DEVELOPMENT OF A THERMAL STORAGE MODULE USING MODIFIED ANHYDROUS SODIUM HYDROXIDE

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PROJECT OUTLINE

Project Title: Latent Heat (NaOH) Storage for Total Energy Systems

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Project Goals: To conduct laboratory scale testing of a modified anhydrous NaOH latent heat storage concept for small solar thermal power systems such as total energy systems utilizing organic Rankine systems.

Project Status: Under a previous contract, NAS3-20615, a module was tested and a computer simulation code developed. This follow-on effort consists of diagnostic test on the module and investigation of alternative heat transfer fluids and heat exchange concepts.

Post test analysis of the previously tested module indicated no internal corrosion or leakage. The module has been refilled with Thermkeep (91.8% Anhydrous NaOH, 8% $NaNO_3$, and 2% MnO_2) and prepared foir a second test series using an alternative heat transfer fluid, Caloria HT-43. Silicone B was initially to be used; however, this fluid was found to be mildly reactive with the NaOH. The computer simulation model has been modified to predict the performance of this module in a solar total energy system environment. In addition, the computer model has been expanded to investigate parametrically the incorporation of a second heat exchange inside the TES module which will vaporize and superheat the Rankine cycle power fluid.

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INTRODUCTION

The program reported herein is a continuation of a prior program (ref. 1) which included the design, construction, and testing of an experimental one-tenth scale-model of a phase change thermal energy storage (TES) system suitable for use in electricity generating systems such as the Sandia Solar Total Energy Test Facility (SSTETF) at Albuquerque, New Mexico. This was used to generate data with which to verify a previously developed computer model of the TES unit. The TES unit employs a single passive internal heat exchanger which is used both for charging and discharging heat by means of a non-phase change heat transfer fluid such as Therminol-66. The TES unit and test bed are described in ref. 1.

The nominal composition of the TES medium (Thermkeep) is:

Anhydrous NaOH, commercial grade	91.8% (wt)
$NaNO_3$	8.0
MnO_2	0.2

The commercial grade of NaOH typically contains 1-2% of NaCl and 1-2% of Na_2CO_3.

The program which is approximately 50% completed includes the following tasks:

1. The experimental model developed under the prior contract is to be examined to determine whether or not deterioration has occurred during the testing, such as mechanical damage to the heat exchanger, or chemical changes in the TES medium.

2. Restoration of the TES system to operating condition, installation of a different heat transfer fluid approved by the NASA Program Manager, and the running of a series of thermal charging and discharging cycles to obtain additional experimental data for correlation with the computer model for further validation.

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* The program is being performed under Contract No. DEN3-138 issued by NASA Lewis Research Center.

3. Extension of the computer model of the TES system to include a second heat exchanger in the TES unit, so that the unit can be charged by means of a non-phase change fluid (e.g. from solar collectors) flowing in one heat exchanger, and discharged by a phase change fluid flowing in the other (e.g. the power fluid of a Rankine cycle engine).

4. Upon completion of the computer model a reference design of a lowest cost TES system is to be developed suitable for use in solar electric power generation.

POST-TEST ANALYSIS OF TES UNIT

During the prior program the TES unit was used to obtain data from 23 cycling tests which ranged in duration from 4 hours to 48 hours, and in temperature from approximately 230 C to 315 C. These tests extended over a period of about 5 months during which the unit was maintained continuously within the operating temperature range. Thereafter the unit self-cooled very slowly to ambient temperature.

Chemical Analysis of Thermkeep

The first step of the post-test analysis was the removal of samples of Thermkeep for chemical analysis to determine whether or not segregation of components occured (Thermkeep being a non-eutectic mixture), and whether reduction of $NaNO_3$ resulted in an increase in $NaNO_2$. The latter is formed at a very slow rate by oxidation of the steel tank and heat exchanger and is reoxidized to $NaNO_3$ by air "breathed" into the clearance space above the Thermkeep during cycling, thus maintaining chemical stability. Samples for analysis were obtained through holes cut in the wall of the tank. Because the heat exchanger sustantially fills the tank, the samples were removed from locations within 5 cm of the tank wall. Tank height is 244 cm and diameter is 71.8 cm.

The samples were analyzed in pairs, one pair taken from the original lot of Thermkeep and seven pairs taken from seven locations in the tank. The results of the analysis are shown in table I. The six components were independently determined and the small deviation of the total from 100% indicates the precision of the analyses. The analyses show that the $NaNO_2$ content of the Thermkeep did not increase in the TES unit, indicating chemical stability of the system.

The $NaNO_3$ content of Thermkeep (8%) is lower than that of the $NaOH-NaNO_3$ eutectic (33% $NaNO_3$). Upon cooling, the solid phase which forms on heat exchanger surfaces, and on the tank walls due to insulation loss, has a higher ratio of NaOH to $NaNO_3$ than the liquid phase. The samples of Thermkeep (which were close to the tank wall) all show an increased $NaOH/NaNO_3$ ratio. Since it is believed unlikely that nitrogen was lost from the system, this is tentatively attributed to a small-scale segregation of components during solidification, which would be reversed upon remelting. To obtain more information on this point, additional samples which are awaiting analysis were taken after the Thermkeep had been completely remelted by a method which prevented segregation of components during sampling.

The cycling mode of the TES unit during the testing program that preceded the sampling was such that the Thermkeep near the bottom (location 7) was permanently solid. The upper portion (locations 1-4) was substantially completely liquefied during each cycle. Table I shows that the $NaOH/NaNO_3$ ratio is higher at sampling locations 5 and 6 than at others. This is believed to indicate a small degree of vertical segregation of the components of Thermkeep in the tank. Further testing is required to determine whether or not this represents a stable state in the TES tank or whether further segregation would occur with continued cycling. In either case this condition could be reversed by periodically remelting the Thermkeep in this zone of the tank.

Examination of Heat Exchanger

Following removal of the Thermkeep samples, the Thermkeep was melted and partially drained to expose the upper third of the heat exchanger. The heat exchanger consists of 25 helical coils of .64 cm diameter steel tubing formed in a helix 10 cm in diameter, manifolded at top and bottom for parallel flow of the heat transfer fluid. Figure 1 shows the heat exchanger during fabrication and figure 2 shows it in the tank, exposed for examination. No significant changes were observed and it was concluded that no repair was required before proceeding with the test program.

EXPERIMENTAL VALIDATION OF COMPUTER MODEL

The selection of a heat transfer fluid for the computer model validation program was based on several factors. It must have thermo-physical properties significantly different from those of Therminol-66 which was used in the prior program in order to extend the range of correlation. It must not react violently nor produce toxic reaction products when in contact with Thermkeep at the operating temperature, and it must be a fluid which would be suitable for use in a demonstration system. From among the candidates, the NASA Program Manager approved Caloria HT43, a product of Exxon Corp. The heat transfer fluid system has been flushed and recharged with HT43.

Data for experimental validation of the computer model (details of which can be found in ref. 1) are to be obtained from several types of charging and discharging runs during which HT43 flow rates and temperatures, the Thermkeep temperature, and the TES tank surface temperature will be measured. The runs will include charging and discharging at constant rates, consecutive cycles at constant charge and discharge rates, and cycles simulating a solar daily cycle. This actual performance is to be compared with performance predicted by the computer model.

This phase of the program is just starting and only preliminary results are available. Figures 3 and 4 show partial results of a slow discharge test with HT43 entering at 235 C and flowing upward through the heat exchanger at 0.0489 kg/s (1.1 gal/min). The temperature of the Thermkeep in the TES tank was measured by thermocouples located inside the tank, 11 cm (4.3 in) and 27 cm (10.8 in) from the wall, and others on the wall. Temperatures of the Thermkeep are plotted against distance from the top of the tank, as measured, and as predicted by the computer model. Figure 3 shows the initial condition of the TES tank resulting from an immediately preceding charging which left the temperature of the wall about 17 C lower than the interior. The computer response to the initial temperatures is also shown. Figure 4 shows the state after one hour of discharging and the computer prediction. The Thermkeep is liquid above 292 C and most of the latent heat is delivered between 292 C and 270 C. This is reflected in figure 4 by an increase in the vertical thermal gradient below the latent heat range, and a decrease within it. The location of the upper surface of the Thermkeep is also shown. This will move downward due to the decrease in specific volume of the Thermkeep as solidification continues in later stages of the run, which will be continued to a total of about 6 hours.

ADVANCED HEAT EXCHANGER MODEL

Figures 5 and 6 show schematically how the TES unit can be used in a solar powered electricity generating system such as the SSTETF. The experimental TES unit and computer model presently being tested correspond to figure 5. Heat transfer fluid heated by solar collectors to approximately 310 C flows to a heat exchanger where the Rankine cycle fluid (e.g. toluene) is vaporized and superheated. Excess heat is delivered to the TES unit. The return temperature to the collectors is 243 C. In the absence of solar heat, flow through the TES is reversed.

The advanced computer model will provide for two heat exchangers in the TES unit, one for the heat transfer fluid and one for the Rankine cycle fluid, as in figure 6. The algorithms provide for heat transfer within the TES unit from the heat transfer fluid to Thermkeep, from Thermkeep to the Rankine fluid, and directly from the heat transfer fluid to the Rankine fluid. This will allow analysis of two configurations: 1) two independent heat exchangers with the total output from the solar collectors flowing through the Thermkeep; 2) two thermally coupled exchangers with only stored heat flowing through the Thermkeep. Potential advantages of these configurations are the elimination of the external heat exchanger and, more importantly, potential improvement in performance of the TES unit resulting from the fact that during discharging the temperature of the Rankine fluid entering the bottom of the TES is much lower than that of the heat transfer fluid in the case of the single heat exchanger.

REFERENCE

1. Development of a Phase-Change Thermal Storage System Using Modified Anhydrous Sodium Hydroxide for Solar Electric Power Generation, DOE/NASA/0615-79/1, NASA CR-159465.

TABLE I. ANALYSIS OF THERMKEEP FROM TES VESSEL, AND ORIGINAL MATERIAL (% BY WEIGHT)

Sample No.	Location No.	cm*	NaOH	$NaNO_3$	$NaNO_2$	MnO_2	Na_2CO_3	NaCl	Total
1	Orig.Mat'l	N/A	86.94	8.467	.0306	.172	2.62	2.03	100.26
2			88.74	7.477	.0307	.171	1.45	1.98	99.85
3	1	172	91.50	4.652	.0020	.101	2.85	1.73	100.84
4			91.55	5.278	.0021	.085	1.48	1.35	99.75
5	2	144	91.17	5.041	.0023	.113	1.55	1.47	99.35
6			91.74	5.326	.0022	.110	1.43	1.63	100.24
7	3	117	91.88	4.503	.0019	.083	1.38	1.68	99.53
8			92.23	4.377	.0023	.110	1.35	1.85	99.92
9	4	89	89.50	5.623	.0023	.102	2.89	1.65	99.77
10			91.66	4.878	.0026	.095	1.36	1.76	99.76
11	5	62	94.30	2.791	.0017	.042	1.44	1.53	100.10
12			---	---	---	---	--	--	----
13	6	34	93.93	2.707	.0021	.057	1.40	1.76	99.86
14			94.59	2.546	.0032	.053	1.32	1.25	99.76
15	7	6	89.17	5.772	.0098	.137	2.88	1.58	99.55
16			89.88	5.138	.0095	.172	2.90	1.43	99.53

* Distance from bottom of tank

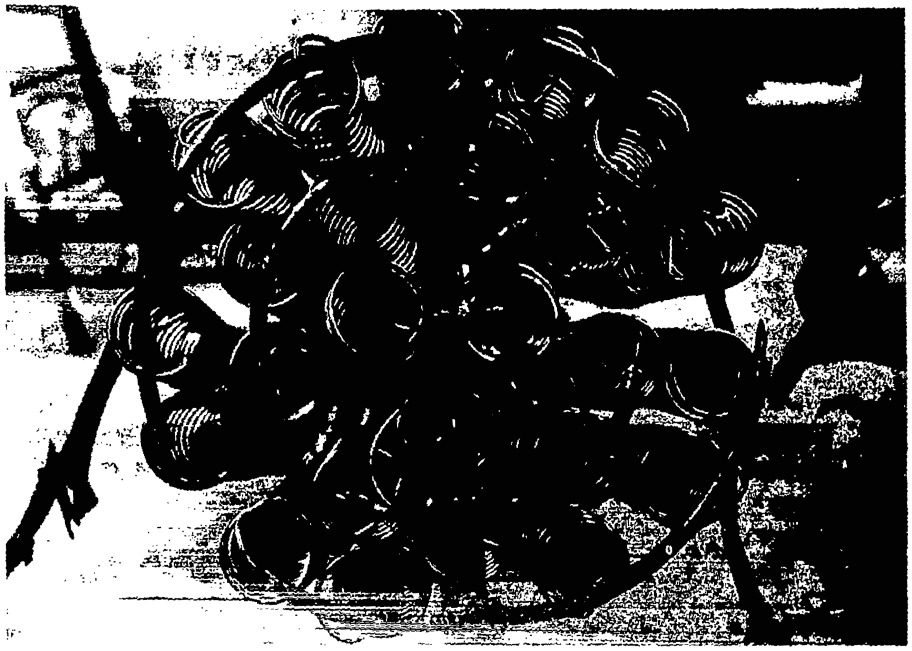

Fig. 1. Heat Exchanger During Fabrication

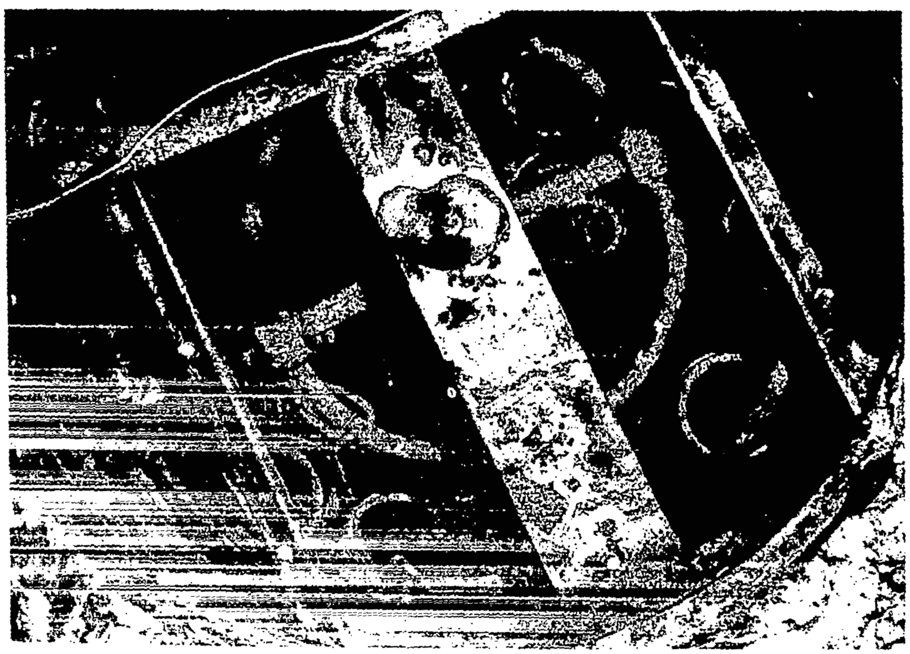

Fig. 2. Heat Exchanger Exposed for Examination

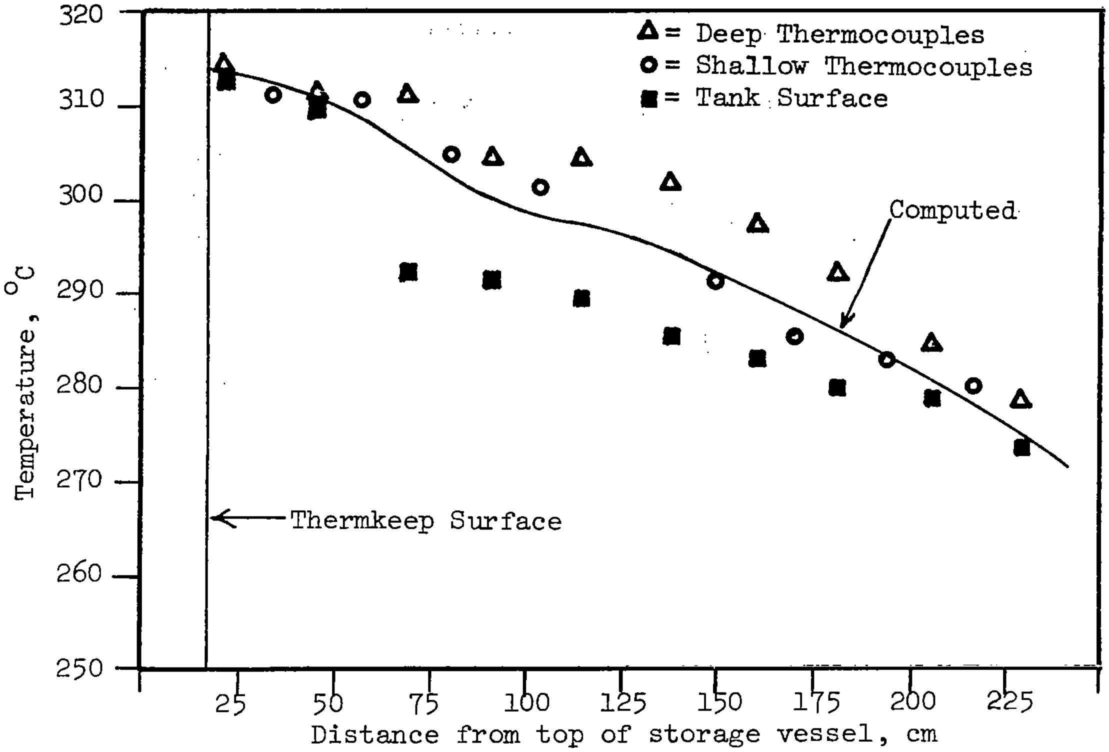

Fig. 3. Thermkeep Temperature vs. Axial Distance, Initial Condition

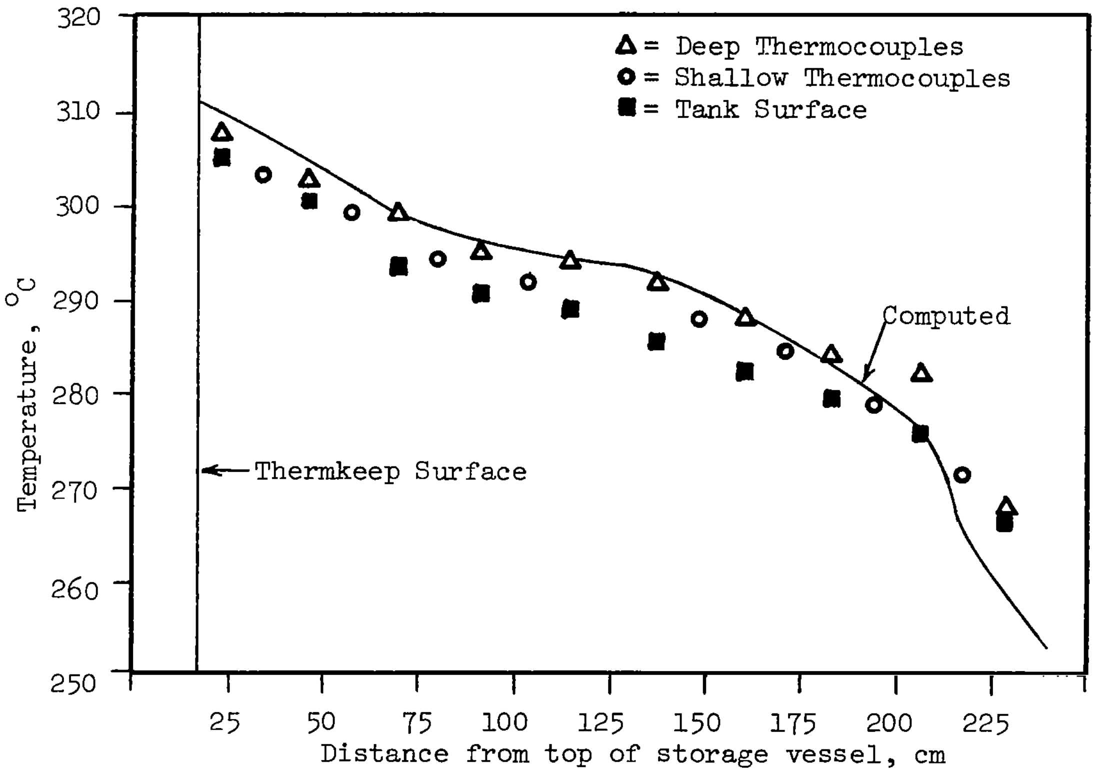

Fig. 4. Thermkeep Temperature vs. Axial Distance, after 1 Hour.

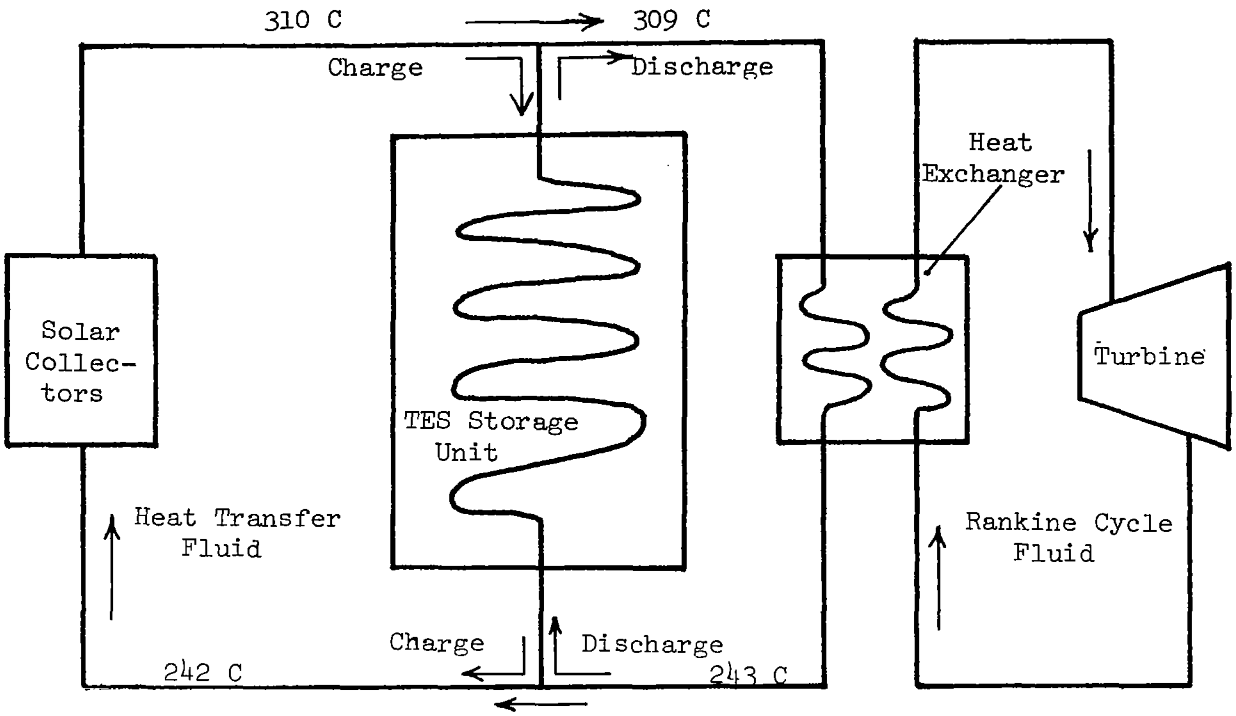

Fig. 5. Schematic of Solar Powered Electricity Generating System

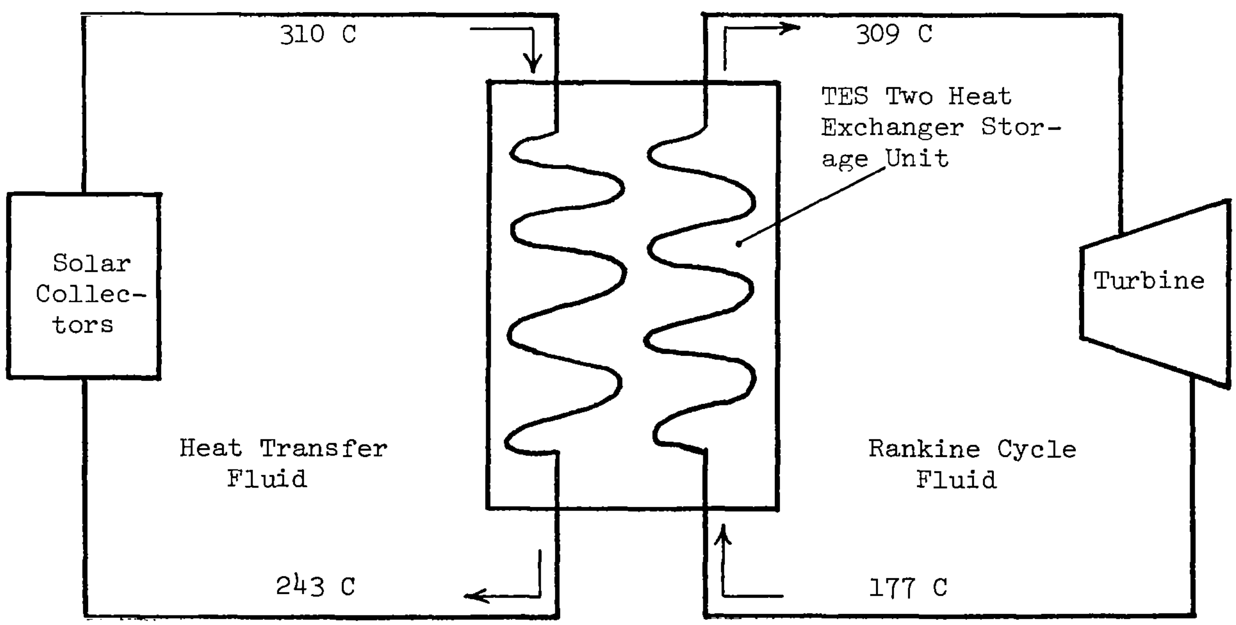

Fig. 6. Advanced Computer Model