Chemical Hydride Slurry for Hydrogen Production and Storage

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Safe Hydrogen, LLC

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Project ID # STP16

Overview

Timeline

- Project start date: 1/1/2004
- Project end date: 12/31/2007
- Percent complete: 80%

Barriers

- Barriers addressed for On-Board Storage

Project also applicable for Delivery, Off-board storage, and MgH_2 Cost reduction

  - A. System Cost
  - K. System Life-Cycle Assessment
  - R. Regeneration Processes

Budget

- Total project funding
  - DOE share: $1.8M
  - Contractor share: $437K
- Funding in FY06: $400K
- Funding for FY07: $450K

Partners

- Interactions/ collaborations
  - TIAX LLC
  - Professor T. Alan Hatton, MIT
  - Jens Frederiksen, PF&U Mineral Development ApS
  - Hatch Technology, LLC
  - Boston University
  - Metallurgical Viability, Inc.
  - HERA Hydrogen Storage Systems, Inc.
  - Massachusetts Technology Collaborative

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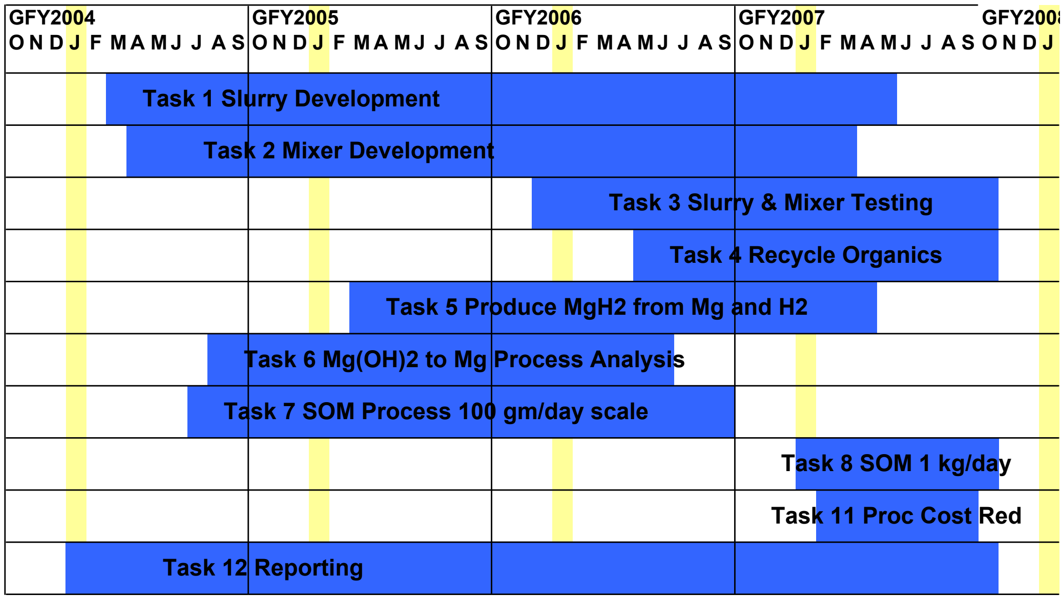
Objective and Approach

- **Objective** - Demonstrate that Magnesium Hydride Slurry is a cost effective, safe, and high-energy-density hydrogen storage, transportation, and production medium
  - Pumpable and high energy density slurry offers infrastructure advantages
  - High system energy density with high vehicle range
- **Approach**
  - **Slurry** - Develop a stable and very fluid MgH_2 slurry with slurry energy density of 3.9kWh/kg and 4.8kWh/L necessary for transportation and distribution
  - **Mixer** - Develop mixing system to use MgH_2 slurry and to meet 2kWh/kg and 1.5kWh/L system targets
  - **Cost** - Evaluate and develop Mg reduction and slurry production technologies to show potential cost of hydrogen, slurry, and system
    - Comparative evaluation of alternate Mg reduction technologies
    - Experimental Solid-oxide Oxygen-ion-conducting Membrane (SOM) process
    - Slurry production and component recycling
    - Mg hydriding, slurry mixing, Oil separation and recycle, Mg reduction

Approach



- Address Show-stopper issues first
- Focus on
  - Slurry development
  - Mixer development
  - Recycling cost estimate
    - Overview study
    - Exp SOM
- Plan two to three investigate-and-review cycles in each area to identify and address design issues

Issues and Options

- Issues that are being address in this project
  - Cost of: hydrogen from a *large scale* magnesium hydride slurry system
  - Cost of: reducing $Mg(OH)_2$, making MgH_2, recovering the oils
  - Slurry stability: continued pumpability for lengthy storage and delivery to the market
  - Speed and control of hydrogen generation. Mixer needs to enable rapid reaction, with very compact and simple footprint to meet on-board requirements
- Benefits of slurry technology
  - Slurry system can deliver hydrogen to the market with only slight modification to the existing transportation and delivery infrastructure.
  - Slurry based system can be used both as *fueling station* or an *on-board* storage and generation technology
  - Project Research will yield new magnesium and magnesium hydride production technology know-how which will benefit other metal based hydrogen storage technologies

Progress Slurry Development

target: a pumpable slurry that stays liquid for months

- Slurry characteristics depend on:
  - Carrier liquid and dispersant
  - Particle size, size mix and loading
- Continuing size reduction tests
  - Bimodal particle size distributions tested so far has not improved solids loading
- Significant achievements
  - Energy density and fluid stability are continually improving
  - Demonstrated stability of MgH_2 slurry with 70% milled solids loading. This provides a fresh material storage capacity of 3.6 kWh/kg and 4.2 kWh/L (capacity based on spent slurry 1.8 kWh/kg and 3.1 kWh/L)
  - Viscosity measured versus temperature

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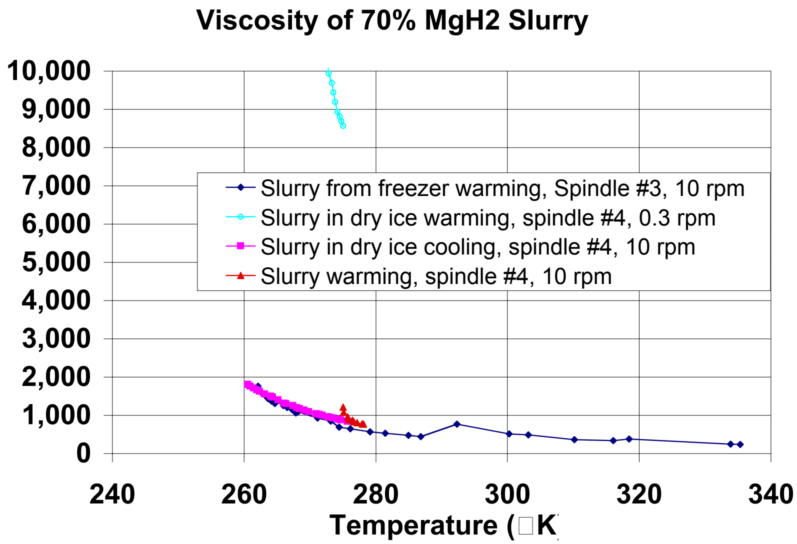
Progress Slurry Development

target: a pumpable slurry that stays liquid for months

70% milled slurry
Viscosity after 1 week 321-332cP at 25°C
Viscosity after 8 months 307-334cP at 21° C



Viscosity Measurements
Using Brookfield Model LVDVE115 viscometer

- 70% milled MgH_2 slurry has performed well and has been selected as the new standard slurry
- Slurry viscosity measurements indicate that slurry is non-Newtonian and exhibits characteristics of shear thinning
- Testing continues to evaluate additional slurry preparation strategies

Slurry Stability Evaluation

- Observe settling rate
- Measure viscosity and density

8 months of settling time

•The slurry on the right settled after 1 week. It shows a clear layer of oil over the settled solids.

•The slurry on the left has a very thin layer of oil on top that indicates some settling. This however did not show up for several months indicating a clear improvement in stability. This slurry remixed readily and flows in a manner similar to when it was made.

Progress Mixer Development

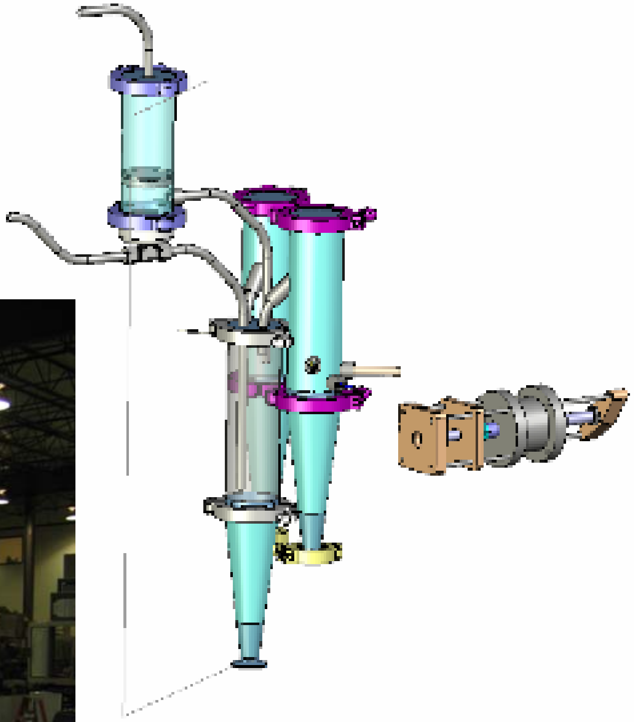
target: simple compact design providing efficient reaction control

- Desired characteristics of ideal mixer
  - Simple, lightweight, compact
  - Low energy input
  - Reliable cycling on/off
  - Control moisture in hydrogen
  - Rapid start
  - Byproduct handling
- Significant achievements
  - Tested airless paint pump with 70% slurry
  - Demonstrated that piston pump moves slurry reliably
  - Began design, fabrication, and testing of semi-continuous mixer system using piston pumps

Progress Mixer Development

target: simple compact design providing efficient reaction control

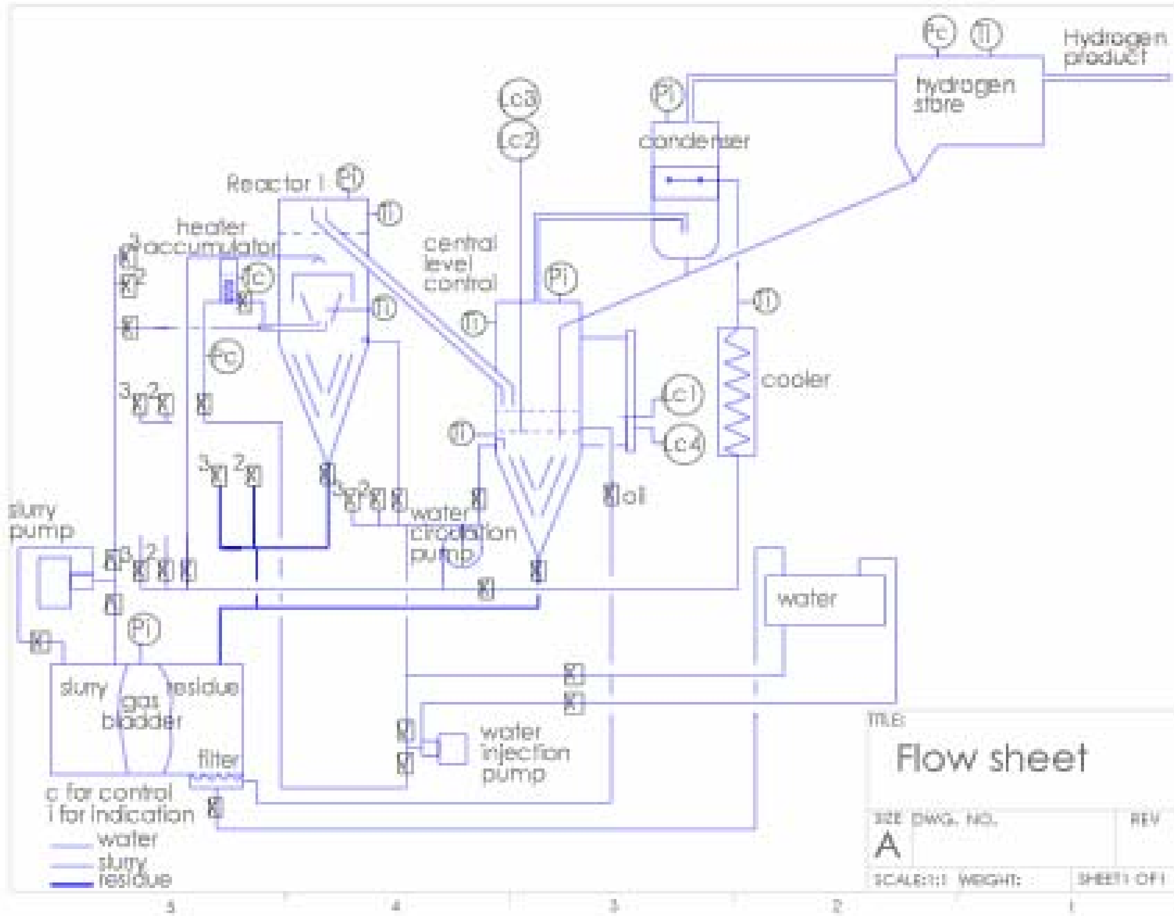
- Model #4 mixer system designed
  Fabrication in progress
- Slurry and water pumps along with pneumatic actuated valves are being tested with Parr autoclave apparatus
  - Slurry mixed with water jet
  - Slurry and water are homogenized as they enter reactor



Progress Mixer Development

target: simple compact design providing efficient reaction control

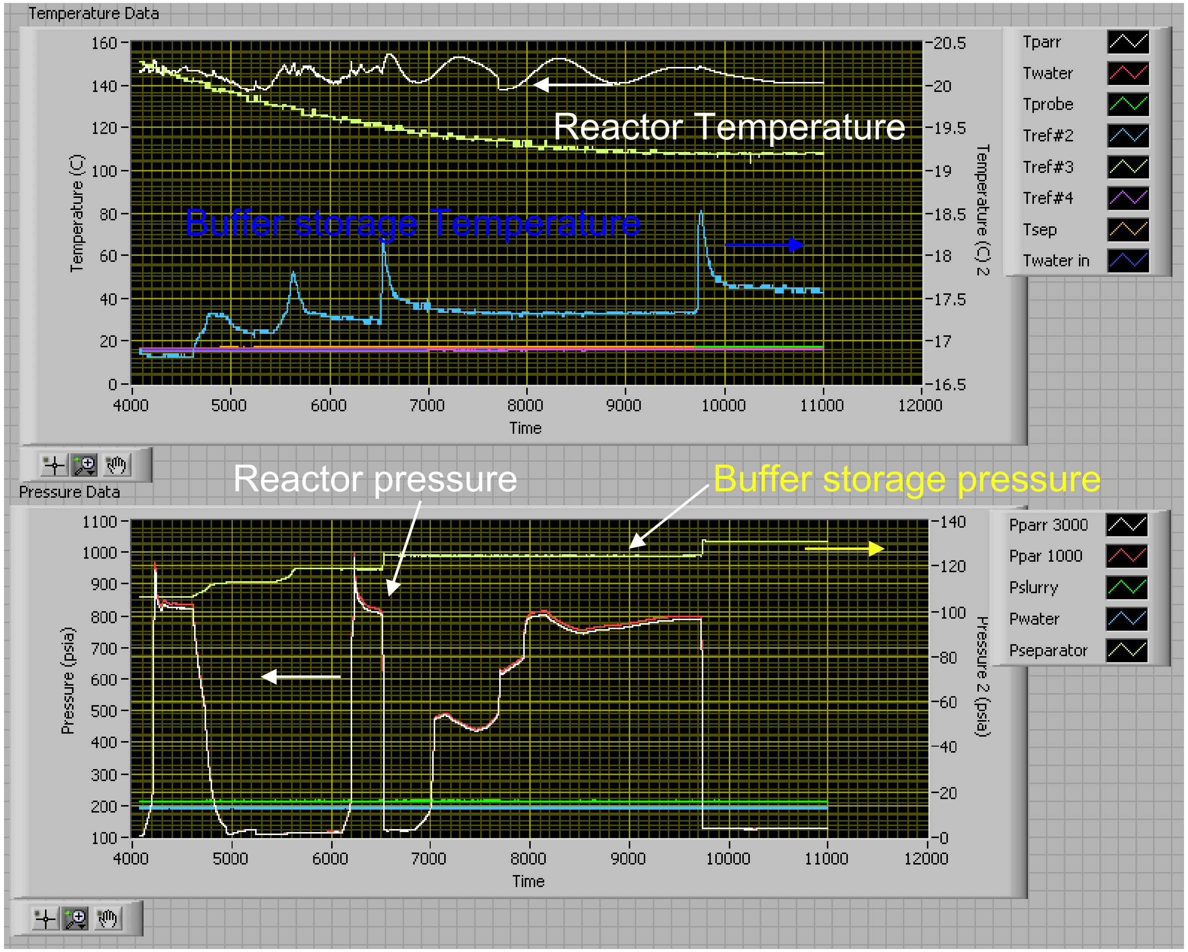
- Semi continuous mixer system flowsheet
- System mixes water and slurry as they are being injected into reactor
- Multiple reactors provide means of separating byproducts while maintaining flow of hydrogen
- Circulation of reaction water reduces need for external heat



Progress Mixer Development

target: simple compact design providing efficient reaction control

- Reaction rates are relatively rapid
- Chart shows sequence of reactions where cold slurry was injected into hot water.
  - Some reactions occurred in sealed reaction vessel showing large pressure rise in the reaction vessel
  - Other reactions proceeded with reaction vessel open to large buffer storage



Progress Recycling Oils

target: Low cost method of recovering oils from byproduct

- Characteristics sought
  - Simple, low cost, low energy process to separate oils from byproducts
  - Recovered oil undamaged from H_2 production process
- Significant achievements
  - Recycled oils used in the preparation of slurry
  - Slurry with recycled oil used in continuous mixer tests

Progress Hydriding Mg

target: Low cost method of hydriding

- Characteristics sought
  - Low cost process
  - Low energy consumption
- Opportunity
  - MgH_2 is reported to be autocatalytic
- Significant achievements
  - MgH_2 autocatalytic nature confirmed
  - MgH_2 produced from mixture of Mg and MgH_2
  - Hydriding process appears to be relatively simple and thus relatively inexpensive
  - Hydriding work resulted in patent application

Progress - Recycling MgO

Target: determine energy efficiencies and costs of alternative recycling processes

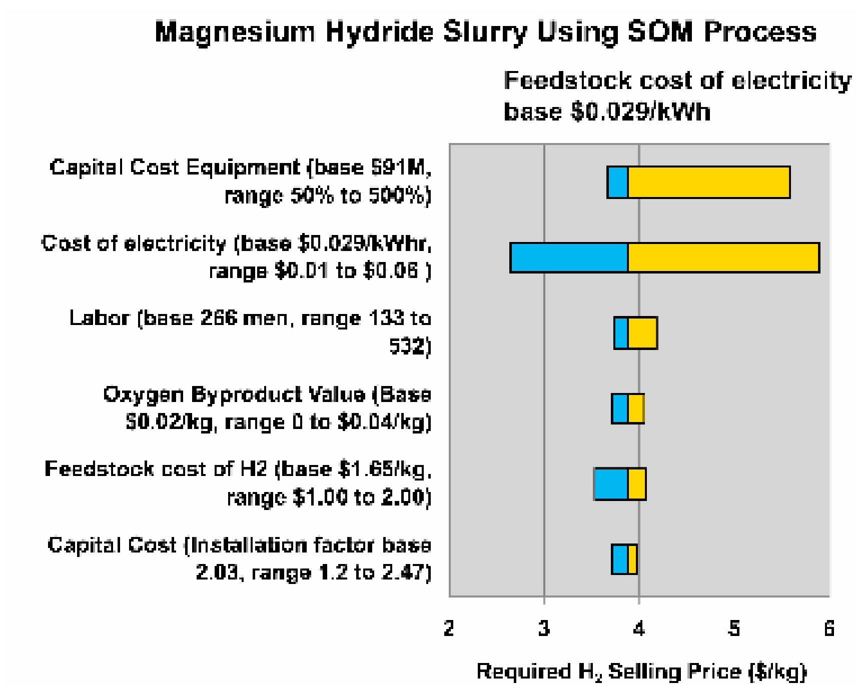
- Task plan
  - Evaluate Mg reduction alternatives
  - Determine operating and capital costs using bottom up approach
  - Evaluate cost of hydrogen using H2A framework

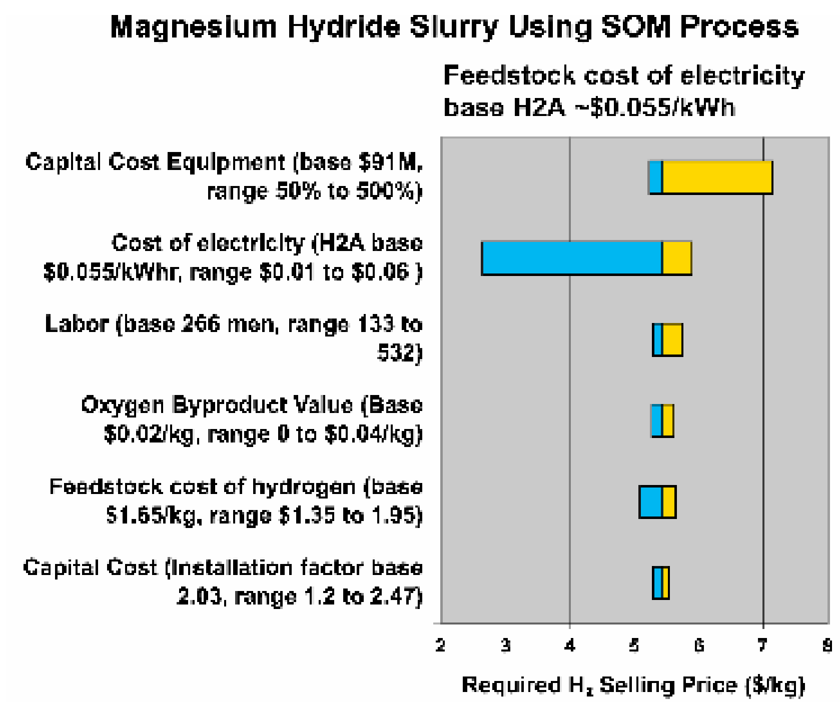
- Process steps
  - Reclaim oil
  - Calcine $Mg(OH)_2$ to MgO
  - Reduce MgO to Mg
  - Hydride $Mg + H_2 = MgH_2$
  - Mix slurry

- Significant Results
  - SOM offers lowest energy consumption, reduction process can operate at 10 kWh/kg of Mg
    - Demonstrated in laboratory experiments at Boston University
  - H2A analysis of SOM based Safe Hydrogen slurry system resulted in estimated cost of hydrogen at \$3.88/kg at plant gate; \$4.50/kg at pump.

Progress - Recycling MgO

H2A tornado chart showing effect of varying costs of energy, labor, O_2 byproduct, capital, and process H_2





Tornado charts with baseline cost of electricity of $0.029/kWhr

Tornado charts with baseline cost of electricity of $0.055/kWhr

Conclusion: Cost of hydrogen from SOM process is strongly affected by the cost of electrolysis energy but industrial scale energy costs should produce plant gate hydrogen costs <$4/kg H_2

Progress - Recycling MgO

Assumptions used in H2A analysis of resulting hydrogen cost

- Baseline case
  - Mature large-scale plant, all power produced from captive power plant
  - 2.4 GWth power plant producing
    - electricity (45% eff)
    - hydrogen (50% eff from thermal energy)
  - Cost of electricity $0.029/kWhe
  - Cost of H_2 $1.65/kg
  - Electrical energy needed to produce Mg 10kWhe/kg Mg
  - Based on above assumptions, power plant will use 1.85 GWth for Mg and 545MWth for H_2 production. The plant will produce 731,174 metric ton/yr of Mg, 60,629 metric ton/yr of H_2 and 481,176 metric ton/yr of O_2 as byproduct for sale
  - Slurry will produce 121,257 metric ton/year of hydrogen
  - Mg plant would be comparable to some of today's larger Al plants
  - The slurry production plant is assumed to have a capital cost about 25% of that of current $MgCl_2$ plants. Cost analysis, using a bottom up approach, still has much uncertainty but seems reasonable.

Cost of Hydrogen

Using H2A Framework

- SOM Production at large scale
  - \$3.884/kg H_2 at the plant gate
- Chemical hydride terminal cost
  - \$0.158/kg H_2
- Transportation 200 km cost
  - \$0.198 to 0.231/kg H_2
- Distribution - Forecourt Chemical Hydride Slurry
  - \$0.243/kg H_2
- Total
  - \$4.483 to \$4.516/kg H_2 at pump

Progress SOM

target: low cost method of reducing MgO to Mg

- Significant achievements
  - Demonstrated Mg production at a rate of 160gm/day with a single membrane tube
  - Estimated operating and capital costs of the SOM cell module producing 2 metric ton/day of Mg using 37 tubes
  - SOM experiment was operated for 2 days with periodic addition of MgO
  - Successful operation without an anode reductant using a liquid silver anode
- Current focus
  - Modeling the single and three tube SOM reactor
  - Defining design options for a condenser to produce Mg powder and MgH_2

Accomplishments

- Improved slurry stability and flow characteristics with modifications to dispersants and with particle size reduction. Current 70% milled solids loading.
- Demonstrated continuous production of hydrogen from continuous mixer using heat recovery and start/stop of slurry and water
- Observed simple method of separating oils from byproducts
- Demonstrated MgH_2 production from Mg and H_2 using mixture of Mg and MgH_2
- Mg reduction studies show \$3.88/kg H2 production cost estimate using H2A analysis framework. \$4.50/kg H_2 at pump
- SOM process demonstrated for 2 days with periodic replenishment of MgO producing Mg at rate up to 160 g/day

Future Work

- FY07 Plans
  - Completing fabrication and testing of semi-continuous batch mixer system
  - Testing of slurry and mixer for robustness and hydrogen purity
    - Evaluate operation at lower temperatures
  - Organics recycle process cost analysis
  - MgH_2 production process cost analysis
  - Updating production cost analysis
  - SOM cell experiments using 3 tube cell
- FY08 Plans
  - Complete project testing and reporting
  - Seek additional funding to design commercial scale prototypes of chemical hydride slurry systems for R&D users and for prototype fueling station evaluations
  - Seek funding to develop rechargeable slurry technologies discovered during this project

Project Summary

What have we done & what does it mean

- The primary technical, cost, and efficiency concerns have been addressed
  - Technical
    - Pumpable, stable slurry can be made enabling the use of current distribution infrastructure
    - Slurry can be mixed with water in a simple, low cost device to produce H_2 from both water and slurry
    - SOM process development is progressing well
  - Cost & Efficiency
    - Oils can be easily separated from byproducts ensuring a low cost recycling process (detailed cost estimate remains)
    - Mg can be easily hydrided promising a low cost regeneration process (detailed cost estimate remains)
    - Mg reduction process costs can likely be reduced to provide \$3.88/kg H_2 using estimate of SOM 37 tube cell and H2A framework shows cost path to meet DOE targets
    - Full system efficiency appears to be comparable to LH_2 and cH_2 options
- Upcoming work will refine and improve the results achieved to date