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ENHANCEMENT OF LOW GRADE HEAT VIA THE HYCSOS CHEMICAL HEAT PUMP

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ABSTRACT

The Argonne HYCSOS system is a thermally driven chemical heat pump based on two metal hydrides with different free energies of formation that functions in heating, cooling and energy conversion modes. Hydrogen is transferred by means of thermal gradients from one hydride bed to another and the heat released on hydride formation or absorbed on hydride decomposition is available for heating or cooling purposes. With three beds of the same hydride cycling between a higher temperature and a lower one, a continuous supply of high pressure hydrogen can be generated, do useful work in an expansion engine-dynamo unit supplying electricity and then be absorbed on the alloy at a lower temperature.

An interesting mode of HYCSOS operation is made feasible by the recent development of a series of ternary alloys whose hydrogen decomposition pressures at a given temperature can be varied by several orders of magnitude. By proper choice of pairs of alloys with properties suitable for the available temperature regime, low grade solar energy, such as can be obtained from inexpensive flat plate collectors in northern climes with low levels of insolation, can be enhanced to provide domestic hot water. Using the $LaNi_5$ and $CaNi_5$ currently in the HYCSOS system, 34 kcal of thermal energy raised the temperature of water from 39°C to 66°C.

INTRODUCTION

The Argonne HYCSOS system is a two hydride concept [1-6] operating as a chemical heat pump for storage and recovery of thermal energy for heating, cooling, and energy conversion. Low grade thermal energy, as from a solar collector, can be used to decompose a metal hydride with the higher free energy of dissociation and the released hydrogen is reabsorbed at an intermediate temperature and stored as a second hydride with a lower free energy of dissociation. The heat of reabsorption of the second hydride at the intermediate temperature can be used for space heating. The heat pump mode of the heating cycle is the use of low temperature outdoor heat to decompose the second hydride and reabsorb the hydrogen at the intermediate temperature as the first hydride. The heat of absorption of the first hydride can now be used for space heating. By rejecting the intermediate temperature heat of hydrogen absorption to the outdoors and withdrawing the low temperature from indoors, the heat pump cycle can be used for space cooling. The HYCSOS system also lends itself to conversion of thermal energy into useful shaft work. High pressure hydrogen from the high temperature dissociation of a hydride could do work in an expansion engine driving an electric generator before being reabsorbed on another bed of the same hydride at a lower pressure and temperature. The heat pump cycle can also be used to raise the temperature available from an inexpensive flat plate solar collector or which is available as waste heat in many industrial operations.

THE HYCSOS SYSTEM

The Argonne HYCSOS system is a demonstration test facility to evaluate materials and components for use in the hydride heat pump concept. The dual metal-metal hydride demonstration unit consists of four heat exchangers of approximately one-half gallon volumetric capacity each, containing two different types of metal powders or metal hydride powders. The Hydride heat exchangers and hydrogen piping system are made of 316 type stainless steel. A hydrogen filter, one micron retention, is incorporated immediately above the hydride heat exchangers to preclude transfer of hydride powder through the lines and to prevent contamination of other hydride material. Safety relief valves, filters, flowmeters, shutoff valves, and manifolds between the hydride beds are provided in the hydrogen process system. For personnel safety considerations, the hydride containers are surrounded by a well ventilated hood through which a large volume flowrate of air (2000 CFM) is drawn and exhausted outdoors. Continuous hydrogen concentration monitoring, with an alarm set below the flammability limit, is provided to warn of potential danger. The test facility is large enough that heat losses, kept to a minimum by insulating the system and minimizing its heat capacity by reducing the heat transfer fluid volume, do not seriously impair the accuracy of the measurements (see figure 1).

Because the hydride reactions are heat transfer limited, design consideration of the heat exchangers containing the alloy powder is important. The current units are tanks with internal heat transfer surfaces in the form of coiled tubing with the heat transfer cooling or heating fluid circulating inside the tubing. The alloy powder is between the loops of the coils such that no powder is more than 1/8 inch from a coil surface. Advanced design heat exchangers are being investigated in order to reduce cycle times and increase the heat transfer in the alloy beds. A heat exchanger containing the alloy powder in the small interstícies of an aluminum foam matrix bonded to heat transfer fluid channels is being developed and constructed.

A preliminary examination of such a unit showed a heat ransfer rate approximately eight fold greater than a coiled tubing heat exchanger. Compactions of metal hydrides with high thermal conductivity metal powders are reported [7] to have a thermal conductivity 10-20 times better than the alloy powder. Commercially available high performance compact fin-plate heat exchangers are also being evaluated.

Many variables are followed during the operation of the system. Information from the various sensors, e.g., temperature, pressure, flow and power is digitized and transmitted by a data logger to a Tektronix data handling system. Important variables are also displayed on a remote graphic panel. The instrumentation system can be used to provide real-time indication of important system characteristics, provide for logging of data generated during system operation, provide a means of processing raw data, and provide a way to automatically control HYCSOS system operation.

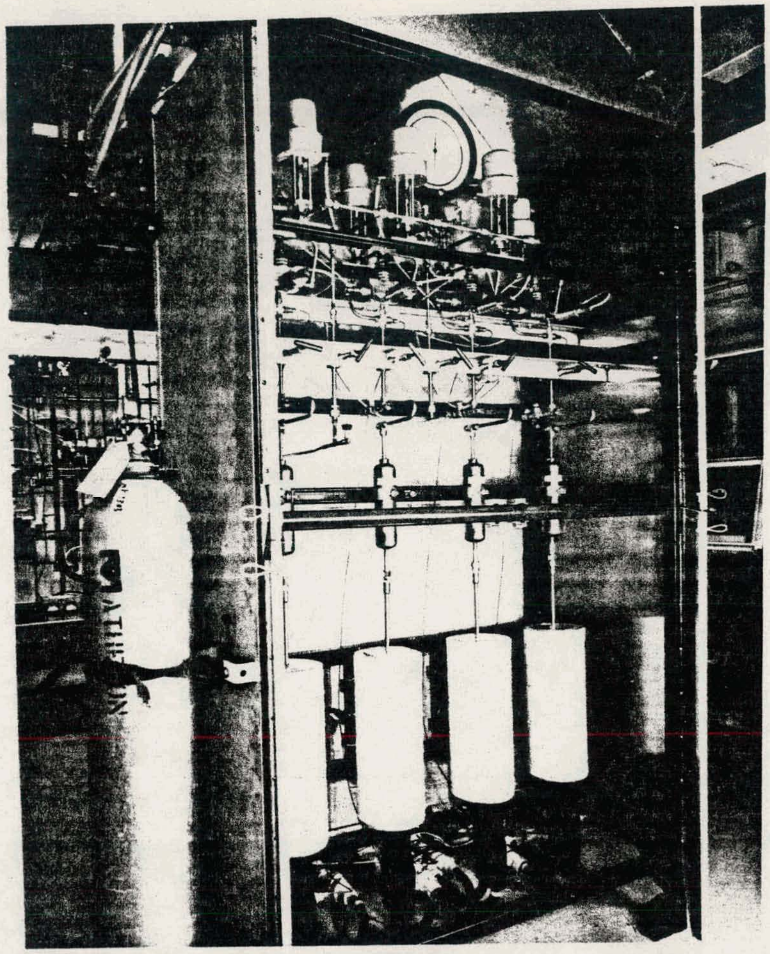

Figure 1. The HYCSOS System

THERMODYNAMICS OF HYDRIDE MATERIALS

The selection and availability of desirable pairs of hydrides to function as a chemical heat pump are important to the efficient and economical operation. In recent years, lanthanide-nickel hydride systems have been investigated which have properties that make them attractive candidates for solar energy utilization purposes.

Van Vucht, Kuijpers and Bruning [8] reported the ability of intermetallics of the form AB_5, where A can be a lanthanide and B is nickel or cobalt, easily to absorb and reversibly desorb large amounts of hydrogen with excellent kinetics. These compounds have hexagonal structure. For example, stoichiometric $LaNi_5$ can absorb over six hydrogen atoms while undergoing a 25% lattice expansion. A two-phase region is bounded by solid solution at low H/M ratios and the hexagonal $LaNiH_6$ hydride phase at higher H/M ratios. The H/M range of the two-phase plateau region is shortened somewhat with increasing temperature. A hysteresis effect between the absorption and desorption plateau pressures increases with temperature and is probably related to the internal stresses associated with the large volume change on hydriding. Although temperature dependent, the kinetics of the system are rapid, with over 95% of the equilibrium hydrogen pressure attained in a few minutes at room temperature. The heat of formation of $LaNi_5H_6$ is 7.2 kcal/mole H_2.

The hydrogen pressure required for absorption and desorption determine the material and construction of the system. From the treatment [9] of chemical heat pumps and figure 2, where the dissociation pressure in the plateau region is approximated by the van't Hoff equation

$$\ln P = \Delta H/RT - \Delta S/R$$

where ΔS and ΔH are the entropy and enthalpy changes per mole of hydrogen for the hydriding reaction, it can be seen that the most efficient heat pump operation, being able to pump from the lowest temperature, occurs when the entropy for the hydride reaction is the same for the two hydrides. The temperature regime over which a given pair of hydrides can function, however, is determined primarily by the enthalpy for the hydride reaction.

The use of free energy charge-cell volume correlations has been useful in obtaining hydrides with specified properties. Although varying the ratio of nickel to lanthanum in $LaNi_5$, partially substituting other lanthanides for lanthanum or other transition metals for nickel have been known [10,11] for some time to change the plateau dissociation pressure by a factor of about 4, there has been no systematic way of changing the enthalpies of hydriding reactions over a wide range. It has recently been shown [12-14] that aluminum substitutions for nickel, forming the $LaNi_{5-x}Al_x$ ternary alloy system, lowers the plateau pressure by a factor of about 10^3 in going from $LaNi_5$ to $LaNi_4Al$. Measurements on well annealed samples in the $LaNi_{5-x}Al_x$ system show the entropy

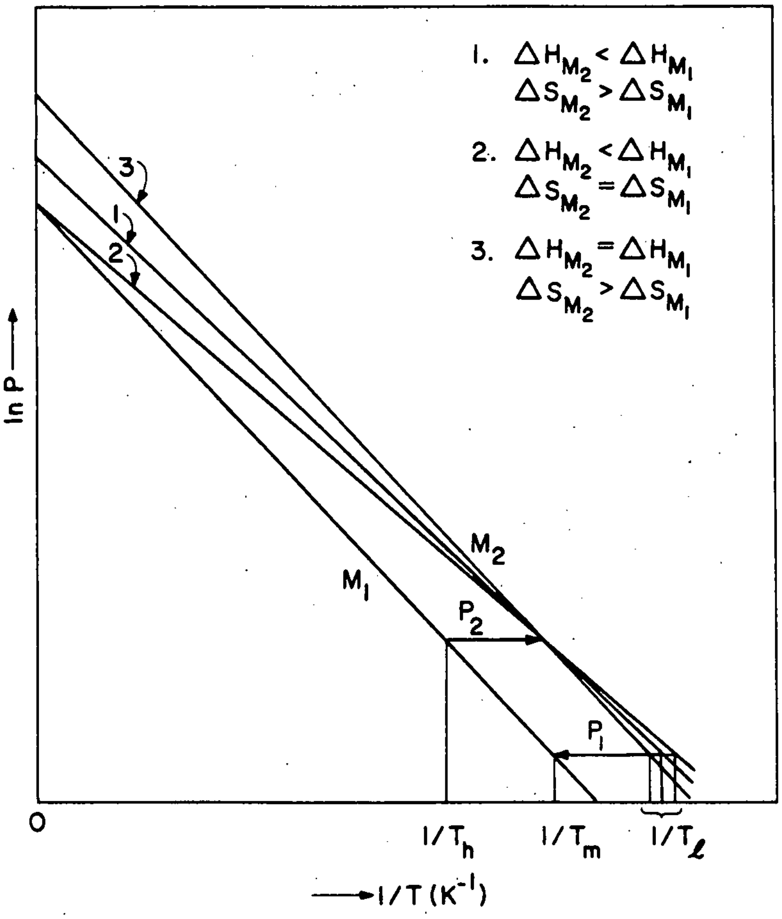

Figure 2. Thermodynamics of Metal Hydride Chemical Heat Pumps.

changes over a wide composition range to be virtually constant [15].

Also, a linear relationship has been observed between the aluminum content and the heat of formation for the hydriding reaction. Within experimental error, a 0.1 change in "x", the aluminum content, changes the heat of formation by about 0.5 kcal/molH_2 [16]. Aluminum has also been substituted for nickel in mishmetal* (Mn) pentanickel alloy with similar reduction in plateau dissociation pressure [17]. A substantial additional benefit is the reduction in the high hysteresis which renders the unsubstituted alloy unusable. The use of low cost mishmetal results in alloy raw material costs 35-45% that of present $LaNi_5$ costs and about 70% of future costs on a per unit hydrogen storage basis. The advent of these ternary alloys adds flexibility to the selection of alloy pairs for the optimization of engineering design and performance characteristics of the hydride heat pump system.

To be useful for chemical heat pump purposes, hydrides must be sufficiently stable to undergo many hydride-dehydride cycles without decomposition. Since the binary hydrides of the A intermetallic component (which can also be calcium) are very stable, the ternary hydrides tend to be metastable and form the binary hydride of A, pure B metal (or a compound more rich in B) and hydrogen [18]. That ternary hydrides do form is due to the limited diffusion of the A and B atoms at the temperatures used. The plateau capacity of $CaNi_5$, currently used as M_1 in HYCSOS systems, has been found to be substantially reduced when contained in a hydrogen atmosphere for an extended period of time [19]. Figure 3 shows the effect of a several year exposure to hydrogen on the $CaNi_5$ in the HYCSOS system. Regenation of the original alloy can be achieved by annealing the material in a vacuum at a moderate temperature [20].

TEMPERATURE ENHANCEMENT

An interesting mode of HYCSOS operation is made feasible by the ability to select alloys with a particular decomposition pressure. By proper choice of pairs of alloys with properties suitable for the available temperature regime, low grade solar energy, such as can be obtained from inexpensive flat plate collectors in northern climes with low levels of insolation, can be enhanced to provide domestic hot water. The addition of heat pump operation to the solar collector system enables longer periods of usefulness with lower available solar temperatures.

To cycle between a solar collector temperature as low as 40°C and produce a high temperature of 75°C, thermodynamic considerations [9] of hydride heat pumps suggest a ratio of 1.1 for the enthalpy of hydride formation for two alloys having the same entropy. Such a mode of operation is shown in figure 4. Using $LaNi_5$, with an enthalpy of 7.2 kcal/mole H_2, as M_2 and 8.1 kcal/mole H_2 for the enthalpy of the more stable hydride M_1, a heat pump input temperature of 40°C could be enhanced to 75°C. The same 40°C input temperature could also be used to complete the cycle at a reject temperature of 4.5°C. In late spring, summer and early autumn during the time of day when solar collector output temperatures are sufficient, direct water heating can be used. At other times the heat pump addition would decrease the need for auxiliary heating.

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*Mishmetal is the unrefined rare earth mixture of average composition; 48-50% Ce, 32-34% La, 13-14% Nd, 4-5% Pr and 1-2% other rare earth.

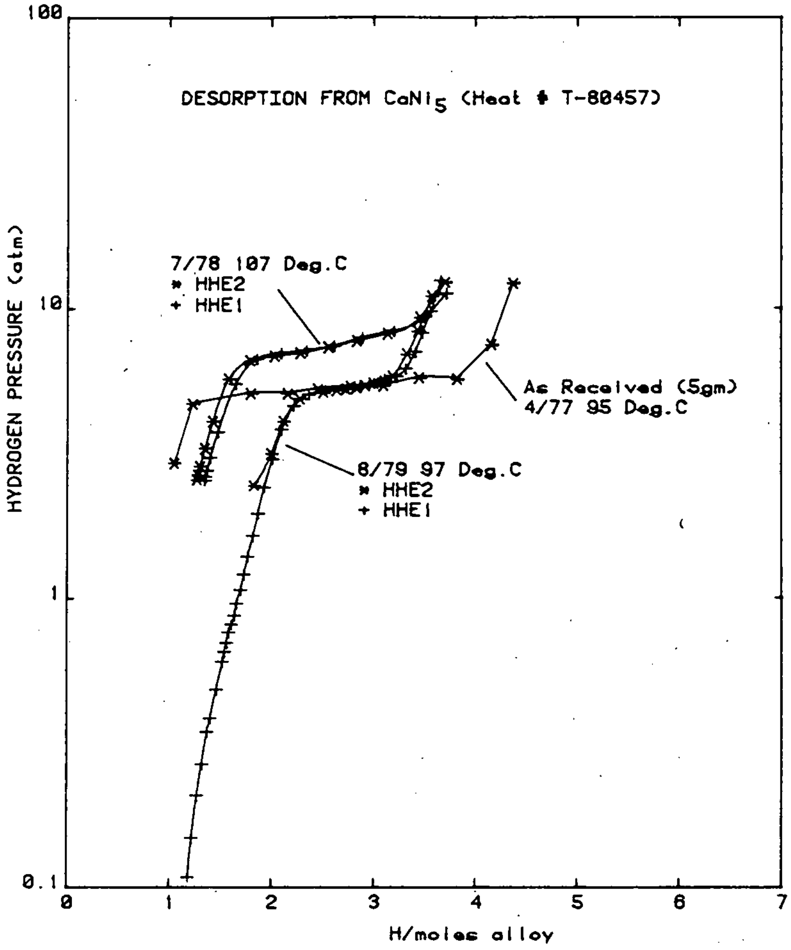

Figure 3. Metastability of $CaNi_5$.

The operation of the HYCSOS system containing $LaNi_5$(ΔH = 7.2 kcal/mole H_2) as M_2 and $CaNi_5$(ΔH = 7.5 kcal/mole H_2) as M_1 is shown in figure 5. In two minute approximately 5 moles of hydrogen (IF-3H, integrated H_2 flow) was desorbed from $LaNi_5$ at 39°C (T-3HTF-0, outlet heat transfer fluid temperature) and absorbed on $CaNi_5$ at 66°C (T-2HTF-0, outlet heat transfer fluid temperature). The transient decrease in $LaNi_5$ temperature with desorption and the increase in $CaNi_5$ temperature with absorption are evident.

The temperature enhancement of the thermal energy is observed in the behavior of the integrated power into the desorbing $LaNi_5$ (IPC) and the absorbing $CaNi_5$ (IPA). A base-line determination of the power required to maintain each hydride bed (and associated heat transfer fluid loops) at the desired temperature is obtained for about 10 minutes before the transfer of hydrogen is initiated. During the hydrogen desorption from $LaNi_5$, the temperature drops to 36° before the increased heating power returns it to 39°C. No heating power to the absorbing $CaNi_5$ is required until the temperature is again returned to 66°C from its peak at 70°. Approximately 34 kcal of thermal energy was used to increase the temperature of the heat transfer fluid from 39°C to 66°C. Higher temperatures (75°C) could have been achieved with the optimum alloy pair, but 66°C is considered a safe maximum for domestic hot water. Because the alloys are not optimum, 60°C, rather than the 40°C assumed available from the solar collector, would be required to return the hydrogen from $CaNi_5$. However, using $LaNi_{4.8}Al_{0.2}$ to form the more stable hydride would permit the return of hydrogen at 40°C to the $LaNi_5$ as the less stable hydride at 4°C. The 34 kcal

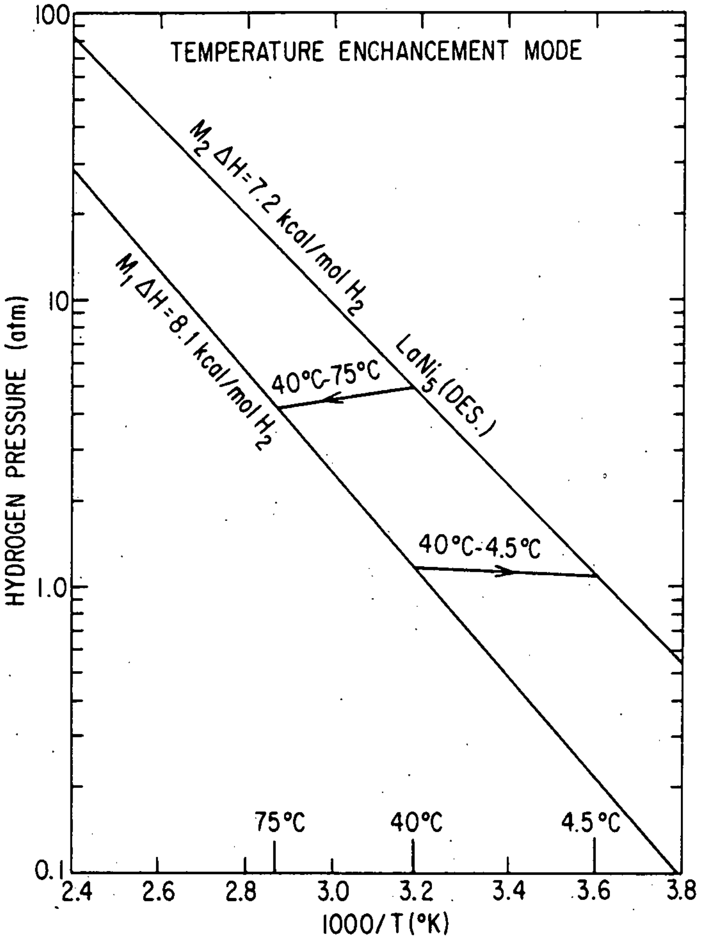

Figure 4. Temperature Enhancement by Heat Pump Operation.

transferred compares well with the 37 kcal calculated from the enthalpies of the hydrides.

In many commercial operations, e.g. factories, hospitals, foundries, etc., low temperature thermal energy is rejected to the environment. Because of wide temperature range available by proper selection of alloy pairs, hydride chemical heat pumps can up-grade the heat to useful temperatures.

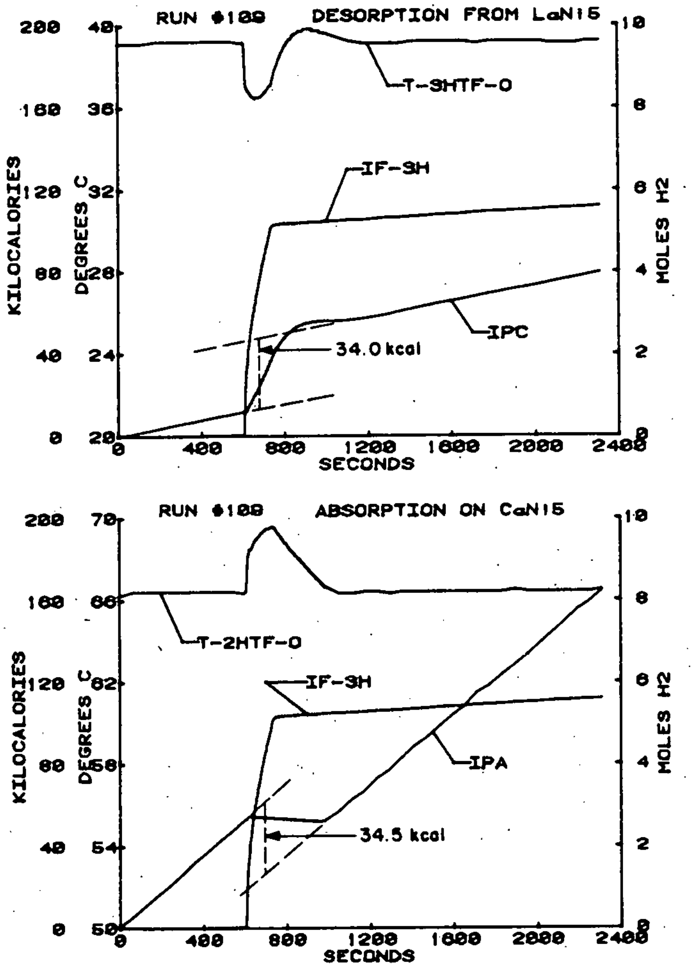

Figure 5. HYCSOS Operation in Temperature Enhancement Mode. IPA is integrated thermal energy into $CaNi_5$, IPC is integrated thermal energy into $LaNi_5$, IF-3H is moles of hydrogen transferred, T-2HTF-O is outlet temperature of heat transfer fluid to $CaNi_5$, and T-3HTF-O is outlet temperature of $LaNi_5$ heat transfer fluid.

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