



Chemical Hydride Slurry for Hydrogen Production and Storage

2006 DOE Hydrogen Program Review

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Overview

Timeline

- Project start date: 1/1/04
- Work start: 4/1/04
- Project end date: 12/31/06
- Percent complete: 59%

Budget

- Total project funding
 - DOE share: \$1.8M/ 3-4 years
 - Contractor share: \$457K
- Funding received in FY05: \$300K
- Funding for FY06: \$400K

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

Collaboration

- TIAX LLC
- Professor T. Alan Hatton, MIT
- Jens Frederiksen, PF&U Mineral Development ApS

Partners

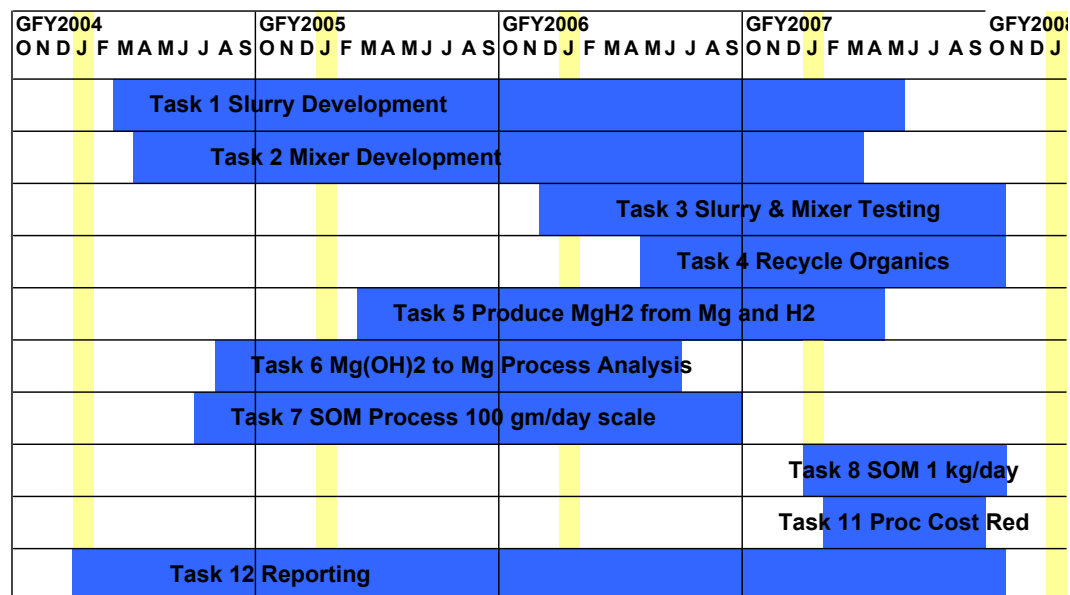
- Hatch Technology, LLC
- Boston University
- Metallurgical Viability, Inc.
- HERA Hydrogen Storage Systems, Inc.
- Massachusetts Technology Collaborative₂

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, 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

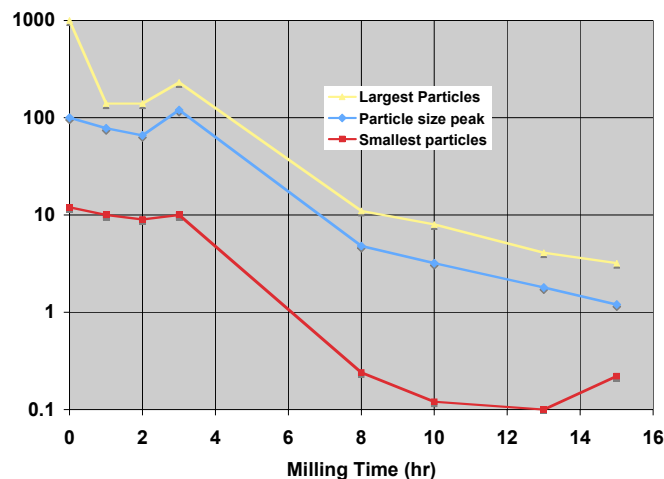
- Slurry characteristics depend on:
 - Carrier liquid and dispersant
 - Particle size, size mix and loading
- Completed tests of commercial MgH_2 powder with original dispersant
 - Partial success – but average particle size may be too large
- Performing size reduction tests
 - Slurry prepared with MgH_2 milled for 15 hours has stayed in suspension without settling
 - Bimodal particle size distribution may allow higher solids loading
- Significant achievements
 - Smaller particle sizes increase slurry stability
 - Energy density and stability are continually improving

Progress Slurry Development

target: a pumpable slurry that stays liquid for months



50% slurry without milling



Size reduction vs time

Using Horiba LA-910 Particle Size Distribution

Analyzer

- 50% slurry of as-received MgH_2 is acceptable but needs to be stirred occasionally
- Slurry made from MgH_2 ball milled for 15 hours has stayed in suspension for the several weeks since it was made
- Tests of 60% slurry in progress
- Testing continues to evaluate additional slurry preparation strategies

Progress Mixer Development

target: simple compact design providing efficient reaction control

- Desired characteristics of mixer
 - Simple, lightweight, compact
 - Low energy input
 - Reliable cycling on/off
 - Control moisture in hydrogen
 - Rapid start
 - Byproduct handling
- Significant achievements
 - Demonstrated heating only at startup
 - Demonstrated reliable cycling on/off
 - Model 2 mixing improved over Model 1 system

Progress Mixer Development

target: simple compact design providing efficient reaction control

- 1st continuous mixer
 - Designed, fabricated, tested
 - Double annulus to heat slurry and water
 - Slurry feed had difficulties
- 2nd continuous mixer
 - Designed, and fabricated
 - Testing in progress
 - Slurry can be started and stopped
 - Water preheating in annulus
- Important design features
 - Injection of slurry must allow cycling
 - Mixing of slurry and water
 - Heat management



Double Annulus Mixer



Single Annulus Integrated Head Mixer

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 H₂ production process
- Significant achievements
 - Observed that oils separate readily from byproducts when allowed to settle
 - Oils can be removed by oil skimming techniques
 - Solids and water can be removed by pumping
 - Recycled oils have been used in the preparation of new slurry for mixer testing

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
 - Tested techniques reported in the literature using the Parr Autoclave
 - MgH_2 demonstrated to be autocatalytic
 - Mg and MgH_2 mixture absorbed H_2 readily and cycled reliably
 - Evaluated milling of MgH_2



Progress - Recycling MgO

Target: determine energy efficiencies and costs of alternative recycling processes

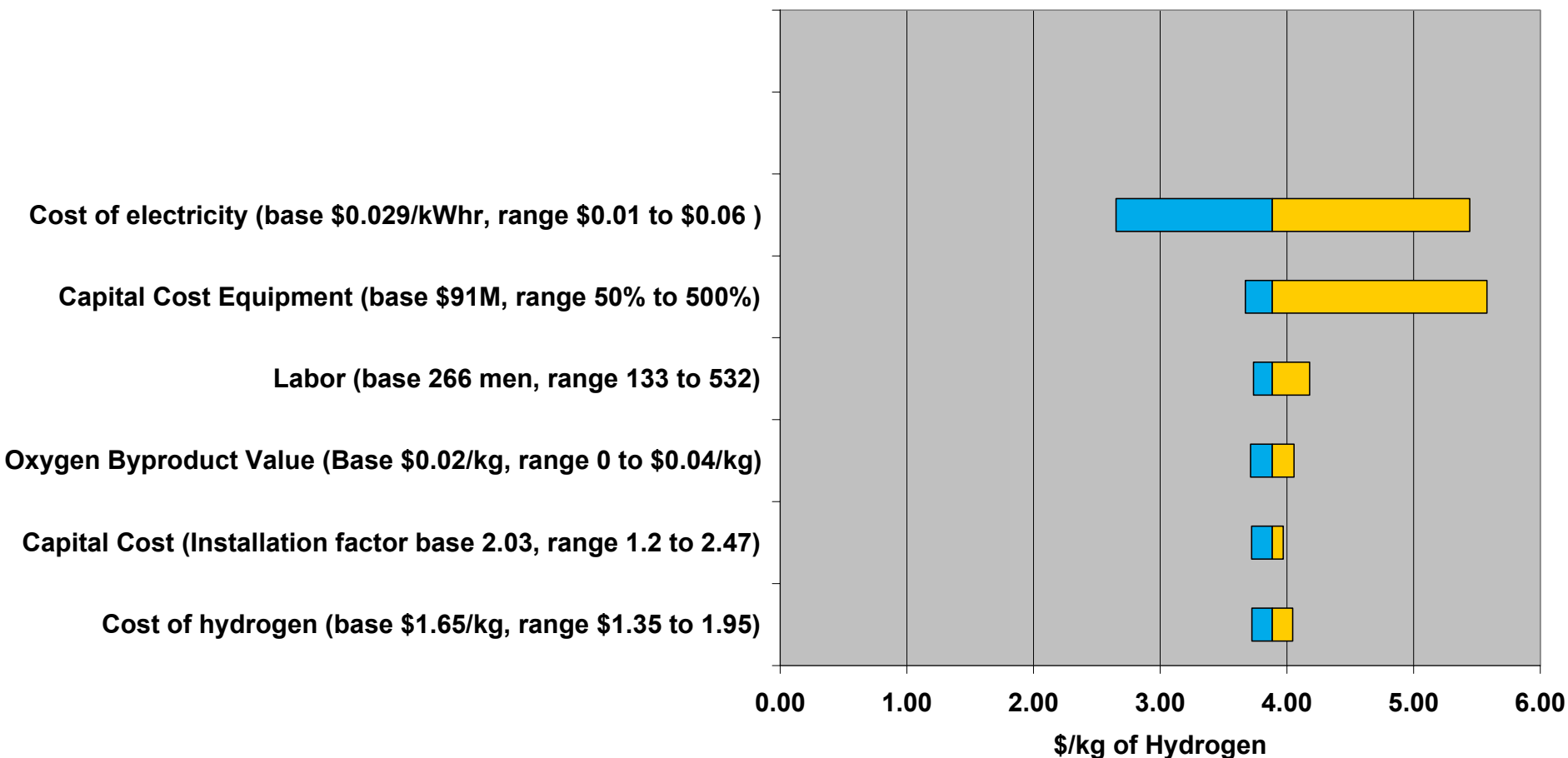
- Task plan
 - Evaluate Mg reduction alternatives
 - Determine operating and capital costs using bottom up approach
 - Evaluate cost of hydrogen using H2A framework
- Process steps
 - Reclaim oil
 - Calcine $\text{Mg}(\text{OH})_2$ to MgO
 - Reduce MgO to Mg
 - Hydride $\text{Mg} + \text{H}_2 = \text{MgH}_2$
 - 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



Progress - Recycling MgO

H2A tornado chart showing effect of varying costs of energy, labor, O₂ byproduct, capital, and process H₂

Safe Hydrogen Magnesium Hydride Slurry Using SOM Process





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 H₂ \$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 H₂ production. The plant will produce 731,174 metric ton/yr of Mg, 60,629 metric ton/yr of H₂ and 481,176 metric ton/yr of O₂ 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 MgCl₂ plants. Cost analysis, using a bottom up approach, still has much uncertainty but seems reasonable.



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 with modifications to dispersants and with particle size reduction
- 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 H_2 production cost estimate using H2A analysis framework
- SOM process demonstrated for 2 days with periodic replenishment of MgO producing Mg at rate up to 160 g/day

Future Work

- FY06
 - Continued slurry development using smaller particles
 - Mixer prototype improvements
 - Testing for hydrogen purity
 - Review of Mg reduction studies
 - Continued hydriding evaluation
 - Focus SOM development on
 - Modeling of SOM 1 and 3 tube cells
 - Condenser designs
- FY07 Plans
 - SOM cell experiments using 3 tube cell
 - Testing of slurry and mixer for robustness and hydrogen purity
 - Organics recycle process cost analysis
 - MgH_2 production process cost analysis
 - Updating cost analysis

Project Summary

- Many of the primary concerns have been addressed
 - Pumpable, stable slurry can be made
 - Slurry can be mixed with water to produce H₂
 - Oils can be easily separated from byproducts (cost estimate remains)
 - Mg can be easily hydrided (cost estimate remains)
 - Mg reduction process costs can likely be reduced to provide \$3.88/kg H₂ using estimate of SOM 37 tube cell and H2A framework
 - SOM process development is progressing well
- Upcoming work will refine and improve the results achieved to date

Supplementary Slides



Response to Reviewers Comments

- Freeze protection for on-board water
 - Freeze protection is a concern that will need to be addressed
 - Issue has been postponed in order to focus attention on show-stopper issues
 - If H_2 can be produced, transported, and stored cheaply enough then freeze protection techniques may be easy
 - The use of antifreeze and insulating and heating the water have been proposed
- Bladder - premature H_2 evolution and bladder wear
 - Our experience with the slurry indicates that H_2 will not be released from the slurry at the temperatures likely to be seen in the bladder
 - Byproduct is smooth and soft, not likely to cause wear on bladder
- Hydrogen purity
 - We are planning to perform H_2 purity tests this year
 - Until mixer system performs reliably, hydrogen purity tests don't aid the development effort



Publications and Presentations from the past year

- 12. 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
- 13. 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
- 14. Sigmar H. Tullmann, “Chemical Hydride Slurry for Hydrogen Distribution and Storage”, AltWheels Conference, Larz Anderson Auto Museum, Brookline, MA 17-18 September 2005
- 15. Andrew W. McClaine, “Chemical Hydride Slurry for Hydrogen Production and Storage”, Chemical Hydrogen Storage Systems Analysis Meeting, Argonne National Laboratory, October 12, 2005
- 16. Uday B. Pal and Srikanth Gopalan of Boston University, “Clean Energy Research at Boston University”, Clean Energy Conference, Boston, 8 November 2005



Critical Assumptions and Issues

- Mg reduction cost analysis
 - The cost analysis indicates that the cost of hydrogen could be \$3.88/kg.
 - Analysis is based on SOM/LSM process which should be cheaper than MgCl_2 processes because
 - SOM is a direct MgO reduction process
 - No minerals processing equipment
 - Minimal Mg processing required
 - Analysis based on single tube experiments
 - Need modeling of process with multiple tubes
 - Need further scale-up development
 - Used 6/10ths scaling law to scale from 21,773 metric ton/yr to 731,174 metric ton/yr
- Slurry solids loading
 - Process is most attractive with high solids loading
 - 60% solids loading may be acceptable, higher would be better
 - MgH_2 has not been behaving the same as LiH in the slurry
 - Particle shape may be causing difference
 - Milled particle testing should reveal if this is the case
- Mixer design must eventually be small, light, and robust
 - Slurries are generally handled with large scale equipment
 - Mixer must use smaller scale slurry handling equipment
- Hydrogen specifications are not well defined
 - Some fuel cell manufacturers are looking for humid hydrogen
 - Other fuel cell manufacturers are designing for dry hydrogen
 - Amount to store on vehicle has varied from 3kg to 10kg