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HYDROGEN TRANSMISSION/STORAGE WITH A METAL HYDRIDE/ORGANIC SLURRY

Ronald W. Breault, Jon Rolfe, and Andrew M^cClaine
Thermo Power Corporation
45 First Avenue
Waltham, MA 02254-9046

Abstract

Hydrogen has immense potential as an efficient and environmentally-friendly energy carrier of the future. It can be used directly by fuel cells to produce electricity very efficiently (> 50%) and with zero emissions. Ultra-low emissions are also achievable when hydrogen is combusted with air to power an engine or to provide process heat, since the only pollutant produced, NO_X, is then more easily controlled. To realize this potential, however, cost effective methods for producing, transporting, and storing hydrogen must be developed.

Thermo Power Corporation has developed a new approach for the production, transmission, and storage of hydrogen. In this approach, a chemical hydride slurry is used as the hydrogen carrier and storage media. The slurry protects the hydride from unanticipated contact with moisture in the air and makes the hydride pumpable. At the point of storage and use, a chemical hydride/water reaction is used to produce high-purity hydrogen. An essential feature of this approach is the recovery and recycle of the spent hydride at centralized processing plants, resulting in an overall low cost for hydrogen. This approach has two clear benefits: it greatly improves energy transmission and storage characteristics of hydrogen as a fuel, and it produces the hydrogen carrier efficiently and economically from a low cost carbon source.

Our preliminary economic analysis of the process indicates that hydrogen can be produced for $3.85 per million Btu based on a carbon cost of $1.42 per million Btu and a plant sized to serve a million cars per day. This compares to current costs of approximately $9.00 per million Btu to produce hydrogen from $3.00 per million Btu natural gas, and $25 per million Btu to produce hydrogen by electrolysis from $0.05 per Kwh electricity. The present standard for production of hydrogen from renewable energy is photovoltaic-electrolysis at $100 to $150 per million Btu.

Introduction

The overall objective is to investigate the technical feasibility and economic viability of the chemical hydride (CaH_2 or LiH) organic slurry approach for transmission and storage of hydrogen with analysis and laboratory-scale experiments, and to demonstrate the critical steps in the process with bench-scale equipment. Specific questions which have been addressed in work to date include:

- What is the formulation and physical properties of slurries that meet the energy density criteria?
- What are the organics which can be used to form the slurry?
- What are the conditions required for hydrogen generation?
- What are the properties of the slurry after hydrogen generation?
- What is the projected efficiency and cost of hydrogen production?

Background

Hydrogen (H_2) has been suggested as the energy carrier of the future. It is not a native source of energy, but rather serves as the medium through which a primary energy source can be transmitted and utilized to fulfill our energy needs. Hydrogen has a number of advantages:

- It can be made from renewable energy sources such as biomass, solar, and hydroelectric.
- In combustion, water is the main product, with zero to low emissions when used as a combustion heat source.
- It can be directly used in fuel cells for high efficiency, zero emission electric power generation.
- H_2 is a widely-used chemical raw material for chemical synthesis.

At present, H_2 is used industrially primarily as a chemical synthesis raw material. It is generally produced on-site by steam-reforming of methane. The primary problems restricting widespread use of H_2 as an energy carrier are its:

- Very high cost compared to fossil fuels.
- Poor gas pipeline transmission characteristics relative to natural gas.
- Poor energy storage characteristics.
- Supply from native energy sources.

The concept under development addresses a new approach which greatly improves the energy transmission and storage characteristics of H_2 as a fuel for industrial and transportation applications. Further, a method of producing the H_2 carrier from a low cost carbon source such as biomass, both economically and with high energy efficiency, is described.

Application of Metal Hydride/Water Reaction for Hydrogen Storage and Transmission

The way in which the metal hydride/water reaction would be used in a closed loop system for the storage and transmission of hydrogen is illustrated in Figure 1. The process consists of the following major steps:

1. Slurrying the metal hydride with a liquid carrier and transporting it to the point(s) of use.
2. Generating hydrogen on demand from the metal hydride/liquid carrier slurry at the point of use by adding water and then transporting the resulting metal hydroxide/liquid slurry back to the hydride recycle plant.
3. Drying, separating, and recycling the metal hydroxide to the metal hydride at the centralized recycle plant and returning the liquid carrier for reuse.

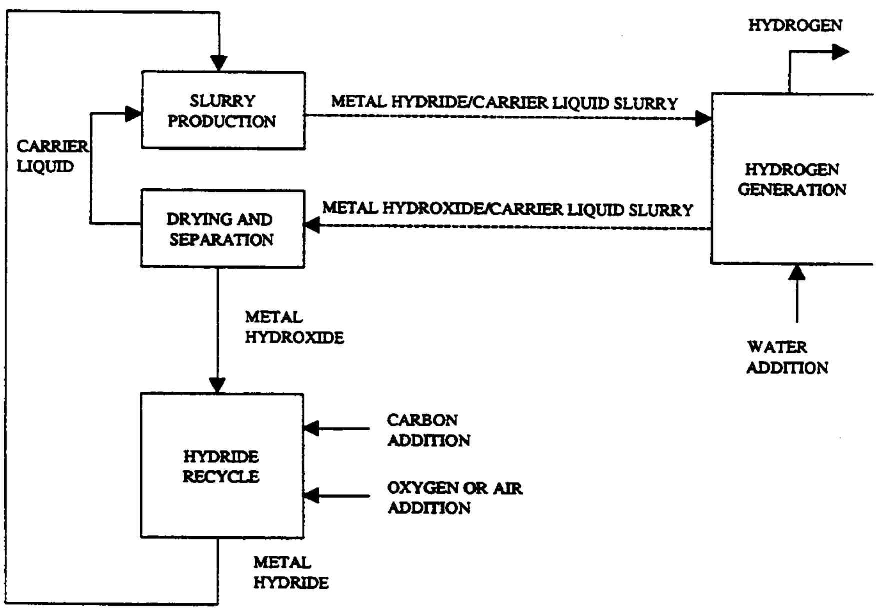

Figure 1. Simplified Process Diagram for Hydrogen Transmission/Storage With a Metal Hydride

Metal Hydride/Water Reactions and Hydrogen Storage Characteristics

A variety of metal hydrides react with water at ambient temperature to produce high purity hydrogen. Examples of reactions are:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$
$$LiH + H_2O \rightarrow LiOH + H_2 \uparrow$$
$$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2 \uparrow$$
$$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2 \uparrow$$

The hydrogen generation capability of these hydrides when reacted with water is outstanding. For example, the volume of H_2 (STP) produced by complete hydrolysis of 1 kg (2.2 lb) of lithium hydride is 2800 liters (99 ft^3) and by 1 kg (2.2 lb) of lithium borohydride is 4100 liters (145 ft^3).

In Table 1, the energy density of these hydrides when reacted with water is presented and compared to gasoline, as well as the storage of H_2 as a liquid, gas, and a reversible hydride. The energy densities of the reactive hydrides are given on the basis of the initial hydride mass. The energy densities of the hydride/water reaction are respectable when compared to gasoline or methanol, with $LiBH_4$ having the highest energy densities on both a mass and volume basis. The heat of reaction must be removed during the H_2 generation.

Comparing the chemical hydrides of Table 1 with the volumetric and gravimetric energy density goals results in Table 2.

The comparison is based on the energy densities of the initial hydride as a 50% slurry and the mass and volume of the storage container assuming a 20% void in the container when the hydride is completely spent. The LiH, $LiBH_4$, and $NaBH_4$ hydrides exceed the volumetric energy density goal by moderate factors (1.09 to 1.64). LiH and $LiBH_4$ exceed the gravimetric energy density goal by moderate factors (1.03 to 1.41), with CaH_2 slightly lower than the goal. It should be noted that energy density is not the only criterion which needs to be compared. Other factors such as cost and ease of handling must also be considered.

In summary, several hydride/water reactions exceed the performance goals of the solicitation for both the volumetric and gravimetric energy densities. An additional feature is the ability to generate H_2 on demand and to control the rate of reaction by regulating the rate of water addition to the hydride bed. If desired, H_2 can also be generated at a high pressure for direct use in pressurized fuel cells without compression.

Table 1. Comparison of Metal Hydrides to Other Hydrogen Storage Methods and Gasoline

Hydride	H_2 Volume Per Mass Hydride (STP ft^3/lb)	Energy Density		Water Reaction Enthalpy per HHV	Fraction Hydrolysis H_2 (lb H_2 per lb Hydride)	Hydride Density (gm/cm^3)
		HHV/Mass, Btu/lb	HHV/Bulk Volume (Btu/gallon)			
Ca H_2 (1)	17.1	5,850	92,800	0.396	0.0958	1.90
Li H(1)	45.2	15,500	99,600	0.388	0.254	0.77
Li B H4(1)	65.9	22,600	124,500	0.212	0.370	0.66
Na B H4(1)	38.0	13,000	116,700	0.157	0.213	1.074
Fe Ti H(1.6)(2)	2.7	935	42,900	0.122(4)	0.0153	5.5
Liquid Hydrogen (3)	—	61,100	35,650	—	—	0.07
Gaseous Hydrogen (5000 psia, 300 K)	—	61,100	15,574	—	—	0.03058
Gasoline	—	20,600	130,000	—	—	—

(1) Reaction with Water
(2) Dissociation by Heating
(3) Liquid Fuel
(4) Based on Dissociation Energy

Table 2. Comparison of the Volumetric and Gravimetric Energy Densities

Component	Volumetric Energy Density (Btu/gallon)	Average Gravimetric Energy Density (Btu/lb)
Goal	106,367	6,138
CaH_2	61,065	2,552
LiH	147,632	6,295
$LiBH_4$	174,366	8,655
$NaBH_4$	116,255	5,326

Program Activity Discussion

The program goal is to investigate the technical feasibility and economic viability of the chemical hydride (CaH_2 or LiH) organic slurry approach for transmission and storage of hydrogen through a research program which consists of technical and economic analyses and laboratory-scale and bench-scale experiments.

The initial program was structured to gain a more detailed understanding of the technical and economic aspects of the overall process, and of key elements for each of the three critical steps in the process: metal hydroxide to metal hydride conversion, metal hydride/organic slurry formation and pumping, and hydrogen generation from the slurry by addition of water.

In the next phase, we will demonstrate the critical steps in the process with bench-scale equipment and perform a more in-depth technical and economic evaluation of the process. Successful completion of this work will provide the technical basis and economic justification for proceeding to the next logical step in the development, a pilot-scale plant.

This approach has been chosen as the most logical and cost-effective way to advance the state-of-the-art of this promising technology past the conceptual stage. Advancing this technology to a stage where a sufficient technology base has been developed will establish the technical and economic feasibility of the concept with a level of confidence that warrants the further development and ultimate implementation of the technology.

System Component and Processing Selection

A preliminary analysis of the chemical hydride slurry approach for storing hydrogen was performed. An initial selection of mineral oil, decane, and dodecane for the initial slurry liquid was made. The organic material required for the slurry must not react with the chemical hydride. It must provide a coating for the hydride particles to protect them from atmospheric moisture in the event that the hydride comes in contact with the atmosphere. It must be useable in the normal temperature range of operation, 20°C to 150°C, and it must be removable from the spent slurry so that the spent slurry can be regenerated without consuming the organic material. Mineral oils and alkanes meet these requirements.

The final issue in the choice of the organic carrier component of the slurry is the volatility of the organic. One means of removing the organic from the spent slurry will be to boil it off the slurry. It must not be so volatile that it becomes an air pollution problem. Mineral oil, which is a mixture of several alkanes, is another alternative organic material for the slurry. It is frequently used in the production of sodium hydride and lithium hydride to protect the hydride from contact with the atmosphere. Mineral oils come in various viscosities ranging from near that of water to quite viscous.

We decided to begin the experimental slurry evaluations using light mineral oil rather than the more refined decane. The plan will be to separate the mineral oil from the spent slurry with a centrifuge.

Metal Hydride/Organic Slurry

Discussion of Slurry Setup

Currently, simple tests have been completed and observations have been made based on the ASTM descriptions of sedimentation characteristics. Size classification sieves have been obtained for the optimization stages of the slurry development. A ball mill, with its associated alumina jars and media, has been obtained for size reduction of the candidate hydrides. A small laboratory centrifuge has been obtained for accelerated age stability tests, and the appropriate disposable sedimentation tubes have been obtained. Cup-type viscometers have been purchased to allow standard centistoke values of the slurries to be determined. A shaker table is being used to evaluate the potential for milling of the hydride during transportation and movement and the subsequent effect of particle attrition on the slurry properties.

Discussion of Chemical Stability of the Organic Medium

Infrared Absorption Spectrophotometry is performed on the organic compound as supplied, and then on a sample which has been subjected to the heat and pressure of the hydrogen generation process. In the reaction of light metal hydrides and water, strong bases result. The purpose of this test is to detect gross molecular changes in the organic medium. As the preferred slurry system becomes better defined, GC/MS will be performed on the preferred organic medium after one or more reaction cycles. Figure 2 displays a typical result from the infra-red spectroscopic analysis.

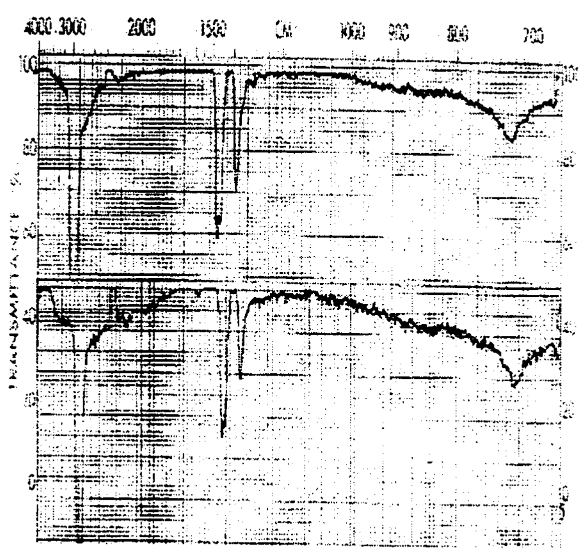

Figure 2. Example of Infrared Spectroscopic Analysis Results for a Test Using Sodium Hydride and Light Mineral Oil

Discussion of Hydride Slurry Results

Slurries have been prepared of sodium hydride, lithium hydride, sodium borohydride, and calcium hydride.

Least practical appear to be the slurries made from sodium borohydride. While the materials are relatively safe to handle and have a favorable hydrogen content, their complete hydrolysis requires the presence of an acid. Regeneration of these compounds is potentially problematic. Unlike the single light metal hydrides, the exhausted material consists of borates and boric acid.

The most promising hydrides appear to be calcium hydride and lithium hydride. In the former case, the end product is harmless slaked lime, consisting of calcium hydroxides and its hydrates. We have shown that hydrolysis is limited to relatively safe pressures (c.a. 300 psig), and because of the formation of compounds of low solubility, does proceed to completion without requiring additives or other reactants, delivering >80% of the theoretical hydrogen yield. This is an important safety consideration, as it is desired that the waste product be completely exhausted and nonreactive.

From the consideration of energy density per weight of hydride, lithium hydride is superior. Both hydrides are practical to regenerate.

Sodium hydride has a base-limited hydrolysis reaction. When the pH of the system reaches approximately 13.6, the hydrolysis reaction stalls. One method by which this problem can be addressed is by the addition of aluminum metal to the slurry. The resulting aluminate reaction with the base forces the hydrolysis reaction to completion by consuming the base, forming an inert aluminate end product. The formation of the aluminate also releases still more hydrogen, splitting oxygen from the hydroxide. Regeneration issues regarding aluminates will need to be investigated if this method is to be further explored.

For the slurries to be useable in practical systems, they must be relatively safe to handle, have an attractive energy density, and be stable in storage. Further refinement of the dispersant system with a surfactant could depress viscosity enough to allow higher hydride concentrations with attendant increased hydrogen content per weight. For our purposes, the slurries should consist of at least 50% hydride. The upper limit of hydride loading is determined by the viscosity of the slurry. At loadings greater than this amount, viscosity and shear rise abruptly. Surfactants such as silicone-terminated alkyls can collapse these systems, resulting in hydride loadings of at least 60%, while still producing easily-pumped formulations. The slurries presently prepared from calcium and lithium hydrides by ball milling with alumina media have particle sizes between 5 and 10 microns. Good physical stabilities have been achieved by the use of polymeric dispersants which sterically stabilize the hydride/mineral oil system. Polymeric dispersants allow the use of higher molecular weight lyophiles than do conventional alkyl terminated systems, which are generally limited to 12-carbon chains. With the use of polymeric dispersants, the slurries are stable and do not present the sedimentation or settling difficulties of the initial slurry formulations. More than twenty minutes are required in a clinical centrifuge at 5,125 X G for sedimentation to begin with the current slurries. The slurries of calcium and lithium hydrides, at

50% hydride content, are pourable liquids with the consistency of heavy cream or paint. Their measured viscosities are 20 seconds with a #4 Zahn cup (approximately 210 cPs).

The following photomicrograph, Figure 3, taken at 1,000X in polarized light, shows a calcium hydride slurry made by the above method.

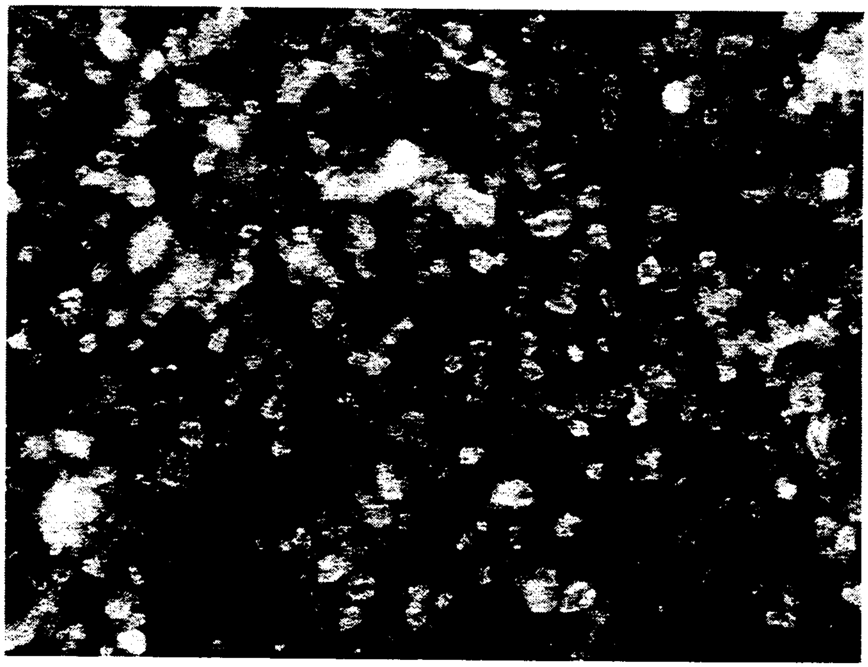

Figure 3. Photomicrograph (1000X) of Calcium Hydride Slurry

Hydrogen Generation

Tables 3 and 4 display various characteristics of the chemical hydrides of interest. Calcium hydride and lithium hydride offer an attractive option for the metal hydride/slurry program and have been selected for the initial evaluation of the metal hydride/slurry storage. Other hydrides which should eventually be investigated are Lithium-boro-hydride, Lithium-alumino-hydride, Sodium-boro-hydride, and Sodium-alumino-hydride. From Table 4, one can see that LiH offers the opportunity to provide 0.25 g of hydrogen per gram of hydride. This is very attractive when compared to the 1.5% to 6% of the more traditional metal hydrides. $LiBH_4$ and $LiAlH_4$ offer even greater storage capacity.

Table 3. Physical Characteristics of Light Metal Hydrides

		Temperature		Density
		Melting	Decomp	g/ml
Calcium Hydride	CaH_2	816 (in H_2)	600	1.9
Lithium Hydride	LiH	680		0.82
Sodium Hydride	NaH	800	800	0.92
Sodium Hydride 60% in oil	NaH			
Sodium Aluminum Hydride	$NaAlH_4$	178		1.28
Sodium BoroHydride	$NaBH_4$	500	400	1.074
Lithium Aluminum Hydride	$LiAlH_4$		125	0.917
Lithium BoroHydride	$LiBH_4$	278	275	0.666

Table 4. Hydrogen Storage Capabilities of Chemical and Absorption Hydrides

	Moles H_2 Released per Mole Hydride	Mass per Mole H_2 Released	Mass H_2 Released per Mass Hydride	Reactions
Mg	1	24.31	0.083	$Mg + 2H_2O = Mg(OH)_2 + H_2$
LiH	1	7.95	0.254	$LiH + H_2O = LiOH + H_2$
NaH	1	24.00	0.084	$NaH + H_2O = NaOH + H_2$
CaH_2	2	21.05	0.096	$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$
MgH_2	1	26.33	0.077	$MgH_2 = Mg + H_2$
$LiBH_4$	4	5.45	0.370	$LiBH_4 + 4H_2O = LiOH + H_3BO_3 + 4H_2$
$NaBH_4$	4	9.46	0.213	$NaBH_4 + 4H_2O = NaOH + H_3BO_3 + 4H_2$
$LiAlH_4$	5	7.59	0.266	$2LiAlH_4 + 2H_2O = 2LiH + 2H_2O + 2Al + 3H_2 = 2LiOH + 2Al + 5H_2$
$NaAlH_4$	5	10.80	0.187	$2NaAlH_4 + 2H_2O = 2NaH + 2H_2O + 2Al + 3H_2 = 2NaOH + 2Al + 5H_2$
$FeTiH_{1.6}$	0.8	131.70	0.015	
$LaNi_5H_{6.7}$	3.35	131.11	0.015	
Mg_2TiH_6	3	34.19	0.059	
$MgTi_2H_6$	3	42.05	0.048	

Slurries of lithium hydride and calcium hydride were contacted with water to measure the hydrogen release rates. Figure 4 displays the reaction of half a mole of lithium hydride with one mole of water.

The reaction rates can be calculated from the pressure rise and temperature data collected during the hydrogen generation testing. These rates are derived from the data by calculating the number of moles of gas required to produce the pressures measured within the closed volume. From this value, the number of moles of argon used to drive the water into the autoclave is subtracted as well as the number of moles of water vapor calculated from the measured temperature of the hydride/water mixture. Figure 5 displays a typical hydrogen generation curve for lithium hydride and water.

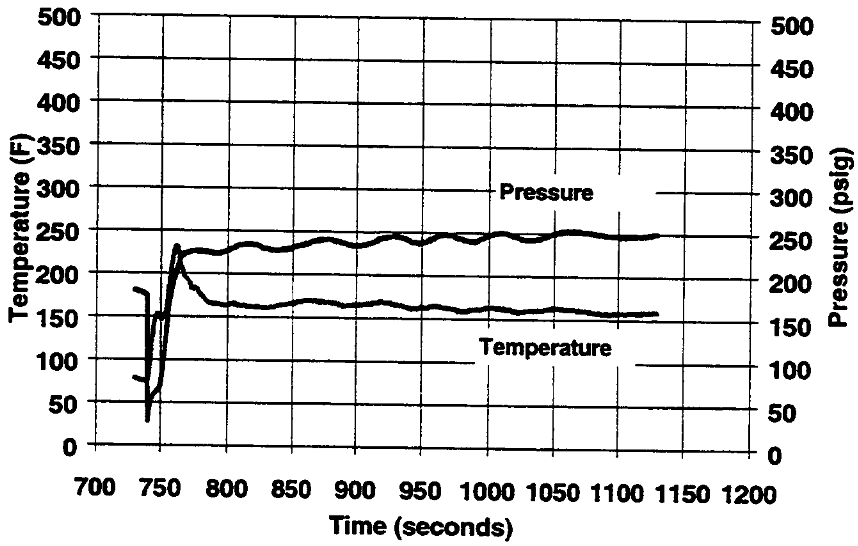

Figure 4. 40% Lithium Hydride Slurry with Mineral Oil - 0.5 mole LiH, 1.0 mole H_2O

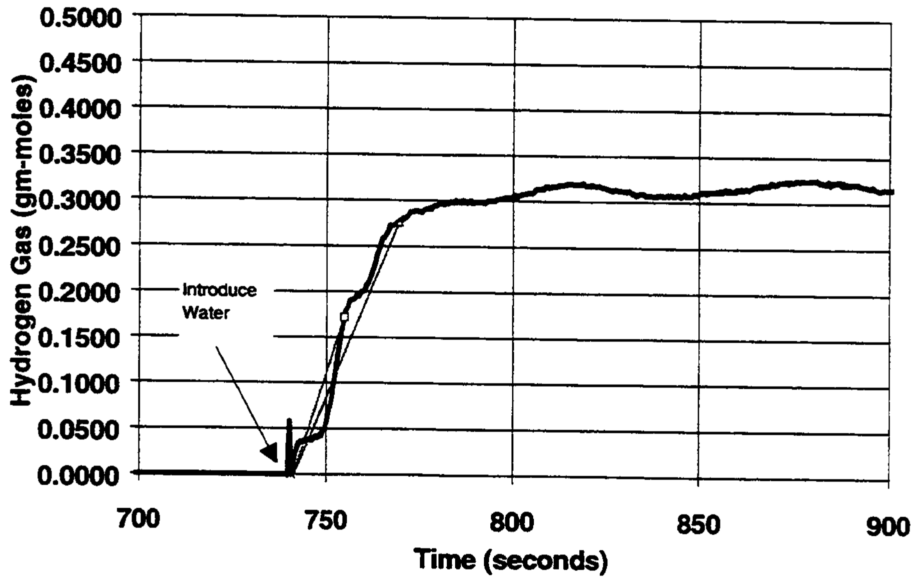

Figure 5. Lithium Hydride in 50% Slurry with Light Mineral Oil

The rates range from 0.0015 to 0.0165 gmole/s depending on the hydride, oil fraction, water stoichiometry, and mixing rate. No attempt has been made to assess the impact each of these properties have on the rate. In general:

- The calcium hydride was observed to be considerably slower than the sodium hydride and the lithium hydride.
- The greatest consistency was achieved with the calcium hydride.
- The sodium hydride with aluminum was observed to be the fastest reacting hydride, but the results of the two tests performed vary dramatically.

The conclusion from these tests is that the reaction rates are sufficiently rapid to be of interest in a hydrogen generation system. Further testing needs to be performed to determine the effect of the particle size, the water availability, the pressure of the reaction, and the temperature of the reaction. These characteristics will be needed to define the design of a demonstration reactor.

Preliminary Design and Economics

Preliminary Design of Hydroxide Regeneration System

A preliminary design of the hydroxide to hydride regeneration system has been conducted to identify process stream conditions and to allow the major equipment components to be sized such that a capital equipment cost could be developed. The system is shown in Figure 6. The analysis has been conducted for both lithium hydroxide and calcium hydroxide regeneration.

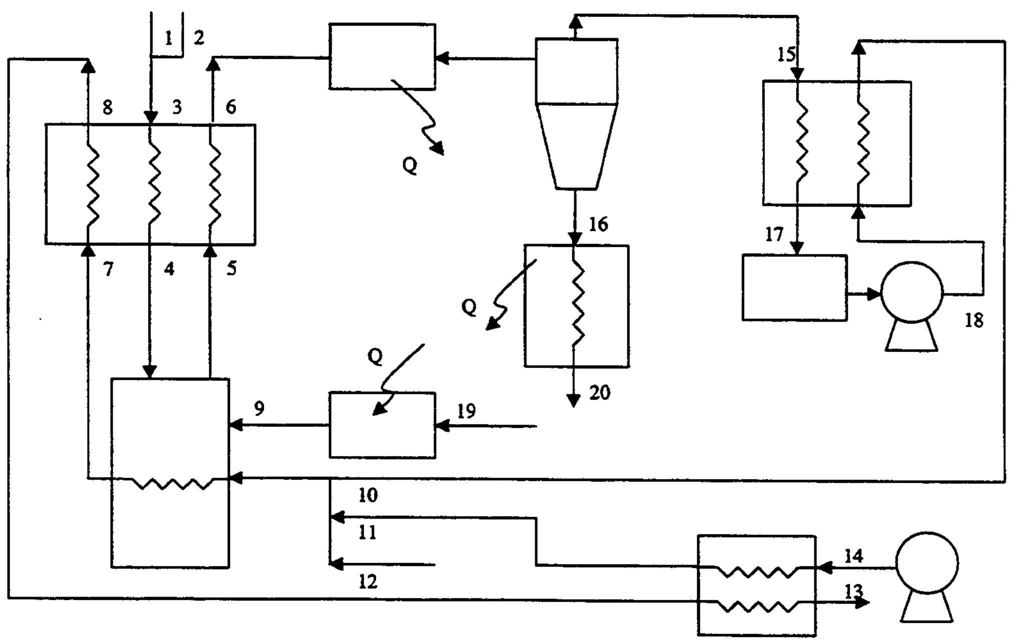

Figure 6. Hydroxide Regeneration System

The material and energy balances for the two metals were conducted for a plant supplying hydrogen to 250,000 cars.

Plant size- Service 250,000 cars

- 6.4 billion Btu/hr
- 13 tons H_2/hr
- 1876 MW_t
- 1/3 size of First FCC unit
- 1/25 size of Today's FCC units

The results are shown in Tables 5a,b,c for lithium. Lithium hydroxide is combined with carbon for the reduction and fuel, streams 1, 2a and 2b, to form stream 3 and is fed to the top of an indirect vertical heat exchanger which preheats the incoming reactants while cooling the stream containing the lithium hydroxide, streams 5 and 6. The possibility for removing heat from the indirect fired process heater is also provided, streams 7 and 8.

The hot preheated and partially reacted reactants, stream 4, enter the reduction reactor in which they are heated indirectly to the reaction temperature by combustion of the recycled carbon monoxide, stream 10, and additional fuel, stream 12, with preheated air, stream 11. The possibility of adding direct heat to the reactor is accomplished by adding oxygen to the reduction reactor by stream 9. The products of reduction leave the reduction reactor through stream 5. Within the reactant preheater, the lithium hydride is formed through the non-equilibrium kinetics as the mixture of lithium, hydrogen and carbon monoxide is cooled. Additional heat is taken out of the product stream for the generation of electrical energy which is added back into the reduction reactor to reduce the additional fuel.

The product, lithium hydride, is separated form the carbon monoxide in the hot cyclone, stream 16. This is further cooled to produce additional power which is also added to the reduction reactor. The hot carbon monoxide, stream 15, is passed through a self recuperator to get a cold stream of CO which could have a barrier filter installed to remove all the lithium hydride and a blower to circulate the CO, stream 18. This stream is reheated with the incoming CO and fed into the indirect process heater as discussed above.

The hot combustion products leaving the solids preheater, stream 8, are used to preheat the combustion air and produce power which is fed back into the reduction reactor.

The energy efficiency of the hydrogen storage is obtained by dividing the heat of combustion of the hydrogen in the metal hydride by the heat of combustion of the carbon used for the reduction and the additional fuel. The results are:

- Lithium - 52.1%
- Calcium - 22.9%

Table 5a. State Points - Lithium Hydroxide to Hydride Regeneration

Stream		1	2a	2b	2	3	4	5	6
Name		Hydroxide feed	Carbon for heat	Carbon for metal reduction	Carbon Feed	Hydroxide and Carbon Feed	Preheated Hydroxide and Carbon	Reduction Reactor Output	Lithium Hydride Condenser Offgas
Pressure	Bar	1	1	1	1	1	1	1	1
Temperature	K	298	298	298	298	298	1650	1850	950
Mass Flow Rate	kg/hr	139,601	0	70,022	70,022	209,623	209,623	209,623	209,623
Component Mass Flows	kg/hr								
metal gas								40,452	
metal (l)									
metal (s)									
metal hydride (s)	46,329								46,329
metal hydroxide (s)		139,601				139,601			
metal oxide (s)							87,089		
H2O									
H2O(l)									
C			0	70,022	70,022	70,022	35,011		
CO2									
CO							81,647	163,294	163,294
H2							5,876	5,876	0
O2								0	
N2									
Hydrocarbon feed									
Organic removed prior	30,577								
Total Enthalpy	kJ/hr	-2.827E+09	0.000E+00	0.000E+00	0.000E+00	-2.827E+09	-1.393E+09	9.092E+08	-7.881E+08

Table 5b. State Points - Lithium Hydroxide to Hydride Regeneration

Stream		7	8	9	10	11	12	13	14
Name		Combustor Exhaust	Exhaust Exchanger outlet	Preheated Oxygen for Direct Heating	Preheated CO	Preheated Combustion Air	Additional Fuel	Stack Gases	Combustion Air
Pressure	Bar	1	1	1	1	1	1	1	1
Temperature	K	2000	2000	298	800	1800	298	400	298
Mass Flow Rate	kg/hr	328,775	328,775	0	163,294	151,008	14,473	328,775	648,079
Component Mass Flows	kg/hr								
metal gas									
metal (l)									
metal (s)									
metal hydride (s)	46,329								
metal hydroxide (s)									
metal oxide (s)									
H2O		32,505	32,505					32,505	
H2O(l)									
C									
CO2		296,270	296,270					296,270	
CO					163,294				
H2					0				
O2		0	0	0		151,008		0	151,008
N2		0	0					0	497,071
Hydrocarbon feed							14,473		
Organic removed prior	30,577								
Total Enthalpy	kJ/hr	-2.313E+09	-2.313E+09	0.000E+00	-5.473E+08	2.950E+08	-6.755E+07	-3.034E+09	0.000E+00

Table 5c. State Points - Lithium Hydroxide to Hydride Regeneration

Stream		15	16	17	18	19	20
Name		Separator CO product	Hot Hydride	CO Cooler Product	CO Pressurized	Oxygen In	Cold Hydride Product
Pressure	Bar	1	1	1	1	1	1
Temperature	K	950	950	400	400	298	355
Mass Flow Rate	kg/hr	163,294	46,329	163,294	163,294	0	46,329
Component Mass Flows	kg/hr						
metal gas							
metal (l)							
metal (s)							
metal hydride (s)	46,329		46,329				46,329
metal hydroxide (s)							
metal oxide (s)							
H2O							
H2O(l)							
C							
CO2							
CO		163,294		163,294	163,294		
H2		0		0	0		
O2						0	
N2							
Hydrocarbon feed							
Organic removed prior	30,577						
Total Enthalpy	kJ/hr	-5.183E+08	-2.698E+08	-6.247E+08	-6.247E+08	0.000E+00	-5.059E+08

Economics of the Approach

The preliminary economics for the process are obtained by first developing a capital cost for the process equipment and then estimating the operating cost to define the needed sales price of the metal hydride for the required after tax return on the investment.

The capital equipment costs for the process are shown in Table 6 for the lithium process. These estimates, as well as the operating cost estimates, were obtained using standard chemical engineering practice. The operating cost assumptions are shown below:

- Carbon — Variable, \$0.67 to 1.67/10^6 Btu
- Fuel — \$2.5/10^6 Btu
- Labor
  - -Operators — 25 at \$35,000/yr
  - -Supervision & Clerical — 15% of Operators
- Maintenance & Repairs — 5% of Capital
- Overhead — 50% of Total Labor and Maintenance
- Local Tax — 2% of Capital
- Insurance — 1% of Capital
- G&A — 25% of Overhead
- Federal and State Tax — 38% of Net Profit

Table 6. Capital Cost - Lithium Hydride Regeneration

		Total cost
1	Furnace Cost, base 70m3	9,236,116
2	Solids preheater, 70 m3	9,236,116
3	Condensor, base 100MW	-
4	Hydride Reactor, Base 35m3	720,417
5	Blower, H2 from sep.base, 75m3/s	270,254
6	Steam Turbine Generator	25,693,663
7	Cent Slurry sep.	189,413
8	Hydride cooler, base 70 m3	9,236,116
9	Heat Exch/recuperator, base 20e9J/s	2,814,328
10	Hydrocarbon Decomp, base 100MW	-
	Sum, Total Cost	57,396,424

The manufacturing cost summary is presented in Table 7 for lithium.

Table 7. Manufacturing Cost Summary - Lithium Hydride Regeneration

Plant Size	No. cars per day served	2,000,000		
Physical Plant Capital Cost($)				
	Fixed Capital	199,865,957		
	Initial charge LiOH	32,759,101		
	Working Capital	19,986,596		
	Total Capital	252,611,653		
Direct Cost				
	carbon cost, $/lb			0.02
	carbon cost, $/yr		212,955,679	
	Fuel cost, $/lb			0.0575
	Fuel cost, $/yr.		126,549,051	
	Op. Labor, $/yr.		875,000	
	# Staff	25		
	Annual Salary	35,000		
	Sup&Clerical, $/yr.		131,250	
	Maint&Repairs, $/yr.		9,993,298	
	Total Direct, $/yr.		350,504,278	
(Indirect Op. Exp)				
	Overhead, $/yr.		5,499,774	
	Taxes, $/yr.		3,997,319	
	Insur, $/yr.		1,998,660	
	Total Indirect Cost, $/yr.		11,495,753	
Total Mfg Exp			362,000,030	
	Depreciation, $/yr.		19,986,596	
	G&A, $/yr.		1,374,943	
	Distrib&Sales, $/yr.		0	
	R&D, $/yr.		0	0
Total Genl Expenses, $/yr.			1,374,943	
Total Expenses, $/yr.			363,374,974	
Revenue From Sales Hydride, $/yr.			505,650,462	0.0708
Total Revenues, $/yr.			505,650,462	
Net Annual Profit, $/yr.			142,275,488	
Income Taxes, $/yr.			46,469,779	
Net Annual Prof after Taxes, $/yr.			95,805,709	
After-Tax Rate of Ret (%)		37.93		
$/10^6 btu		4.57		

The sensitivity of the cost of the hydride and the rate of return as a function plant size and carbon cost is shown in Figures 7 and 8 for lithium and 9 and 10 for calcium. In Figure 7, the cost of hydrogen is plotted versus the plant size for four values of the cost of carbon. For a 250,000 car-per-day plant, the cost of hydrogen is on the order of $3.61 per million Btu at a carbon cost of one cent per pound and a fixed return on the investment of 15 percent. In Figure 8, the effect of plant size and carbon cost for a fixed hydrogen cost on the rate of return is shown. In this case, if the hydrogen can be sold for a value of $4.57 per million Btu, the return to the investors can range from 15 to 65 percent depending on plant size and carbon price. The same trends are seen for calcium.

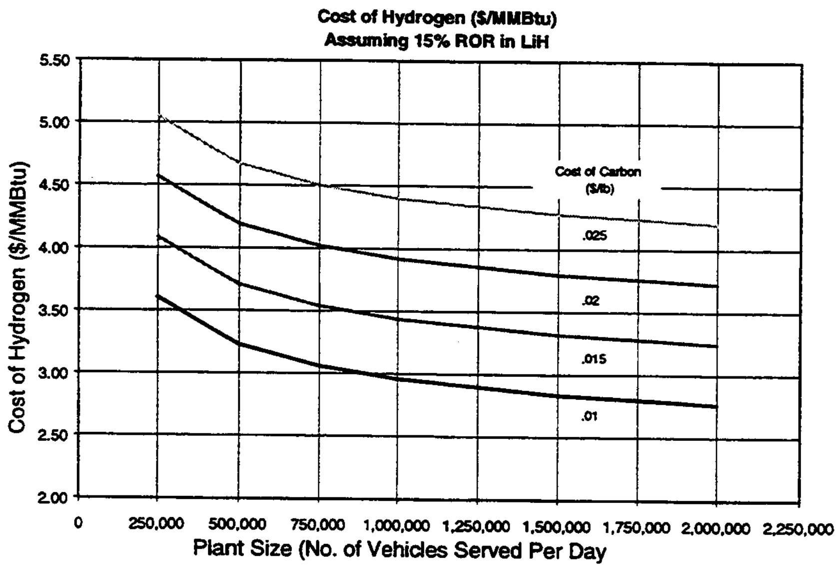

Figure 7. Sensitivity of Hydrogen Cost to Carbon Cost and Plant Size for Lithium Hydride

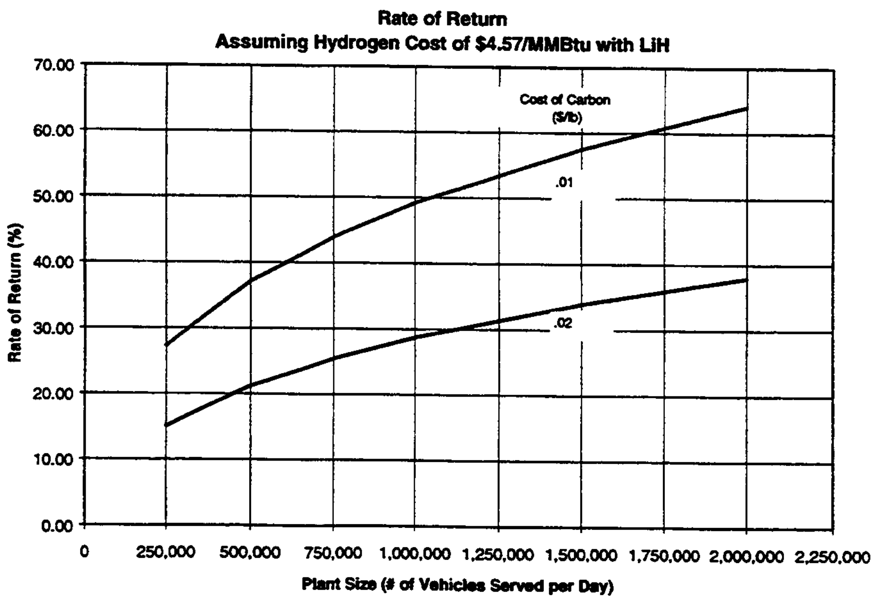

Figure 8. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Lithium Hydride

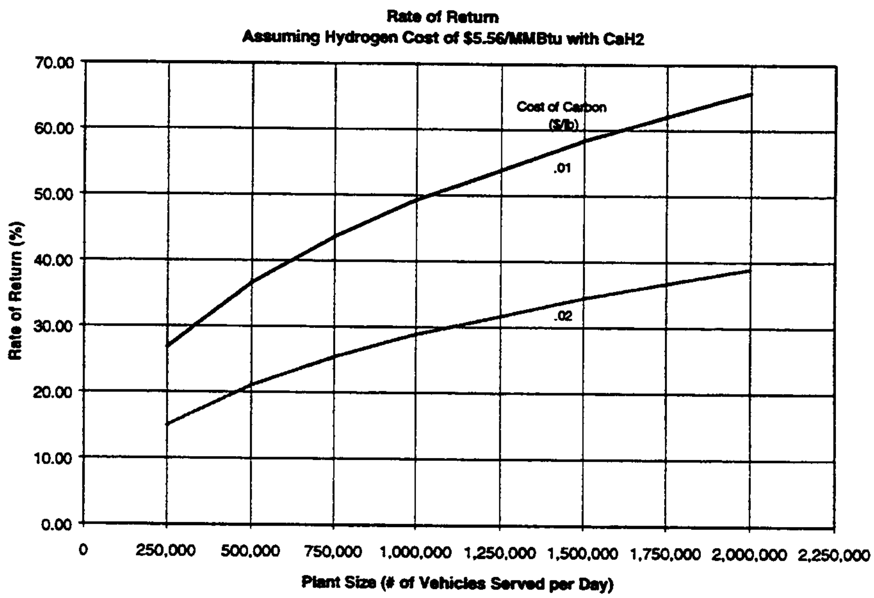

Figure 9. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Calcium Hydride

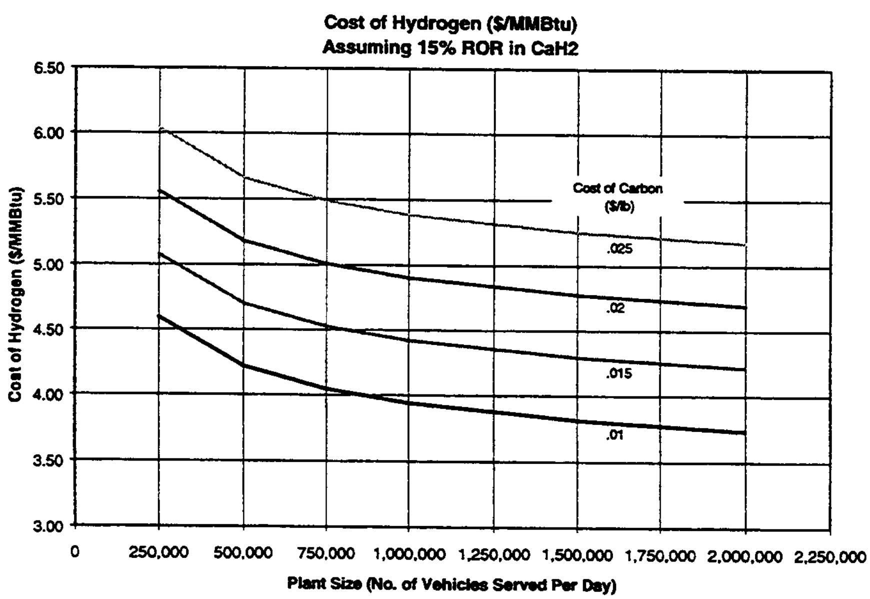

Figure 10. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Calcium Hydride

Summary and Follow On Activities

The results of the work to date are:

- Best Organic - Light Mineral Oil
- Best Hydrides -LiH & CaH_2
- +95% Hydrogen Release/Recovery
- Reaction rate controllable
- pH/Pressure Control
- Stable slurry
- Polymeric dispersants sterically stabilize the suspension
- Cost of Hydrogen $2.75 to $6.00 per 10^6 Btu

The follow on activities are:

- Conduct laboratory-scale experiments of the chemical hydroxide to chemical hydride conversion process.
- Update analysis of the complete cycle.
- Development of final process specifications and plans for bench-scale demonstrations of the components.
- Demonstrate the bench-scale recycle experiment and the slurry production and pumping experiment.

References

1 "Plans For A U.S. Renewable Hydrogen Program," Block, D. and Melody I., Florida Solar Energy Center, Proceedings of 10th World Hydrogen Energy Conference, Cocoa Beach, FL, June 20-24, 1994.

2 Ulrich, "A Guide To Chemical Engineering Process Design And Economics", John Wiley & Sons, 1984.