

2-7
7/19/79
240 NT/5

MASTER



ARGONNE NATIONAL LABORATORY

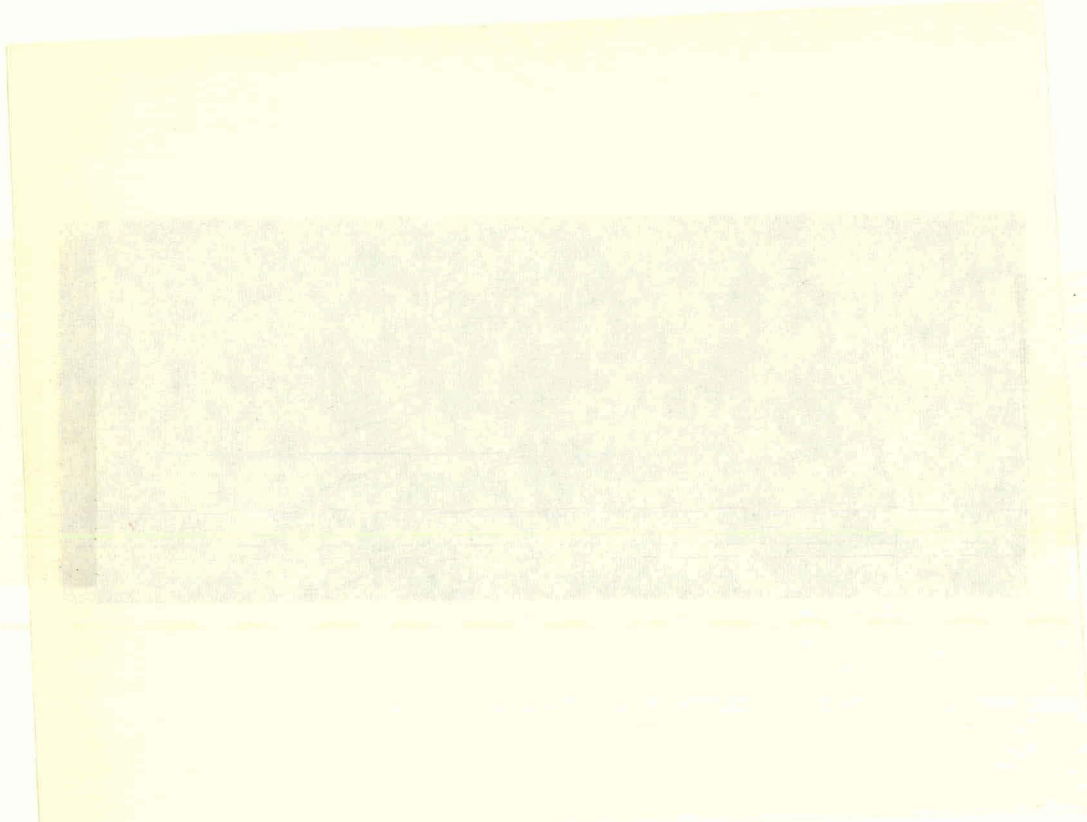
ENERGY AND ENVIRONMENTAL SYSTEMS DIVISION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.



This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Department of Energy.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Department of Energy, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

Informal Report ANL/EES-TM-50

ARGONNE NATIONAL LABORATORY
Argonne, Illinois 60439

HYCSOS: CHEMICAL HEAT PUMP AND
ENERGY CONVERSION SYSTEMS
BASED ON METAL HYDRIDES
Mid-Year Program Report*

June 1979

prepared by
C.A. Blomquist

contributions by
J.G. Asbury, J.M. Clinch, D.M. Gruen,
J.S. Horowitz, J.M. Nixon,
P.A. Nelson, I. Sheft

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Work sponsored by
U.S. Department of Energy
Assistant Secretary for Energy Technology
Division of Energy Storage Systems

*Project Number C8-03-02-01-3, ANL 49405

~~DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED~~

Rey

This report is available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

1.0 HYCSOS PROGRAM

The Argonne National Laboratory (ANL) HYCSOS Metal Hydride Chemical Heat Pump Program activities for FY 1979 involve the ANL Chemistry and Energy and Environmental Systems (EES) Divisions. The Chemistry Division is investigating hydride materials by evaluating the chemical thermodynamics of various hydrides in their laboratory, and also heat exchanger evaluations. The activities of the EES Division include program planning and management, engineering systems analysis, hydride heat transfer studies, and hydride heat exchanger evaluations.

The funding level for HYCSOS during FY79 is \$240K with allocations of approximately \$165K for the Chemistry Division, and \$75K to support the EES Division systems engineering activities. Figure 1 shows the current HYCSOS program activities together with the scheduling and cost of each activity.

In regard to accomplishments, the proof of the HYCSOS concept has been demonstrated and the viability of a residential-size unit established. In addition, an engineering development phase is now underway. The objective of the program is to develop a residential-size HYCSOS chemical heat pump for space heating and cooling. Solar energy or waste heat will be used to operate the pump and thus eliminate or reduce fossil fuel requirements. To meet the program objectives, a draft program plan was prepared which identifies the work tasks, subtasks, manpower, budget and schedule. (See Appendix A.)

In support of the HYCSOS program a management plan for FY 1979 and a WPAS for FY 1980 were prepared and submitted to DOE.

2.0 SYSTEMS ENGINEERING

In a 1978 HYCSOS hydride heat pump study for Argonne, TRW Energy Systems Group developed a computer program to aid in the design and performance analysis of a residential-sized hydride heat pump. The program is designed to size some of the components, estimate the cost, and determine the performance of the system. The basic design process is to iterate the performance and cost calculations, changing system parameters in order to define a system with near optimum cost and performance. The computer program calculates some of the system sizing and the cost and performance for each set of system parameters.

Figure 1.
HYCSGS PROGRAM ACTIVITY, SCHEDULING & COST BAR CHART (FY 79)

ACTIVITY	FY 1979												COSTS
	OCT.	NOV.	DEC.	JAN.	FEB.	MAR.	APR.	MAY	JUNE	JULY	AUG.	SEP.	
Program Planning and Administration													+
													\$20K
Engineering Systems Analysis													+
													\$25K
Hydride Heat Transfer and Heat Exchange Evaluation													+
													\$35K
Hydride Material Studies													+
													\$70K
Experimental Studies													+
													\$90K
Total													\$240K

 completed

 planned

The parameters are inputs to the program and are changed by the operator in an interactive mode. The optimum system depends on the cost and performance of the solar collectors supplying the input heat, and the design/analysis of the solar collector subsystem was not within the scope of this study. As such, this analysis does not attempt to define the "true" optimum system.

The TRW program was converted from a CDC version to one compatible with the ANL computer system. During program checkout, several small operational problems were found and corrected. The intended use for the TRW program is to investigate the cost and performance of hydride heat pumps as a function of various parameters. Specifically these are:

- Cycle and regeneration time
- Hydride bed composition
- Solar input temperature
- Heat transfer fluid
- Heat transfer assumptions used in analyzing the hydride heat exchanger
- Other types of hydride heat exchangers

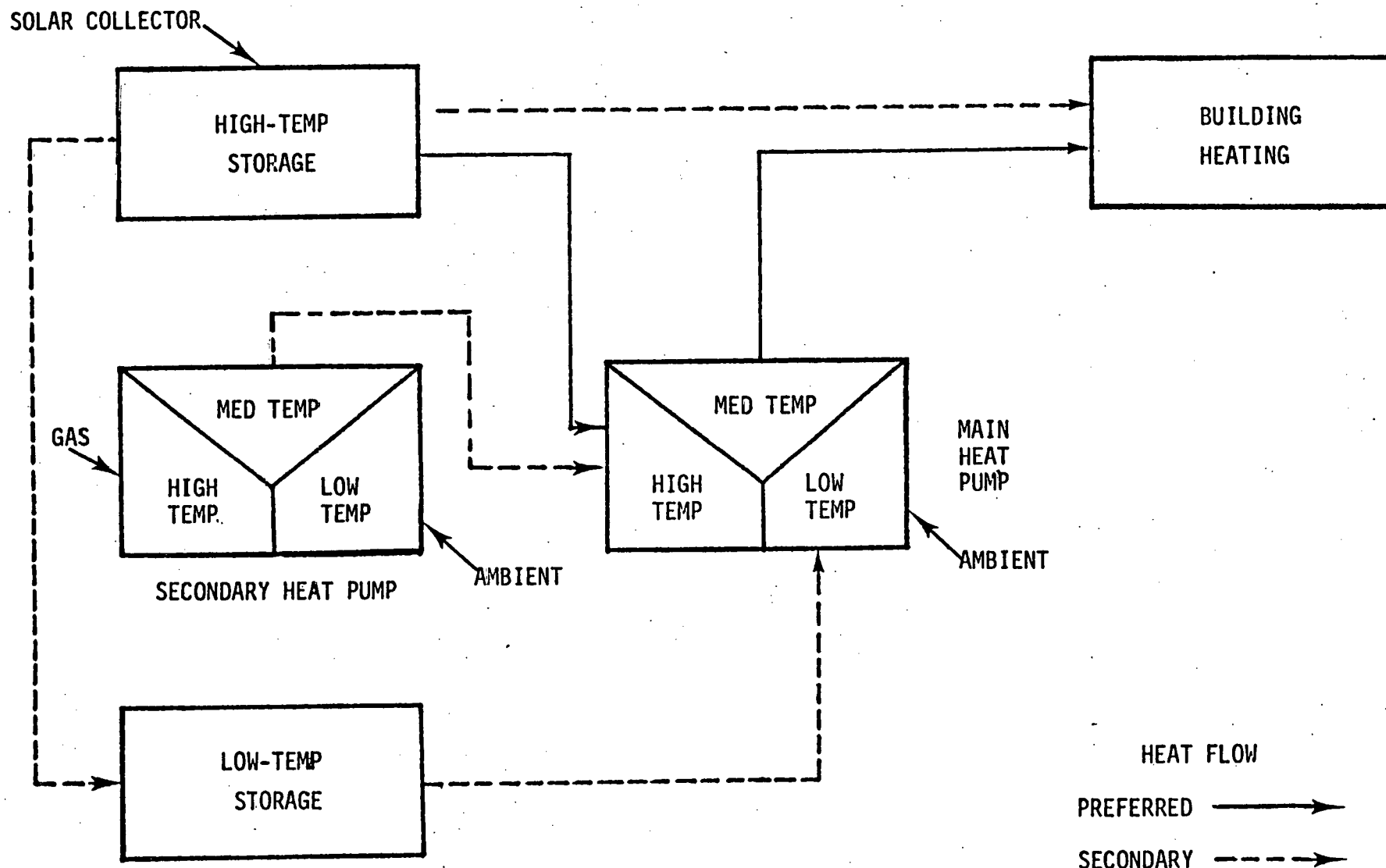
A number of computer runs were made with this program and some preliminary conclusions are:

- System cost and coefficient of performance (COP) increase with cycle time for cycle times larger than about 1 minute.
- A minimum system cost occurs at a cycle time slightly less than 1 minute.
- System costs increase slightly with regeneration time, whereas the COP is relatively insensitive to regeneration time.
- System costs decrease with heat flux while COP increases with heat flux.
- Cooling and heating COPs are directly related.
- There is no clear conclusion as to the effect of alloy composition on cost or performance.

2.1 CONCEPTUAL HYCSOS DESIGNS

The schematic in Figure 2 is one conceptual HYCSOS design being considered. This concept of a hydride heat pump system is capable of heating and cooling a building and is shown in the building heating mode in the diagram. The system provides two heat pumps. The main unit is for heating and cooling

SCHEMATIC OF HYDRIDE HEAT PUMP IN BUILDING-HEATING MODE



the building with energy stored from a solar collector. A secondary heat pump is provided for operation with gas heat. The output from this secondary unit is delivered directly to the high-temperature side of the main heat pump.

Two hot water storage tanks are provided and these are designed for minimum mixing and efficient thermal gradient retention. The water stored in these tanks is both the heat transfer medium for the solar collector and the operating fluid for the main heat pump. It must contain antifreeze, because it would be in direct contact with the solar collector during the winter. This large amount of antifreeze will increase the cost and, therefore, the storage tank sizes must be minimized.

The house is heated and cooled with air passing over a large heat exchanger in a plenum leading to the air distribution system in the house. The heat exchanger is heated and cooled by water circulated from the main heat pump or directly from the high-temperature storage tank. The selection of the most advantageous mode of operation is done by a microcomputer as discussed below.

The use of water as a heat transfer medium in the heat pumps requires careful design of those systems in order to achieve acceptably high coefficients of performance. An alternative coolant which might be considered is a freon refrigerant. However, that would require a complete redesign of the system and is an alternative to the system described here. Such alternatives will be considered to determine the most feasible system for development.

2.1.1 Order of Preference for Energy Sources

As a study of Figure 2 will reveal, there are several ways in which the building can be heated and cooled by means of the proposed system. The method of operation will depend on the exterior temperature, the availability of solar heat, and the temperature of the storage tanks. A microcomputer will consider these factors and select the method of operation which controls the building temperature at the desired level with minimum cost and, as a secondary consideration, maximum energy efficiency in order to conserve stored energy. The order of preference of the energy sources for each of the major components of the system are shown in Table 1. For heating the building, lowest cost and highest energy efficiency are achieved by method one, which would utilize the main heat pump with heat supplied from the high-temperature storage tank and

TABLE I
ORDER OF PREFERENCE FOR ENERGY SOURCES

Order of Preference	Energy Sources	Heat Pump Sources			Requirements
		High Temp. (Heating)	Mid. Temp. (Cooling)	Low Temp. (Heating)	
<u>BUILDING -- HEATING MODE</u>					
1.	Main Heat Pump	HT Store	Building	Ambient	{ HT Store >180°F, Ambient Air >30°F
2.	Main Heat Pump	HT Store	Building	LT Store	
3.	High-Temp. Storage Tank	-	-	-	HT Store >100°F
4.	Natural Gas Burner with both:				
	Secondary heat pump	Gas flame	Main heat pump	Ambient or LT Store	None
	Main heat pump	Secondary heat pump	Building	Ambient	
<u>BUILDING -- COOLING MODE</u>					
1.	Main Heat Pump	HT Store	Ambient	Building	HT Store >180°F Ambient <100°F
2.	Natural Gas Burner with both:				
	Secondary heat pump	Gas flame	Main heat pump	Main heat pump	None
	Main heat pump	Secondary heat pump	Ambient	Building	
<u>HIGH-TEMPERATURE STORAGE TANK</u>					
1.	Solar Collector (only source)	-	-	-	Collector outlet >220°F
<u>LOW-TEMPERATURE STORAGE TANK</u>					
1.	Under flow from HT Store (LT Store + Solar Collector + HT Store + LT Store)				Collector outlet >220°F
2.	Solar Collector				Collector outlet <HT store temp.

an ambient temperature heater. This would require a temperature in the high-temperature storage tank of at least 180°F and an ambient air temperature of at least 30°F. If the ambient temperature air is less than 30°F, the second method shown in Table 1 can be used for heating the building by using the main heat pump and the low-temperature storage tank as the low-temperature heat source. If the temperature of the high-temperature storage tank is less than 180°F but greater than 100°F, the heat pump cannot be operated, but the building could be heated directly from the high-temperature storage tank (method three in Table 1).

If there is no stored energy, the building may be heated by method four which uses natural gas as a heat input to the secondary heat pump in a cascade arrangement with the main heat pump. It is proposed that both the secondary heat pump and the main heat pump use ambient air as the low-temperature heat source. With this arrangement the theoretical COP would be 4.0. In practice it might be possible to achieve a COP of between 1.5 and 2.0. This high COP when operating with the gas backup system reduces the cost penalty for exhausting the storage capacity. Therefore, small storage tanks might be economically optimal.

Building cooling would be carried out in much the same way as building heating, except that for cooling the low-temperature heat source for the heat pump would be the building air and the medium temperature heat would be discharged to the ambient air. It is estimated that the main heat pump could be operated with heat input from the storage tanks at water temperatures down to 160°F if the ambient temperature is 80°F. When the usable energy in both water tanks is exhausted, the building would be cooled with natural gas heat input and use of the secondary heat pump in cascade configuration with the main heat pump. With both heat pumps in operation, the theoretical COP would be about 2.0 and the actual obtainable COP would be about 1.0.

It should be noted that the high-temperature storage tank would be heated only by the solar collector and not by the natural gas burner. The preferred method for heating the low-temperature storage tank would be by underflow from the high-temperature storage tank when the tank was being heated from the solar collector. When the solar collector is in operation, the water to the solar collector would be directed from the low-temperature storage tank. The return from the solar collector would be directed to the

top of the high-temperature storage tank, and the underflow would feed the low-temperature storage tank. A second method of transferring energy to the low-temperature storage tank is by direct transfer from the solar collector when the collector outlet temperature was less than the temperature at the top of the high-temperature storage tank. This would be expected to occur if the solar collector is drained when solar insolation is interrupted by cloud cover.

2.1.2 Estimated Operating Temperatures

Operating temperatures can be estimated by (1) selecting storage tank temperatures and ambient temperatures, (2) estimating temperature differentials between the various heat exchange fluids, and (3) calculating the medium temperatures in the heat pumps by assuming that they will be approximately the geometric mean of the low-temperature and high-temperature zones. Three sample cases for building heating are listed in Table 2. In Case I it is assumed that the high-temperature storage tank was operating at 220°F and the ambient temperature was 30°F. Water from the high-temperature storage tank at 220°F is delivered to the high-temperature zone of the heat pump and results in a maximum hydride bed temperature of 210°F. The ambient temperature of 30°F results in a temperature of 20°F in the water returning from an outdoor heat exchanger. This water, then pumped to the low-temperature zone of the heat pump, would result in a temperature in the hydride bed of 10°F. The hydride bed temperature in the medium temperature zone of the heat pump was estimated to be about 105°F. Water circulated through the medium temperature zone would reach a temperature of 95°F and when circulated to a heating unit in the air duct of the building ventilation system, would result in an air temperature of 85°F.

Various other high-temperature storage tank temperatures and ambient air temperatures were assumed in Case II and Case III of Table 2 and it was demonstrated that reasonable temperatures could be calculated. It should be noted that the temperature between heat exchange fluids was assumed to be 10°F in all cases. Further calculations are required to demonstrate whether such small temperature differences are practical.

A HYCSOS concept that is being evaluated is a tubular version which is shown in Figure 3. This concept consists of sealed tubes with an enhanced

Table 2. Operation of Main Heat Pump for Building Heating

	HT	Ambient	Heat Pump Zones		
	Store Temp., °F	Air Temp., °F	High Temp.	Med Temp.	Low Temp.
<u>CASE I</u>	220	30			
Hydride Bed Temp., °F			210	105	10
Water Temp., °F			220	95	20
Air Temp., °F			-	85 ^a	30 ^b
<u>CASE II</u>	190	50			
Hydride Bed Temp., °F			180	100	30
Water Temp., °F			190	90	40
Air Temp., °F			-	80 ^a	50 ^b
<u>CASE III</u>	180	<30 ^c			
Hydride Bed Temp., °F			170	105	50
Water Temp., °F			180	95	60 ^c
Air Temp., °F			-	85 ^a	c

^aTemperature of air exiting heating coils in plenum leading to hot air ducts.

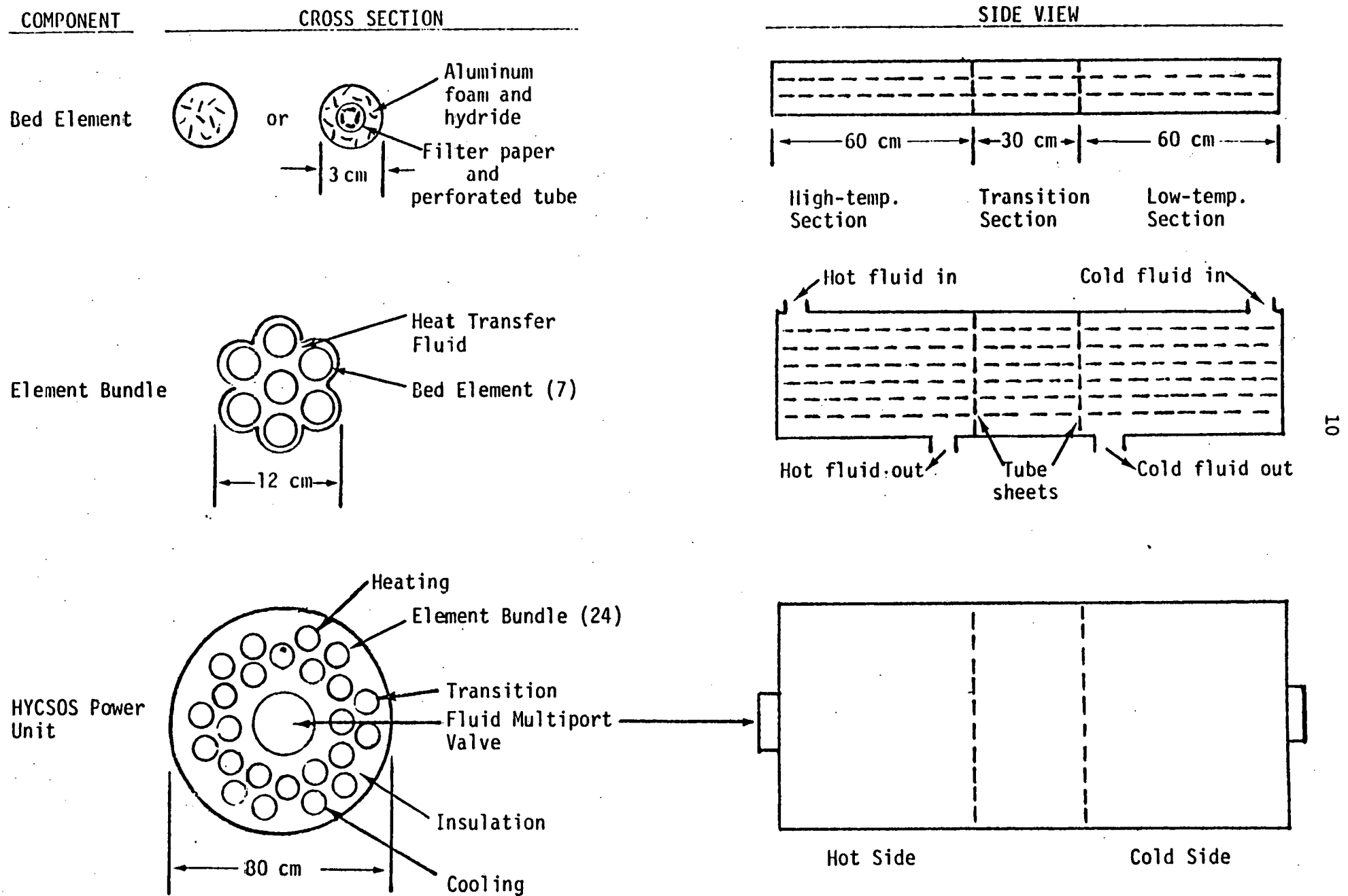
^bTemperature of air providing heat to water pumped to low-temperature zone of heat pump.

^cAt ambient temperatures below 30°F, heat is provided to the low temperature zone of the heat pump by means of water from the low-temperature storage tank, which was assumed to be at 60°F in Case III.

internal surface. Different hydride material is located at each end of the tube and separated by a transition section. The individual tubes are assembled into an enclosed element bundle to permit circulation of a heat transfer fluid around the elements. The element bundles are then assembled into a power unit whose size depends upon the required heating or cooling load. Continuous operation will be possible because in the power unit some of the element bundles will be desorbing hydrogen, some absorbing hydrogen, and some undergoing regeneration. Some advantages of this concept are:

- Flexibility in design
- Eliminates hydrogen valves
- Minimizes loss of hydrogen due to leaks

Figure 3. Schematic of HYCSOS Power Unit



- Utilizes temperature gradients in heat transfer fluid
- Simpler to fabricate

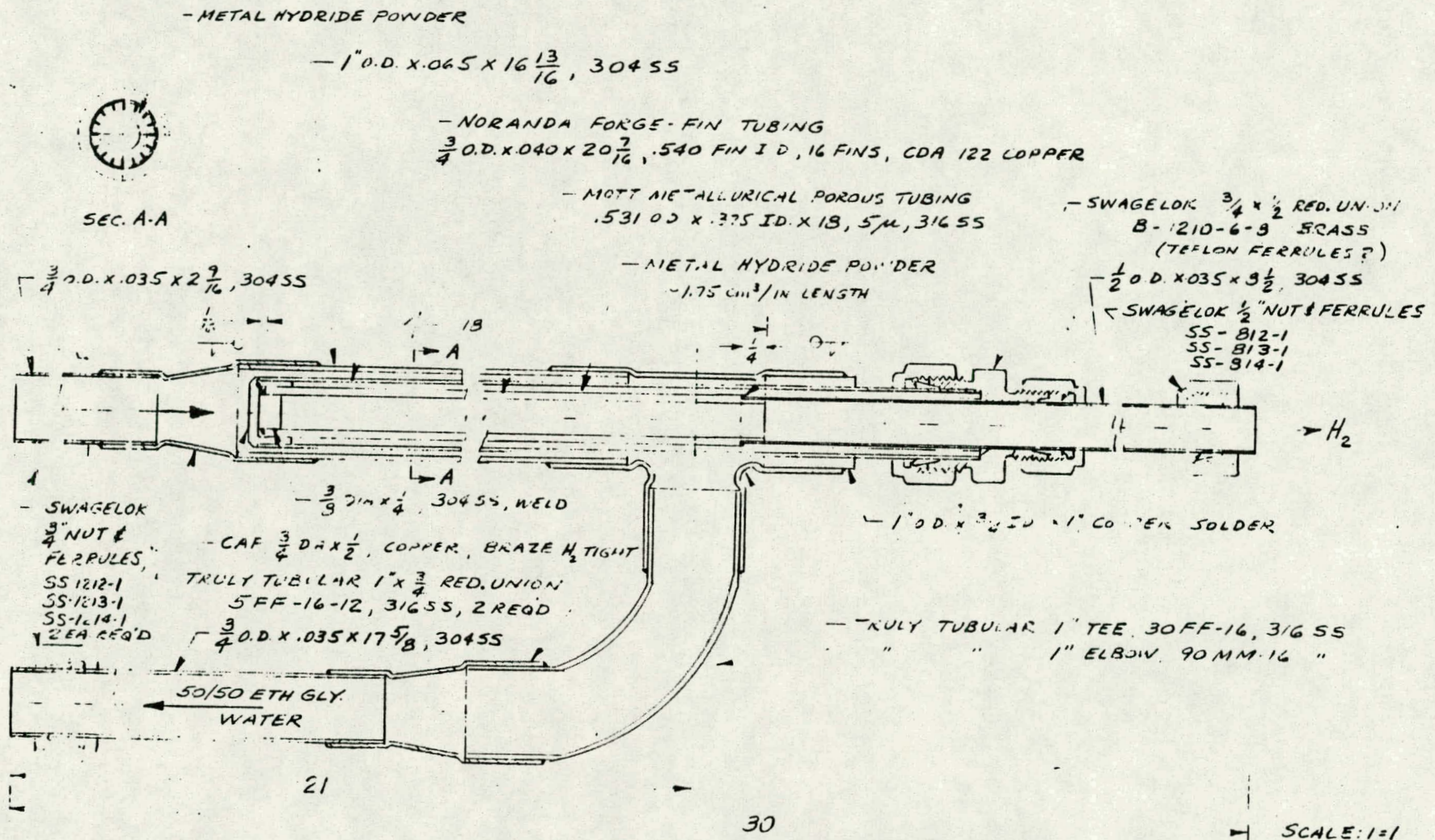
A single tube version, Figure 4, of this concept was designed and is under construction. Basically it consists of three (3) concentric tubes. The outer tube is the containment for the heat transfer fluid. The middle tube is internally finned and provides the enhanced surface. The inner tube is sintered stainless steel and acts as a filter. The metal hydride is in the annulus formed by the finned and sintered tubing. The unit was designed to utilize available material, to simplify fabrication, and to permit installation in the Chemistry Division laboratory facility. Assembly of this unit is awaiting delivery of the finned tubing.

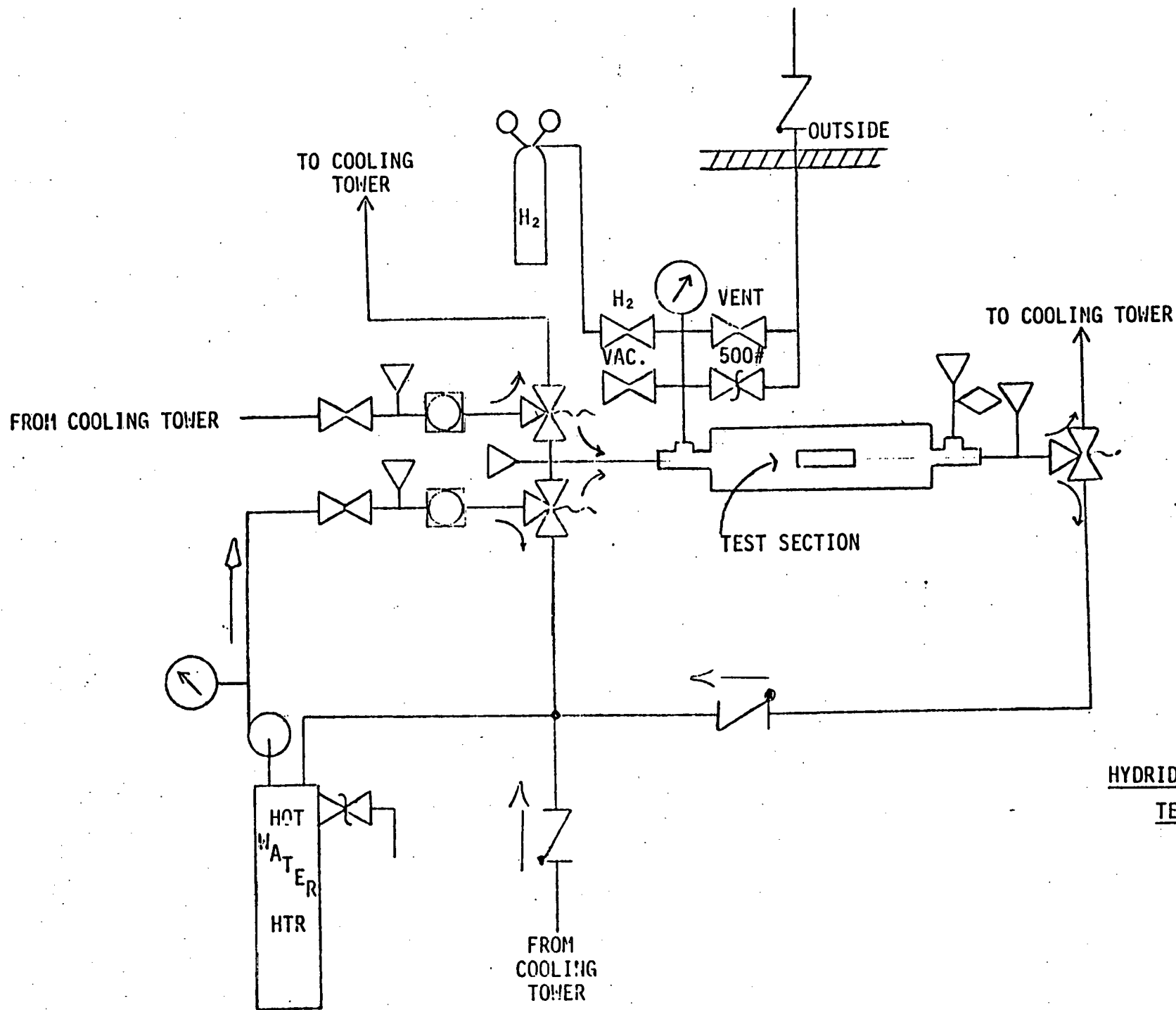
3.0 HYDRIDE HEAT TRANSFER AND HEAT EXCHANGER STUDIES

Hydride heat transfer and the design of a suitable heat exchanger are key elements for the successful development of a metal hydride chemical heat pump. In order to obtain basic heat transfer data, a small scale test program was initiated and a single-tube test facility was designed. This facility is shown schematically in Figure 5. Heat transfer surfaces up to 2 in. in diameter and 6 ft long can be accommodated inside the hydrogen pressure vessel. Hydride material of varying thickness will be contained between a filter element and the heat transfer surface. Conditioned water will be circulated through the heat transfer surface to desorb hydrogen from the metal hydride. Pressure, temperature and flow measurements will be taken by a computer based data acquisition system. A computer program has been written to analyze the data to determine the heat transfer rate, response time, and amount of hydrogen desorbed. The test facility is nearing completion and checkout should be started in early July.

The heat exchangers in the Chemistry Division laboratory facility consist of coiled tubing inside and outside a heavy-wall stainless steel vessel. These exchangers were fabricated for hydrides with high hydrogen desorption pressures to demonstrate proof of the HYCSOS concept. These units are inadequate, and a heat exchanger which contains the alloy powder in interstices of an open-cell aluminum foam was ordered from Energy Research and Generation (ERG) Inc. in 1978. The pressure vessel container for this unit was received but the aluminum-foam section has not been delivered. The manufacturer keeps

Figure 4. Prototype Metal Hydride Heat Exchanger Element





Legend

- ▽ - Temperature
- ◇ - Pressure
- - Flow
- ⤴ - Pressure Gage

HYDRID HEAT EXCHANGER
TEST FACILITY

FIGURE 5

promising delivery and cites a backlog in brazing and other high priority Department of Defense work as reasons for the delay.

In January, 1979, a search was started for compact plate-fin type heat exchangers manufacturers that have the following capabilities:

1. Engineering expertise and experience in the design and analysis of efficient, lightweight, compact heat exchangers.
2. Manufacturing facilities that included vacuum furnaces for aluminum brazing.
3. A willingness to explore the possibility of adapting their standard heat exchanger designs to the difficult problem of heat transfer between a liquid and finely divided metal hydride powders.

In the Chicago area there are firms that do aluminum dip brazing but none that specialize in heat exchangers fabricated by vacuum brazing. Three potential firms in the New York City area that were contacted are Hughes-Treitler Manufacturing Corp., Limco Manufacturing Corp. and Precise Metal Products Corp. From catalog information and discussions with these firms, it was determined that Hughes-Treitler and Limco had the qualifications and sufficient interest in fabrication of a hydride heat exchanger.

A set of specifications for the hydride heat exchanger was prepared and submitted to these firms in March, with the request that they utilize their standard corrugated fin stack heat exchanger design. Both firms submitted preliminary sketches and proposals for the heat exchanger. After discussing the designs and reviewing their manufacturing capabilities, it was concluded that Hughes-Treitler was the preferred company. Hughes-Treitler have a larger and more experienced engineering department, and their manufacturing and vacuum brazing facilities are more extensive than those of Limco. In addition, they also have a sophisticated heat exchanger design computer program that was developed for NASA, and their proposed design satisfies most of the requirements of the HYCSOS experimental program. This design provides a hydride side surface area that is an order of magnitude larger than the present heat exchangers. In addition, the design has short hydrogen paths and large filter areas for low pressure drop, the capability for easy loading or removal of hydride powders, and fits directly into the laboratory facility with very little modification of the piping system.

In May, Hughes-Treitler submitted a quotation and sent a computer generalized design analysis with core geometry specifications, heat transfer parameters, pressure drop and mass calculations. Procurement of 2 to 4 of these heat exchangers is in process. Hughes-Treitler has a large backlog of work, but have promised delivery of two units by the end of September.

4.0 MATERIAL STUDIES

The heat of reaction for the absorption, ΔH_{abs} , and the desorption, ΔH_{des} , of hydrogen on LaNi_5 was measured calorimetrically. In a single determination, ΔH_{abs} was 5.49 kcal/mole H_2 and ΔH_{des} was 7.68 kcal/mole H_2 . The generally accepted values, calculated from van't Hoff plots for an alloy formulation not necessarily the same as in the HYCSOS system, are 7.2 kcal/mole for desorption and approximately 6 kcal/mole for absorption.

A small prototype of the aluminum foam heat exchangers that Energy Research and Generation (ERG) Inc. is fabricating was used to measure kinetics of hydriding reactions with LaNi_5 . Hydrogen quantities large enough to follow pressure changes but small enough not to produce large temperature changes, are isothermally absorbed on the alloy. Preliminary results show a complicated relation for absorption, which may indicate a multiple-step reaction.

Kinetic measurements were run on the hydriding reaction of CaNi_5 hydride and LaNi_5 hydride. Small amounts of hydrogen, between 0.3 moles and 0.06 moles were absorbed on or desorbed from the alloy hydrides contained in the coiled tube heat exchangers and the LaNi_5 loaded aluminum foam test unit. The course of the reaction was followed by changes in hydrogen pressure above the alloy. Complete reaction would cause a 5-10 psi change. A rapid initial reaction, perhaps indicative of the true reaction kinetics, occurred in the first second or less. A longer time to complete reaction, extending to about five minutes or longer in the case of the aluminum foam unit, is probably due to a heat transfer limitation. Table 3 shows reaction time and fraction reacted. The last column shows the temperature change expected from the amount of hydrogen transferred. The reaction rates seem related to the expected temperature change and imply a heat transfer effect even in the initial rapid rate. Use of heat transfer fluid did not affect the reaction in the room temperature experiments.

Table 3. Kinetics of Hydride Reactions

System	Reaction		Temperature Change (°C)
	%	time (sec)	
CaNi ₅ (desorb. at 84°C)	75	0.2	0.12
	90	1.0	
LaNi ₅ (desorb. at 22°C)	50	0.2	0.18
	75	1.8	
LaNi ₅ (absorb. at 22°C)	50	0.2	0.23
	75	1.0	
	90	4.5	
LaNi ₅ in Al foam			
(desorb. at 22°C)	50	4.0	0.73
(desorb. at 22°C)	50	>10	1.38

To study the kinetics of the rapid initial hydride reaction, the pressure change during desorption was monitored with a cathode ray oscilloscope. Based on fraction of hydrogen desorbed from LaNi₅ hydride at intervals during the first 1/2 second, the desorption reaction is second order in the coiled tube heat exchanger and zero order in the aluminum foam unit. The reaction order for CaNi₅ hydride desorption was indeterminate.

A seven liter standard volume was incorporated into the hydrogen filling manifold of the HYCSOS laboratory system to facilitate measurement of the large amount of hydrogen required to activate the alloys.

Thermal conductivity is an important characteristic determining heat transfer of powder beds. Using data from the transfer of 5.74 moles of hydrogen from CaNi₅ to LaNi₅, the thermal conductivity of these materials were calculated and are shown in Table 4. These results are based on a mean fluid temperature in the coils, a bed thickness of 0.32cm, a filling factor based on a lightly poured LaNi₅ powder density of 4 g/ml, and a heat of reaction of 7.5 kcal/mole for CaNi₅ and 7.2 kcal/mole for LaNi₅. Although these results are, at best, approximate, the relative consistency of the values indicates the importance of factors other than composition or filling factor, e.g., bed disruption during hydrogen mass transport, on the effective conductivity of powder beds in these heat exchangers.

Table 4. Thermal Conductivity of CaNi_5 Hydride and LaNi_5 Hydride

Comp. Range	Heat (kcal)	Δt (°C)	Surface (cm^2)	Filling Factor	Conductivity Cal °C·cm·sec
$\text{CaNi}_5\text{H}_{2.66}$ - $\text{CaNi}_5\text{H}_{1.99}$	43.0	9.0	3125	0.6	0.0040
$\text{LaNi}_5\text{H}_{2.26}$ - $\text{LaNi}_5\text{H}_{3.30}$	41.3	9.1	2690	0.4	0.0045
$\text{CaNi}_5\text{H}_{2.66}$ - $\text{CaNi}_5\text{H}_{1.99}$	43.0	5.1	3125	0.6	0.0036*

*5 minutes heat transfer time.

5.0 EXPERIMENTAL STUDIES AND OPERATIONS

To evaluate the thermodynamic operation of the HYCSOS system and reduce the effect of the piping and heat transfer fluid in the system beyond the hydride heat exchangers (HHE) in lowering system efficiency, the heat capacity of the HHE including the contained alloy and heat transfer fluid was determined.

In a calorimetric measurement the temperature rise caused by the absorption in the center of the plateau region of approximately 5 moles of hydrogen on the alloy, i.e., 30-40 kcal, was measured. This data was used to calculate the heat capacity of the heat exchangers containing LaNi_5 and CaNi_5 and these results are shown in Table 5.

Table 5.

HHE*	MOLES H_2 Added	Alloy Comp. Range	Temp. °C Initial Final	ΔH_{abs} kcal/mole	Heat Capacity kcal/°C
3	4.90	$\text{LaNi}_5\text{H}_{1.75}$ - $\text{LaNi}_5\text{H}_{2.52}$	19.0 35.4	7.2	2.15
3	4.92	$\text{LaNi}_5\text{H}_{2.59}$ - $\text{LaNi}_5\text{H}_{3.36}$	17.6 34.5	7.2	2.10
2	5.66	$\text{CaNi}_5\text{H}_{1.43}$ - $\text{CaNi}_5\text{H}_{2.07}$	19.1 39.5	7.5	2.08
2	6.43	$\text{CaNi}_5\text{H}_{2.08}$ - $\text{CaNi}_5\text{H}_{2.81}$	18.0 41.2	7.5	2.08

*Hydride Heat Exchanger

For comparison, a value for the heat capacity was calculated from the blueprint dimensions for the volume of water and the mass of metal in the heat exchanger. A Dulong and Petit value of 6.2 cal/°C was used for the atomic heat capacity of the metal. A heat capacity 37.02 cal/deg mole was used for

LaNi_5 and for CaNi_5 a value of 37.16 cal/deg mole was calculated from its atomic heat of 6.2 cal/deg. A heat capacity of 1.88 kcal/deg was calculated for HHE-3 and 2.08 kcal/deg for HHE-2.

The prototype unit of a LaNi_5 loaded aluminum foam heat exchanger was readily hydrided and dehydrided three times. No difficulties were encountered even though no heat transfer fluid was used to remove heat of absorption. A hot air blower was used to speed desorption. In a single adiabatic experiment, 1.74 moles H_2 were desorbed from the activated bed. The subsequent rapid adiabatic absorption of 1.07 moles H_2 was followed by recording pressure changes on magnetic tape at three second intervals. Equilibrium absorption pressure was reached in approximately 30 seconds showing the temperature of the unit to be uniform. Since the heat capacity of the LaNi_5 is estimated to be approximately 30% of the entire unit, bed temperature drift toward equilibrium would be observable. A slight pressure rise after 10 minutes was due to absorption of ambient heat and temperature rise of the unit. Although a similar experiment was not done with a current tank, the rapid achievement of equilibrium pressure indicates significantly better heat transfer in the aluminum foam unit than in the current coiled tube design.

Radiographs taken after hydrogen cycling show some rippling in the steel endplate. Since the radiograph and photographs taken before cycling also show rippling, this effect is probably not due to the reaction, but possible to thermal effects when the filters were beam welded to the unit.

The unit was disassembled in a nitrogen box. Approximately 6-7 gm of powder was found outside the filter in the annular H_2 space. A microscopic examination showed over 90% of the particles to be greater than 5 micron with most over 15 to 30 micron. Since the filter has a 1 micron nominal pore size, the powder likely came through defects in the brazing or welding.

The performance of "old" hydride beds cycled at least 70 times was compared with that of "new" beds which had been hydrided and dehydrided about 10 times including the initial activation of three cycles. With an initial composition near the center of the plateau in both "old" and "new" alloy beds, approximately 5 moles of hydrogen were transferred from LaNi_5 to CaNi_5 and then back. The hydrogen pressure behavior of the "old" and "new" beds are similar which indicates no deterioration of the "old" beds.

In order to obtain baseline heat exchanger data, a test was conducted on the laboratory facility coiled-tubing heat exchangers. Steady flow conditions of hydrogen and heat transfer fluid were established and data taken at 12-second intervals for a period of 6.2 minutes, during which 12.08 moles of hydrogen were transferred. The results of this test are given in Table 6.

Table 6. Baseline Data on Coil-Tube Heat Exchangers

Parameter	Average of 31 12-sec data intervals	Average of 6.2 min period
Heat rate from H ₂ flow and heat of reaction, W	1020	1020
Heat rate based on heat transfer fluid flow and temperature difference, W	810	808
Bed temperature based on H ₂ pressure, °C	61.4	62.3
Log mean temperature difference, °C	40.0	40.9
Overall heat transfer coefficient based on H ₂ heat rate, W/m ² °C	87.2	80.2
Overall heat transfer coefficient based on heat transfer fluid rate, W/m ² °C	64.9	62.8
Number of transfer units	0.060	0.058
Effectiveness	0.058	0.056

From these data, it is evident that the performance of the coil-type heat exchangers is poor. Additional tests will be conducted to fully characterize these exchangers.

Software development for HYCSOS manual mode operation has been completed. Routines to handle data acquisition, logging, compression, correction, and plotting, using the new Tektronix 4907 flexible disk data storage system provide a more rapid and versatile means of presenting HYCSOS data for analysis.

The design of interface and control circuitry for the automatic control mode of HYCSOS operation has been completed. This design will enable the Tektronix 4051 Graphic System computer, acting as systems controller, to communicate with and issue control commands to HYCSOS. All remote operated

hydrogen and heat transfer fluid valves, integrator resets, pump and heater on/off relays and heater temperature can be computer controlled. Designed-in variable delay activation of pneumatically actuated valve pairs will prevent cross-feeding of fluids between isolated loops. Provision has been made for later additions of controlled devices when required.

Logic circuits for automatic systems operation were completed and tested. Cabling and software tasks require additional work.

6.0 MEETINGS, PUBLICATIONS, PRESENTATIONS, AND DISCUSSIONS

6.1 PUBLICATIONS AND PRESENTATIONS

"Performance Characteristics of HYCSOS," D. M. Gruen, I. Sheft, G. Lamich, and M. Mendelsohn. Presented at Chemical Heat Pump Workshop, Sandia Laboratories, Dublin, CA, Nov 7-8, 1978.

"New AB₅ Hydride and Their Application in Chemical Heat Pump Systems," D. M. Gruen, M. Mendelsohn, and I. Sheft, Proc. of Symp. on Solar Energy Conversion and Storage, 1978 ACS Southeastern Regional Meeting, Savannah, GA, Nov. 9, 1978.

ANL personnel presented the HYCSOS concept, material development, engineering aspects, and program plans to T. Bramlette and R. Carling from Sandia Livermore Laboratory during their visit to ANL on March 7.

"Status Report on the HYCSOS Chemical Heat Pump and Energy Conversion System," D. M. Gruen, M. Mendelsohn, I. Sheft, and G. Lamich, Proc. of DOE Chemical Hydrogen Energy Systems Contractor Review, Washington, D.C., Nov. 27-30, 1978, p. 307.

I. Sheft presented the paper "HYCSOS Chemical Heat Pump and Energy Conversion System" at the 4th Annual Heat Pump Technology conference held at Oklahoma State University, April 8-11, 1979.

On May 25, C.A. Blomquist presented the HYCSOS program to the Argonne Universities Association Review Committee for the Energy and Environmental Systems Division.

An abstract of a paper "Engineering Development of a HYCSOS Chemical Heat Pump" was accepted for presentation at the 2nd Miami International Conference on Alternative Energy Sources, Dec. 10-12, 1979.

A report "HYCSOS: A Chemical Heat Pump and Energy Conversion System based on Metal Hydrides-1979 Status Report," I. Sheft, D.M. Gruen, and G. Lamich, ANL-79-8 is in preparation.

6.2 MEETINGS AND DISCUSSIONS

- On March 12, Carl Hiller from Sandia Livermore Laboratory visited ANL for discussions on HYCSOS primarily related to the engineering aspects and proposed program.

- R. Giese made a presentation on HYCSOS at the Heat Pump Technology Information Exchange Meeting on March 7, 1979 at the National Bureau of Standards in Gaithersburg, Maryland.

- J.M. Nixon visited G. Benson at Energy Research and Development, Inc. on March 14 to discuss their fabrication and delivery of a foam heat exchanger.

- J.M. Nixon and I. Sheft visited Limco Manufacturing Co., Glen Cove, N.Y. and Hughes-Treitler Manufacturing Co., Garden City, New York on March 28 and 29, respectively, to discuss the suitability of their compact plate-fin heat exchangers for use as HYCSOS hydride heat exchangers.

- J.M. Nixon and I. Sheft visited International Nickel Co., Suffern, N.Y. for discussions on hydride materials and hydride heat exchangers.

- I. Sheft and J.M. Nixon visited Matt Rosso at Brookhaven National Laboratory on March 29 for information on iron-titanium hydride and thermal conductivity measurements of powder.

- I. Sheft and J.M. Nixon visited Roger Thomas at Exxon Corp., Linden, N.J. on March 30, for discussions on alternative chemical heat pumps and their magnesium chloride-methanol chemical heat pump experimental system and program.

- Pierre Turillon, Marketing Manager, International Nickel Company, Suffern, N.J. visited ANL on April 4, for discussions on HYCSOS with the Chemistry Division Personnel.

- Discussions on HYCSOS were held on May 25 with Dr. Jim Drewry, Manager, Residential and Commercial Utilization, from the Gas Research Institute, Chicago, Illinois.

APPENDIX A HYCSOS PROGRAM PLAN

1. SYSTEMS ENGINEERING

1.1 Heat Transfer Fluid Evaluation

There are several heat transfer fluids than can be used with a HYCSOS chemical heat pump. Their properties, advantages, disadvantages, storage requirements, quantity, costs, etc., will be evaluated to select the fluid for system design and operation.

1.2 Conceptual Analysis

Thermal and hydraulic analyses will be conducted on several different HYCSOS chemical heat pumps to evaluate the effects of heat source temperature, ambient temperatures, storage, unit size, and component and system performance.

1.3 Heat Source

Heat sources suitable for a HYCSOS chemical heat pump will be identified and assessed to determine their performance, storage requirements, and cost. Primary emphasis will be placed on a solar heat source. A similar assessment will be conducted for backup heat sources. A solar collector and appropriate storage unit will be designed and fabricated as the primary heat source. A backup heat source will be selected and sized for a residential HYCSOS heat pump.

1.4 Residential Pilot Unit Design and Fabrication

Utilizing the results of the heat source and heat-transfer fluid evaluation, system studies, and laboratory operating experience, a residential-size HYCSOS chemical heat pump will be designed, fabricated, and installed.

1.5 Data Evaluation

Data from the laboratory unit will be continuously evaluated to determine heat losses, pressure losses, coefficient of performance, thermal response time, heat transfer, hydrogen flow rates, and component performance.

1.6 Advanced Concepts

Studies will be conducted on a system consisting of several alloy hydrides arranged to effectively utilize temperature gradients. The concept of using individually sealed hydride pairs without a hydrogen valve will be investigated. The feasibility of using automobile waste heat to provide air-conditioning with a HYCSOS chemical heat pump will be evaluated. The concept of using two or more stages to form a cascade system will be studied.

1.7 System Analysis

Perform detailed analyses on systems and their components necessary to support the experimental program and commercialization efforts.

2. HYDRIDE HEAT EXCHANGER

2.1 ERG Unit Testing

Energy Research and Generation, Inc. is designing and fabricating a hydride heat exchanger which contains the alloy powder in interstices of an open-cell aluminum foam. Preliminary tests on a small unit indicated good heat transfer characteristics. When the full-scale unit is delivered, its thermal performance will be evaluated.

2.2 Heat Exchanger Alternatives

The poor thermal conductivity of the metal hydrides and the need for rapid thermal cycling poses stringent requirements for the hydride-bed heat exchangers. A detailed search for commercially available or adaptable heat exchangers will be conducted. Suitable equipment will be obtained and tested. The effective thermal conductivity of metal hydride heat transfer surfaces will be investigated. Small-scale heat exchangers will be fabricated and tested to determine heat-transfer coefficients, pressure losses, thermal response, and hydride-bed stability. The results of these studies will be used to design and fabricate larger units for pilot testing. An investigation of suitable filter material for hydride retention will also be undertaken.

3. COMPONENT DEVELOPMENT

Studies will be conducted on heat exchangers, valves, pumps, blowers, and controls to determine the appropriate type, size, cost, and performance of these components. Particular emphasis will be placed on valves. Elimination of the hydrogen valves is highly desirable. Due to the rapid cycling of the heat-transfer fluid, minimization of the number of these valves is required. The use of single-acting or multi-port valves will be investigated. The arrangement of these components to obtain an optimum system will be undertaken.

4. POWER GENERATION

4.1 Expander-Generator

Obtain and review data on commercially available expanders. Purchase and test any suitable units to determine operating characteristics. If a suitable expander is not available, initiate a contract to design one. Evaluate this design and if suitable, fabricate and test a prototype. Obtain and review data on available generators for use with the expander. Purchase a suitable generator and couple it to the expander for testing.

4.2 System Integration

Assess the integration of the expander-generator in the HYCSOS system to determine available generation time and operational requirements and conditions. Define electrical circuit and control requirements for utilization of the power generated.

5. EXPERIMENTAL STUDIES

5.1 Laboratory

5.1.1 Kinetics and Cycling Effects

The kinetics of absorption and desorption of metal hydrides will be studied in a continuing effort to classify materials suitable for a chemical heat pump. Beds will be cycled to measure hydrogen transfer rates and to determine changes in bed performance and characteristics which may affect long-term performance.

5.1.2 Operating Data

The laboratory-scale facility will be operated to obtain material, system, and component performance data.

5.1.3 Automatic Operation

The laboratory-scale facility will be modified for automatic operation, control, and data acquisition.

5.2 Residential Pilot Unit

5.2.1 Performance Data

A pilot HYCSOS chemical heat pump will be operated with a simulated heat source to obtain performance data and operational characteristics.

5.2.2 Heat Source and Sink Integration

If acceptable heat pump laboratory test results are obtained, an appropriate heat source will be coupled to the heat pump for further system evaluation.

5.2.3 Power Generation

After successful completion of the expander-generator tests, this unit will be added to the chemical heat pump to demonstrate its feasibility for power generation.

5.2.4 Cascade System

If prior system studies show that a Cascade system is attractive, additional equipment will be designed, fabricated, and added to the pilot unit for further testing and evaluation.

6. MATERIAL STUDIES

6.1 Advanced Materials

Development of improved hydride materials will continue. The addition of aluminum to lanthanum-nickel alloys has the beneficial effect of reducing hysteresis without reduction of hydrogen capacity. The use of mischmetal alloys is also promising and could result in substantial material cost reduction. The use of compactions of alloy powder with metals, e.g., Cu, Ni, or Al, to increase the alloy thermal conductivity will be investigated.

6.2 Property Data

Thermodynamic and physical properties of promising alloy materials will be determined.

7. COMMERCIALIZATION

7.1 Market Analysis

An analysis of the users, suppliers, and regions suitable for using a HYCSOS chemical heat pump will be undertaken.

7.2 Manufacturer

Industrial firms will be contacted and informed about the HYCSOS chemical heat pump. Input from these firms will be solicited on the fabrication and marketing of these units.

7.3 Prototype

A manufacturer will be selected to design and fabricate a prototype commercial unit for ANL evaluation and testing.

8. PROGRAM MANAGEMENT

The ANL HYCSOS chemical heat pump program will be developed and managed. Assistance will be provided to DOE on matters related to the national chemical heat pump program. Subcontracts for required technical and economic data or equipment design will be initiated and managed.

27
Table 1A
MANPOWER ALLOCATION - Man-Months

TASK	FY79	FY80	FY81	FY82	FY83
1. SYSTEMS ENGINEERING					
1.1 Heat Transfer Fluid Evaluation	1				
1.2 Conceptual Analysis	3				
1.3 Heat Source	1	3			
1.4 Residential Pilot Unit		8	12		
1.5 Data Evaluation	2	2	2	2	2
1.6 Advanced Concepts		3	3	3	3
1.7 Systems Analysis		3	3	3	3
2. HYDRIDE HEAT EXCHANGER					
2.1 ERG Unit Testing	2				
2.2 Alternatives	2	6	8	3	
3. COMPONENT DEVELOPMENT					
3.1 Pumps, Blowers, etc.		3	1		
3.2 Valves		3	3		
3.3 Heat Exchangers		3	1		
3.4 Controls		3		2	2
4. POWER GENERATION					
4.1 Expander-Generator		6	9		
4.2 System Integration		6			
5. EXPERIMENTAL STUDIES					
5.1 Laboratory					
5.1.1 Kinetics & Cycling Effects	6	6	6	6	6
5.1.2 Operating Data	4	4	4	4	4
5.1.3 Automatic Operation	6				
5.2 Residential Pilot Unit					
5.2.1 Performance Data			6	18	18
5.2.2 Heat Source				6	
5.2.3 Power Generation				6	
5.2.4 Cascade System					6
6. MATERIAL STUDIES					
6.1 Advanced Materials	3	3	3	3	3
6.2 Property Data	3	3	3	3	3
7. COMMERCIALIZATION					
7.1 Market Analysis	1	1	1	1	1
7.2 Manufacturer			1	2	1
7.3 Prototype					3
8. PROGRAM MANAGEMENT					
	2	6	6	6	5
TOTAL	36	72	72	68	60

Table 2A.
PROJECT COST
Thousands of Dollars

	FY79	FY80	FY81	FY82	FY83
Operating Cost					
Effort Related	179	375	400	400	375
Materials and Service	21	150	175	200	175
Major Procurements	20	75	75	150	250
Equipment Cost	20	50	150	200	100
TOTAL COST	240	650	800	950	900

Figure 1A. Project Schedule

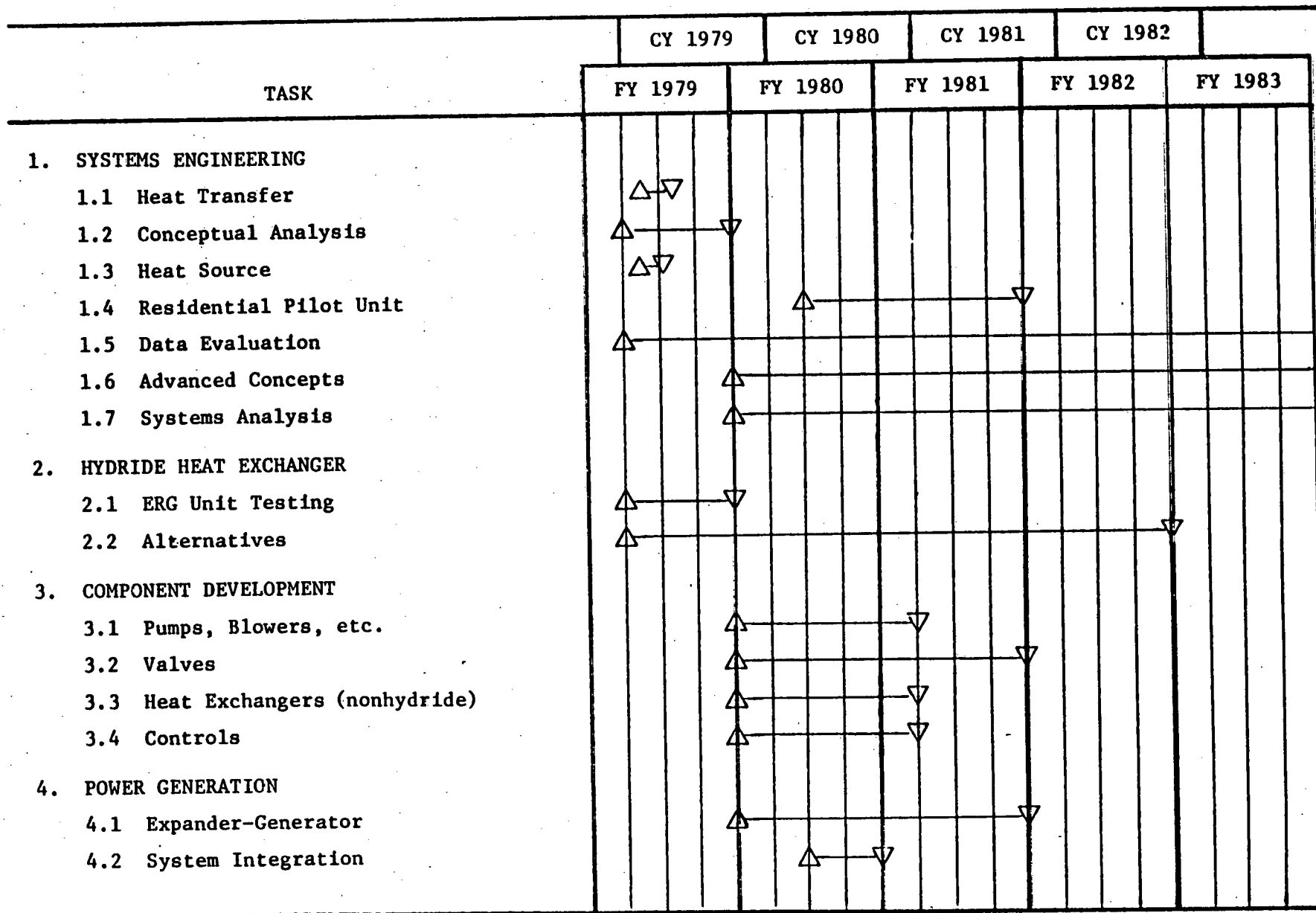


Figure 2A. Project Schedule

