Engineering Tasks for the MHCOE

METAL HYDRIDE CENTER OF EXCELLENCE

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SAVANNAH RIVER NATIONAL LABORATORY

We Put Science To Work

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Project ID #: STP 20

Overview

Timeline

- Start - Oct. 1 2006
- End - Sept. 30, 2009
- % complete – 10%

Budget

- Funding Received in FY08
  - $180K
- Funding for FY07
  - $300k
- Funding Reduced Due to Overlap with Future Hydrogen Storage Engineering Center of Excellence

Barriers Addressed

- System Gravimetric Capacity
- System Volumetric Capacity
- System Discharge Rate
- System Charging Time

Partners

- NASA-Jet Propulsion Laboratory
- University of Nevada-Reno
- Sandia National Laboratory
- University of Utah

Objectives

- Determine Heat Management Requirements for Refueling Station Based on Metal Hydrides
- Determine Sorption Kinetics for LiMgN Sufficient for Initial Design of Storage System Utilizing this Material

Milestones

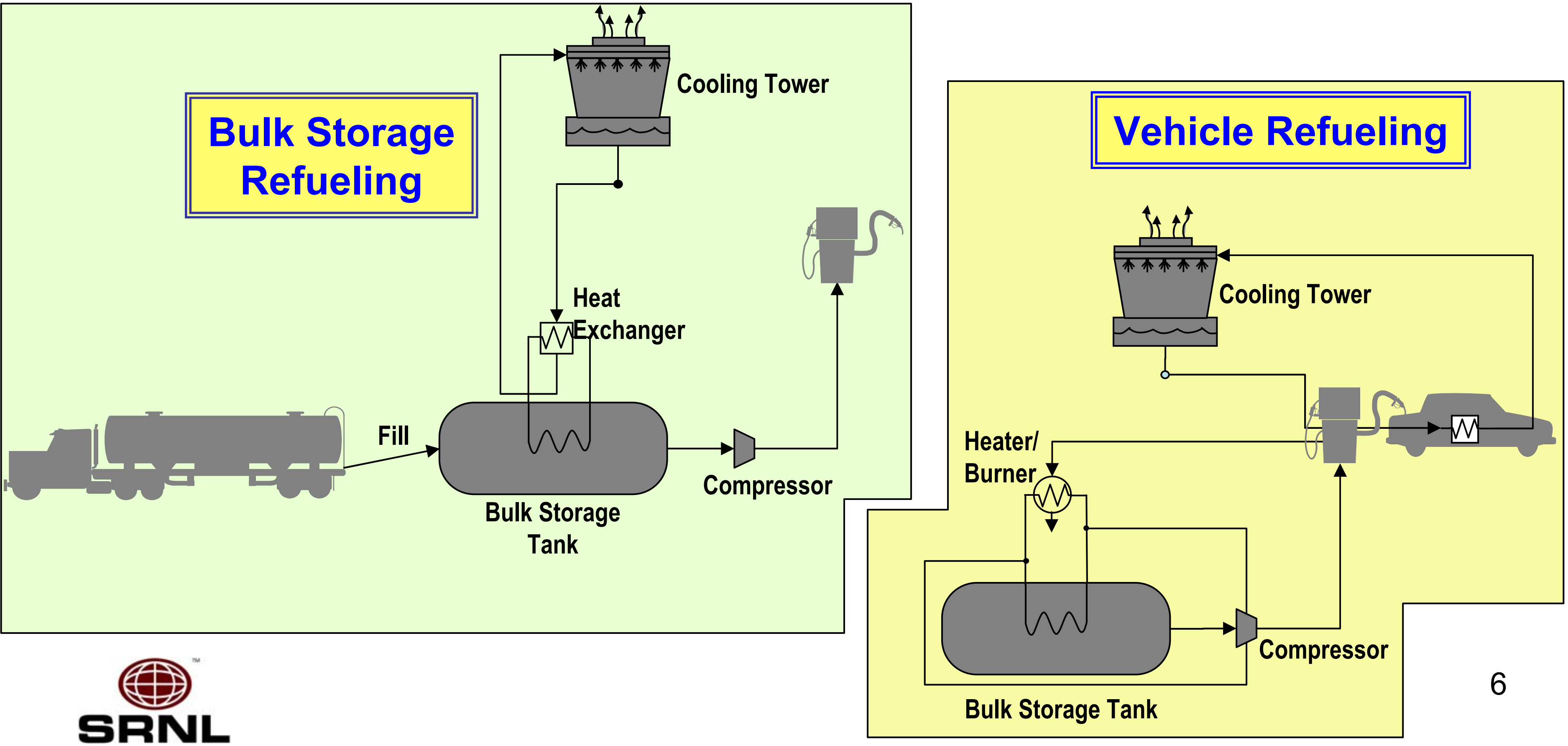
- **System Analysis** (9/’07 end)
  - **Develop heat and mass transfer models to assess MHCoE storage materials’ performance in a hydrogen storage system *(reported at ’07 annual review)* and determine thermal management requirement during refueling for at least three different heats of reaction. 9/07**
- **LiMgN Kinetics** (1/’08 start)
  - **Determine the hydrogen sorption kinetics and mechanisms of LiMgN over the temperature and pressure range of interest to DOE for automotive hydrogen storage applications. 9/08**

System Analysis Approach

- Developed System Model Using ASPEN+® Software
- Determine Fueling Station Parameters
- Modeled Required Heat Transfer
  - Modeled Required Heat Removal From On-Board Storage System
  - Modeled Heat Transfer to Bulk Storage Tank
    - Based heat generation rates on metal hydrides with range of overall heats of reaction
    - Charged at rates given in DOE Technical Targets
      - Varied number of vehicles refueling simultaneously

Refueling Station System Diagram

- Two Stages of Hydrogen Transfer Occur at the Refueling Station
- Only Vehicle Refueling Modeled Here

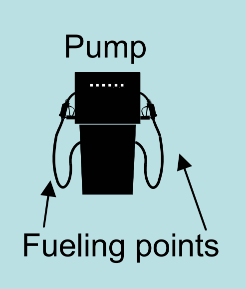


Fuel Storage Requirements

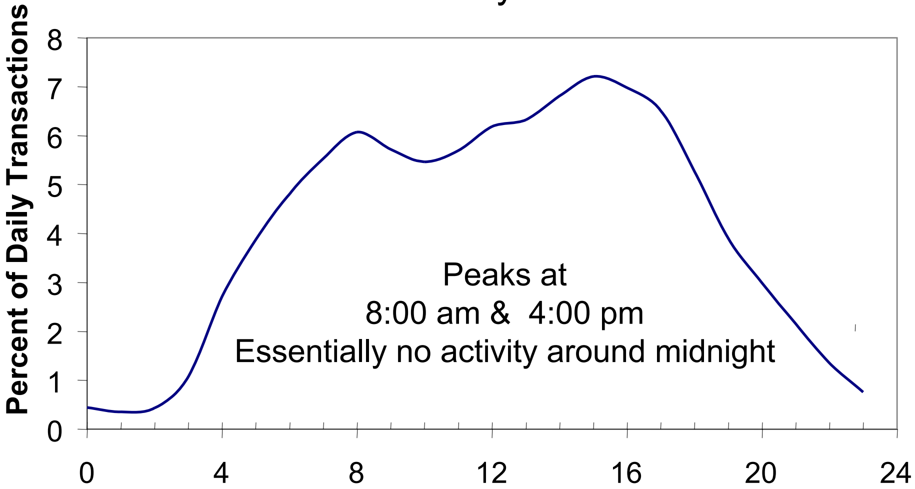
Station Design

2 fueling points per pump
8 pumps per station
4 kg H_2 dispensed per vehicle
3 minutes refueling per vehicle
5 minutes per car for payment, connecting and disconnecting hoses and grounds
7.5 vehicles fueled/hour/fueling point (maximum)
1 kg H_2 = 1 gal gasoline (energy equivalent)

480 kg H_2 peak hourly fuel demand
6,850 kg H_2 daily fuel demand
20,000 kg H_2 for 3-day on-hand fuel supply



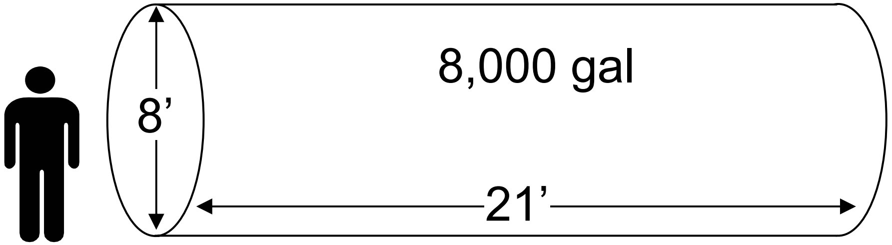
Station Fueling Profile
- Thursdays*



Peaks at
8:00 am & 4:00 pm
Essentially no activity around midnight

* From Hydrogen Delivery Infrastructure Option Analysis delivered at *DOE and FreedomCAR & Fuel Partnership Hydrogen Delivery and On-Board Storage Analysis Workshop* January 25, 2005 Washington DC

Standard Gasoline Bulk Storage Tank



20,000 kg of Hydrogen Would Occupy:

689 bar (10,000 psi)	**540,000 L**	**140,000 gal**	**17.5 Std Tanks**
Liquid	**280,000 L**	**73,333 gal**	**9.2 Std Tanks**
Metal Hydride**	**200,000 L**	**50,000 gal**	**~6.3 Std Tanks**

**Averaged over all metal hydrides in Figure 4 of
Hydrogen Storage Materials Workshop Proceedings 2002

Modeling Assumptions

- Steady State Process
  - Reasonable for high flows of heat transfer fluid
    - Rapid transfer of energy
  - Neglects change in bed temperatures at onset of refueling
    - Both for vehicle and bulk tank
  - Immediate response of coolant system
  - Energy balance
    - Uniform temperature in storage media is maintained
    - Instantaneous transfer of energy
- Ambient Temperature of 25°C

Modeling Assumptions (cont)

- Hydride used as Fuel Supply Source
  - Identical hydride for bulk storage and vehicle storage
- No Recovery of Heat Accounted for
  - All heat dissipated through cooling tower
  - Cooling tower sized for hourly peak fueling
  - Cooling tower is sized such that bulk refueling heat dissipation can occur during off hours

Mass and Energy Balances

Basic steady-state energy balance, mass balance, and mass diffusion relations used for cooling tower design

$$\frac{dT_w}{dV} = \frac{\frac{dh_a}{dV} - C_{p,w}\left(T_w - T_{ref}\right)\frac{dw_a}{dV}}{\left[\frac{\dot{m}_{w,i}}{\dot{m}_a} - \left(w_{a,o} - w_a\right)\right] C_{p,w}}$$

$$\frac{dw_a}{dV} = -\frac{Ntu}{V_T}\left(w_a - w_{s,w}\right)$$

$$\frac{dh_a}{dV} = -\frac{Le \cdot Ntu}{V_T}\left[\left(h_a - h_{s,w}\right) + \left(w_a - w_{s,w}\right)\left(1/Le - 1\right)h_{g,w}\right]$$

where:

T_w is the water temperature

T_{ref} is the reference temperature, typically 25ºC

m_a is the mass flow rate of air through the cooling tower

$m_{w,i}$ is the mass flow rate of water through the tower

h_a is the enthalpy of the moist air per pound of dry air

$h_{s,w}$ is the enthalpy of saturated air at the water volume

$h_{g,w}$ is the enthalpy of saturated water vapor

dV is a differential volume

V_T is the total volume

w_a is the humidity ratio at the water temperature

$w_{a,o}$ is the humidity ratio at exit water conditions

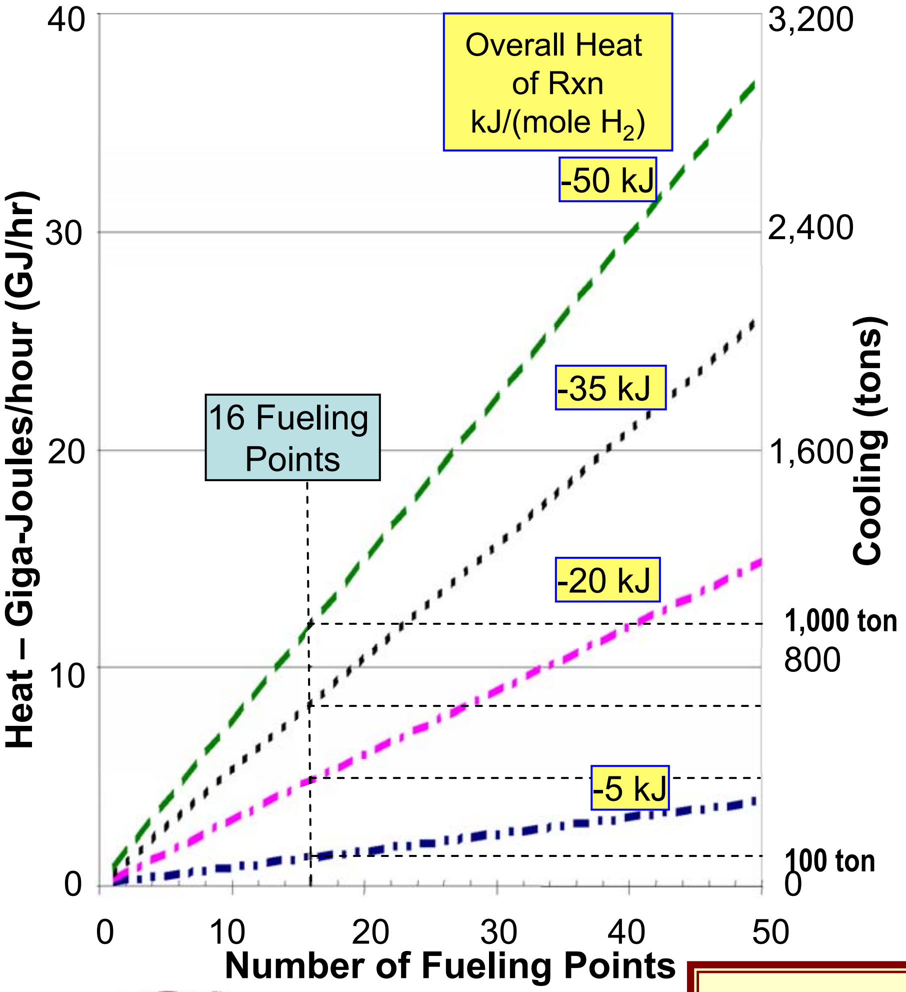
$w_{s,w}$ is the humidity ratio of saturated air

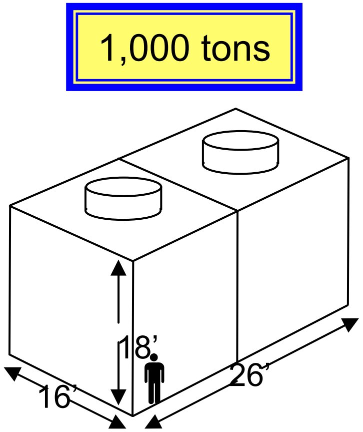
$C_{p,w}$ is specific heat of water

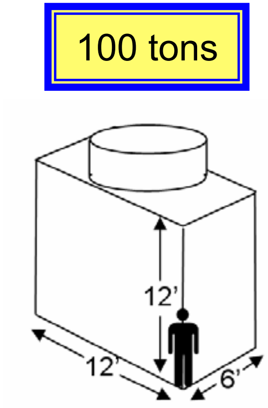
Ntu is the number of transfer units for the cooling tower

Le is the Lewis number

Maximum Hourly Heat From Fueling Vehicle







The cooling tower requirements for fueling stations are significant but technologically feasible

Cooling Tower Water Rates Calculation

Cooling = 100 tons
Cycles = 4

Cooling = 1,000 tons
Cycles = 4

Recirculation – typically 0.03 gpm per ton of cooling required

Recirculation = 3 gpm * 100 tons
= 300 gpm

Recirculation = 3 gpm * 1,000 tons
= 3,000 gpm

Evaporation – typically 1% of recirculation rate

Evaporation = 0.01 * 300gpm
= 3 gpm
4,320 gpd

Evaporation = 0.01 * 3,000gpm
= 30 gpm
43,200 gpd

Blowdown = 3 gpm / (4 – 1)
= 1 gpm
1,440 gpd

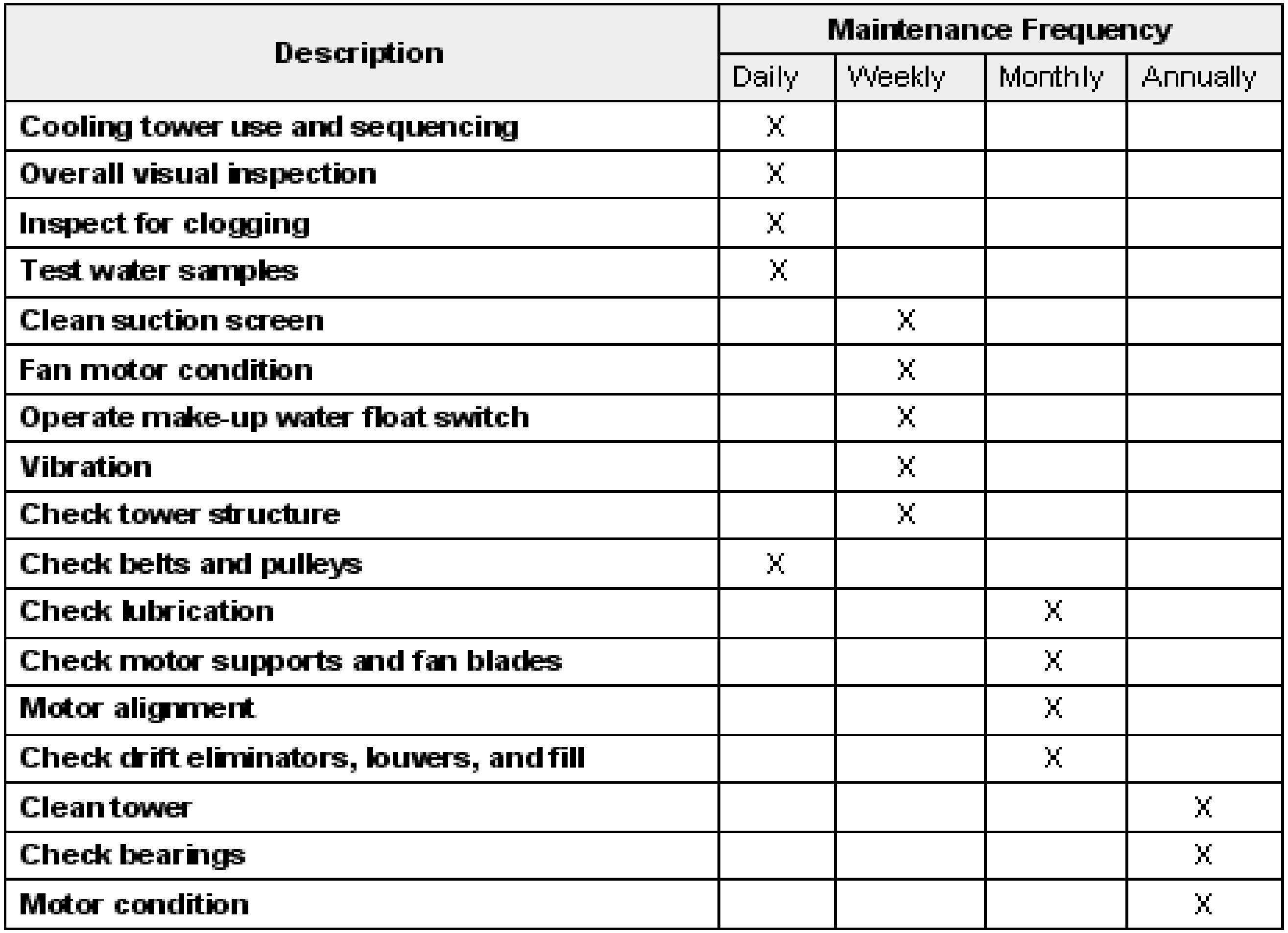
Blowdown = 30 gpm / (4 – 1)
= 10 gpm
14,400 gpd

Make-up = 4,320 gpd + 1,440 gpd
= 5,760 gpd

Make-up = 43,200 gpd + 14,400 gpd
= 57,600 gpd

Make-up cooling water requirements for continuing operation are substantial

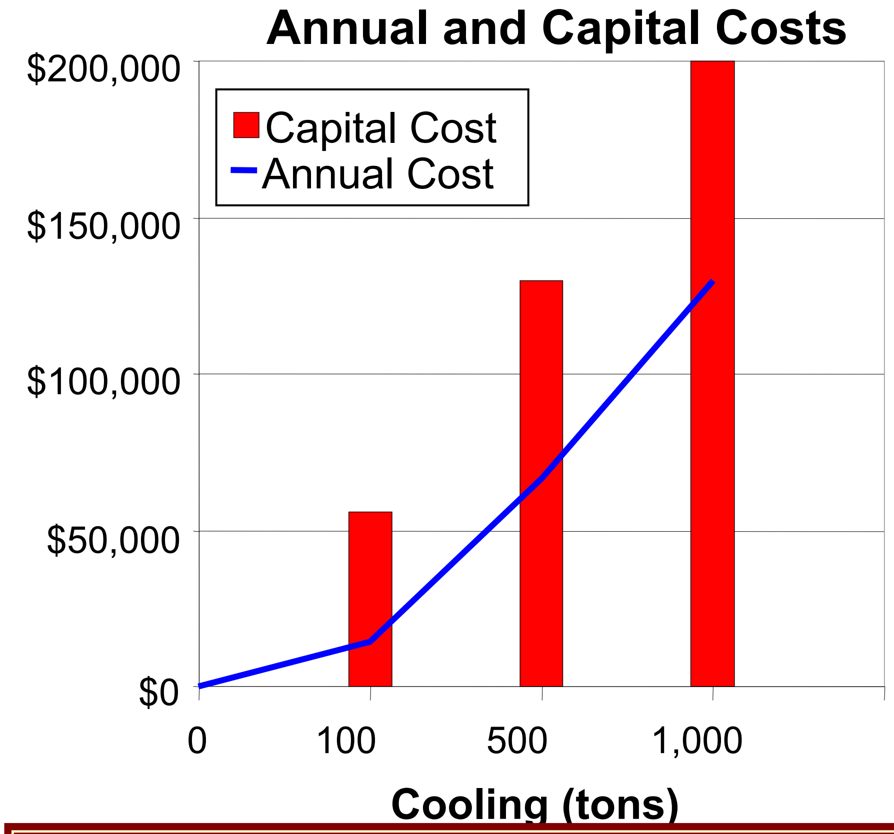
Cooling Tower Maintenance Checklist

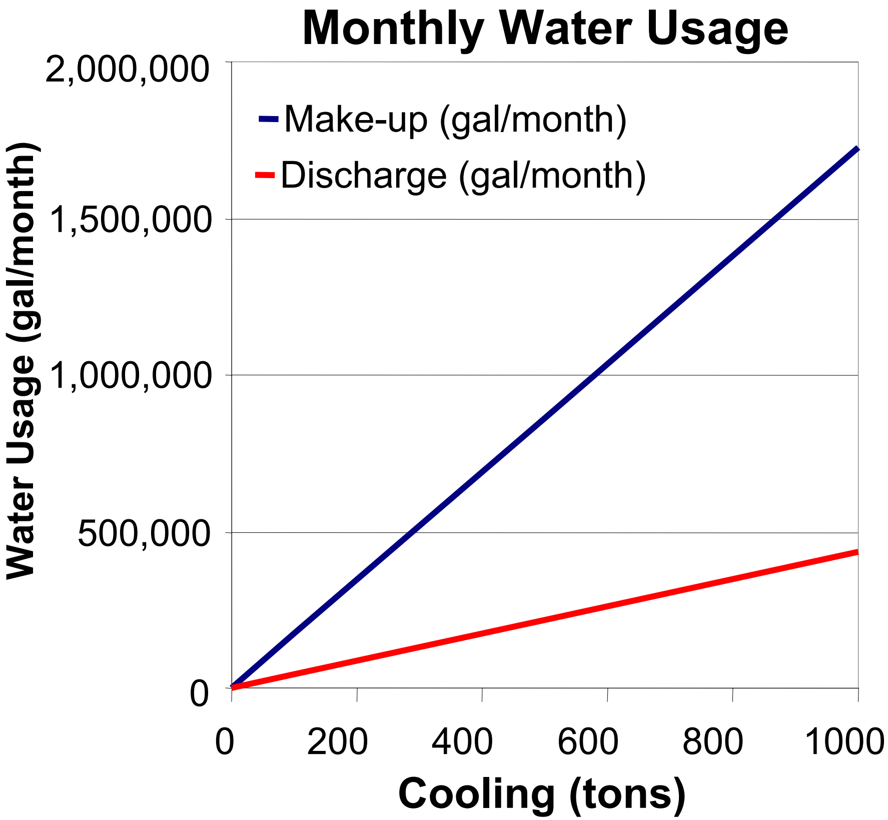


Description	Maintenance Frequency			
	Daily	Weekly	Monthly	Annually
Cooling tower use and sequencing	X			
Overall visual inspection	X			
Inspect for clogging	X			
Test water samples	X			
Clean suction screen		X		
Fan motor condition		X		
Operate make-up water float switch		X		
Vibration		X		
Check tower structure		X		
Check belts and pulleys	X			
Check lubrication			X	
Check motor supports and fan blades			X	
Motor alignment			X	
Check drift eliminators, louvers, and fill			X	
Clean tower				X
Check bearings				X
Motor condition				X

Maintenance costs need to be considered as part of overall fueling costs

Cost and Water Usage





The operating cost and water demands for a given size cooling tower must be considered in fueling station design

1 ton of cooling = 12,000 Btu/hr
= 351.7 MW

Conclusions

- Large quantities (8-10 GJ/hr) of heat are generated during hydrogen refueling.
- Cooling towers (100-1000 tons) will occupy a large footprint and have significant operating costs.
- Bulk fuel storage tanks will need to be approximately 4 times as large as those in existing gasoline filling stations to match capacity if hydrides are used for storage.
- Significant water and waste water resources are needed for cooling tower operation.

Future Work

- Investigate alternative cooling methods.
- Investigate different hydrides for the bulk and vehicle storage medias.
- Identify different fueling station designs.
- Identify uses of low grade waste heat.

Overview: LiMgN Kinetics

- Theoretical H_2 storage capacity is also 8.2 wt% by Lu et. al.* within the MHCoE
  - 8.0 wt% observed experimentally

$$\mathrm{LiMgN + H_2 \leftrightarrow \tfrac{1}{2}\,Mg(NH_2)_2 + \tfrac{1}{2}\,MgH_2 + LiH}$$

- Rapid discharge observed at 160-220°C
- Rehydrogenation observed under moderate temperature and pressure
  - 160°C and 140 bar
- Dehydrogenation proceeds through an intermediate step

$$\mathrm{\tfrac{1}{2}\,Mg(NH_2)_2 + \tfrac{1}{2}\,MgH_2 + LiH \rightarrow Li_{2x}Mg_{1-x}(NH)_2 + MgH_2 + H_2 \rightarrow LiMgN + H_2}$$

- Accelerated reversibility has been observed using 4 wt.% $TiCl_3$ dopant.*

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* Lu *et al. J. Phys. Chem. C*, **111**,pp. 12129. (2007)

Objectives

- Verify reversibility conditions of 4wt% $TiCl_3$ doped LiMgN
- Outline dehydrogenation and hydrogenation kinetics under various temperature and pressure conditions anticipated for **hydrogen storage system design**
- Explore Li:Mg ratio and transition metal content on both hydrogenation and dehydrogenation kinetics.

Experimental Plan

- Perform isothermal kinetic studies under well-defined, controlled reaction conditions utilizing Seivert's apparatus
- Experimental conditions to be explored:

- Broad Range Kinetics Characterization
  - Composition: 1LiH:1Mg(NH)$_2$+4wt% TiCl$_3$
    - Charge: 100 – 180°C/70 & 140bar
    - Discharge: 100 – 260°C/1bar

- Kinetics Optimization
  - Charge: 100°C/140bar
  - Discharge: 100°C/1bar
    - LiH:Mg(NH)$_2$= 2 & 3
    - TiCl$_3$ = 0.5, 1, 2wt%

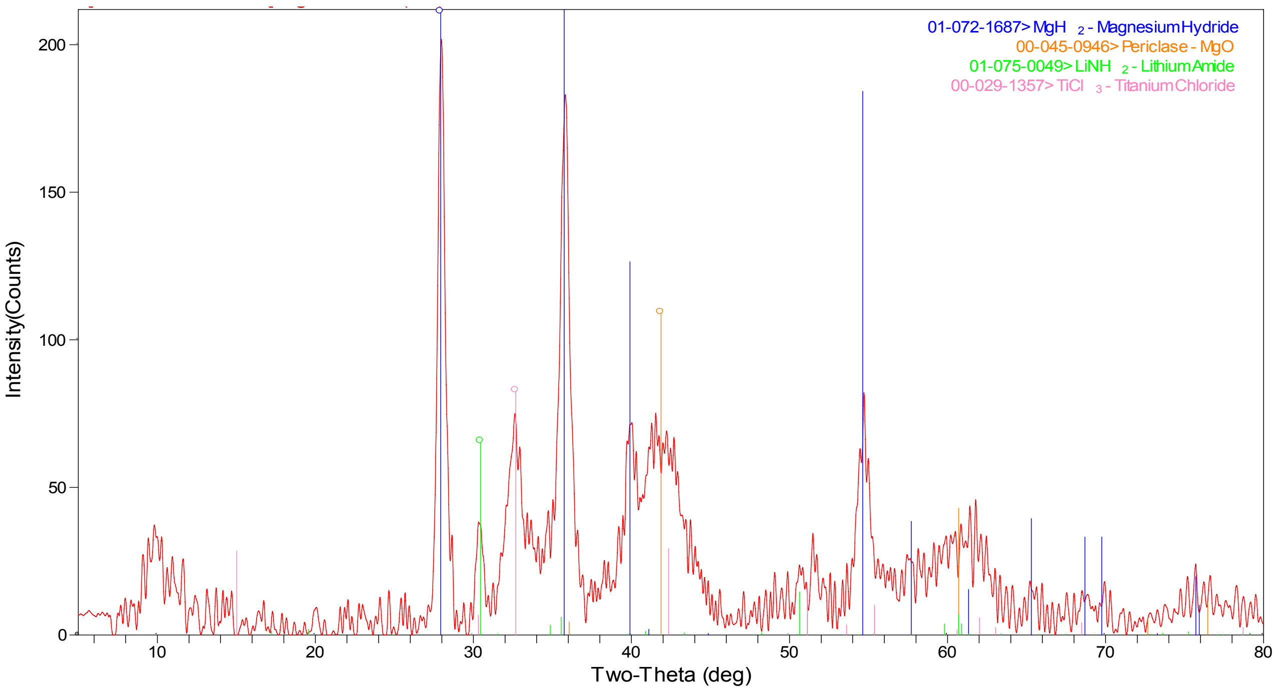
- XRD analysis at various points in hydrogenation/dehydrogenation cycle

- *Deliverable*:
  - Experimental data required to determine storage system heat load and performance characteristics.
  - Optimized composition for kinetics and capacity.

Material Characterization for LiMgN System

$LiNH_2$:MgH_2 Preparation:

- Fritsch milled 1$LiNH_2$:1MgH_2 + 4 wt% $TiCl_3$ for 2 hr. at 500 rpm under Ar Rotation changed every 30 min.



Identified primarily $LiNH_2$ and MgH_2 present, with unreacted $TiCl_3$ and residual contamination oxides.

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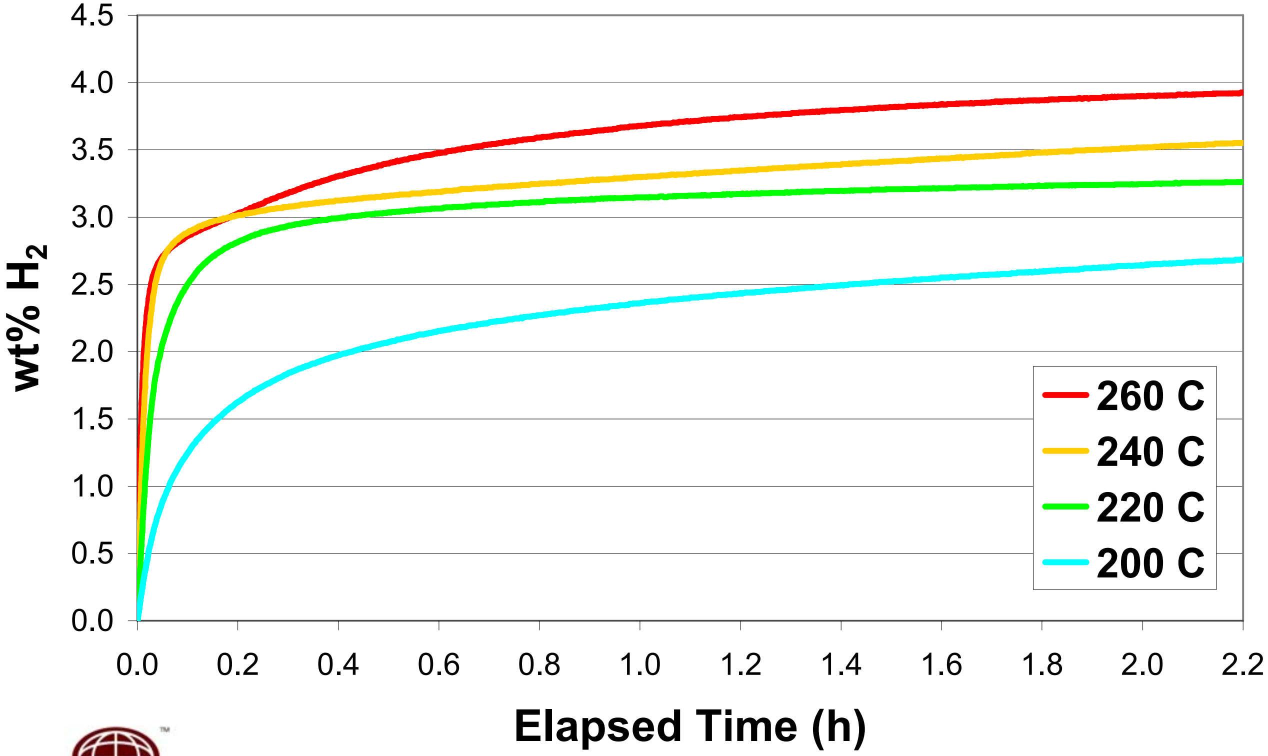
Isothermal Discharge Kinetics

- 1MgH_2:1$LiNH_2$ + 4wt% $TiCl_3$
- Dehydrided from as-milled condition
- Nominal reservoir pressure is 1 bar to

(maximum 0.1 bar pressure rise)



- As milled material readily dehydrides 2.5 - 3wt% in 30 min.
- Max wt% observed
  - 3.9 over 2 hour period
  - 4.1 wt% after 4.5 hours

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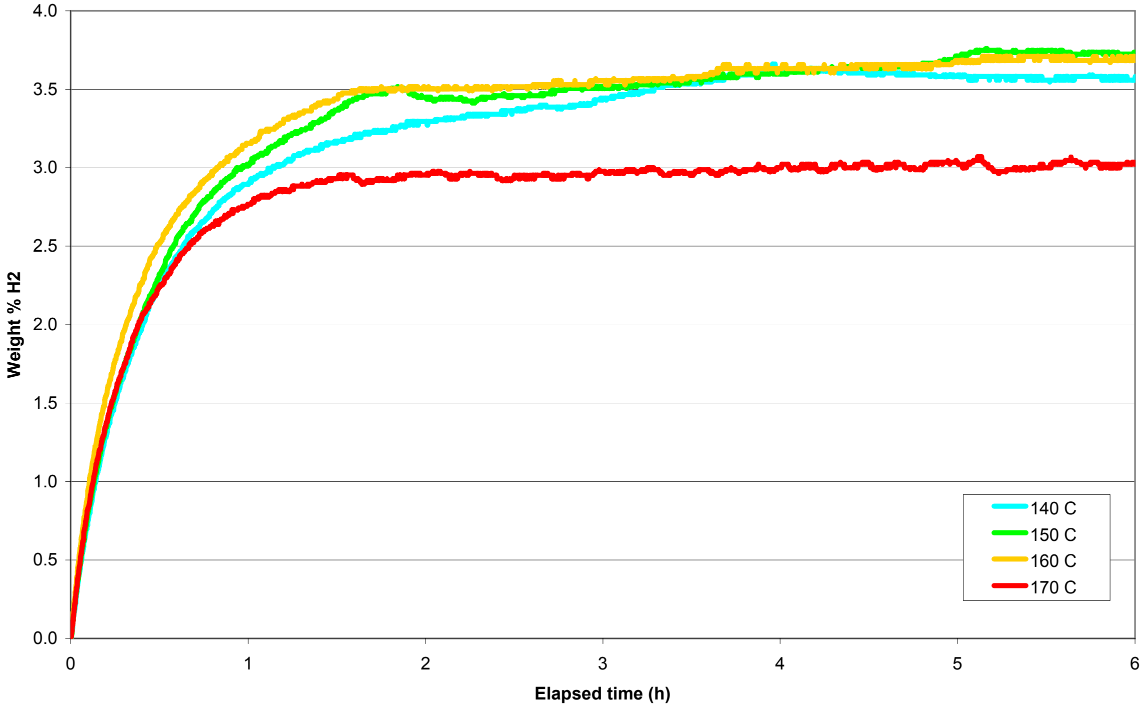
Isothermal Charging Kinetics

- $1MgH_2$:$1LiNH_2$ 4 wt% $TiCl_3$
- Charged after discharged at 220°C/3 hrs
- Nominal charging pressure 140 bar

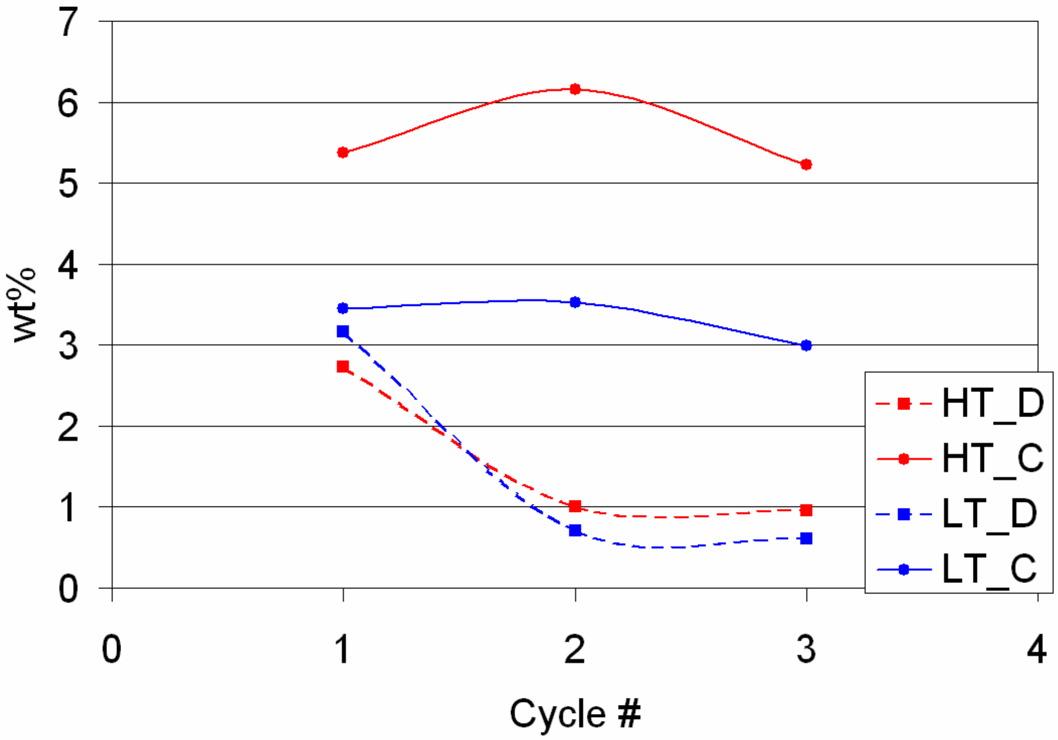
  (maximum 0.5 bar pressure drop)



- Recharging confirmed over a broad range of temperatures
- 140°C -160°C data show similar rehydriding performance with 3.7wt% achieved after 2-3 hrs.
- 170°C data show that thermodynamic limit of hydrogen uptake reached at 3wt%

Cyclic Behavior of LiMgN

- Two Cycles investigated
  - HT Cycle
    - Discharge: 280C/1bar/3hrs
    - Charge: 160C/140bar/6hrs
  - LT Cycle
    - Discharge: 220C/1bar/3hrs
    - Charge: 150C/140bar/6hrs



- Material charges consistently through 3 cycles with some degradation after second cycle.
- Discharge capacity loss of 60% due to lack of full recharging.

Future Plans

Future Plans

- –XRD analysis of products as a function of charge state currently being conducted
- –Perform subsequent discharge tests after recharge to obtain consistent starting state
- –Continuously monitor discharge gas with RGA to observe possible NH_3 loss as a function of temperature
- –Expand discharging temperatures for optimum recharging kinetics
- –Test range of LiH:$Mg(NH)_2$ compositions
- –Test various catalyst concentrations to minimize catalyst mass and cost.

Publications

- Mark P. Jones. “Solid State Hydride System Engineering - Integrated Component and System Model.” *Washington Savannah River Company Document*, WSRC-TR-2007-00391, Rev. 1, **2007**.