

# HYDROGEN TRANSMISSION/STORAGE WITH A CHEMICAL HYDRIDE/ORGANIC SLURRY

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## 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<sub>x</sub>, 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<sub>2</sub> 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: (1) it can be made from renewable energy sources such as biomass, solar, and hydroelectric, (2) in combustion, water is the main product, with zero to low emissions when used as a combustion heat source, (3) it can be directly used in fuel cells for high efficiency, zero emission electric power generation, and (4)  $H_2$  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: (1) very high cost compared to fossil fuels, (2) poor gas pipeline transmission characteristics relative to natural gas, (3) poor energy storage characteristics, and (4) 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) slurring 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, and (3) drying, separating, and recycling the metal hydroxide to the metal hydride at the centralized recycle plant and returning the liquid carrier for reuse.

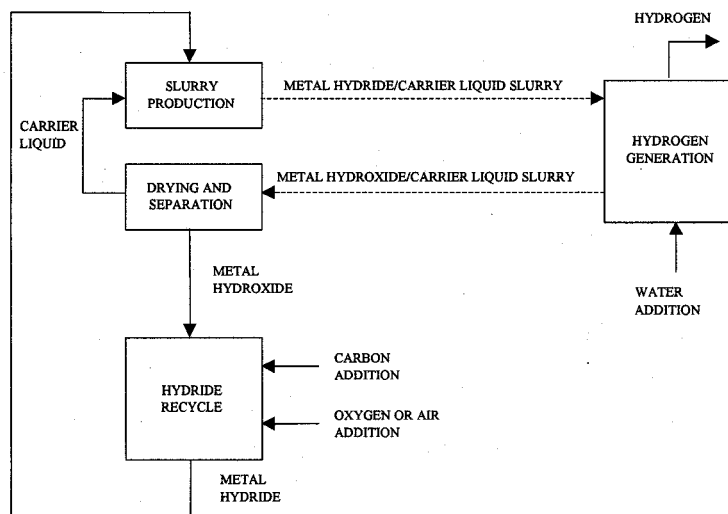
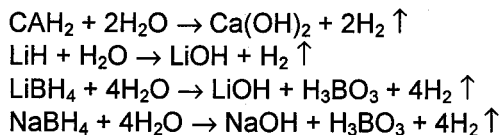


Figure 1. Simplified Process Diagram for Hydrogen Transmission/Storage With a Metal Hydride

**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:



The hydrogen generation capability of these hydrides when reacted with water is outstanding. For example, the volume of H<sub>2</sub> (STP) produced by complete hydrolysis of 1 kg (2.2 lb) of lithium hydride is 2800 liters (99 ft<sup>3</sup>) and by 1 kg (2.2 lb) of lithium borohydride is 4100 liters (145 ft<sup>3</sup>).

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<sub>2</sub> 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<sub>4</sub> having the highest energy densities on both a mass and volume basis. The heat of reaction must be removed during the H<sub>2</sub> generation.

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

Hydride	H <sub>2</sub> Volume Per Mass Hydride (STP ft <sup>3</sup> /lb)	Energy Density		Water Reaction Enthalpy per HHV	Fraction Hydrolysis H <sub>2</sub> (lb H <sub>2</sub> per lb Hydride)	Hydride Density (gm/cm <sup>3</sup> )
		HHV/Mass, Btu/lb	HHV/Bulk Volume (Btu/gallon)			
Ca H <sub>2</sub> <sup>(1)</sup>	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 H <sub>4</sub> (1)	65.9	22,600	124,500	0.212	0.370	0.66
Na B H <sub>4</sub> (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 <sup>(3)</sup>	—	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

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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<sub>4</sub>, and NaBH<sub>4</sub> hydrides exceed the volumetric energy density goal by moderate factors (1.09 to 1.64). LiH and LiBH<sub>4</sub> exceed the gravimetric energy density goal by moderate factors (1.03 to 1.41), with CaH<sub>2</sub> 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<sub>2</sub> on demand and to control the rate of reaction by regulating the rate of water addition to the hydride bed. If desired, H<sub>2</sub> can also be generated at a high pressure for direct use in pressurized fuel cells without compression.

### 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 2. The analysis has been conducted for both lithium hydroxide and calcium hydroxide regeneration.

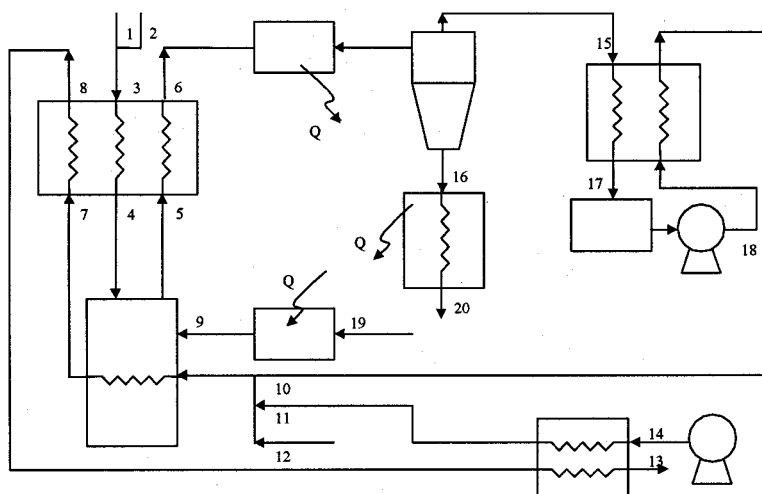


Figure 2. Hydroxide Regeneration System

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<sub>2</sub>/hr
- 1876 MW<sub>t</sub>
- 1/3 size of First FCC unit
- 1/25 size of Today's FCC units

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The results are shown in Tables 3a, 3b, and 3c 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 from 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%) and calcium (22.9%).

**Table 3a. 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

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Table 3b. 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 3c. 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

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### 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 4 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<sup>6</sup> Btu
- Fuel \$2.5/10<sup>6</sup> 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 4. 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 sensitivity of the cost of the hydride and the rate of return as a function of plant size and carbon cost is shown in Figures 3 and 4 for lithium and 5 and 6 for calcium. In Figure 3, 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 4, 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.

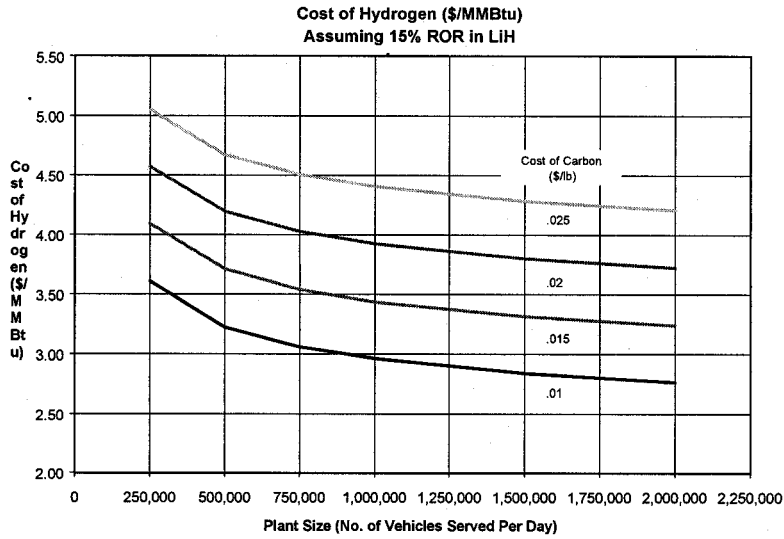


Figure 3. Sensitivity of Hydrogen Cost to Carbon Cost and Plant Size for Lithium Hydride

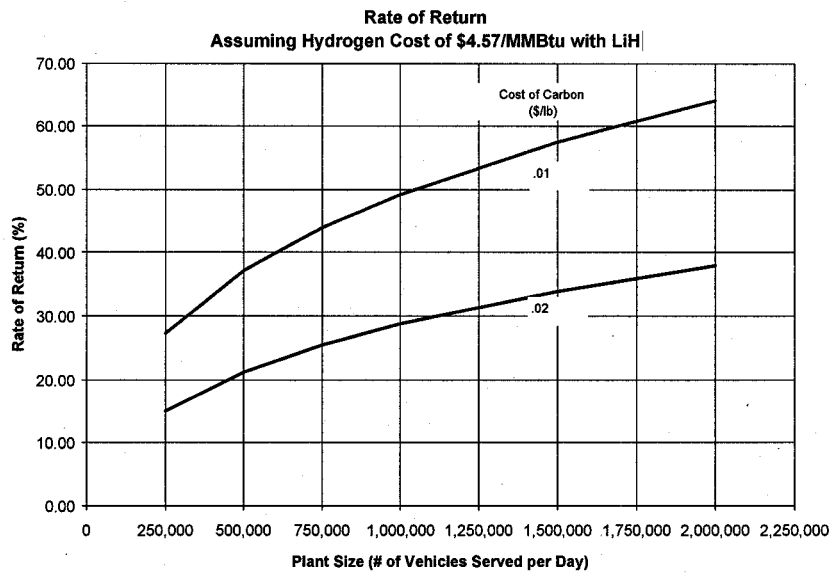


Figure 4. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Calcium Hydride



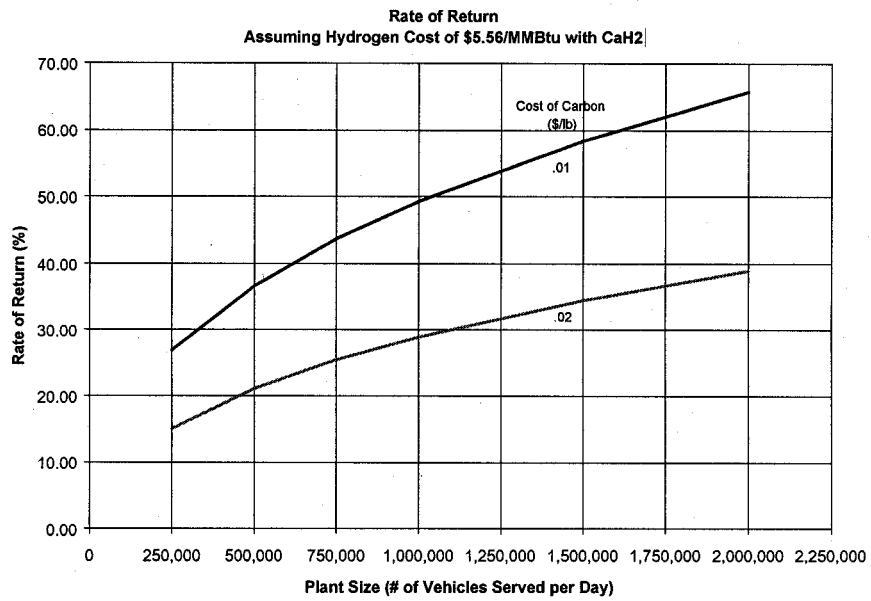


Figure 5. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Calcium Hydride

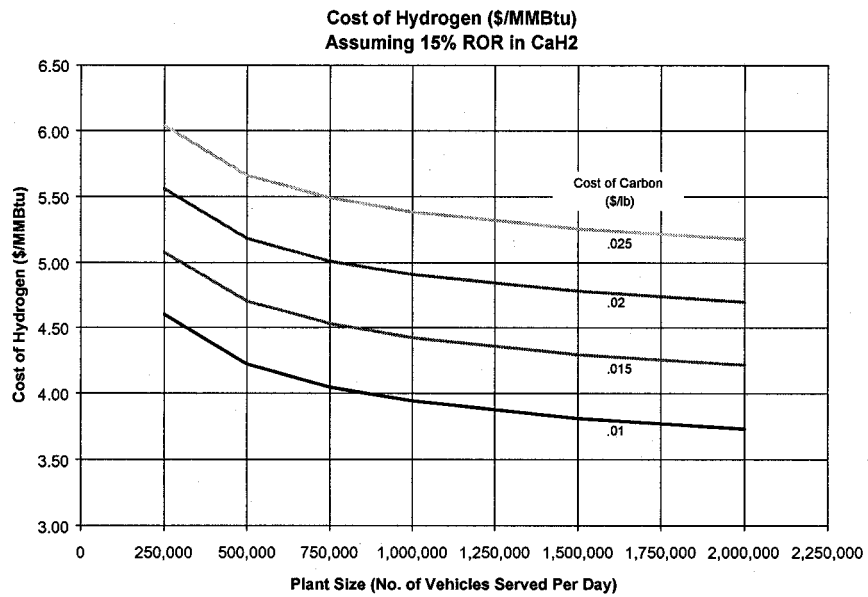


Figure 6. Sensitivity of Rate of Return to Carbon Cost and Plant Size for Calcium Hydride

## Summary and Follow On Activities

The results of the work to date are:

- Best Organic - Light Mineral Oil
- Best Hydrides -LiH & CaH<sub>2</sub>
- +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<sup>6</sup> Btu

## References

- <sup>1</sup> "Plans For A U.S. Renewable Hydrogen Program," Block, D. and Melody I., Florida Solar Energy Center, Proceedings of 10<sup>th</sup> World Hydrogen Energy Conference, Cocoa Beach, FL, June 20-24, 1994.
- <sup>2</sup> Ulrich, "A Guide To Chemical Engineering Process Design And Economics", John Wiley & Sons, 1984.