

## ENGINEERING DEVELOPMENT OF A HYCSOS CHEMICAL HEAT PUMP

by

J.S. Horowitz, P.A. Nelson, and C.A. Blomquist

**MASTER****DISCLAIMER**

This book 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.

Prepared for  
Second Miami International Conference  
on  
Alternative Energy Sources  
Miami Beach, Florida  
December 10-13, 1979



U of C-AUA-USDOE

**ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS**

Operated under Contract W-31-109-Eng-38 for the  
U. S. DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ep*

## **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.**

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) among 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.

#### MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona  
Carnegie-Mellon University  
Case Western Reserve University  
The University of Chicago  
University of Cincinnati  
Illinois Institute of Technology  
University of Illinois  
Indiana University  
The University of Iowa  
Iowa State University

The University of Kansas  
Kansas State University  
Loyola University of Chicago  
Marquette University  
The University of Michigan  
Michigan State University  
University of Minnesota  
University of Missouri  
Northwestern University  
University of Notre Dame

The Ohio State University  
Ohio University  
The Pennsylvania State University  
Purdue University  
Saint Louis University  
Southern Illinois University  
The University of Texas at Austin  
Washington University  
Wayne State University  
The University of Wisconsin-Madison

#### NOTICE

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party 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 United States Government.

ENGINEERING DEVELOPMENT OF A  
HYCSOS CHEMICAL HEAT PUMP

J.S. HOROWITZ, P.A. NELSON, and C.A. BLOMQUIST  
Argonne National Laboratory  
Argonne, Illinois 60439 U.S.A.

ABSTRACT

Argonne National Laboratory (ANL) is developing a hydride conversion and storage system (HYCSOS) that is capable of thermal energy storage, space heating and cooling. As a thermal storage medium, metal hydrides provide a high-energy density; however, the economics of such a system are currently unattractive. As a chemical heat pump, a metal hydride system offers the promise of using solar energy, waste heat, natural gas and other energy sources to provide space heating and cooling. The incorporation of an electrical power generation cycle is also a possibility.

The HYCSOS chemical heat pump utilizes the heat of absorption and desorption of hydrogen from different metal hydride beds to provide space heating or cooling. In its simplest form, a hydride heat pump consists of two different hydride beds that are interconnected to allow hydrogen gas transfer between them.

Past work at ANL has concentrated on demonstrating the feasibility of the concept, and on the development of metal alloys suitable for this application. Recently, an engineering development program has been initiated to study the various system aspects of the hydride chemical heat pump. This study has included conceptual designs of various systems.

This paper will concentrate on the engineering development of a heat pump which uses a unique tubular hydride bed that can be cycled rapidly. This design features a large number, about 200, of individual tubes. Each tube contains a high temperature hydride at one end, and a low temperature hydride at the other end. The central portion of the tube is designed to allow hydrogen to flow freely between the ends, but retard the flow of heat between the ends.

This proposed design has several advantages including:

- no hydrogen valves required;
- high reliability due to the large number of independent hydride bed elements;
- potentially high coefficient of performance (COP) due to a unique method of heating and cooling the hydride beds;
- potentially high COP by cascading units for gas-fired applications; and

- simple control system and minimal valves outside of the unit.

This concept can be applied to a number of applications including: gas fired heating and cooling, solar assisted heat pump, automobile air conditioning, and truck refrigeration. Most of the systems engineering and experimental efforts are directed toward the gas-fired application.

## INTRODUCTION

### Heat Pumps

A heat pump is a device which transfers heat from a cold body to a hot body with the expenditure of energy. The presently available heat pumps are driven by electricity. The electricity is used to drive a compressor which is the source of energy input. The principle of operation of these units is identical to that of a household refrigerator. In the summer heat is pumped from inside the house to outside the house. In the winter the process is reversed, and heat is pumped from the cold outside air into the house.

Presently available heat pumps suffer from the disadvantage of requiring high priced electricity. In an attempt to eliminate this drawback, heat pumps are being developed which use little or no electricity. These heat pumps can be divided into two types: absorption and chemical. Absorption units utilize the heat of solution of a fluid, such as ammonia in water, to reduce the need for electricity by replacing the compressor. It should be noted that a high temperature heat source is required. Chemical heat pumps use the heat of a chemical reaction to produce the heat pump effect. Various types of chemical heat pumps have been proposed including: metal hydrides<sup>1</sup>, sulfuric acid-water<sup>2</sup>, methylated salts<sup>3</sup>, and ammoniated salts.<sup>4</sup>

### Metal Hydrides

About 10 years ago, it was discovered that intermetallics of the form AB<sub>5</sub> (A is a lanthanide and B is a transition metal) possessed the ability to easily absorb and reversibly desorb large amounts of hydrogen. At constant temperature there is a pressure plateau where the pressure increases slightly with increasing hydrogen/metal ratio. The absorption and desorption curves for metal alloy hydrides are not identical but exhibit hysteresis. By varying the materials A and B and the ratio B/A, pressure-temperature relationships over wide ranges are obtainable.

Metal hydrides have the property of providing good kinetics while undergoing a reversible thermal decomposition. This feature combined with reasonable cost, and the ability to tailor a system by varying the composition of alloys make hydrides unique in the field of energy conversion. Because of their desirable properties, metal alloy hydrides have been proposed for thermal energy storage applications and for thermal heating and cooling. The incorporation of an electrical power generation cycle is also possible, but at this time it is not being considered.

### Operation

In its simplest form, a hydride heat pump consists of two different



hydride beds that are interconnected to allow hydrogen gas transfer between them. The heat pumping action of the system involves a four-step process which is shown for a heating mode in Figure 1.

1. High temperature heat is applied to the first bed causing it to desorb hydrogen at a pressure higher than the second bed. Therefore, hydrogen flows to the second bed where it is absorbed with a release of heat at an intermediate temperature. This heat is rejected to the building.
2. The two beds are cooled without hydrogen transfer, the first to an intermediate temperature and the second to a low temperature. This step insures that the correct pressure differential between beds exists for reverse hydrogen flow during the next step.
3. Heat from the outside atmosphere is added to the second bed to desorb hydrogen at a pressure higher than the first bed. Hydrogen now flows to the first bed where it is absorbed and releases heat at the intermediate temperature. This heat is rejected to the building.
4. During this step both beds are heated without hydrogen transfer the first to a high temperature, and second to an intermediate temperature, in preparation to the start of the next cycle.

The theoretical coefficient of performance (COP) defined as the ratio of useful heat to the high-temperature heat added is about two for the heating cycle. For cooling, the cycle is the same as above with "the building" and "the atmosphere" interchanged. For this case the theoretical coefficient of performance is about one. For either mode of operation near continuous heat pumping action can be provided by use of multiple pairs of beds.

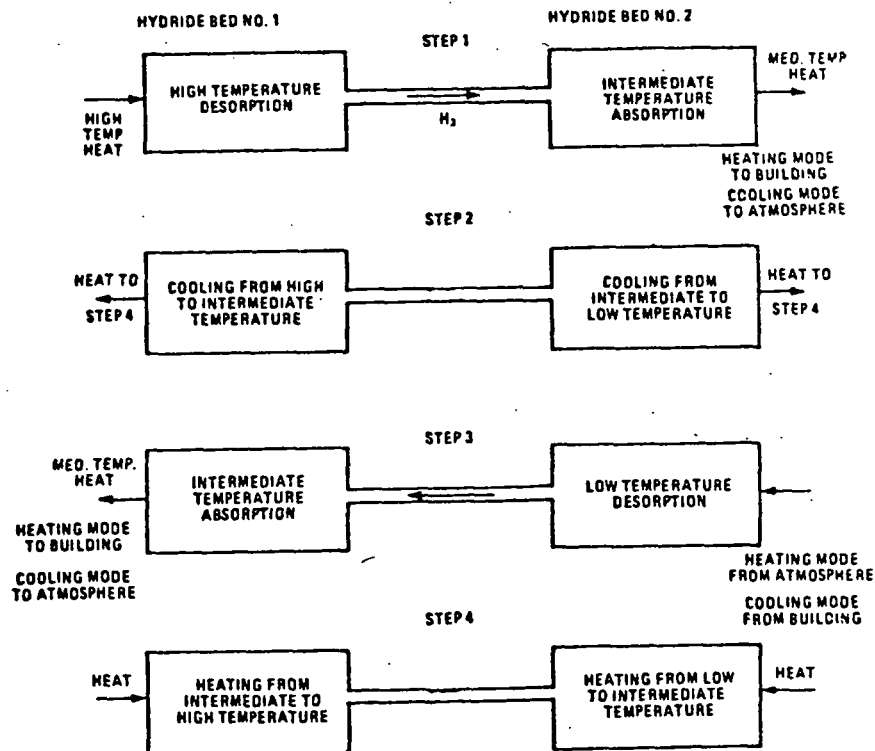


Figure 1. Block Diagram of Theoretical Hydride Heat Pump Operation

## PAST WORK

### Hydride Bed Heat Transfer

The Chemistry Division of ANL has constructed a HYCSOS test facility<sup>1,5</sup> to experimentally evaluate hydride beds. The hydrides of  $\text{LaNi}_5$  and  $\text{CaNi}_5$  are used in a four-bed system. A four-bed system is made up of two pairs of beds. One pair is adsorbing and desorbing hydrogen (step 1 or 3 above), while the other pair is being heated or cooled (step 2 or 4 above).

### System Studies

Under contract to ANL, TRW performed a conceptual design study on a 100-ton solar-powered HYCSOS air conditioning unit (Ref. 6). The study demonstrated that the concept was technically feasible, and design calculations showed that such a unit would have a cost slightly less than current  $\text{LiBr-H}_2\text{O}$  absorption unit selling prices and a competitive coefficient of performance. Since a large fraction of the cost of the HYCSOS system is in the hydride material, and since  $\text{LiBr-H}_2\text{O}$  absorption units exhibit large economics of scale, small scale residential HYCSOS units should show particular promise.

Based upon the above considerations, a second subcontract was awarded to TRW to assess residential applications of HYCSOS for space heating and cooling, and electrical generation using Freon<sup>R</sup> as a heat transfer fluid (Ref. 7). A computer program was developed to optimize the system. In both of these studies a four-bed system was considered.

An economic evaluation based on total annualized cost was prepared for two cities -- Boston and Albuquerque. When compared with conventional systems, the HYCSOS system had a higher annual cost, due to the high capital cost, but it did use considerably less energy. When compared to a solar heating and cooling system, the HYCSOS system had lower costs for both Albuquerque and Boston.

## PRESENT DESIGN

### Four-Bed System

In spite of the fact that the four-bed system has been the design most thoroughly investigated, it suffers from a number of disadvantages. These include:

- only one-half the system is in operation at any time, the other half is in the regeneration cycle.
- effective recovery of heat during regeneration is difficult, and
- one hydrogen leak in a bed will shut down all of the interconnected beds connected.

The last disadvantage may well be the most important as the system would either be unreliable or expensive because of severe quality control requirements.



## Tubular System

In order to overcome these disadvantages, an improved system has been designed. This system features independent, tubular, hydride beds or elements (see Fig. 2). A number of these tubular beds are assembled into a bundle (see Fig. 3). And, finally, a number of bundles are assembled into the complete unit.

Each bed consists of metal tube sealed at both ends containing one alloy at one end, and a different alloy at the other end. The alloy can be contained either as a sintered, doughnut-shaped, briquette, packed around a tubular filter element, or contained in a capsule such as the one patented by the International Nickel Company as shown in Figure 2. In any event, a heat transfer fluid flows outside the tube, and the hydrogen flows back and forth within the bed. In this way the hydrogen is completely contained, and hydrogen valves are eliminated.

Ten beds are combined to form a bundle as shown in Figure 3. The bundle has fittings on the ends to allow for the heat transfer fluid to enter and exit. Note that the central tubesheet keeps the two fluid coolant paths separate, and also inhibits heat transfer between the two sides. Care must be to design the shell with a small coolant volume to minimize the losses during regeneration.

Twenty-four bundles are combined into a unit as shown in Figure 4. Into each end of the unit there are three flows. On the hot end there are flows to and from the heat source, the intermediate-temperature sink, and the high temperature regeneration loop (explained below). The low-temperature side is connected to the low temperature source, the intermediate temperature, and the low temperature regeneration loop.

On each side of the unit there is a multi-port rotating valve. This valve directs the flow of heat transfer fluid from each bundle to the appropriate heat exchanger and back to the bundle. Each bundle undergoes a complete cycle per revolution of the valve. The valves in this design are not believed to be standard, and they are within state of the art.

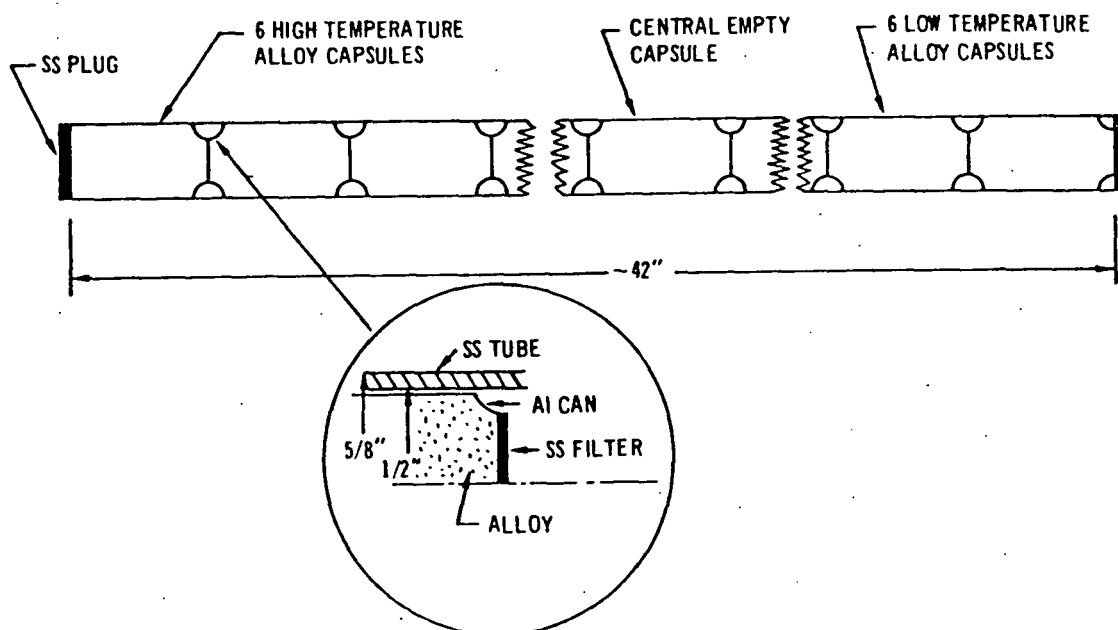


Fig. 2. Tubular Hydride Bed

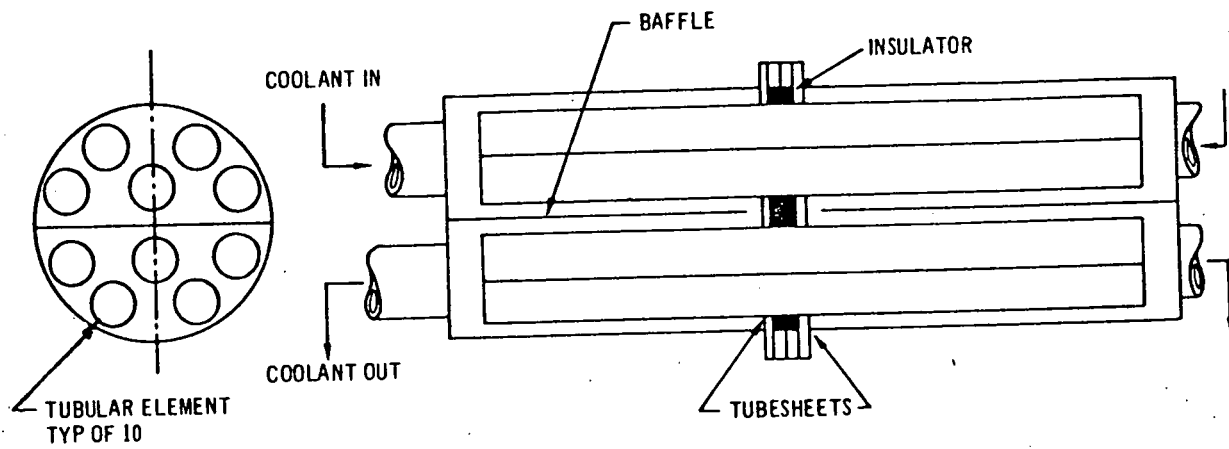


Fig. 3. Hydride Element Bundle

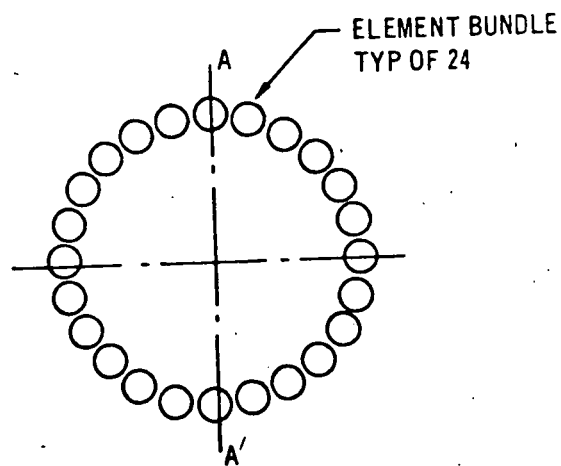
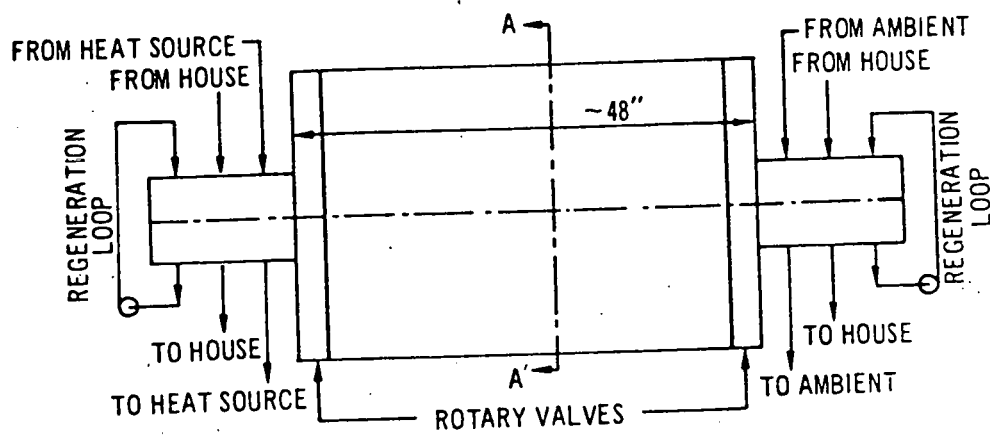


Fig. 4. HYCSOS Unit

The operation of the system can be understood by following a complete cycle for space heating. Consider a bundle just about to be exposed to the high-temperature fluid (see Fig. 5). The high-temperature end of the elements are heated by the fluid. They accept heat and desorb hydrogen. The hydrogen flows down the elements where it is adsorbed at the low-temperature end rejecting heat to the fluid flowing to the house. The cycle time is set so that when this process is virtually complete, the valves place the bundle into the regeneration mode.

In this mode, a closed loop circulates heat transfer fluid from the bundles being cooled to the bundles being heated as shown in Figure 6. With this method the bundles are efficiently heated and cooled. At the end of the regenerative cooling, the bundle reaches the low-temperature portion of the cycle.

At this portion of the cycle heat is added to the low-temperature alloy causing the hydride to desorb hydrogen. The hydrogen flows down the element to the high temperature end where heat is rejected (into the house in the heating mode). The bundle is then regeneratively heated back up to the start of the high temperature heating where the cycle continues.

#### Conceptual Design

ANL has performed a conceptual design study on the tubular concept. The analysis was done to determine the size, performance, and potential cost of a residential-sized heating and cooling system. The results of this analysis are presented in Table 1. This analysis is the basis for continuing work on system design.

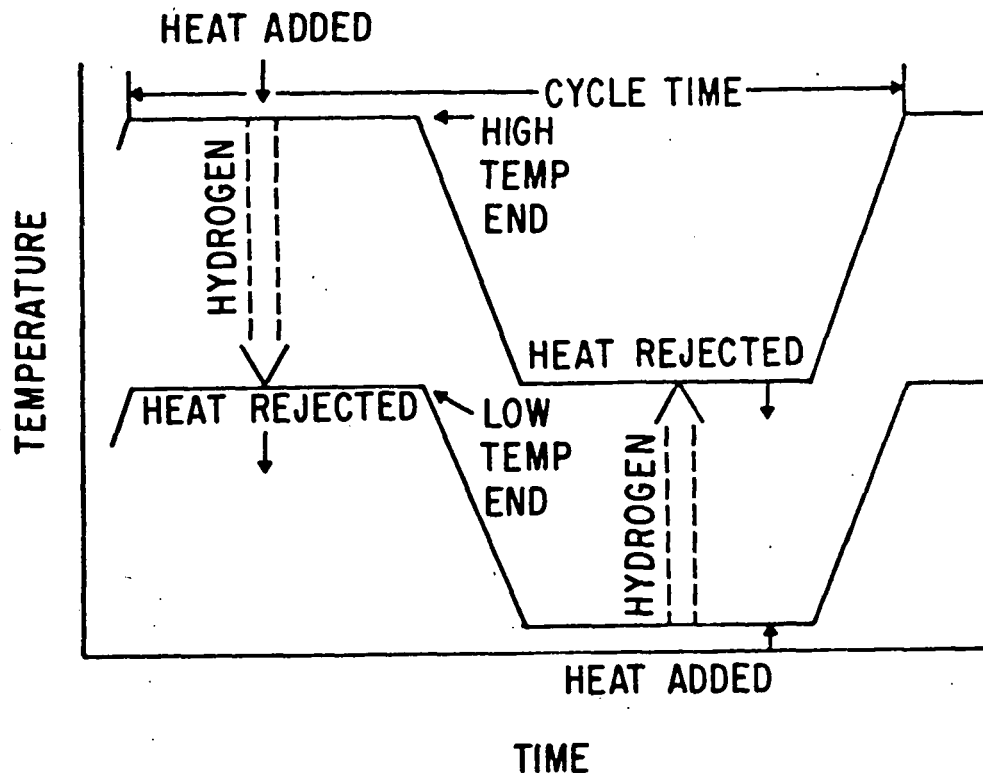


Fig. 5. Schematic of Operation

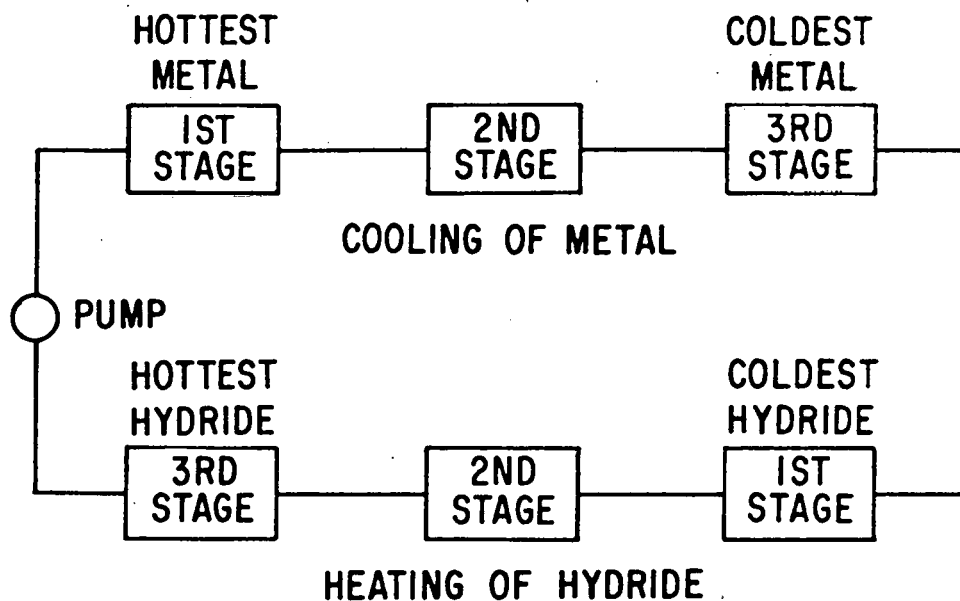


Fig. 6. Schematic of Regeneration Loop

Table 1. Summary of Initial System Design

#### Physical

|  |     |
|--|-----|
| Number of element bundles              | 24  |
| Number of bundles in regeneration made | 6   |
| Number of tubular elements per bundle  | 10  |
| Total weight of hydride, lb            | 110 |
| Cycle time, min                        | 4   |

#### Performance

|                                      |        |
|--------------------------------------|--------|
| Design Rating, Btu/hr                | 50,000 |
| Coefficient of Performance (Heating) | 1.55   |
| Coefficient of Performance (Cooling) | 0.55   |
| Cost, \$/1000 Btu Heating Capacity   | \$110  |

#### Experimental Work

To implement the results of the system studies, a prototypical bundle is being procured from INCO. This bundle has ten elements. Each element contains 13 capsules. The six outer capsules on each end contain hydride, and the central capsule is empty and provides insulation (see Fig. 2). This bundle will be tested in the Chemistry facility in early 1980.

#### APPLICATIONS

The HYCSOS system has many potential applications. Among the uses that are being or have been studied are:

- large scale (100 ton) refrigeration using waste heat (Ref. 6),

- residential scale heating and cooling using solar energy as input (Refs. 1 and 7),
- residential scale heating and cooling using gas as the input energy supply (Ref. 8), and
- upgrading waste heat (Refs. 9 and 10).

Other potential applications are automotive air-conditioning, truck refrigeration using engine heat, and power generation.

At present no clear choice can be made as to the first commercial application. At present ANL is concentrating on development of a gas fired residential unit, while INCO is under contract to New York State Energy Research and Development Authority to develop a system to upgrade waste heat (Ref. 10).

#### FUTURE PLANS

The ANL HYCSOS program milestone chart is shown in Figure 7. During fiscal years 1980 through 1982, effort will be concentrated on the design, construction, and testing of a HYCSOS system for residential heating and cooling. Also advanced work will be directed at the design of a two-stage system which would be particularly suited for use with a natural gas heat source.

The goals of the one and two stage system are presented in Table 2. By meeting these goals, HYCSOS could become a viable heat pump system.

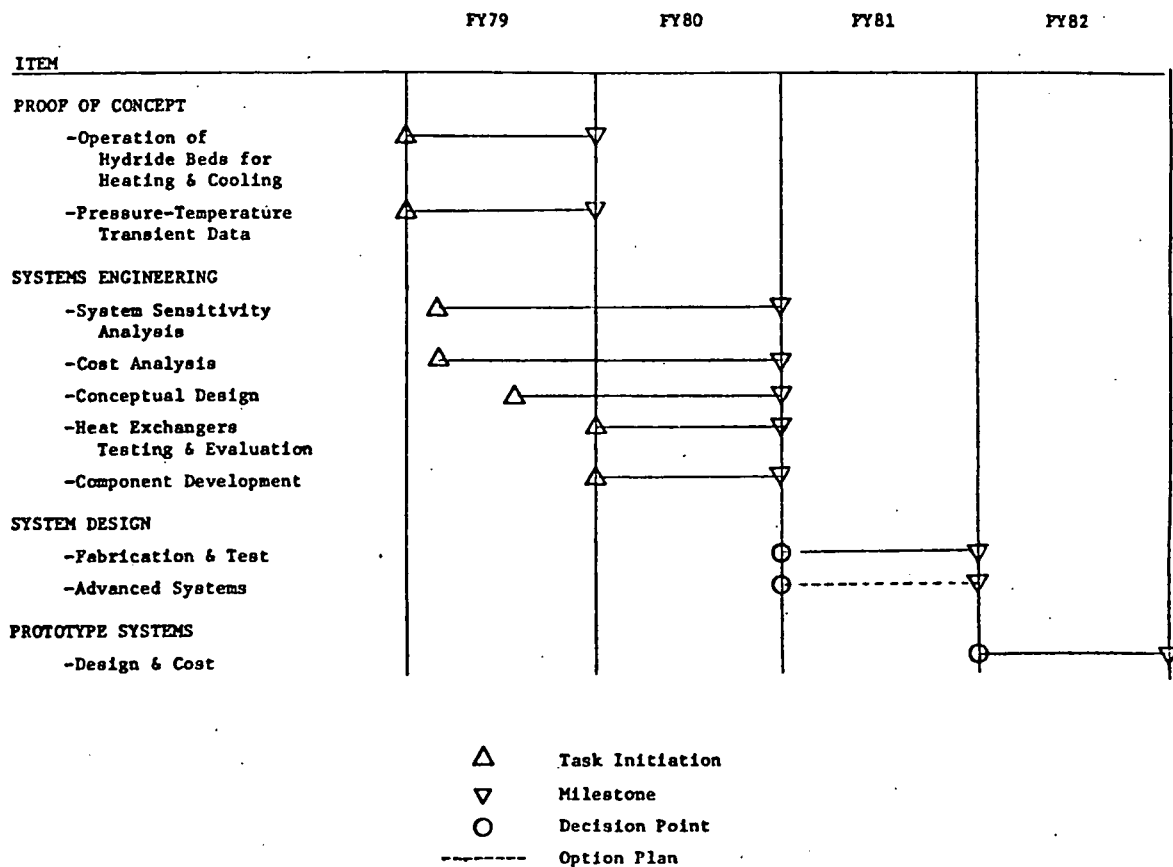


Fig. 7. Hydride Heat Pump Milestone Chart

Table 2. Hydrogen Heat Pump (HYCSOS) Goals and Performance Specifications -- Natural Gas Heat Input

|   | One-Stage | Two-Stage |
|---|-----------|-----------|
| Unit Price for Heating Capacity,<br>\$ per 1000 Btu/hr <sup>a</sup> | 100       | 70        |
| Ratio of Cooling-to-Heating Capacity                                | 0.5       | 0.5       |
| Coefficient of Performance (Btu Output/Btu Input)                   |           |           |
| Heating   | 1.5       | 2.0       |
| Cooling   | 0.5       | 1.0       |
| Heat Transfer Media Temperatures, °F                                |           |           |
| Heating   |           |           |
| Heat Input  | 240       | 340       |
| Minimum Low-Temperature Input <sup>b</sup>                          | -20       | -20       |
| Heat Delivery   | 110       | 110       |
| Cooling   |           |           |
| Heat Input  | 240       | 340       |
| Heat Discharge  | 130       | 130       |
| Coolant   | 40        | 40        |
| Initial Test  | 1981      | 1983      |

<sup>a</sup>Price to building contractor for complete unit, including heat supply and external heat exchangers, having capacity rating in range of 20,000 to 100,000 Btu/hr for heating (10,000 to 50,000 Btu/hr for cooling), when manufactured in quantities of 10,000 units per year.

<sup>b</sup>Based on -10°F ambient temperature and 10°F temperature differential.

#### REFERENCES

1. D.M. Gruen, I. Sheft, G. Lamich, M. Mendesohn, HYCSOS: A Chemical Heat Pump and Energy Conversion System Based on Metal Hydrides, Argonne National Laboratory Report, ANL-77-39, (June 1977).
2. E.C. Clark, Sulfuric Acid and Water Chemical Heat Pump/Thermal Energy Storage, Third Annual Proceedings of Thermal Energy Storage Contractors' Information Exchange Meeting, (1978).
3. P. O'D. Offenhartz, Methanol - Based Heat Pumps for Storage of Solar Thermal Energy, Third Annual Proceedings of Thermal Energy Storage Contractors' Information Exchange Meeting, (1978).
4. F.A. Jaeger and W.R. Haas, Development of Ammoniated Salts, Thermochemical Energy Storage System - Phase II, Third Annual Proceedings of Thermal Energy Storage Contractors' Information Exchange Meeting, (1978).
5. I. Sheft, D.M. Gruen, G. Lamich, HYCSOS: A Chemical Heat Pump and Energy Conversion System Based on Metal Hydrides, Argonne National Laboratory Report, ANL-79-8, (April 1979).

6. R. Gorman, Performance and Cost Analysis of a Hydride Air Conditioning System, prepared by TRW Energy Systems Group for Argonne, ANL/EES-TM-65, (April 1977).
7. R. Gorman and P. Moritz, Hydride Heat Pump. Vol. I: Users Manual for HYCSOS System Design Program and Vol. II: Cost, Performance, and Cost Effectiveness, prepared by TRW Energy Systems Group for Argonne, ANL/EES-TM-66, Vol I and Vol. II, (May 1978).
8. P.A. Nelson, unpublished information, (Oct. 1979).
9. D.M. Gruen, I. Sheft, G.J. Lamich, Enhancement of Low Grade Heat Via the HYCSOS Chemical Heat Pump, proceedings of the 2nd Miami International Conference on Alternative Energy Sources, (Dec. 1979).
10. E. Snape, Ergenics, Inc. subsidiary of INCO, personal communication, August 1979.