

IV.B.2 Chemical Hydride Slurry for Hydrogen Production and Storage

Andrew W. McClaine (Primary Contact),
Kenneth Brown, Sigmar Tullmann
Safe Hydrogen, LLC
30 York Street
Lexington, MA 02420-2009
Phone: (781) 861-7016; Fax: (781) 942-7413
E-mail: AWMcClaine@SafeHydrogen.com

DOE Technology Development Manager:
Grace Ordaz
Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

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Subcontractors:

Hatch Technology LLC, Fall River, MA
Boston University, Boston, MA
Metallurgical Viability, Inc., Newark, DE
HERA Hydrogen Storage Systems
Longueuil, Quebec, Canada

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Projected End Date: December 31, 2006

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (K) System Life-Cycle Assessments
- (R) Regeneration Processes

Technical Targets

This project is investigating the capability of magnesium hydride (MgH_2) slurry to meet the DOE 2010 hydrogen storage targets listed in Table 1.

TABLE 1. Magnesium Hydride Slurry Development Capability

Storage Target	Target Value	MgH_2 Slurry Estimate
Gravimetric Energy Capacity	2.0 kWh/kg	1.8 kWh/kg
Volumetric Energy Capacity	1.5 kWh/L	1.7 kWh/L
Price of Hydrogen	\$3/kg at the pump	\$4.32/kg at the pump
System Cost	\$4/kWh (\$133/kg H_2)	No estimate yet

Objectives

Demonstrate that a magnesium hydride slurry can meet the cost, safety, and energy density targets for on-board hydrogen storage of hydrogen fuel cell vehicles.

- Develop a stable and pumpable magnesium hydride slurry with energy density of 3.9 kWh/kg and 4.8 kWh/L.
- Develop a compact robust mixing system to produce hydrogen from the slurry and to meet the 2 kWh/kg and 1.5 kWh/L system targets.
- Define and assess the capital and operating costs of the recycling system required to make new magnesium hydride slurry from the materials remaining after the hydrolysis of magnesium hydride slurry and water.
 - Separate and recycle the organic compounds from the hydroxide byproduct
 - Reduce the magnesium hydroxide to magnesium
 - Prepare magnesium hydride from magnesium and hydrogen
 - Prepare magnesium hydride slurry from the magnesium hydride and recycled organics

Accomplishments

- Demonstrated stability of MgH_2 slurry with 70% solids loading. This provides a fresh material storage capacity of 3.6 kWh/kg and 4.2 kWh/L (capacity based on spent slurry having 2.2 kWh/kg and 4.3 kWh/L). This is a 16% improvement over the slurry we were testing last year. Slurry has remained in suspension for periods exceeding two months. Our goal remains to achieve a 76% solids loading slurry with a fresh material storage capacity of 3.9 kWh/kg and 4.8 kWh/L (capacity based on spent slurry having 2.3 kWh/kg and 4.8 kWh/L).
- Demonstrated continuous mixer operation with no external heat addition. Slurry and water injection has been started and stopped to show that the mixing system can be restarted. Hydrogen production rates have been between 7 and 10 sL/min for several hours duration.
- Explored simple method of separating oils from byproducts.

- Explored MgH_2 production from Mg and H_2 using mixture of Mg and MgH_2 .
- Mg reduction studies show \$3.88/kg H_2 production cost estimate using H2A analysis framework.
- Solid-oxide oxygen-ion-conducting membrane (SOM) process operated for 2 days with periodic replenishment of MgO producing Mg at rate up to 160 g/day.

Introduction

Magnesium hydride slurries provide a means of transporting, storing, and producing hydrogen in a single system. The slurry is produced in a large-scale production facility to take advantage of economies of scale and to minimize the cost of producing the slurry. The slurry is transported using the liquid fuels infrastructure including tank trucks on the roads, tank cars on the rails, and barges on water to minimize the cost of transportation. The slurry is pumpable and stable for weeks to months. This minimizes the cost of storage. When hydrogen is needed, the slurry is mixed with water and produces hydrogen. Two moles of hydrogen are produced for each mole of MgH_2 in the slurry. The chemical relationship is $\text{MgH}_2 + 2\text{H}_2\text{O} = \text{Mg(OH)}_2 + 2\text{H}_2$. The slurry can be used to produce hydrogen at a consumer station or on-board a vehicle. The oils of the slurry protect the MgH_2 from inadvertent contact with moisture in the air and the MgH_2 reacts very slowly at room temperatures, so it is relatively safe to handle and can be handled in the air. The byproduct is “Milk of Magnesia” and it also is relatively benign.

This project has been underway for about two years. At this time, we have produced a stable MgH_2 slurry that remains in suspension for weeks to months. We are developing a mixing system to release the hydrogen and have demonstrated continuous operation for several hours with no external heat addition except at the beginning of the test. We have been evaluating the recycling of the byproduct. Using the SOM process under development by Boston University, we have estimated that hydrogen could be supplied, in a mature large-scale system, for about \$4.32/kg of H_2 at the pump. We have also been evaluating the recycling of the oils from the byproducts and the production of MgH_2 from recycled magnesium.

Approach

The approach used in the project is to evaluate the showstopper issues first and then to develop the slurry, the mixer, and the recycle processes in successively greater detail. Significant attention is being paid to estimating the cost of hydrogen resulting from this process. The process involves the production of MgH_2

slurry, the transportation and distribution of that slurry, the production of hydrogen on-board or off-board, the return of the byproduct, and the recycling of the byproduct back to high energy capacity slurry. Recycling involves the separation of the oils from the byproduct for reuse, the calcination of Mg(OH)_2 to MgO, the reduction of MgO to Mg, the hydriding of Mg and H_2 to MgH_2 , and the production of new slurry from the MgH_2 . Tasks have been included in the project for slurry exploration and development, mixer system development, recycling oil byproduct, recycling magnesium hydroxide byproduct, hydriding the magnesium, and estimating the costs of the processes. An experimental task is directed at evaluating a promising technology under development at Boston University to electrolytically convert MgO to Mg.

Results

At this point, we have identified and addressed all the showstopper issues. All experiments and evaluations lead us to believe that the slurry approach is physically and economically achievable. We have shown that MgH_2 can be incorporated into stable slurry. The slurry looks like a thick grey paint (Figure 1). We are currently working with slurries of 70% solids loading. These high solids loadings became possible after milling the MgH_2 delivered from the manufacturer. Milling has reduced the particle size from about 100 micron down to about 1 micron. We believe that we can increase this loading by a few more percent. The 70% slurry has a material energy capacity of 3.6 kWh/kg and 4.2 kWh/L as a



FIGURE 1. Magnesium Hydride Slurry Pouring

fresh slurry and 2.2 kWh/kg and 4.3 kWh/L based on the byproducts. It is important for the slurry to have a high energy capacity in order to minimize the cost of transporting the slurry and to maximize the energy capacity of an on-board system. We are still in the midst of the particle reduction studies. The increase in particulate loading resulting from the use of smaller particles may be due to particle size or it may be due to particle shape. The as-delivered particles had a flake-like shape. The milled particles are expected to have a more rounded shape. Based on the previous work with lithium hydride slurry, we believe that the slurry density can still be improved. Our target remains 76% solids which will have material energy capacities of 3.9 kWh/kg and 4.8 kWh/L based on fresh material and 2.3 kWh/kg and 4.8 kWh/L based on byproduct mass and volumes.

We have shown that the slurry can be mixed with water to produce hydrogen at reasonable rates. We have recently been experimenting with a continuous mixer system that has produced 7-10 liters per minute for several hours of duration. We have shown that the slurry can be started, stopped, and started again and that the hydrogen production follows the slurry flow with only a short delay. We have shown that the production of hydrogen from the reaction is 100% of the theoretical amount expected from the reaction. The current mixer design uses no moving parts except for the pumps and valves. Further work needs to be performed to reduce the mass and volume of the pump system and to improve the handling of the byproduct. Our estimates of the energy capacity of the mature system is 1.8 kWh/kg and 1.7 kWh/L meeting the volumetric goal for 2010 but not quite achieving the gravimetric goal (goals 2.0 kWh/kg and 1.5 kWh/L). This estimate is based on storing 10 kg of hydrogen in 76% slurry. This estimate uses the maximum volume and mass of the system and includes all the water and slurry that will be required to support the system. It does not include the recovery of water from the fuel cell which would offer improved energy densities if achievable.

We have shown that the oils can be separated from the byproduct and that magnesium can be hydrided relatively inexpensively and rapidly. Further work is needed to better estimate the process costs for these two processes but they are expected to be low because the processes are relatively simple.

The slurry byproduct recycle processes can be performed with existing technologies. The process plan is to:

- separate the oils from the byproducts,
- calcine the magnesium hydroxide to magnesium oxide,
- reduce the magnesium oxide to magnesium,
- hydride the magnesium to magnesium hydride, and

- prepare slurry from the magnesium hydride and the recovered oil.

Oils can be separated from the byproducts using skimming techniques or using solvent refining techniques that are relatively simple and highly efficient. Magnesium hydride has been shown to be self-catalytic [1] thus allowing magnesium to be hydrided at temperatures of about 350°C and 10 bar hydrogen pressure. This process is not well developed but its simplicity indicates that it should not be expensive. We have performed this process in the laboratory and confirmed its operating characteristics. The calcination of magnesium hydroxide to magnesium oxide is a well-developed process. Both the hydriding and the calcination processes may be able to use waste heat from downstream processes. The largest cost process is anticipated to be the reduction of MgO to Mg. There are several well-developed processes capable of performing this task. However, the costs of the overall process improve when the magnesium reduction process is improved.

Safe Hydrogen has been working with Boston University to develop and evaluate a process to directly reduce MgO to Mg using a solid-oxide oxygen-ion-conducting membrane (SOM) process. During the first year of the project, Boston University scientists performed laboratory tests of the process providing energy consumption and process data to use for scale-up studies [2]. Boston University estimates of a large-scale process have been used with the H2A framework to estimate the costs of the reduction process. The H2A framework has also been used to estimate the costs of transporting and distributing the slurry. From this analysis we estimate that a mature large-scale process can produce slurry for a required H₂ selling price of \$3.88/kg of hydrogen. The transporting of the slurry from the production plant to the distribution station is estimated to add an additional \$0.206/kg of hydrogen. The distribution of the slurry is estimated to add an additional \$0.24/kg of hydrogen. The total selling price for a mature large-scale system is estimated to be \$4.33/kg of hydrogen. The production cost is dominated by the cost of energy. Figure 2 displays the variations in the required selling price of hydrogen for several factors. This analysis assumes that a power plant will be built to supply energy to the recycle plant. Electricity is assumed to cost \$0.029/kWh and process hydrogen produced from the heat of this plant is assumed to cost \$1.65/kg. The required selling price of hydrogen is most significantly affected by the cost of electricity. The top bar is included to estimate the effect of changes in the assumed capital costs of the magnesium reduction plant. By increasing the capital costs by 500%, the capital costs would be similar to the current magnesium reduction plant costs. The second bar indicates the required selling price of hydrogen if the cost of electricity varies

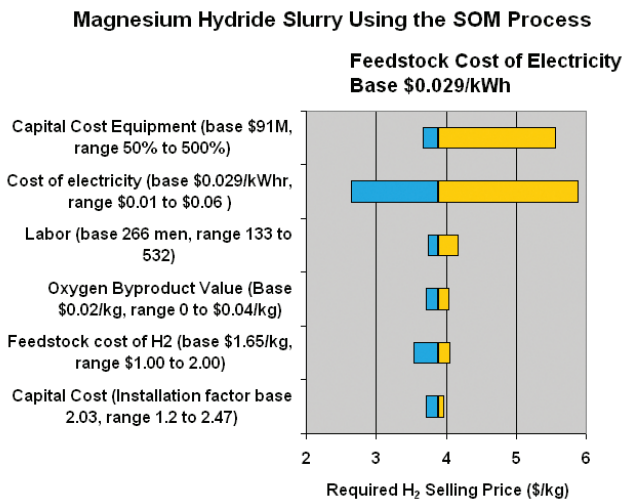


FIGURE 2. MgH₂ Slurry Production Costs

between \$0.01 and \$0.06/kWh. This range extends over the range of industrial electricity costs.

Figure 3 displays a similar analysis but assumes that electricity will be purchased from the electric utility grid. This is an assumption that is generally used by the H2A analysis team. The use of grid power is not anticipated by the author to be a likely design decision in a large-scale mature technology. The large-scale plants will be large enough to consume all the power from large power generation plants, thus benefiting from the base load production of electricity. We have assumed that a large-scale implementation of this technology will probably employ the construction of a large-scale power plant to support it. The use of grid power adds considerable cost

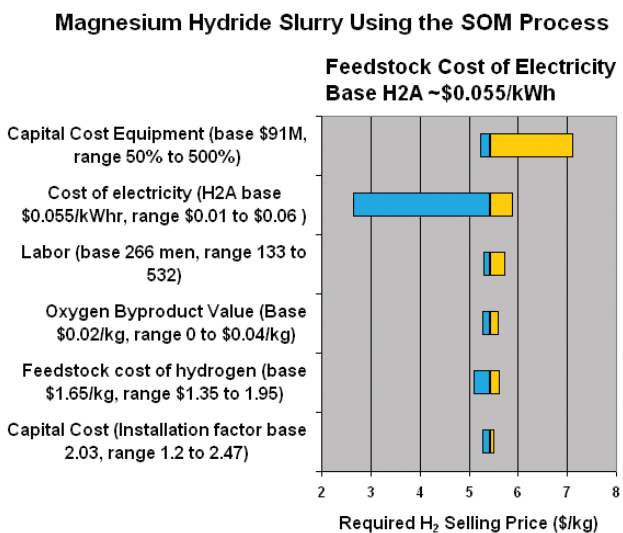


FIGURE 3. MgH₂ Slurry Production Costs Using Grid Power

to electricity as it incorporates the cost of distribution equipment, lines, and power losses. The cost of grid power, as estimated by the H2A framework, ranges from \$0.05 to \$0.06/kWh and results in a required selling price of hydrogen of \$5.445/kg of hydrogen.

The development work at Boston University during the past year has been limited to modeling of the process and evaluation of the possibility for producing magnesium hydride as part of the process. (Reductions in funding required that some of the project effort be postponed). The modeling effort has provided some valuable insights into the design options for multi-tube devices. Modeling has shown that the tube spacing may be important in some design options. The production of magnesium hydride during the condensation of the magnesium as part of the process is particularly attractive as it could further reduce the cost of the process.

Conclusions and Future Directions

During the past year, we have addressed the last of the showstopper issues relating to the development of a magnesium hydride slurry approach for producing, transporting, and storing hydrogen. At this point in the project, the system looks attractive and competitive with all other competing options. In addition, the magnesium hydride slurry approach offers considerable safety and handling characteristics that will make it a very promising mass-market fuel. We have increased the solids loading of the slurry, we have continued to improve the mixer system, we have experimentally evaluated all of the recycle sub-processes, and we have performed a cost analysis that has resulted in a projected required selling price of hydrogen using the magnesium hydride slurry approach that is approaching the cost of gasoline. Further work is required to bring the level of development up to the level that private industry requires before private capital will consider it a good investment.

During the next year, we will be improving the cost estimates while also improving the slurry and mixing technology. We intend to:

- Improve the MgH₂ slurry – more favorable pumpability and flowability characteristics.
- Improve continuous mixer system – to include lower cost and lighter pump systems, and byproduct handling.
- Slurry/mixer testing – to demonstrate the laboratory mixer and slurry robustness and hydrogen purity.
- Develop cost estimate for oil recycle process – to improve the cost analysis.
- Complete estimate of hydriding process – to improve the cost analysis.

- Experimental evaluation of SOM three tube process – to improve the cost analysis.
- Evaluation of process cost reduction options.

Special Recognitions & Awards/Patents Issued

1. United States Patent No. US 7,052,671,B2, May 30, 2006, Storage, Generation, and Use of Hydrogen.

FY 2006 Publications/Presentations

1. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, 2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, Arlington, VA, 24 May 2005.
2. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, DOE Hydrogen Production and Distribution Tech Team Annual Review, Alexandria, VA, 24 August 2005.
3. Sigmar H. Tullmann, “Chemical Hydride Slurry for Hydrogen Distribution and Storage”, AltWheels Conference, Larz Anderson Auto Museum, Brookline, MA, 17-18 September 2005.
4. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, Chemical Hydrogen Storage Systems Analysis Meeting, Argonne National Laboratory, October 12, 2005.

5. Uday B. Pal and Srikanth Gopalan of Boston University, “Clean Energy Research a Boston University”, Clean Energy Conference, Boston, 8 November 2005.

6. Sigmar Tullmann, “Hydrogen Storage Breakthrough – The Safe Hydrogen Story”, Hydrogen and Fuel Cell Summit, Worcester Polytechnic Institute, 5 June 2006.

7. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, 2006 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review, Arlington, VA, 18 May 2005.

8. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, DOE Hydrogen Storage Tech Team Meeting, Detroit, MI, 22 June 2005.

References

1. United States Patent 5,198,207, “Method for the Preparation of Active Magnesium Hydride-Magnesium Hydrogen Storage Systems, Which Reversibly Absorb Hydrogen”, Wilfried Knott, Klaus-Dieter Klein, Gotz Koerner, Th. Goldschmidt AG, October 30, 1991.
2. An Analysis of the Economic, Energy and Environmental Advantages of the Solid-Oxide Oxygen-Ion-Conducting Membrane (SOM) Process By Professor Uday B. Pal and Dr. Christopher P. Manning.