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THE HYCSOS CHEMICAL HEAT PUMP AND ENERGY CONVERSION SYSTEM BASED ON METAL HYDRIDES

BY

Irving Sheft, Dieter M. Gruen and George J. Lamich

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THE HYCSOS CHEMICAL HEAT PUMP AND ENERGY CONVERSION SYSTEM BASED ON METAL HYDRIDES*

Irving Sheft, Dieter M. Gruen and George J. Lamich

Argonne National Laboratory

Argonne, IL 60439

Summary

The Argonne HYCSOS system is a two hydride concept, operating as a chemical heat pump for storage and recovery of thermal energy for heating, cooling and energy conversion. Hydrogen gas is transferred from one hydride bed by solar thermal energy input at a characteristic temperature to a second bed where hydrogen is absorbed and thermal energy is released at another temperature appropriate for the mode of operation in use.

The basic HYCSOS concept uses thermal energy from a low grade source such as a solar collector to decompose a hydride, e.g. $CaNi_5$, and the released hydrogen is absorbed at a lower, intermediate, temperature and stored as a second hydride, e.g. $LaNi_5H_6$. The heat pump mode is the low temperature dissociation of the $LaNi_5H_6$ and the absorption of the hydrogen at the intermediate temperature. The intermediate temperature is available for space heating, using solar energy during periods of insolation and using low temperature ambient heat via heat pump action during other times. Operated in a reverse mode, the system can be used for refrigeration, eliminating the mechanical compression required in the operation of a conventional air conditioner. With three hydride heat exchangers containing the same hydride cycling between a high temperature and a lower one, a continuous supply of high pressure hydrogen can be generated to do useful work in an expansion engine-dynamo unit supplying electricity, the hydrogen being absorbed after expansion on the alloy at a lower temperature.

The demonstration test facility in the ANL Chemistry Division has four stainless steel hydride heat exchangers of approximately 2.5 liter capacity each for holding the metal hydrides. The facility is instrumented to measure and record system characteristics on a data logger and graphics computing system. Three isothermal heat transfer fluid loops which can be remotely valved and fluid pumped into the appropriate hydride heat exchanger are available. The unit is of sufficient size that thermal losses are small compared to measured heat transfer rates in a heat storage mode, refrigeration mode and power generation mode.

Although the system currently contains the alloy pair, $CaNi_5$-$LaNi_5$, recent developments of aluminum substituted ternary alloys have provided a versatile class of materials whose hydrogen dissociation pressure can be varied in a predetermined manner by almost three orders of magnitude and can provide a wide range of preselected temperatures and pressures for chemical heat pump operation.

The current status of the HYCSOS system is discussed.

Introduction

Application of the "heat pump" concept, the use of heat available at a lower temperature to warm a space at a higher temperature, has been discussed for many years and was first pointed out by Lord Kelvin.[1] Interest in solar energy driven heat pumps, including chemical heat pumps has recently been shown.[2-4]

The Argonne HYCSOS system is a two hydride concept,[5-8] 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, is used to decompose one of a pair of metal hydride with the higher free energy of dissociation and the released hydrogen is reabsorbed at an intermediate temperature to form 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 uses 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 low temperature heat 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 Argonne HYCSOS system[9] designed and constructed to show the scientific feasibility of the concept and to evaluate system components and materials for use as hydrides has been operational for approximately a year. The scientific feasibility was demonstrated by the rapid cycling of hydrogen between $CaNi_5$ hydride and $LaNi_5$ hydride at experimental conditions approaching design specifications. Optimum operational characteristics for this first pair of hydrides are yet to be determined. Because

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the unit was designed to be a versatile test facility and does not yet have capability for regenerative heat exchange between hydride beds, thermal efficiency measurements of the cycles would not be meaningful. Advanced concept heat exchangers and new versatile ternary alloys are available for future testing.

Hydride Systems as Chemical Heat Pumps

A heat pump is a device which absorbs heat at a low temperature and delivers it at a higher temperature. Mechanical heat pumps generally use a compressor to supply the driving action. A chemical heat pump uses the thermal energy of reversible chemical equilibrium to pump heat from a low temperature to a higher one. For such a thermally driven heat pump, which could be used for either heating or cooling purposes, the thermal energy need not first be converted to mechanical energy. An additional advantage in the heating mode is the ability to also use the driving thermal energy for heating purposes.

The rapid kinetics of hydrogen absorption and desorption with AB_5 alloys, the ability to vary the dissociation pressure by controlling the chemical composition of either the A or B component and the high hydrogen carrying capacity of these alloys make them especially useful for chemical heat pump applications. Alloys can be selected so that low grade heat sources such as solar collectors, automobile heat exhaust or reject heat from a power plant could be used to drive hydride heat pumps.

The treatment[10] of the following general heat pump equations can be applied to any pair of compounds and can be used to determine alloy properties for best heat pump operation at specified temperatures.

Consider a thermally driven heat pump used for heating purposes. A quantity of heat Q_h is supplied to the heat pump at a high temperature T_h, heat Q_m is delivered by the heat pump at the intermediate temperature Tm used for space heating, and heat Q_ℓ is extracted from a lower temperature T_ℓ. For a reversible process,

$$Q_m = Q_h + Q_\ell$$

and

$$\frac{Q_m}{T_m} = \frac{Q_h}{T_h} + \frac{Q_\ell}{T_\ell}$$

An index of the efficiency of such a heat pump, the coefficient of the performance, COP_h, the ratio of the useful heat delivered to the required high temperature heat input, can be seen to be

$$COP_h = \frac{Q_m}{Q_h} = \frac{T_m}{T_h}\left[\frac{T_h - T_\ell}{T_m - T_\ell}\right].$$

The coefficient of performance for the refrigeration mode is

$$COP_c = \frac{Q_\ell}{Q_h} = \frac{T_\ell}{T_h}\left[\frac{T_h - T_m}{T_m - T_\ell}\right].$$

For both cases the highest performance is reached as the low temperature approaches the intermediate temperature to which the low temperature heat is pumped.

For the specific case where the heat pump consists of a pair of metal hydrides M_1 and M_2 with hydrogen flowing freely between them, M_2 cycles between T_ℓ and T_m with corresponding dissociation P_1 and P_2 and M_1 cycles between temperatures T_m and T_h where its dissociation pressures are P_1 and P_2 respectively. The equilibrium dissociation pressures in the two phase region, which are plotted in Fig. 1, are determined by the enthalpies ΔH_{M_2} and

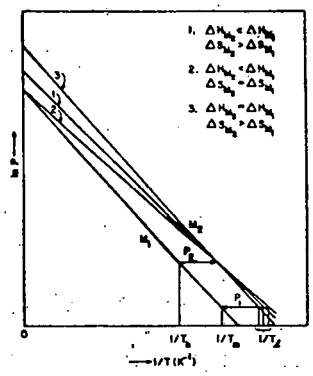

Figure 1. Thermodynamics of Metal Hydride Chemical Heat Pumps.

ΔH_{M_2} of the hydride formation reactions and by the entropies ΔS_{M_2} and ΔS_{M_1}.

To operate the hydrides M_1 and M_2 in the heat pump mode, start with M_1 saturated with hydrogen at T_m and P_1. Heat M_1 to T_h causing the pressure to rise to P_2 and hydrogen to desorb. The released hydrogen is absorbed by M_2 at T_m and P_2, the heat of absorption ΔH_{M_2} being released at T_m. The temperature of M_1 is now lowered to T_m and that of M_2 to T_ℓ. Hydrogen desorbing from M_2 at T_ℓ absorbs heat from the environment while the heat of reaction, ΔH_{M_1}, is again released at T_m. Hydrogen gas is the working fluid in this closed cycle which can be repeated indefinitely.

It is clear that to optimize the choice of metal hydride pairs for a particular mode of heat pump operation, the relationship between the thermodynamic quantities governing the hydride formation reactions and the operating temperatures T_h, T_m and T_ℓ needs to be established.

For the general case in both heating and cooling cycles, $\Delta H_{M_2} \neq \Delta H_{M_1}$, $\Delta S_{M_2} \neq \Delta S_{M_1}$, inspection of Fig. 1 shows that

$$-R \ln p_2 = \frac{\Delta F_{M_2}}{T_m} = \frac{\Delta F_{M_1}}{T_h}$$

$$-R \ln p_1 = \frac{\Delta F_{M_2}}{T_\ell} = \frac{\Delta F_{M_1}}{T_m}$$

Straightforward substitution and rearrangement gives

$$\frac{\Delta H_{M_2}}{\Delta H_{M_1}} - \frac{T_m(\Delta S_{M_2} - \Delta S_{M_1})}{\Delta H_{M_1}} = \frac{T_m}{T_h} \qquad (1)$$

and

$$\frac{\Delta H_{M_2}}{\Delta H_{M_1}} - \frac{T_\ell(\Delta S_{M_2} - \Delta S_{M_1})}{\Delta H_{M_1}} = \frac{T_\ell}{T_m} . \qquad (2)$$

Since ΔH_{M_1} is the high temperature, T_h, heat (Q_h) used to drive ΔH_{M_2} (Q_ℓ) from the low temperature, T_ℓ, to T_m, and is itself used for heating at T_m, the heating cycle performance of the hydride heat pump is

$$COP_h = \frac{\Delta H_{M_2} + \Delta H_{M_1}}{\Delta H_{M_1}} = 1 + \frac{\Delta H_{M_2}}{\Delta H_{M_1}} .$$

Combining with equations (1) and (2) shows that for the general case the performance of a hydride heat pump in the heating cycle,

$$COP_h = \frac{T_m(T_h - T_\ell)}{T_h(T_m - T_\ell)}$$

is the same as that for a mechanical heat pump operating reversibly for heating purposes.

For operation in the cooling cycle where

$$COP_c = \frac{\Delta H_{M_2}}{\Delta H_{M_1}},$$

equations (1) and (2) reduce to

$$COP_c = \frac{T_\ell}{T_h}\left[\frac{T_h - T_m}{T_m - T_\ell}\right],$$

also the same as for a mechanical heat pump.

It can be seen that, as shown graphically in Fig. 1, the lowest temperature, T_ℓ, is reached for a given M_1, M_2 pair when $\Delta H_{M_2} = \Delta S_{M_1}$, thus making this special case of particular interest for chemical heat pump applications.

For this special case $\Delta S_{M_2} = \Delta S_{M_1}$ then

$$\frac{\Delta H_{M_2}}{\Delta H_{M_1}} = \frac{T_m}{T_h} = \frac{T_\ell}{T_m} \qquad (3)$$

from which it follows that

$$T_m^2 = T_h T_\ell . \qquad (4)$$

It is of interest to determine the solar collector temperatures required to operate a solar energy driven metal hydride air conditioner. A reasonable value for T_ℓ is 8°C (46°F) and for T_m is 40°C (104°F), making T_h = 76°C (169°F). Another set of temperatures might be T_ℓ = 8°C (46°F) and T_m = 45°C (113°F), making T_h = 86°C (189°F). The input temperatures are, therefore, in the *flat plate* collector range.

The four hydride heat exchangers of the HYCSOS chemical heat pump are in fact equivalent to the four elements, evaporator, absorber, generator and condenser of an absorption refrigerator. Starting in the evaporator, refrigerant absorbs heat from the space to be cooled and vaporizes. The refrigerant vapor combines with the absorbent in the absorber, and the heat of reaction is removed. The absorbent-refrigerant mixture is heated in the generator and separated. Pure absorbent is returned to the absorber, while refrigerant vapor continues to the condenser. Heat is removed from the refrigerant in the condenser. Finally, the refrigerant is returned to the evaporator where the cycle is repeated.

The selection and availability of desirable pairs of hydrides are thus seen to be important to the efficient and economical operation of HYCSOS.

It has recently been shown[10-13] that aluminum substitutions for nickel, forming the $LaNi_{5-x}Al_x$ ternary alloy system, lowers the plateau pressure 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 changes over a wide composition range to be virtually constant.[14]

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.[15] Aluminum has also been substituted for nickel in mishmetal* (Mm) pentanickel alloy with similar reduction in plateau dissociation pressure.[16] A substantial additional benefit is the reduction in the impractical high hysteresis in the unsubstituted alloy. 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.

System Design Description

The Argonne HYCSOS system is a demonstration test facility to evaluate materials and components for use in the hydride heat pump concept. In this dual metal-metal hydride concept, hydrogen gas is transferred from heat exchangers containing a metal hydride bed of one composition to heat exchangers containing a metal hydride bed of another composition by the action of applied thermal energy. The heat of formation of one type of hydride compound (termed M1 hydride) and sensible heats associated with system heat capacities will be supplied, at a specific temperature level which is commensurate with required system hydrogen pressure level to decompose the M1 hydride and drive the hydrogen to the other metal (termed M2) system where the hydrogen is absorbed.

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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 and is less expensive than the separated rare earth elements.

The dual metal-metal hydride demonstration unit consists of four hydride heat exchangers (HHE) of approximately one-half gallon volumetric capacity each, containing two different types of metal powders or metal hydride powders (see Figure 2). The

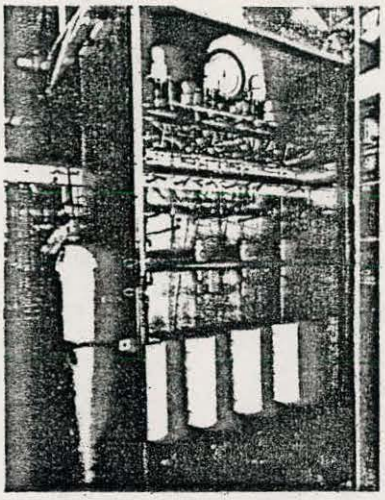

Figure 2. Hydrogen System

hydride heat exchangers and hydrogen piping system are made of 316 stainless steel. For the heat storage and refrigeration tests, two of the heat exchangers contain lanthanum-nickel and/or its hydride, the other two contain calcium nickel and/or its hydride. For the power generation tests, only three heat exchangers are used containing either lanthanum-nickel or calcium-nickel. Safety relief valves, filters, flowmeters, shutoff valves, and manifolds between the hydride beds are provided in the hydrogen process system.

Three isothermal heat transfer fluid loops, Figure 3, are available and can be remotely valved and pumped to the appropriate HHE. The solar or other suitable low temperature thermal energy input is simulated by an 18 kw electric heater. A water cooled heat exchanger of 25 kw heat transfer capacity represents the space being heated in winter and serves for ambient heat rejection during cooling cycles. A heat exchanger cooling water circuit is provided from the building water supply. A third fluid loop with a 6 kw electric heater and water chiller is the refrigeration heat load in the cooling cycle and the ambient heat supply during the recovery cycle.

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 the remote graphic panel, Figure 4, from which the system is controlled.

HYCSOS System Operation

Since most hydride materials are relatively expensive, economic considerations require rapid

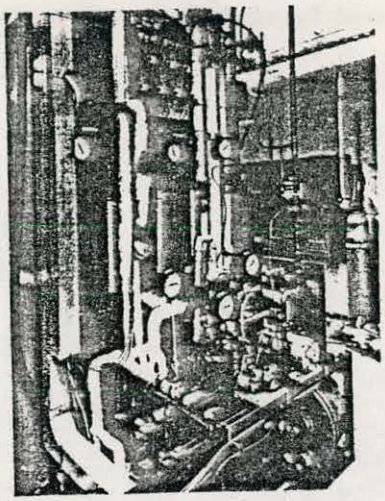

Figure 3. Heat Transfer Fluid System.

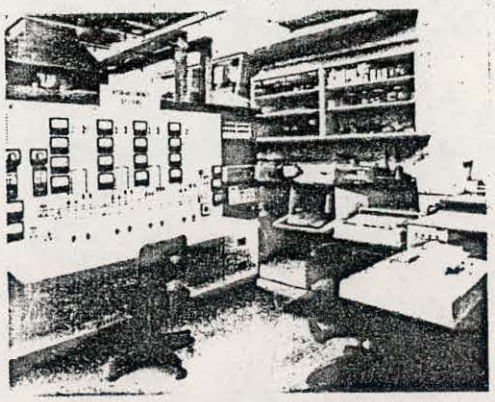

Figure 4. Graphic Control Panel.

cycling of the hydride beds to obtain maximum thermal benefits. Measurement of rapid thermal and pressure transients are thus important for the evaluation of materials and components. The HYCSOS instrumentation and data handling system is designed to measure system transients and output data for further evaluation. In multichannel logging, HYCSOS data can be collected at rates up to eight channels per second. Successive readings of a single channel can be recorded up to four per second.

The heat transfer characteristics of the hydride heat exchangers, a 4" stainless steel pipe

containing four nested coils of circulating fluid immersed in the hydride bed such that no hydride is more than 1/8" from a fluid tube, can be evaluated by comparing the temperature of the hydride bed with temperature of the heat transfer fluid leaving the heat exchanger. The bed temperature, calculated from the measured hydrogen pressure using the appropriate hydride vapor pressure equation and assuming rapid gas sorption kinetics, is a measure of the lowest bed temperature. Figure 5 compares the bed

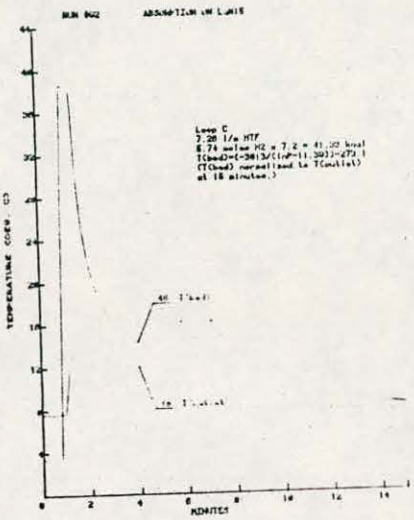

Figure 5. Comparison of Hydride Bed and Heat Transfer Fluid Temperature.

temperature, normalized to the fluid temperature at 15 minutes, with the heat transfer fluid temperature for absorption of approximately 6 moles (equivalent to 41.33 kcal input) of hydrogen. The large lag of bed temperature shows the relatively slow transfer of heat between the bed and the fluid. Since film coefficients are large, the hydriding reaction is seen to be heat transfer limited with the slow step being the transfer of heat from the reaction site in the bed to the first wall of the heat transfer fluid tube.

The heat transfer of powder beds is limited by the point contact between adjacent particles and can be improved by reducing the path length in the powder. In an advanced design hydride heat exchanger, Figure 6, the hydride powder is imbedded in an open-pore aluminum foam with approximately 20 pores to the inch which is brazed to aluminum sheets forming the fluid channels. In a single adiabatic experiment with a test module, 1.74 moles H_2 were desorbed. Figure 7 shows the subsequent rapid adiabatic absorption of 1.07 moles H_2. Equilibrium absorption pressure is reached in approximately 30 seconds showing the temperature of the unit to be uniform. The pressure rise after 10 minutes is due to absorption of ambient heat and the resultant temperature increase of the alloy bed.

Conclusion

An independent assessment[17] of the Argonne HYCSOS system where design was optimized using an

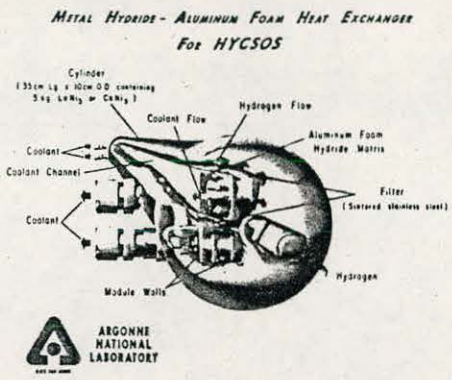

Figure 6. Advanced Design Hydride Heat Exchanger.

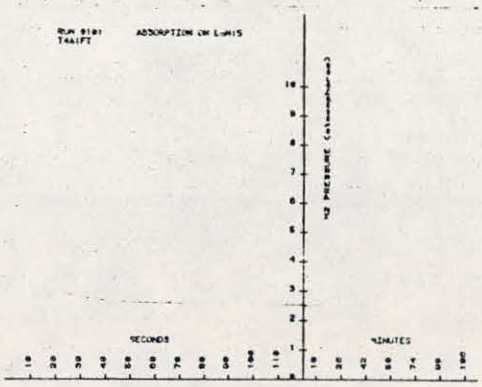

Figure 7. Hydrogen Absorption on Aluminum Foam Heat Exchanger.

iterative computer program concludes that whereas a solar absorption cooling system to provide 3 tons of cooling currently retails for $3000 excluding an expensive cooling tower and an indoor heat exchanger, a HYCSOS system to provide 3 tons of cooling would cost $3700 to $3800, including all heat exchangers. HYCSOS also provides heating with a COP greater than one and electrical power, although it requires a higher solar input than the absorption unit (250° to 280°F as compared with 180°F) and has slightly lower cooling COPs. Thus this HYCSOS system, which can be packaged similar to a conventional heat pump, compares favorably with a solar absorption cooling/ direct solar heating unit.

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