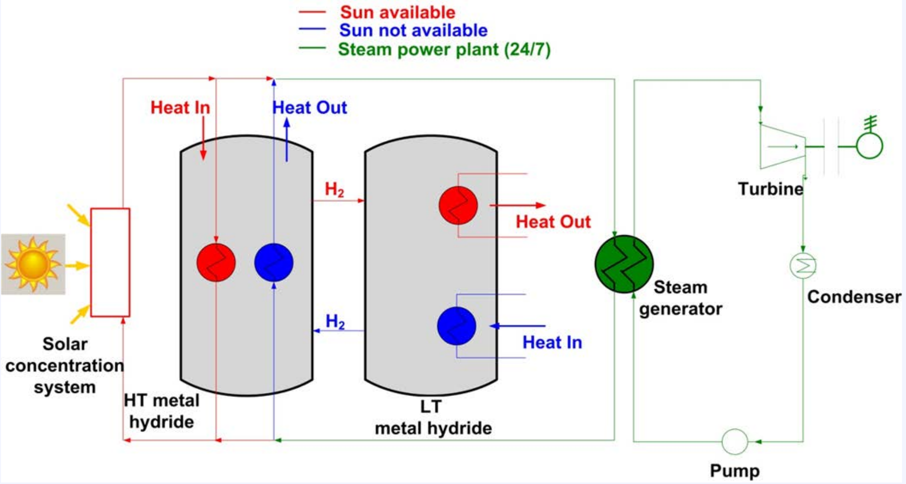
# Low-Cost MH TES Systems for CSP

## Savannah River National Laboratory




Presenter: Ted Motyka

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Project Start: FY13

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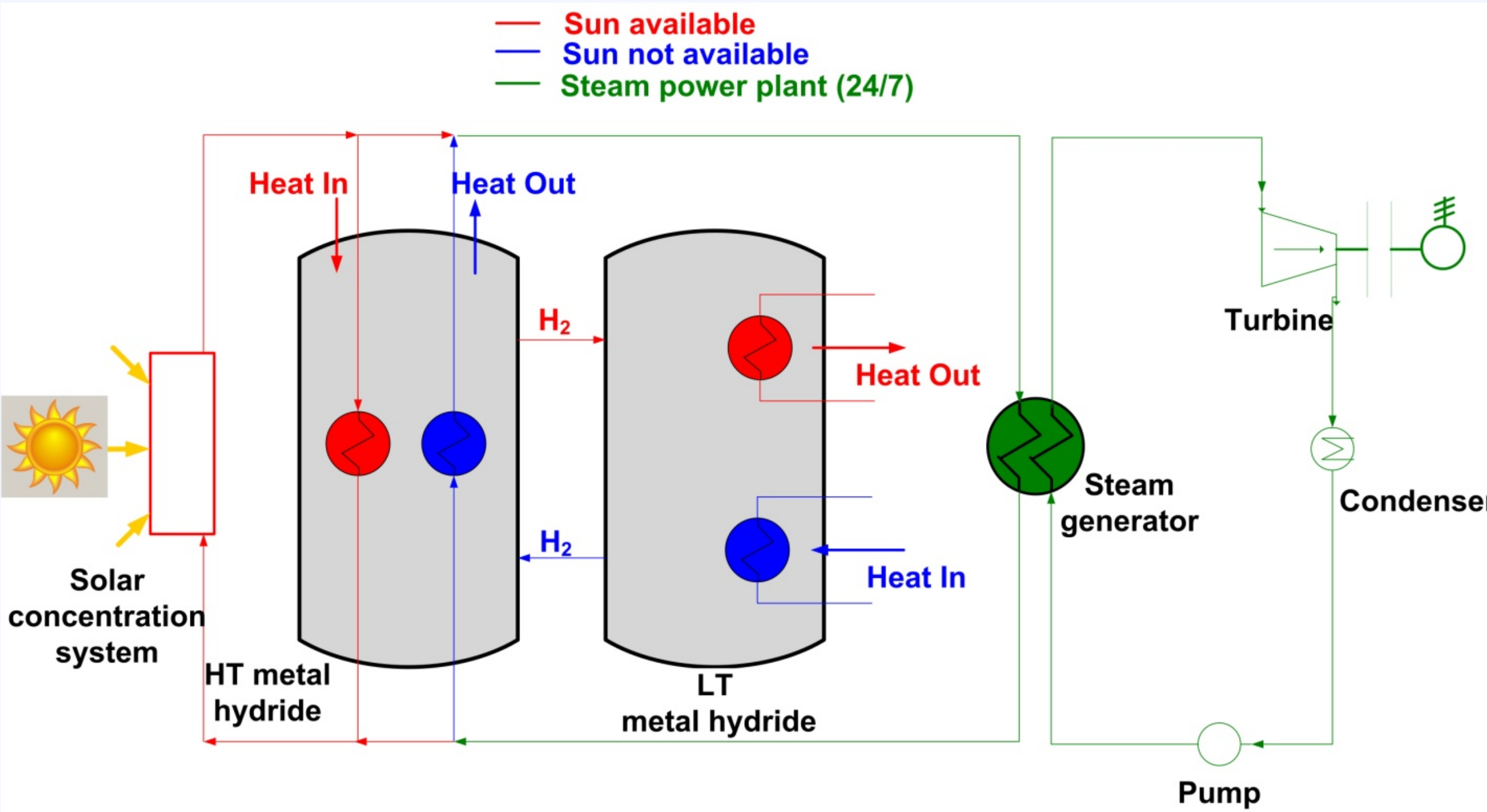
CSP Program Review: April 23, 2013

# Project Objectives

- Objective:
  - Evaluate and demonstrate a metal hydride-based TES system for use with a CSP system.
- Innovation:
  - Metal hydrides have a unique ability to deliver low-cost, high capacity and energy efficient TES systems for CSP applications.
  - New higher capacity and lower cost metal hydride materials have recently become available.
  - SRNL's unique approach, based on integration of modeling and hydride material development, is being applied to help solve this challenge.

# Metal Hydride CSP Schematic



# Overall Project Timeline

| | SRNL CSP MH TES Project | | 1QFY13 | 2QFY13 | 3QFY13 | 4QFY13 | 1QFY14 | 2QFY14 | 3QFY14 | 4QFY14 | 1QFY15 | 2QFY15 | 3QFY15 | 4QFY15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TASKS | LEAD | | | | | | | | | | | | |
| 1.1 | Obtain and generate preliminary material engineering data | SRNL | | | | | | | | | | | | |
| 1.2 | Refine and apply material screening tool (Preliminary System Models) | SRNL | | | | | | | | | | | | |
| 1.3 | Design and fabricate a bench-scale MH TES system | SRNL | | | | | | | | | | | | |
| 2.1 | Generate detailed engineering data for most promising candidate materials and systems | SRNL/Curtin | | | | | | | | | | | | |
| 2.2 | Develop and evaluate transport and system MH TES models | SRNL | | | | | | | | | | | | |
| 3.1 | Operate the bench-scale MH TES system to obtain long-term operational data | SRNL | | | | | | | | | | | | |
| 3.2 | Design and fabricate prototype MH TES vessel and components | Curtin/SRNL | | | | | | | | | | | | |
| 3.3 | Test and evaluate prototype components and vessels | Curtin | | | | | | | | | | | | |
| 3.4 | Update and validate transport and system MH TES models | SRNL/Curtin | | | | | | | | | | | | |

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# Current Year Tasks and Presentation Outline

FY13 tasks for the current budget period:

- Task 1.1: Obtain and Generate Preliminary Material Engineering Data
  - Task 1.1.1: Complete generation of preliminary data on at least 10 candidate MH TES material pairs against targets
- Task 1.2: Refine and Apply Material Screening Tool (Preliminary System Models)
  - Task 1.2.1: Refine material screening tools to apply to CSP TES applications.
  - Task 1.2.2: Screen a minimum of 10 material candidate pairs against targets to arrive at 2 to 3 best preliminary candidate material pairs.
  - Task 1.2.3: Submit a peer reviewed paper on proposed CSP TES system and use of screening tool and criteria.
- Task 1.3: Design and Fabricate a Bench-Scale MH TES System
  - Task 1.3.1: Complete 10-20g bench-scale MH TES design
  - Task 1.3.2: Complete bench-scale MH TES fabrication

# Task 1.1: Obtain and Generate Preliminary Material Engineering Data – Summary of Results

- Preliminary materials data collected (literature and consultation with CU):
  - Thermal physical and chemical properties
  - P-T equilibrium profiles available for all the materials
  - Raw material costs
- New high T& P synthesis and measurement capabilities established (some candidate materials are not readily available and others may need to be modified)
- High temperature metal hydride material ($Mg_2FeH_6$) was synthesized and sample of newly modified material has been obtained.
- Cycling data and the effect on candidate materials ($NaAlH_4$) and their formulation have been initiated.

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# Task 1.1: Material Properties

- Physical and thermodynamic properties of possible candidate materials (HT and LT systems):

| Material | T-high | P at T-high | P at 25°C | Reaction Enthalpy | Theoretical Capacity | Crystal Density | Raw Mat'l Cost |
|---|---|---|---|---|---|---|---|
| | °C | atm | atm | kJ/mol$H_2$ | wt% $H_2$ | kg/m$^3$ | $/kg |
| **HT** | | | | | | | |
| $MgH_2$ | 550 | 110 | | 74 | 7.6 | 1450 | 2.9 |
| $Mg_2FeH_6$ | 600 | 110 | | 77 | 5.5 | 2600 | 1.9 |
| $NaMgH_3$ | 650 | 80 | | 88 | 4.0 | 1470 | 4.2 |
| LiH | 1000 | 5 | | 190 | 12.6 | 800 | 70 |
| $TiH_{1.72}$ | 950 | 110 | | 142 | 3.5 | 3200 | 12 |
| $K_3AlH_6$ | 650 | 130 | | 73 | 4.4 | 1210 | 100 |
| $CaH_2$ | 1100 | 9 | | 186 | 5.0 | 1800 | 6 |
| $ZrMn_2$ | 600 | 100 | | 50 | 1.9 | 4600 | 20 |
| NaH | 650 | 90 | | 130 | 4.2 | 1400 | 4.0 |
| **LT** | | | | | | | |
| $TiFeH_2$ | | | 4.04 | 28 | 1.9 | 5000 | 7 |
| V | | | 2.07 | 43 | 3.8 | 5400 | 400 |
| $LaNi_5H_6$ | | | 1.78 | 31 | 1.5 | 6100 | 33 |
| $MmNi_5$ | | | 1.80 | 30 | 1.2 | 6100 | 22 |
| $CaNi_5$ | | | 0.49 | 45 | 1.2 | 6000 | 20 |
| $TiCr_{1.8}H_{3.5}$ | | | 179.62 | 20 | 2.4 | 4600 | 7 |
| $TiMn_{1.5}H_{2.5}$ | | | 8.29 | 28 | 1.9 | 4400 | 6 |
| $NaAlH_4$ | | | 0.69 | 40 | 5.6 | 1400 | 3.2 |

# Task 1.1: New Material Synthesis & Analysis Capabilities

- The design and assembly of a high pressure and temperature reactor was completed.
- The reactor is capable of handling material synthesis at T > 500° C and P > 6500 psig of hydrogen
- The 75 mL volume reactor is capable of handling up to 50 grams of material.
- In addition to synthesizing and modifying needed materials for this program - this equipment will be used together with our existing high temperature and pressure PCT and calorimeter capabilities to obtain needed material data.

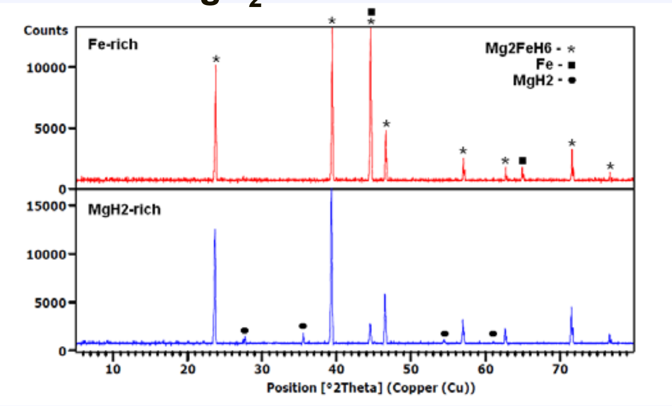
# Task 1.1: New Material Preliminary Synthesis, Modification and Characterization

- Powder XRD confirms the synthesis of the $Mg_2FeH_6$ target material.

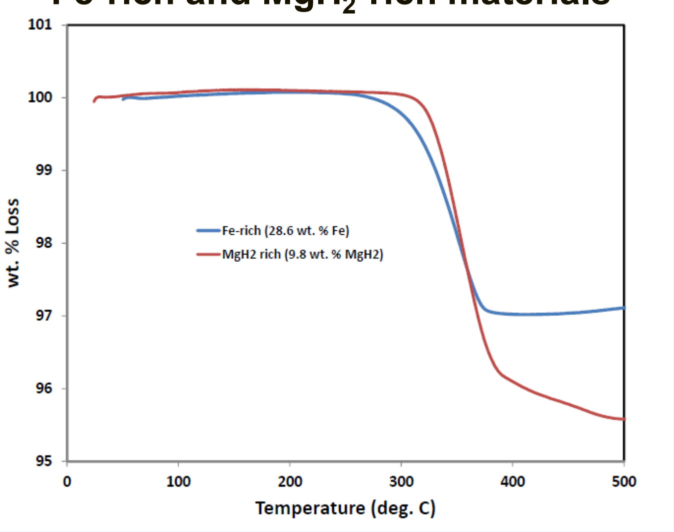
- Further verification is given by thermogravimetric analysis showing results indicative of the $Mg_2FeH_6$ material.

- These results support the operation and efficiency of the newly constructed reactor system.

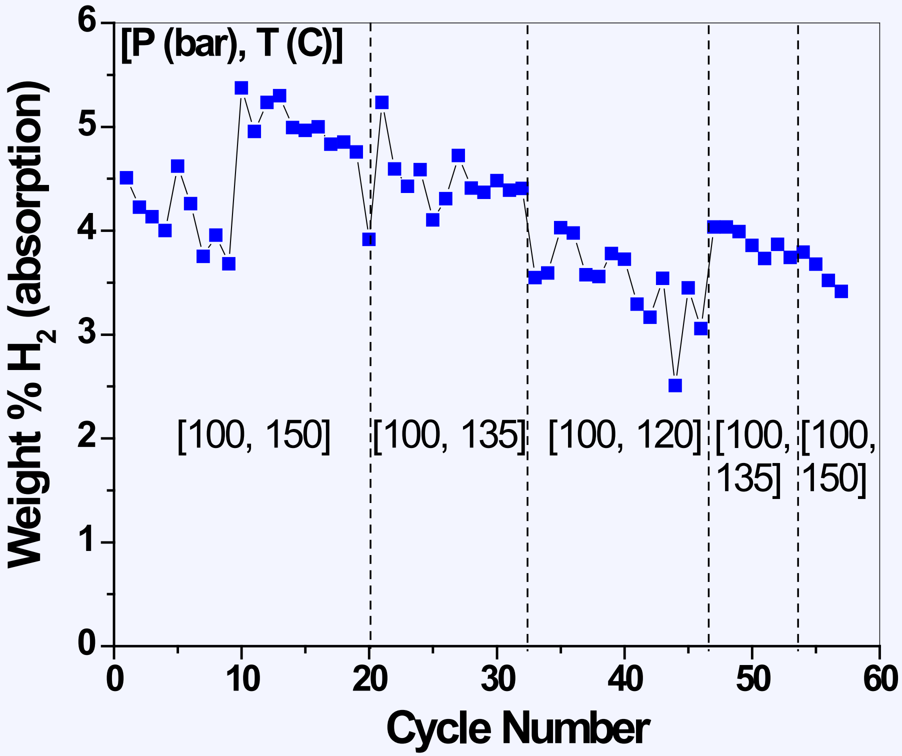
**Powder XRD of Fe-rich and $MgH_2$-rich materials**

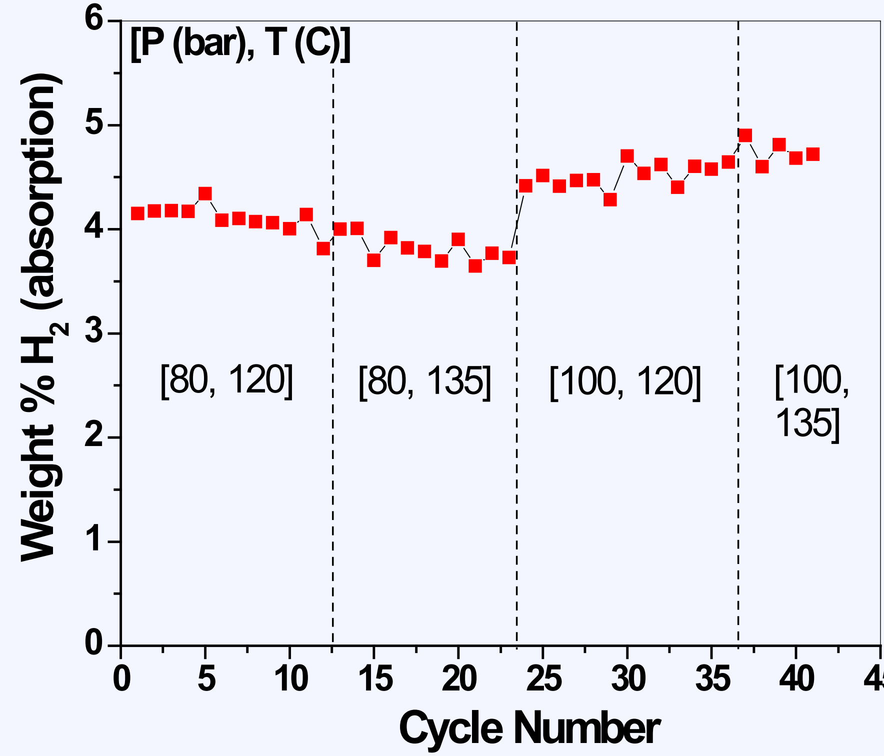



**Thermogravimetric analysis of Fe-rich and $MgH_2$-rich materials**



# Task 1.1 Cycling Comparison for Modified $NaAlH_4$




- $NaAlH_4$-$TiCl_3$ (2 mol%) (blue) vs. $NaAlH_4$-$TiCl_3$ (2 mol%) + Al*(10 wt%) (red)
- $NaAlH_4$-$TiCl_3$ (2 mol%) (blue) shows an inconsistent wt% of $H_2$ absorbed over multiple cycles at various temperatures and pressures
- The $NaAlH_4$-$TiCl_3$ (2 mol%) + Al*(10 wt%) (red) shows a very consistent and reproducible reversible cycling performance over multiple cycles at lower operating temperatures and pressures

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# Task 1.2: Screening Tool (Preliminary System Model) – Summary of Results

- The screening tool allows for the comparison and selection of metal hydride pairs against DOE SunShot targets.
- The screening tool has been (partially) developed. The tool is made of two parts:
    1. Material candidate screening based on CSP properties and TES system cost analysis (Tool 1)
    2. Performance of selected material pairs by a TES preliminary system model including mass and energy balance equations (Tool 2)
- 12 pairs of materials capable of approaching the CSP targets have been selected (Tool 1).
- Selected material pairs performance is being evaluated by the TES system model (Tool 2).

# Task 1.2: Present Screening Tool 1

- Screening tool data

| *INPUTS* | | | *OUTPUTS* |
|---|---|---|---|
| **CSP Plant properties** | **MH Material (HT and LT) properties** | **Heat exchanger properties** | **Material pair properties** |
| Thermal power: $W_{el}$ (W) | Reaction enthalpy $\Delta H$ (J/mol$_{H2}$) | Mean T difference $\Delta T$ (K) | Specific Cost ($/kWh) |
| | Entropy $\Delta S$ (J/mol$_{H2}$ K) | Cooling-heating fluid heat transfer coefficient: h (W/m$^2$K) | Volumetric density (kWh/m$^3$) |
| Power plant efficiency: $\eta_{PP}$ | Density: $\rho$ (kg/m$^3$) | | Max T (K) |
| Plant capacity factor: PCF | Hydrogen weight fraction: wf | | |
| Storage time: $\Delta t_s$ (s) | Raw material cost ($/kg material) | | |
| | Max T (K) | | |
| | Thermal conductivity (W/mK) | | |

- CSP plant properties assumed, based on targets and information available
- Heat exchanger properties assumed
- MH properties available from Task 1.1. This will include other properties in the future development (e.g. specific heat, kinetics data, etc)
- Output will include other properties in the future (e.g. exergy, charging time)

# Task 1.2: Screening Tool 1 – Approach and Assumptions

Different materials have been selected and compared based on the DOE SunShot targets. At the present stage the targets included in the screening tool are:

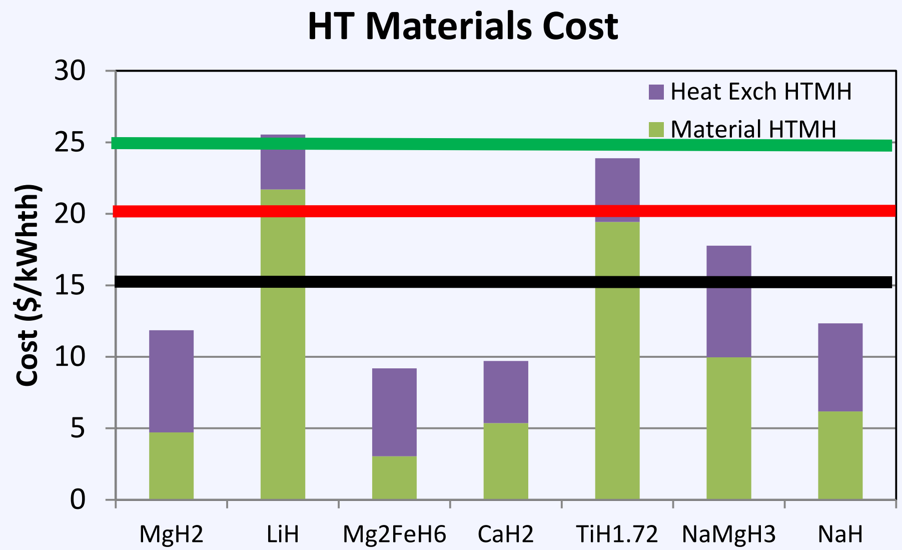
- *Cost target < 15 $/kWhth*
- Volumetric density target > 25 $kWhth/m^3$
- *System target T > 600 °C*

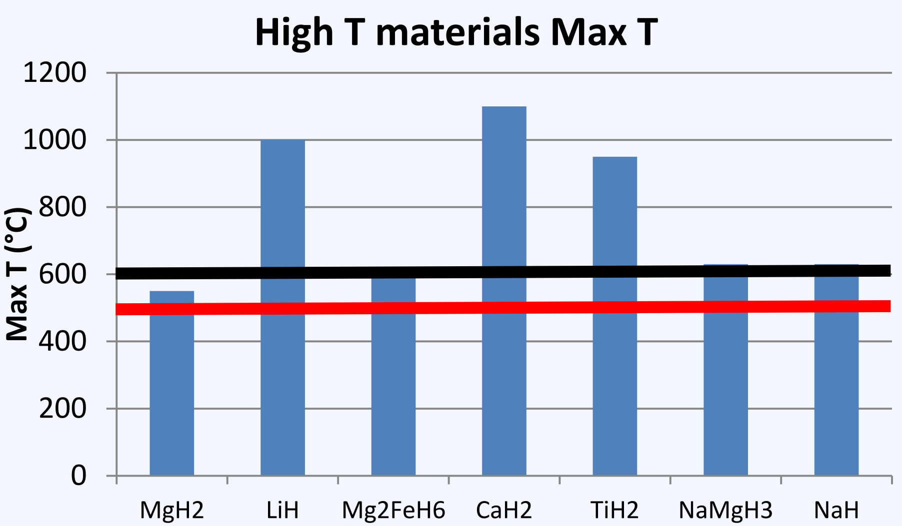
A baseline case has been analyzed making the following additional assumptions, based on the other DOE CSP targets and information available

- Storage time → 13 hours
- PCF → 63%
- Power plant efficiency → 45%
- AVG electric power → 100 MW

Other input values are being investigated and sensitivity analyses will be performed to show the effects of each of the variables.

# Task 1.2: Screening Tool – High Temperature Results




- Based on the project participant's experience in both automotive and stationary applications, the initial list of candidate HT materials included:
  - Mg-family materials
  - LiH
  - $TiH_{1.72}$
  - ✗ $K_3AlH_6$ $C_{SHT} \approx 270$ $/kWhth
  - $CaH_2$
  - ✗ $ZrMn_2$ $C_{SHT} \approx 180$ $/kWhth
  - $NaH_2$
- All the selected materials show T at least higher than 500 ° C
- The high cost of heat exchanger equipment in some material systems may allow for additional cost reductions by further engineering and system optimization.

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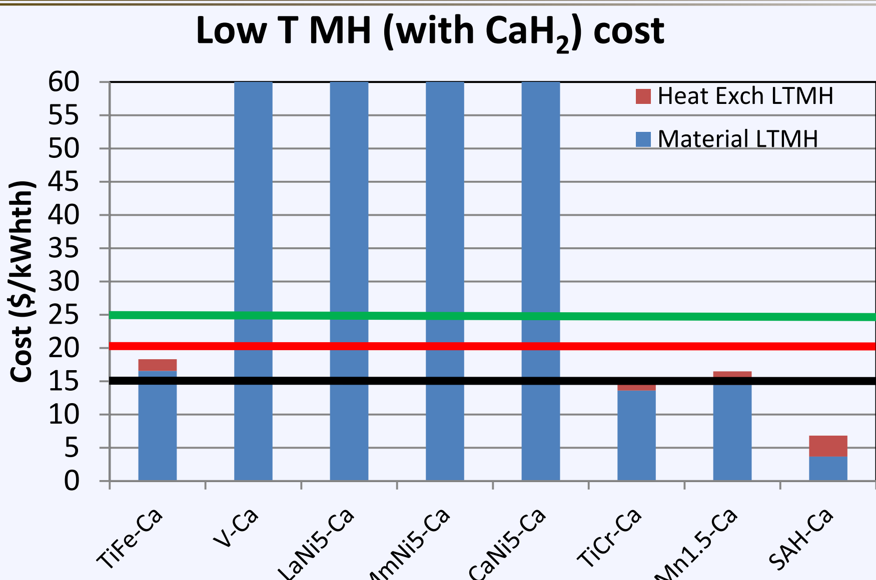
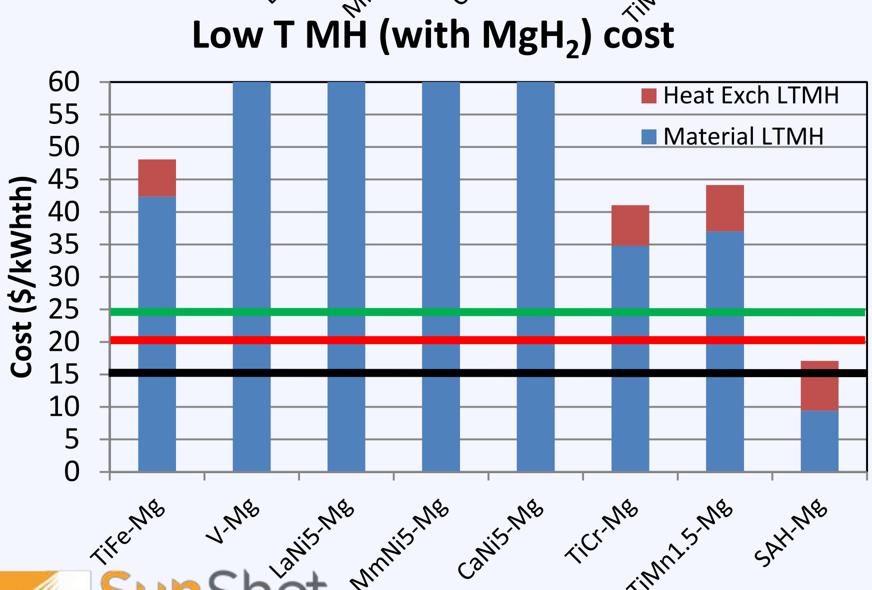
# Task 1.2: Screening Tool – Low Temperature Results



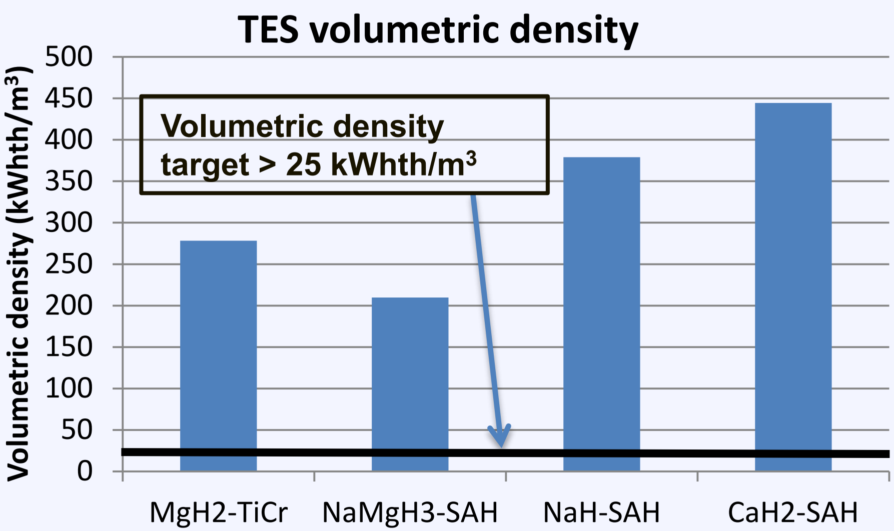




- LT MH system costs are influenced by $\Delta H_{HT}$ which determines hydrogen mass
- Based on the project participant's experience in both automotive and stationary applications the initial list of candidate LT materials included:
  - TiFe
  - ✖ V — $C_{SLT}$ >500 $/kWhth
  - ✖ $LaNi_5$ — $C_{SLT}$ >100 $/kWhth
  - ✖ $MmNi_5$ — $C_{SLT}$ > 85 $/kWhth
  - $TiCr_{1.8}$
  - $TiMn_{1.5}$
  - SAH
  - ✖ $CaNi_5$ — $C_{SLT}$ > 75 $/kWhth
- SAH based materials appear to be the most promising

# Task 1.2: Preliminary Material Pairing Selections and TES Volumetric Density

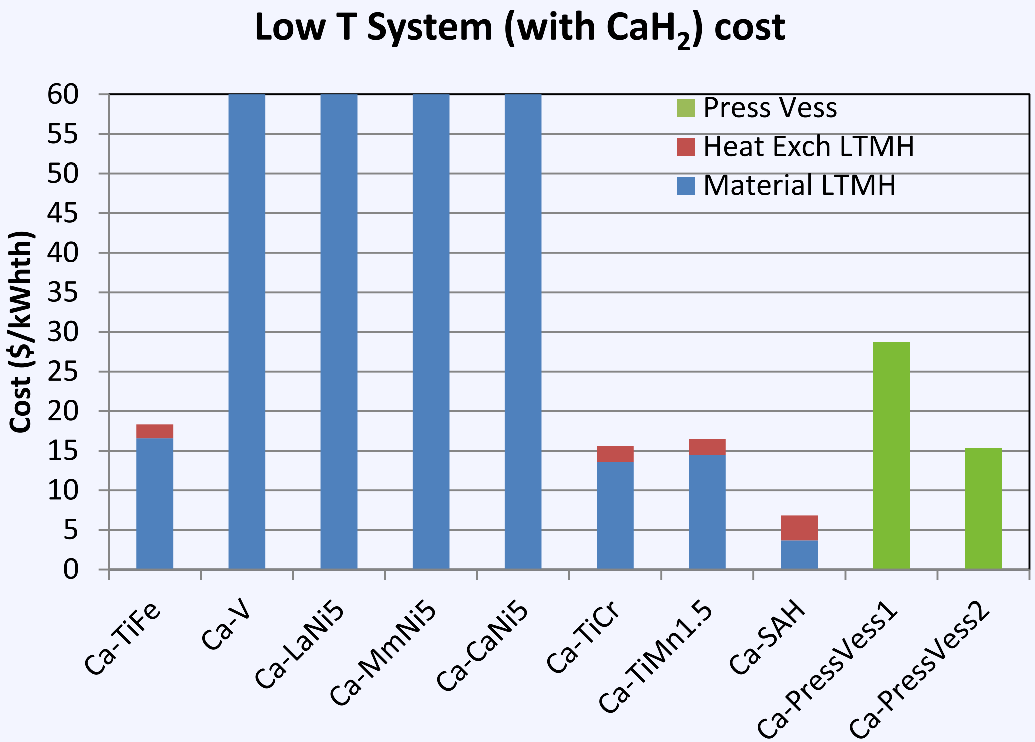
**Selected material pairs**

| | | |
|---|---|---|
| $MgH_2$ – TiCr | $Mg_2FeH_6$ – TiMn | $CaH_2$ – SAH |
| $MgH_2$ – TiMn | $NaMgH_3$ – TiFe | NaH – TiFe |
| $Mg_2FeH_6$ – TiFe | $NaMgH_3$ – TiMn | NaH – TiMn |
| $Mg_2FeH_6$ – TiCr | $NaMgH_3$ – SAH | NaH – SAH |




- 12 material pairs were selected based on:
  - the screening tool results
  - the pair compatibility on the basis of working pressures (P-T equilibrium profiles)
- Volumetric energy density of some selected pairs were evaluated based on the volume occupied by metal hydride materials. The volume occupied by the heat transfer system will be included in the tool in future development when more information and details are required.

# Task 1.2: LTMH vs Pressure Vessel

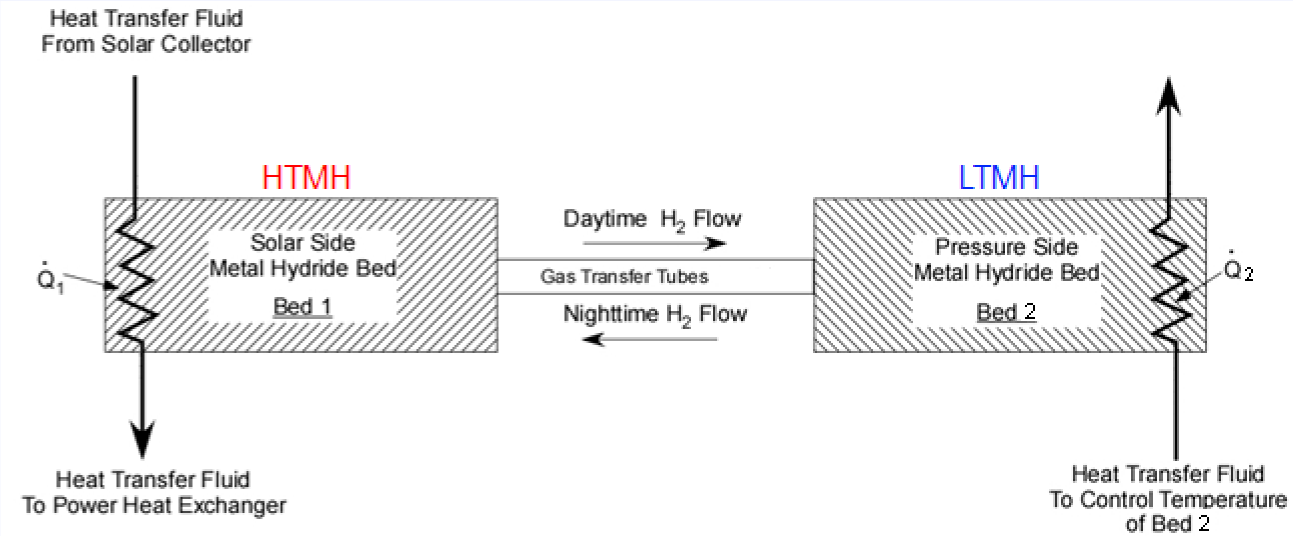



- Pressure vessel-1 cost = 750 $/kg$H_2$ at P=350 bar (DOE 2020 target for $H_2$ Station storage systems)
- Pressure vessel-2 projected cost = 400 $/kg$H_2$ at P=350 bar (DOE proposed target for vehicle application)

# Task 1.2: Pairing Bed System Tool 2 Model

Preliminary system model screening tool under development in Mathcad® including mass and energy balance equations, with the following assumptions:

- Transient lumped parameters model adopted for each TES unit
  - No spatial heat transfer assumed
  - No pressure gradients assumed
- MH heat transfer due to heat exchangers and convective hydrogen flow

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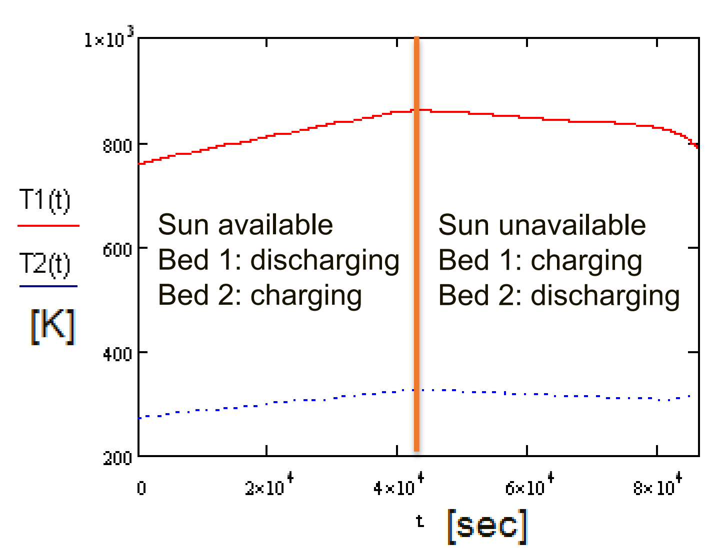
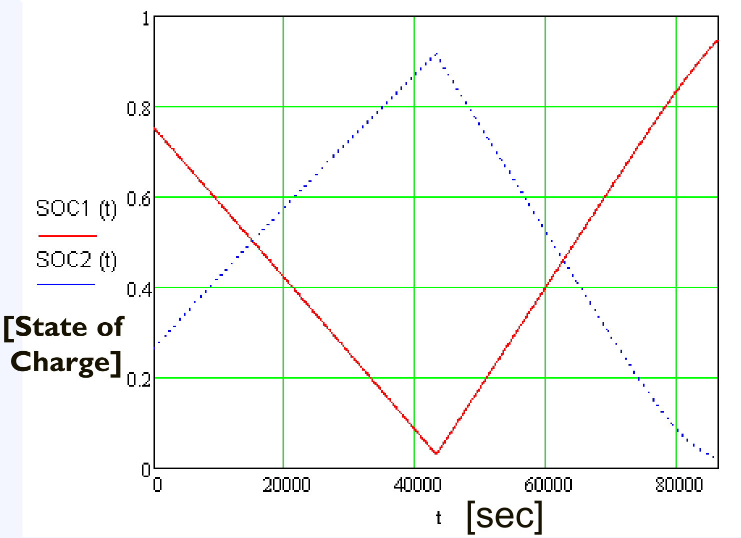
# Task 1.2: Tool 2 Dual Beds with Fast Kinetics




- Baseline case: MgH2 (1) + TiCr (2) pair
- Assumptions:
  - Simulation period equal to one day (86400 s), with storage time = 12 hours
  - Fast kinetics
- Increase of T (and P) of the system due to different kinetics

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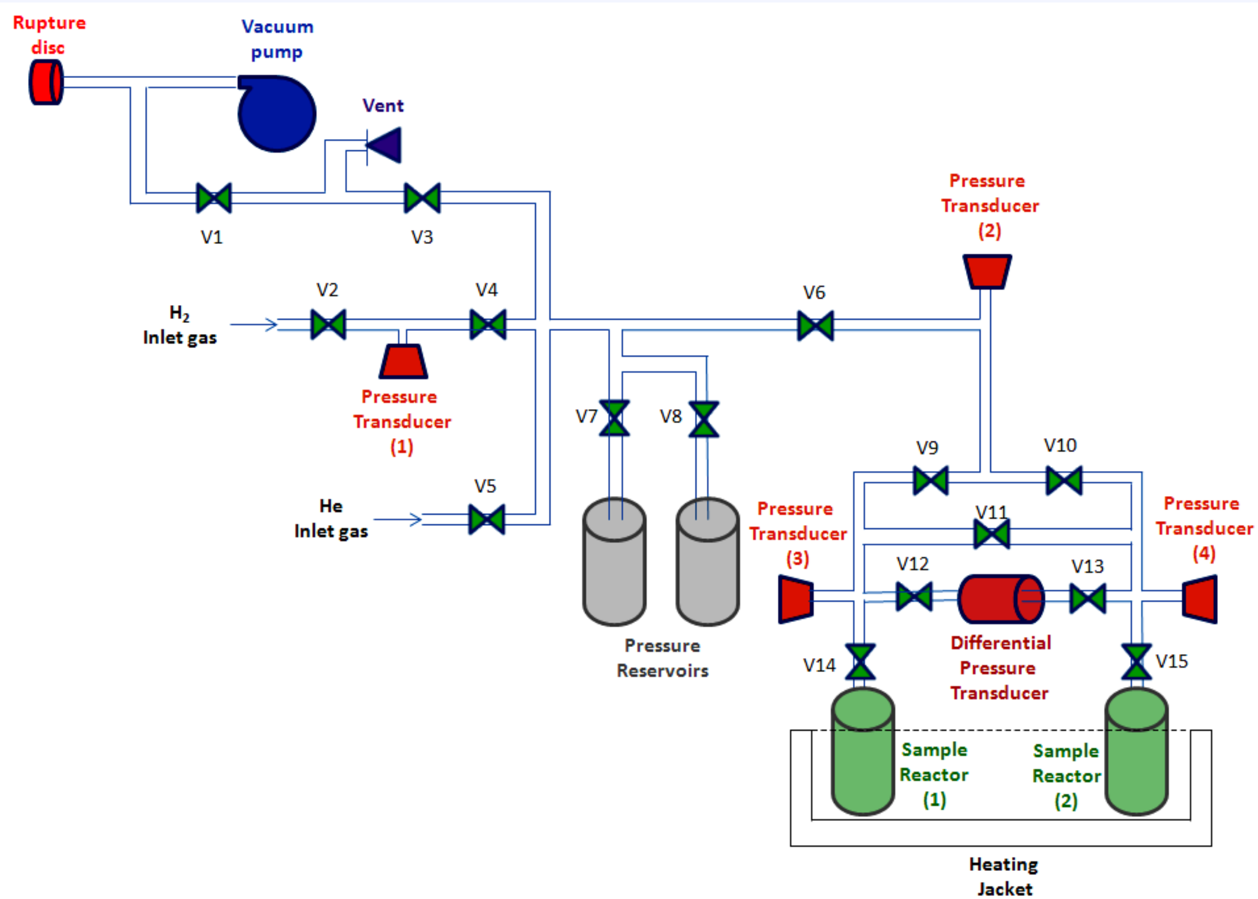
# Task 1.3: Design and Fabricate a Bench-Scale MH TES System – Summary of Results

- MH TES system design has been completed:
  - Design of TES system is modeled after a state-of-the-art Sieverts Pressure-Temperature-Composition technology.
  - TES system will accommodate both the low and high temperature MH materials simultaneously and use differential pressure measurements to improve data quality.
  - TES system design includes computer control to run a series of cycles under simulated thermal collection conditions.
- Construction of the TES system is underway:
  - The use of "80/20" framing will provide a compact and secure platform for the TES system's hardware and software components.
  - Major components of the system have been ordered including high T and P reactor components.

# Task 1.3: Schematic of the Bench Scale TES System

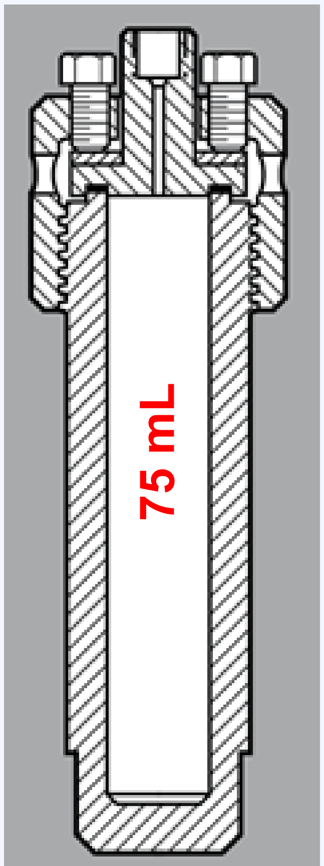
The bench scale TES system will accommodate both the low and the high temperature metal hydrides.




- The system can test individual materials over numerous cycles under a variety of temperatures and pressures.
- The twin reactors allow for operation of both the high and low temperature metal hydride materials.

# Task 1.3: Designing a New and Improved Reactors for the TES System

- System reactors are to be fabricated using the Haynes 230 alloy.
- The 230 alloy is known to resist hydrogen embrittlement as well as to have a high degree of thermal stability.




HAYNES® 230® alloy Information

## Hydrogen Embrittlement Resistance

Notched tensile tests performed in hydrogen and air reveal that 230 alloy is resistant to hydrogen embrittlement. Tests were performed in MIL-P-27201B grade hydrogen, with a crosshead speed of 0.005 in/min (0.13 mm/min). Specimens were notched with a $K_T$ value of 8.0.

| Temperature | | Hydrogen Pressure | | Ratio of Notched Tensile Strength |
|---|---|---|---|---|
| °F | °C | Psig | MPa | Hydrogen/Air |
| 70 | 20 | 3000 | 21 | 0.92 |
| 70 | 20 | 5000 | 34 | 1.07 |
| 1200 | 650 | 3000 | 21 | 1.00 |
| 1600 | 870 | 3000 | 21 | 1.00 |

## Thermal Stability

HAYNES® 230® alloy exhibits excellent retained ductility after long-term thermal exposure at intermediate temperatures. It does not exhibit sigma phase, mu phase, or other deleterious phase formation even after 16,000 hours of exposure at temperatures from 1200 to 1600°F (649 to 871°C). Principal phases precipitated from solid solution are all carbides.

This contrasts markedly with many other solid-solution-strengthened superalloys such as HAYNES 188 alloy, HAYNES 625 alloy, and HASTELLOY® X alloy. These alloys all precipitate deleterious phases, which impair both tensile ductility and impact strength.

The resulting reactor can be operated at high temperature and $H_2$ pressure with little to no reactor material degradation.

* http://www.haynesintl.com/HAYNES230alloy/230HaynesAlloyHE.htm

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# Task 1.3: Partial Assembly of the TES System with Remaining Components On-Order

- The TES system partial assembly provides insight towards current design and construction.
- The 80/20 materials provides a safe and compact platform for the systems hardware.
- Currently, the TES system assembly is 60% complete.
- The final assembly will be completed later this Spring as the remaining on-order items arrive.

Each of the two 230 alloy reactors (similar to the one shown) have been rated to 8500 psi at 600 °C and can be operated at higher temperatures at somewhat reduced pressures

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# Future Work

- Obtain additional material kinetic and initial cycling data as well as additional engineering data (e.g. thermal conductivity, specific heat, detailed data on bulk densities, etc) for material, down selected by the screening tools.
  - SRNL will concentrate on material testing of Mg-based materials including synthesis of lesser available materials like $Mg_2FeH_6$ and $NaMgH_3$
  - CU will be involved directly in the assessment of high temperature data for HT materials based on $CaH_2$ and NaH
- Complete development and application of model screening tool to arrive at best 2-3 material candidate pairs capable of meeting the DOE SunShot CSP TES targets.
- Refine and update screening models to MH TES system model to be used to guide future material development as well as system design and operation.
- Complete and startup bench-scale MH TES system to generate additional long-term material and system performance data.