Chemical Hydride Slurry for Hydrogen Production and Storage

2006 DOE Hydrogen Program Review

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Project ID # STP23

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

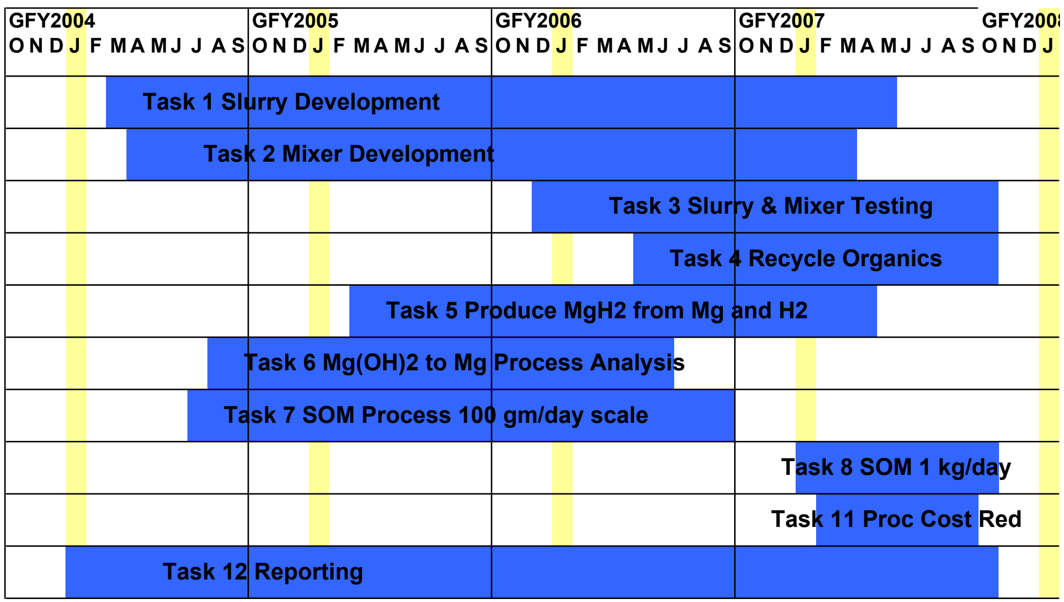
Partners

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

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

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Progress Slurry Development

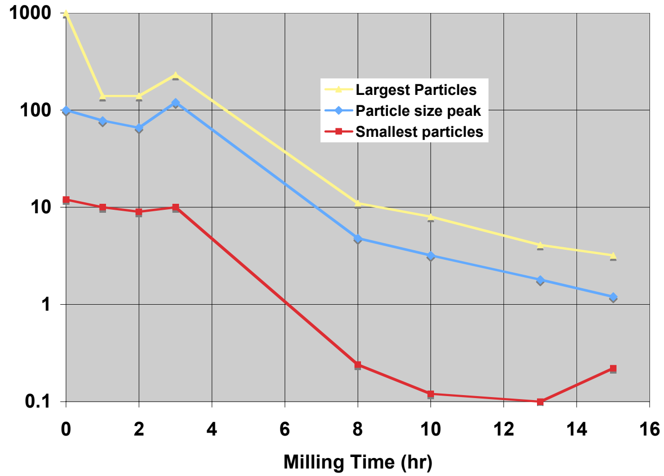
target: a pumpable slurry that stays liquid for months

- 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 MgH2 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

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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

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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
  - 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

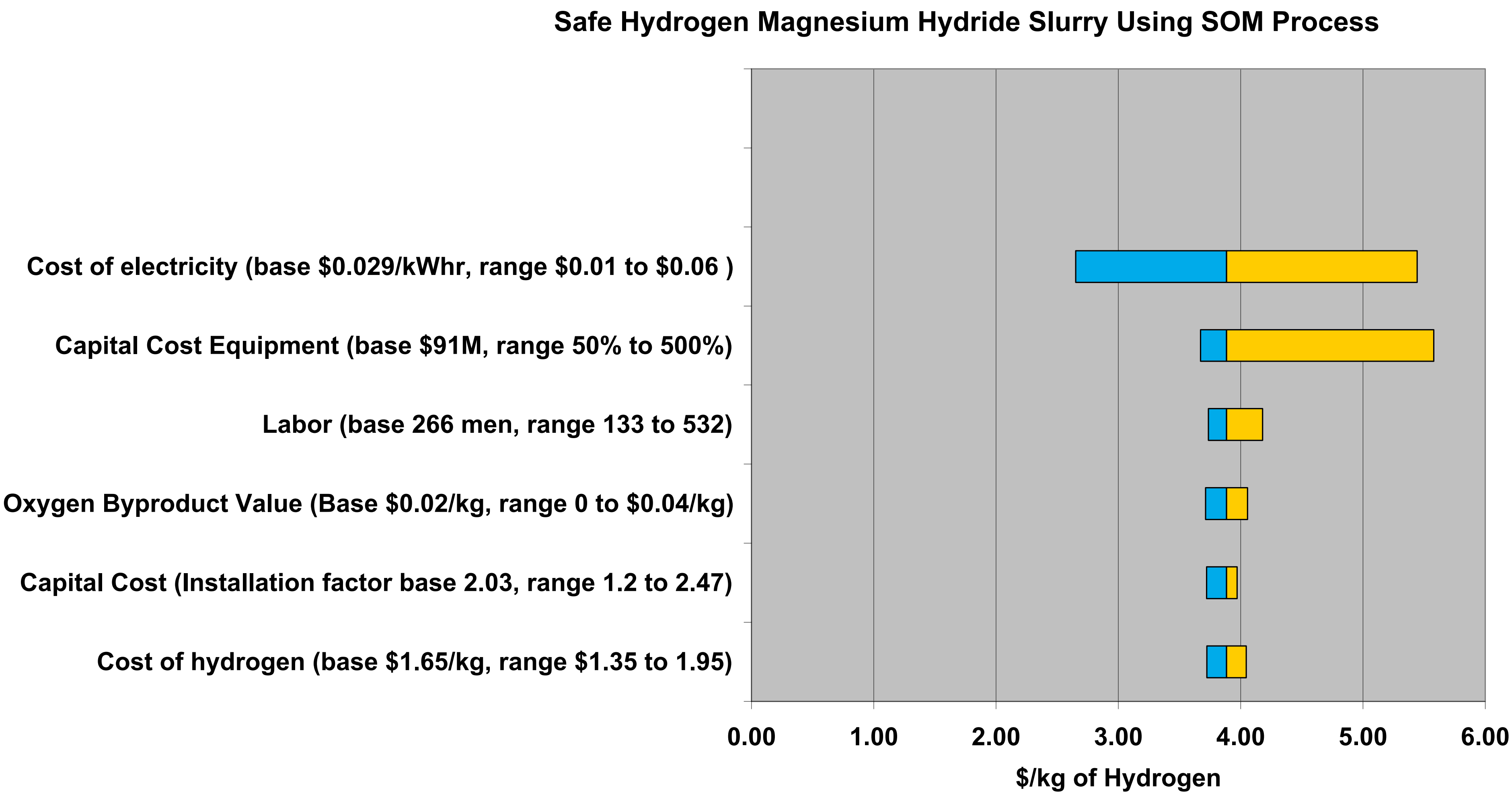
- Task plan
  - Evaluate Mg reduction alternatives
  - Determine operating and capital costs using bottom up approach
  - Evaluate cost of hydrogen using H2A framework

- Process steps
  - Reclaim oil
  - Calcine $Mg(OH)_2$ 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

Progress - Recycling MgO

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

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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 H2 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 H_2
  - 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 H_2 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 a 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