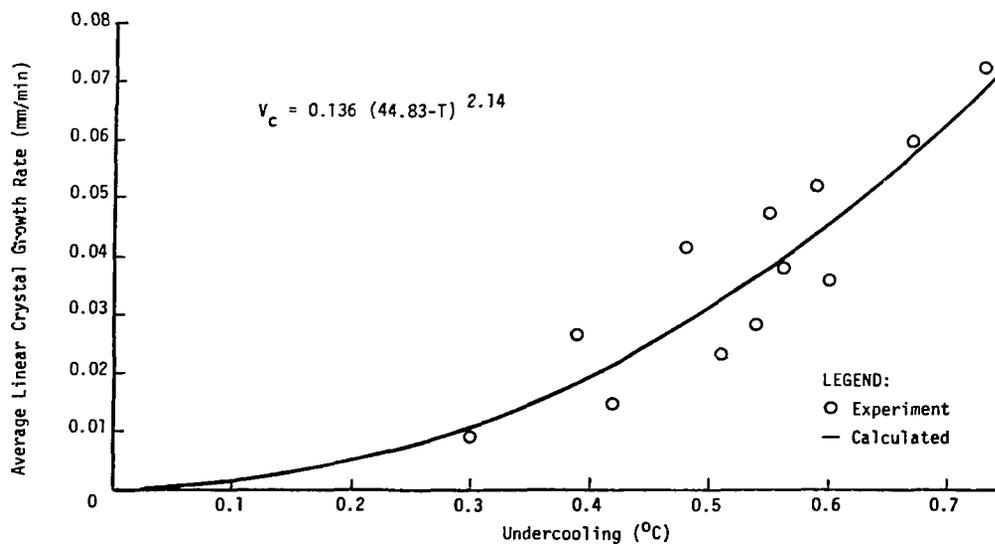


Figure 2. Average Linear Crystal Growth Rate of Sodium Thiosulfate Pentahydrate in a 55.00 Mass Percent Solution as a Function of Undercooling.

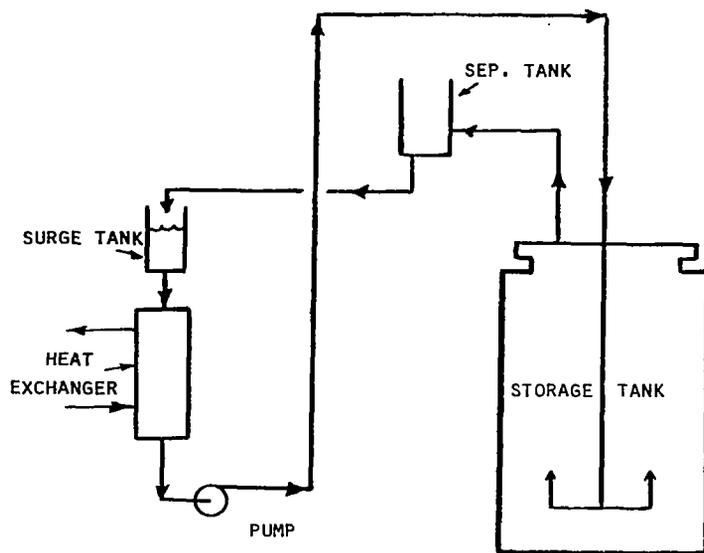


Figure 3. Schematic of Pilot Scale Energy Storage Apparatus

TABLE I. Atomic Absorption Analysis Results for the Extended Salt Run

Day	Concentration of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ($\mu\text{g/ml}$)	Type of Run
13	16.58	Cooling
14	46.10	Heating
15	23.82	Cooling
17	21.85	Cooling
18	106.45	Heating
19	37.01	Cooling
20	137.82	Heating
21	18.15	Cooling
21	134.29	Heating
22	13.94	Cooling

TABLE II. Carry-Over Data for the Extended Salt Run

Day	Period of Collection (hr)	Superficial Velocity (cm/sec)	Amount (ml)	Number of Defrost Cycles
14	24	0.047	11	2
15	22	0.047	13	2
16	24	0.047	15	
17	24	0.047	27	7
18	24	0.047	67	8
19	24	0.047	10790	
20	28	0.047	86	1
21	28	0.046	44	2
23	33	0.043	123	4