Encapsulated Metal Hydride for Hydrogen Separation

(Formerly Separation Membrane Development)

DOE Hydrogen Program

2003 Merit Review and Peer Evaluation

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May 2003

Relevance/Objective

Relevance & Goal

- Develop a metal hydride based packing material for hydrogen separation from low concentration streams.
  - Adsorbent in present PSA process is efficient for high concentration feed stock, not for low concentration
  - Hydrogen economy will need hydrogen recovery from low concentration feed stocks

Objective

- Produce a sol-gel encapsulated metal hydride packing material that will
  - Absorb hydrogen selectively
  - Not break down to fines
  - Resistant to reactive impurities
- Evaluate the material for hydrogen absorption from low concentration streams
  - Design and fabricate experimental apparatus
  - Conduct tests with synthesized gas mixtures
- Develop separation process with the new material

Approach (1)

- Metal hydride preferentially absorbs hydrogen from gas mixtures and has high potential for hydrogen separation.
- Metal hydride particles expands when absorbing hydrogen and contracts when releasing hydrogen that causes the particle to break down to micron size fines.
- The fines self compact and plug up separation column.
- Sol-gel encapsulation technique is used to convert the fines into stable granule that is suitable for packing separation columns.
- Sol-gel process uses a liquid colloidal dispersion method to produce porous silica matrix.

Approach (2)

- Unprotected metal hydride is sensitive to reactive impurities such as oxygen and carbon monoxide.
- Silica matrix protects the metal hydride from impurities by molecular sieving.
- Different recipes are developed to encapsulate the metal hydride fines in a matrix of porous silica to improve performance of the end product.
- Batch hydrogen absorption and flow-through absorption are used to test the performance.
- Performance is evaluated in hydrogen capacity, physical stability, and resistance to impurities.
- Success is defined by a product that maintains its capacity and stability.

Project Timeline

FY98 Project started with an original objective to develop silica based membrane for hydrogen separation. Produced small samples of sol-gel coated membrane on porous support. Permeation tests showed encouraging selectivity and rate.

FY99 Attempted to produce larger membrane for gas separation evaluation. Failed to produce defect free membrane, and encountered difficulty in balancing selectivity and rate. Decided changing the approach from membrane to encapsulated metal hydride.

FY00 Developed two methods to produce silica encapsulated metal hydride. Samples of encapsulated $LaNi_{4.25}Al_{0.75}$ demonstrated hydrogen absorption and resistance to particle breakdown. Designed and fabricated apparatus for testing hydrogen absorption from gas mixtures.

FY01 Started up the hydrogen absorption test apparatus. Demonstrated hydrogen separation from nitrogen mixtures.

FY02 Demonstrated hydrogen separation from gas mixtures containing methane and carbon monoxide. But absorption kinetics and capacity are reduced by carbon monoxide.

FY03 Emphasis placed on: (1) Develop pilot scale encapsulation technique. (2) Develop fabrication conditions and formulation to improve physical strength and CO resistance of the product.

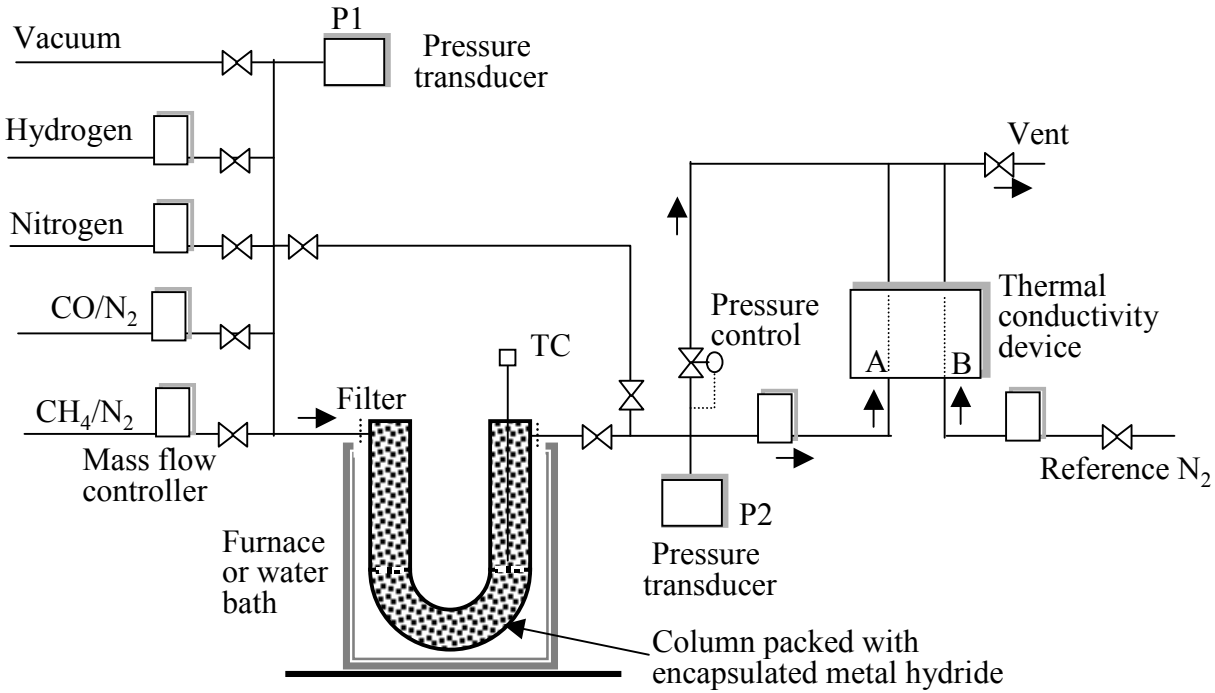
FY04 Plan: Complete pilot scale production development. Design and install pressure(and thermal) swing absorption test apparatus to develop a dual absorption hydrogen separation process combining the special properties of encapsulated metal hydride and molecular sieve. Success Criteria: Kilogram quantity “good” material produced. Hydrogen separation in a dual absorption process Demonstrated.

Accomplishments/Progress (1)

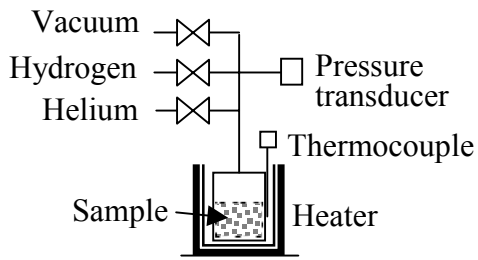
- Milestones:
  1. Begin hydrogen absorption test from mixtures containing nitrogen, methane and carbon monoxide (June 2002). - Accomplished.
  2. Develop variations of encapsulated samples for recipe optimization (March 2003). - Accomplished, 5 variations produced.
  3. Complete cost analysis (September 2003). - Delayed to next year due to insufficient funding.

Accomplishments/Progress (2)

- Apparatus for hydrogen absorption from following gas mixtures:

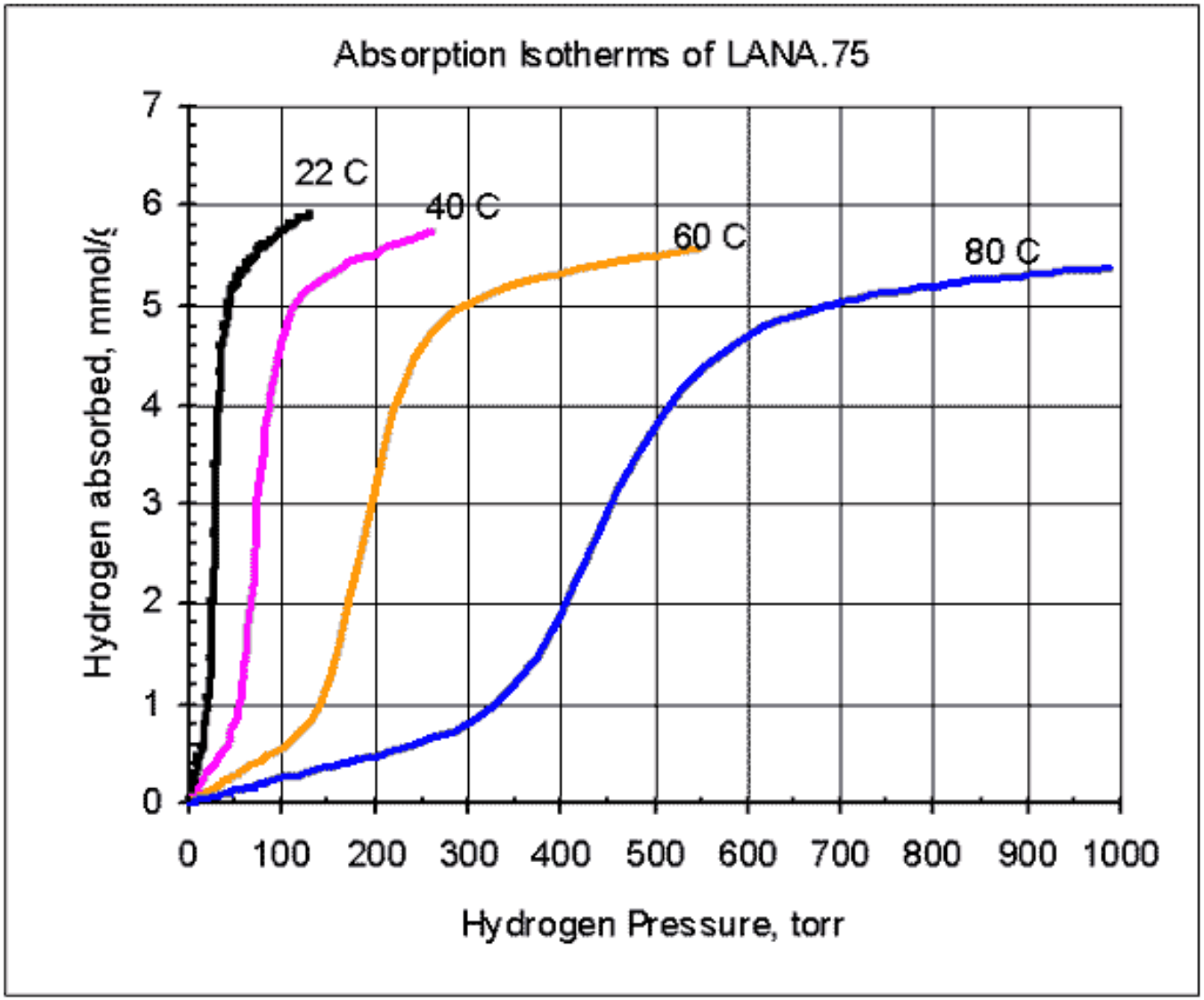


- Apparatus for batch hydrogen absorption tests



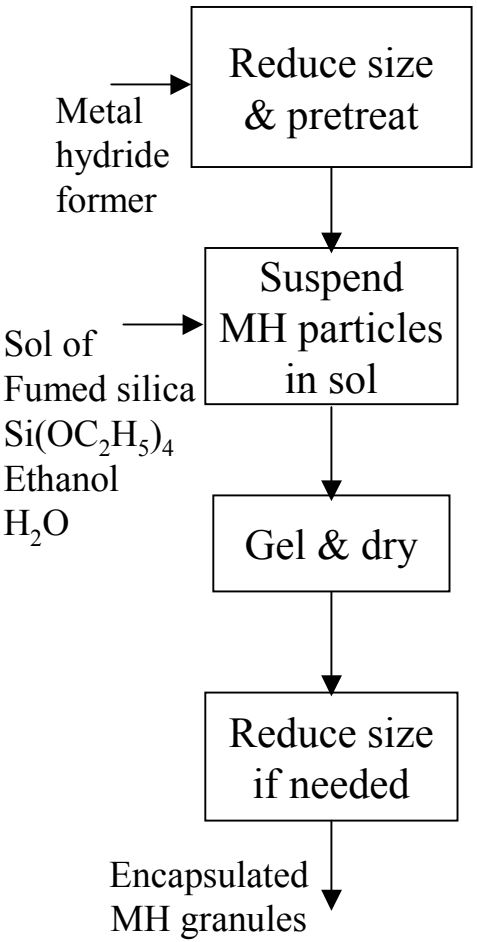
Accomplishments/Progress (3)

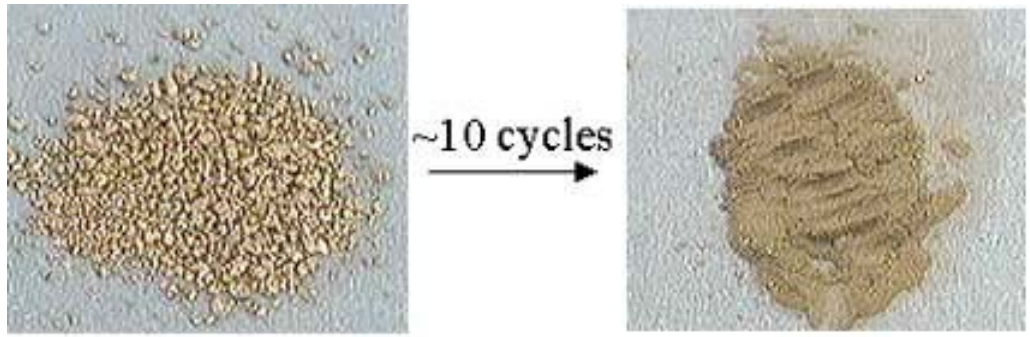
- Hydrogen Absorption Isotherms of the encapsulated metal hydride



Accomplishments/Progress (4)

- Basic steps of sol-gel encapsulation process

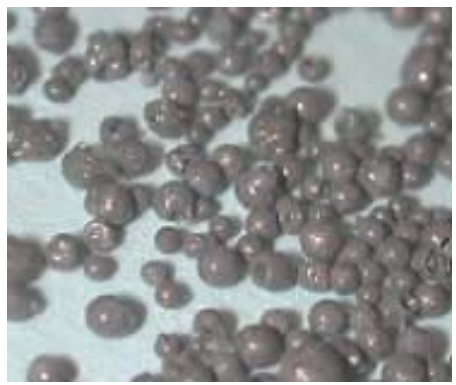




$$M + 1/2\,H_2 \rightleftharpoons MH + Heat$$

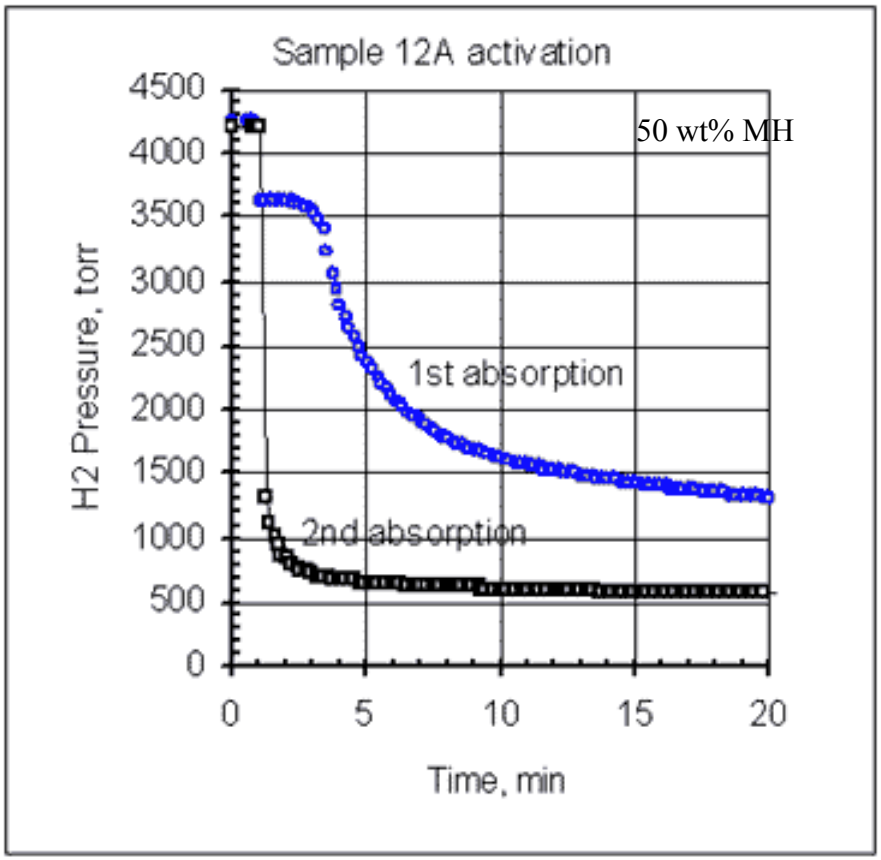
$$Si(OC_2H_5)_4 + 4\,H_2O \rightleftharpoons Si(OH)_4 + 4\,C_2H_5OH$$

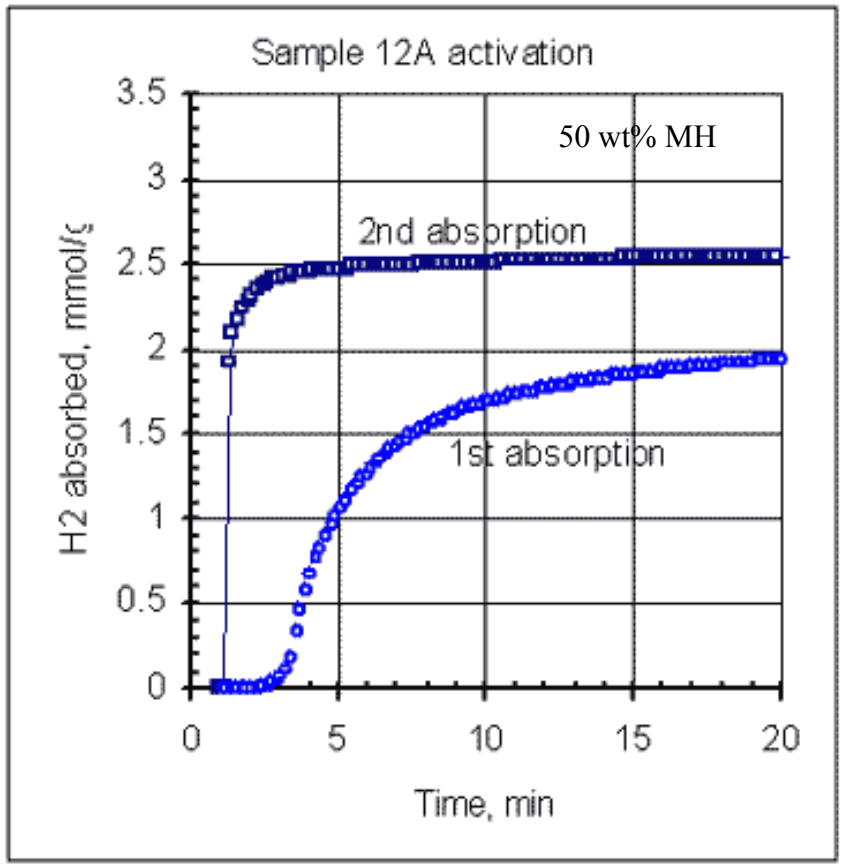
$$Si(OH)_4 \rightleftharpoons \text{Si - O -Si - O} + 2\,H_2O$$



Accomplishments/Progress (5)

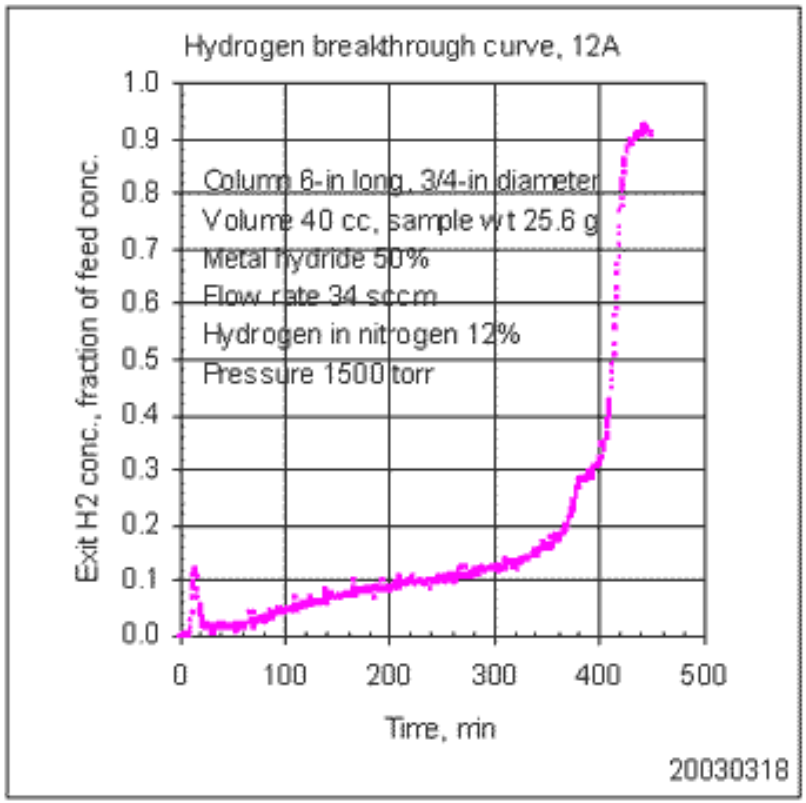
- Encapsulated metal hydride is ready to absorb hydrogen when first exposed to hydrogen

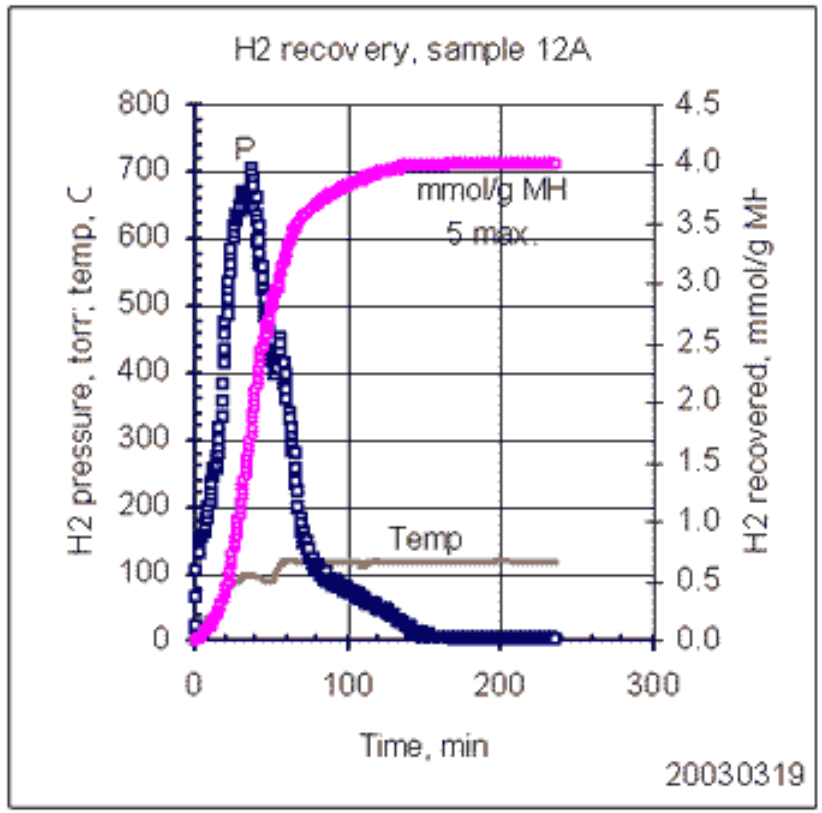




Accomplishments/Progress (6)

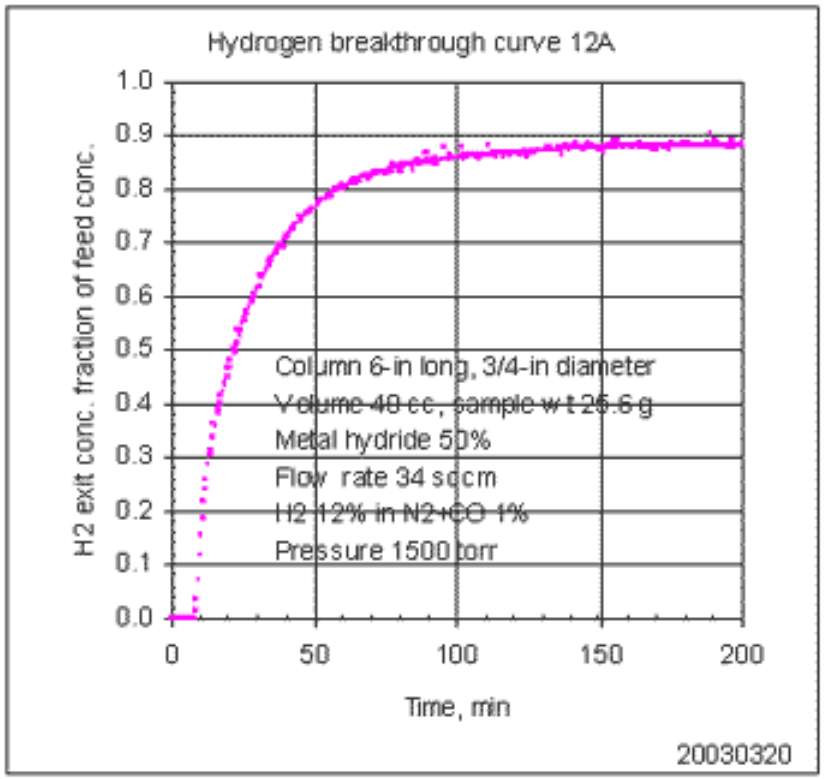
- Hydrogen separation from flowing 12% H_2 in N_2 by a 6-in long 3/4-in diameter column of encapsulated metal hydride

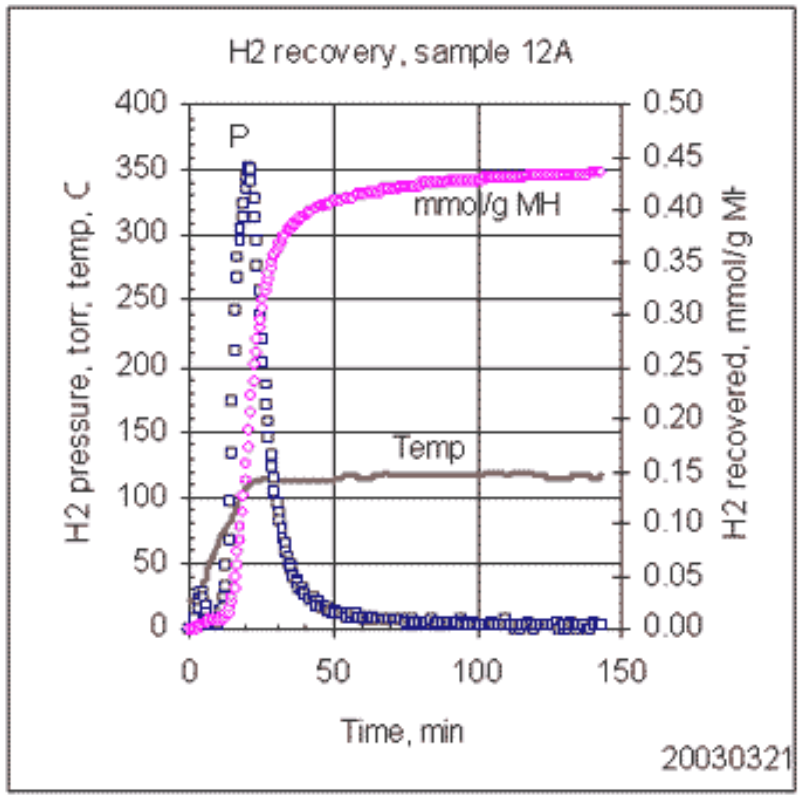




Accomplishments/Progress (6)

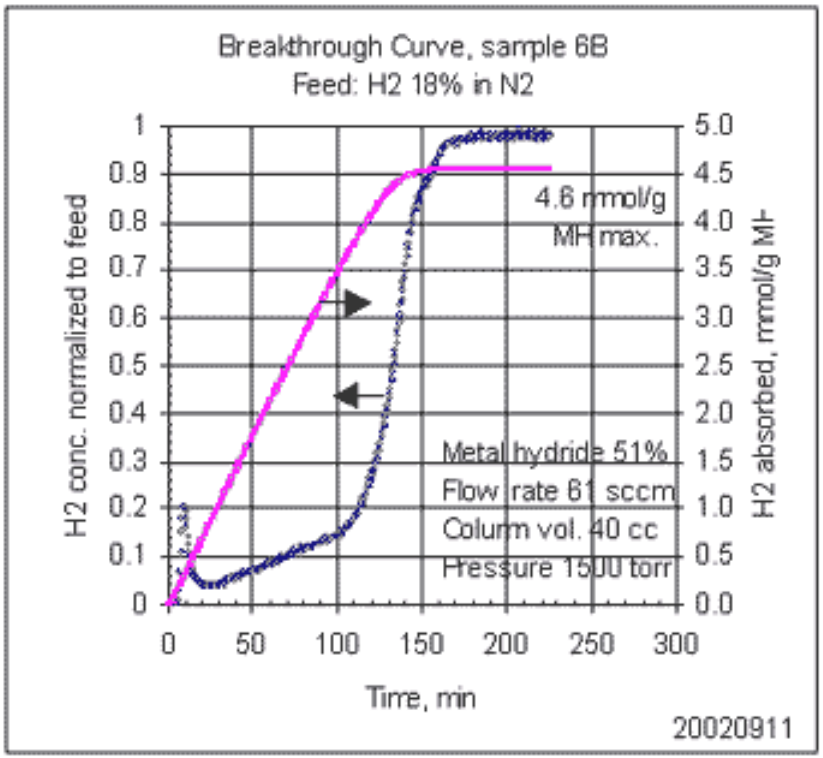
- Hydrogen separation from12% H_2 in (N_2 + 1% CO) by a 6-in long 3/4-in diameter column of encapsulated metal hydride

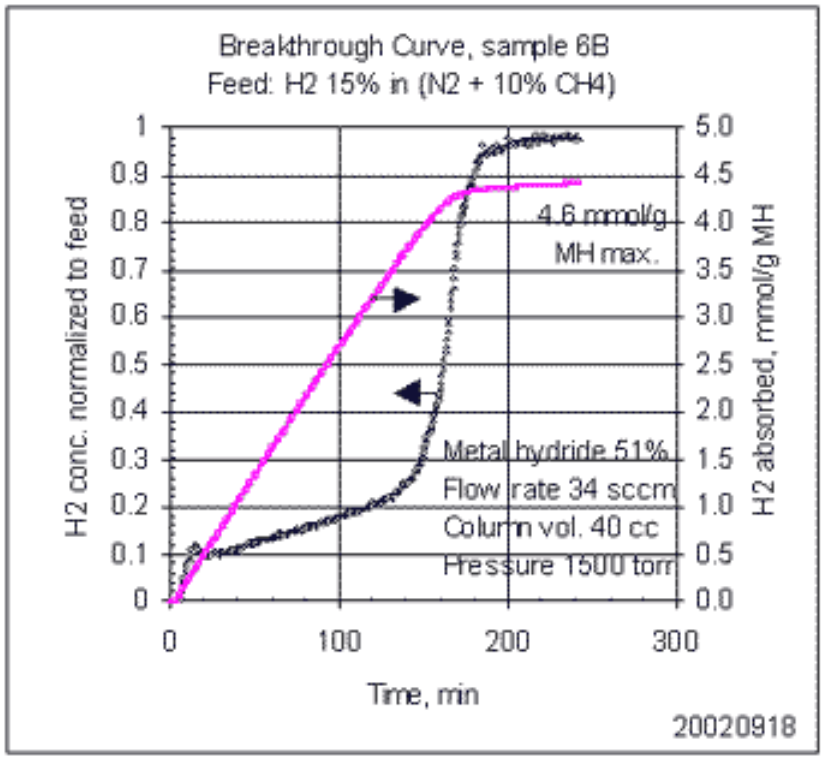




Accomplishments/Progress (6)

- Hydrogen breakthrough curve with and without CH_3 by a 6-in long 3/4-in diameter column of encapsulated metal hydride

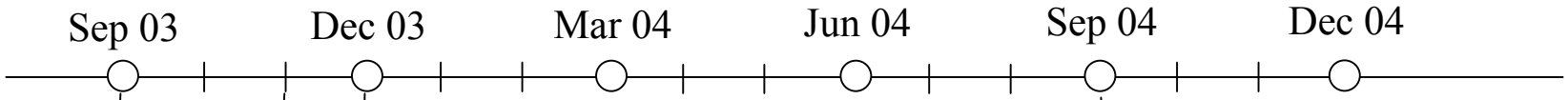




Interaction and Collaboration

- Ongoing join effort with Clemson University via the SCUREF (South Carolina University Research & Education Foundation) program to optimize and scale-up the metal hydride/sol-gel composite fabrication process. Effort has produce two patent disclosures on gelation and pore formation methods.
- Initial discussion with University of South Carolina on using the hydrogen absorbing material to develop a dual absorbent pressure swing absorption process for recovering hydrogen from low concentration streams.

Plans and Future Milestones



- Conduct economic analysis of the new process.
- Complete experimental testing of dual absorbent PSA.
- Startup the experimental, dual absorbent pressure swing absorption process.
- Improve the external gelation process to produce kilogram quantity encapsulated packing material
- Design and begin fabrication a pressure swing experimental apparatus to develop the dual absorbent process concept.
- Fine tune the porous matrix structure to improve its protection for the encapsulated metal hydride against impurities.