IV.B.3 Chemical Hydride Slurry for Hydrogen Production and Storage

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Subcontractors:
- Hatch Technology LLC, Fall River, MA
- Boston University, Boston, MA
- Metallurgical Viability, Inc., Elkton, MD
- HERA Hydrogen Storage Systems, Longueuil, Quebec, Canada

Project Start Date: January 1, 2004
Project End Date: June 30, 2008

Objectives

Demonstrate that 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.

Technical Barriers

This project addresses the following technical barriers from the Storage section 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 slurry to meet the DOE 2010 hydrogen storage targets.

H_2 Storage Target	Units	2010 Target	MgH_2 Slurry System Estimate
System Gravimetric Capacity	kWh/kg	2	1.8
System Volumetric Capacity	kWh/L	1.5	1.7
System Storage Cost Fuel Cost	$/kWh net $/gge at pump	4 2-3	<5 4.50

gge – gasoline gallon equivalent

Accomplishments

- Energy density: demonstrated the process using MgH_2 slurry with 70% solids loading. This provides a fresh slurry storage capacity of 3.6 kWh/kg and 4.2 kWh/L (capacity based on spent slurry 2.2 kWh/kg and 4.3 kWh/L). During the past year a 75% solids loading slurry was demonstrated but not tested in the mixing apparatus. Gains in storage efficiency from a 76% solids loading have been calculated to provide energy densities of 3.9 kWh/kg and 4.8 kWh/L (capacity based on spent slurry 2.3 kWh/kg and 4.8 kWh/L).
- Improved reaction management and control: demonstrated the model #4 mixer system. Demonstrated enhanced mixing of slurry and water into the reaction vessel. Reaction rates between slurry and water remain high. Control of the reaction has been demonstrated with tests of the apparatus that lasted for several hours and produced several cubic meters of hydrogen. The apparatus was designed to produce about 10 L/min and performed at the design conditions.

- Verification of fluidity in cold temperature ranges: viscosity measurements of the slurry versus temperature indicate that slurry pumping should perform well to temperatures below 0°C.
- Cost estimation improvements: the cost of MgH_2 slurry at the pump is estimated to be $4.50/kg of hydrogen delivered. This includes a cost of $3.88/kg H_2 for Mg reduction, $0.16 for terminal cost, $0.20 for transportation costs (200 km round trip), and $0.24 for forecourt costs.
- Regeneration process development: The solid-oxide oxygen-ion-conducting membrane (SOM) process development team performed tests of a three-tube SOM system. Magnesium was produced though some damage to the tubes was observed. Modeling indicates that this damage can be controlled with a small modification to the control system.

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Introduction

Magnesium hydride slurry provides a means of transporting, storing, and producing hydrogen in a single system. The slurry will be produced in large-scale production facilities to take advantage of economies of scale and to minimize the cost of producing the slurry. The slurry will be transported using the existing 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 months. This minimizes the cost of hydrogen. When hydrogen is needed, the slurry is mixed with water. Two moles of hydrogen are produced for each mole of MgH_2 in the slurry. The chemical relationship is $MgH_2 + 2H_2O = Mg(OH)_2 + 2H_2$. 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 was completed at the end of June 2008. We have produced stable MgH_2 slurry that remains in suspension for months. We have demonstrated 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 evaluated 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 $4.50/kg of H_2 at the pump. We have evaluated the recycling of the oils from the byproducts and the production of MgH_2 from recycled magnesium and hydrogen. Our current estimates for system weight and volume compare quite favorably with all other hydrogen storage technologies (1.8 kWh/kg [5.3% H_2], and 1.7 kWh/L [52 g/L]).

Approach

The approach used in the project has been to evaluate the showstopper issues first and then to develop the slurry, the mixer, and the recycle processes in successively greater detail. Significant attention was paid to estimating the cost of hydrogen resulting from this process. The process involves the production of MgH_2 slurry from magnesium and hydrogen, 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 by-product 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 and the recovered oils. Tasks were 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 was directed at evaluating the SOM process, a promising technology under development at Boston University to electrolytically convert MgO to Mg.

Results

Slurry: Figure 1 displays the 70% MgH_2 slurry that we are using now. This slurry consists of a milled MgH_2 powder, light mineral oil, and some dispersants. The dispersants aid in keeping the particles from agglomerating and help to stabilize the slurry. The mineral oil helps to protect the MgH_2 particles from inadvertent contact with moisture in the air and provides the liquid medium for the slurry. Some samples of this slurry have remained in suspension for more than 12 months.

Mixer: During the past year, we have tested a batch reaction concept that has worked well. In this process, slurry is pumped into a stream of hot water to mix the slurry with the water. The mixed stream then flows into a reaction chamber where the bulk of the reaction takes place releasing hydrogen. Several injections take place in quick succession to take advantage of the heat from the previous reaction. The by-products of this reaction collect in the bottom of the reactor. Periodically, the reaction chamber is flushed by filling it with water to recover the oils from the slurry. The water level is reset and the injections resume. Also periodically, the byproducts are moved from the bottom of the reactor to the by-product separation chamber. In the by-product separation chamber, the water is filtered from the solid by-products and returned to the water storage container. For our experiment, we used one reaction chamber. In a commercial version, we envision several reaction chambers sharing heat and operating as needed to supply a continuous flow of hydrogen at the flow rate required. Figure 2 displays the experimental apparatus with the piston pumps and the reaction chamber. The reaction chamber is heavily insulated to retain heat. Figure 3 shows the experimental mixer system from the other side. The water recovery chambers and water control vessels are visible in the middle and right side of the apparatus.

FIGURE 1. 70% Magnesium Hydride Slurry

FIGURE 2. Mixer Showing Reactor and Pumps

By-Product Recycle: Several investigations were performed to evaluate the by-product recycle steps. We evaluated the separation of the oils from the by-product and concluded that they can be reused. We evaluated the SOM process for the reduction of MgO to Mg which will be discussed next. We evaluated the hydriding process and found that we can readily hydride magnesium by mixing magnesium powder with magnesium hydride powder and hydrogen at about 300°C and 10 Bar [1].

SOM Process: The SOM process was evaluated experimentally and analytically. Early tests were performed with a single tube apparatus to demonstrate the efficiency and operation of the basic concept. The tests demonstrated a very high efficiency process consuming less than 10 kWh/kg of Mg produced. The heat produced by the electrolysis process was estimated to be enough to satisfy the heating requirements of the system in continuous operation. Figure 4 displays the three-tube apparatus that has been under test during the past year to evaluate multi-tube operation. The tests of this apparatus also demonstrated the production of Mg. Modeling of this apparatus was used in the design of the apparatus and has aided in understanding the operation.

Cost: The slurry process was evaluated for cost and efficiency. The cost is quite attractive, as noted in the accomplishments section. The estimate of $4.50/kg of H_2 is dominated by the cost to reform Mg from the byproducts. The cost estimate was based on a detailed plant cost estimate with costs estimated for all major components and labor.

FIGURE 3. Mixer Showing H_2 and Water Control Systems

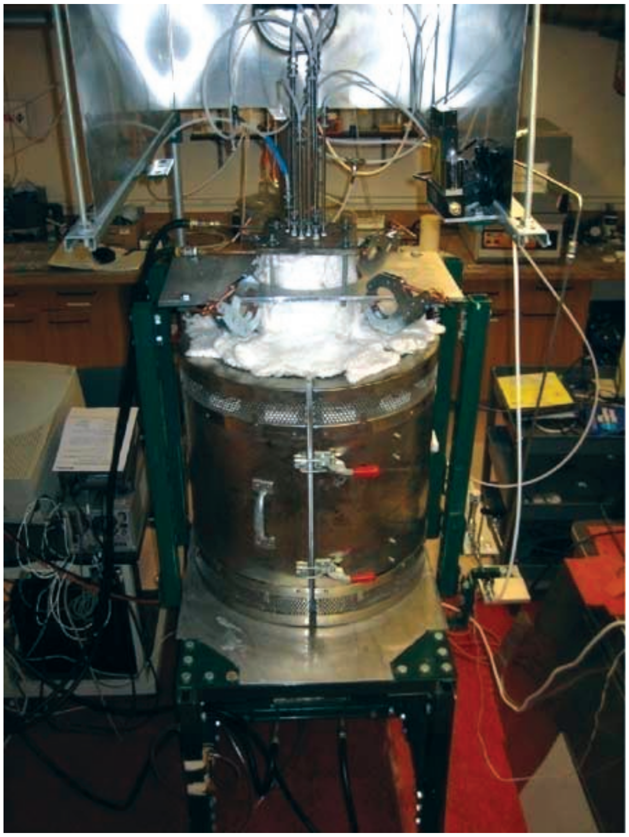

FIGURE 4. SOM 3-Tube Experimental Apparatus

Conclusions and Future Directions

The primary conclusion from the work that the Safe Hydrogen team has performed is that chemical hydride slurry is a viable and cost competitive option for storing, transporting, and delivering hydrogen. Safe Hydrogen has demonstrated that:

- MgH_2 slurry will stay in suspension for months.
- MgH_2 slurry is pumpable and easily moved from tank to tank.
- MgH_2 slurry can be reacted rapidly and safely with water to produce hydrogen at high production rates. The reaction system that was demonstrated is one of two methods investigated. Other methods remain to be evaluated and developed.
- The by-products of MgH_2 slurry can be filtered to recover water to be reused in the system.
- The by-products can be pumped from the recovery vessel and stored in a storage vessel.
- MgH_2 can be produced with Mg powder and 10 bar hydrogen using some MgH_2 as a catalyst.
- The process evaluated includes the recycle of the byproducts to form new MgH_2 slurry. Cost estimates of one SOM-based recycle process indicate that hydrogen can be delivered to an automobile customer for about \$4.50/kg of H_2.
- Boston University researchers have shown that a SOM process can produce magnesium from magnesium oxide and that a multi-tube process is a viable design. Cost estimates of this process were used to estimate the cost of hydrogen from a magnesium hydride slurry process.
- The work performed with MgH_2 slurry demonstrates that chemical hydride slurries are a viable option for storing, transporting, and delivering hydrogen. Future developments in chemical hydrides with greater amounts of H_2 may provide more attractive slurries.
- As part of the hydriding investigation, Safe Hydrogen discovered that the MgH_2 slurry can also potentially be used as a rechargeable slurry. Rechargeable slurry will release hydrogen by heating the metal hydride in the slurry. MgH_2 appears to offer an attractive cost competitive medium for such a slurry. Other metal hydrides currently under development by DOE contractors may be even more attractive.

The work proposed under this contract has been completed. Further development of MgH_2 slurry production facilities and mixer processes is required to commercialize this process at the costs projected. Specifically:

- The SOM process development at the 3-tube laboratory-scale must be completed to provide design data for the design, construction, and testing of a pilot scale process. The pilot-scale process should be able to provide the data necessary to design a full-scale magnesium production plant and to estimate accurately the cost of magnesium from that plant.
- Further development effort needs to be performed to condense magnesium into a powder from the vapor produced by the SOM process. To minimize the hazards associated with magnesium powder, the powder should be immediately hydrided and the resulting magnesium hydride should proceed directly into a slurry production process. Magnesium powder is a significant fire hazard. Magnesium hydride is much more stable than magnesium metal powder and when mixed into a slurry, it is quite benign.
- Further development of the slurry could benefit from the evaluation of other dispersant combinations. One of the issues of the current slurry is that it forms a film rather than flowing completely from a surface. This will create a maintenance issue that might be addressed by the discovery of another combination of dispersants.

- Further development of the mixing system will be required to produce a commercial mixing system. The system tested under this project, demonstrated several of the concepts that will be needed to proceed to a commercial device.
- Based on the evaluation performed on rechargeable slurry, the Safe Hydrogen team also recommends that further investigation be performed on this option.

FY 2008 Publications/Presentations

1. Andrew W. McClaine, Kenneth Brown, "Chemical Hydride Slurry for Hydrogen Production and Storage", presentation made to DOE Headquarters staff, Washington, D.C., 3 August 2007.

2. Adam C Powell IV, "Boundary Element Method (BEM) modeling of electrochemistry", Materials Science and Technology 2007, COBO Center, Detroit, September 16-20, 2007.

References

1. US Patent 5,198,207, Mar. 30, 1993, Method for the Preparation of Active Magnesium Hydride-Magnesium-Hydrogen Storage System, Which Reversibly Absorb Hydrogen, Wilfried Knott, Klaus-Dieter Klein, Götz Koerner, all of Fed. Rep. Of Germany.