Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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Metal Hydride based Thermal Energy Storage Systems for Concentrating Solar Power Systems

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Paper to be Presented at the
ASME 2014 8th International Conference on Energy Sustainability
June 30-July 2, 2014
Boston, MA

Introduction

In the global quest to develop clean renewable sources of energy, solar energy continues to increase its market share especially in the utility and distributed energy markets. While photovoltaic (PV) systems still dominate the solar marketplace, concentrating solar power (CSP) is gaining momentum. Today, there are 80 operational CSP plants around the world, mainly in Spain and the United States, with 1.9 GW of total capacity (1). Another 23 are under construction in India, China, Australia, and South Africa, among other places. Recently, one of the largest solar thermal plant in the world, the Solana plant southwest of Phoenix, Arizona has undergone initial startup activities with full operation scheduled for early 2014 (2). The 280 megawatt plant utilizes 3200 parabolic trough mirrors spread over a 7.8 square kilometers area. The Solana plant has the capability to provide 6 hours of thermal energy storage (TES), making it the largest CSP plant to use substantial TES to help handle intermittency issues common among solar and other renewable energy plants.

A key characteristic of CSP plants is their ability to provide power beyond the daytime sun hours by incorporating TES systems. During summer months, for example, plants typically operate for up to 10 hours per day at full-rated electric output without TES. However, additional generation hours can be added or shifted if TES is available, allowing for greater utilization of the power block and potentially reducing the overall cost of produced electricity (3). One of the first commercial CSP plants to incorporate TES was the Andasol 1 plant in Spain, which incorporates a two-tank molten-salt system. The 50-MW plant uses 28,500 metric tons (MT) of nitrate salts, offering a storage capacity of 1,000 MWt, equivalent to about 7.5 hours of power production. The new 280-MW Solana CSP plant by comparison uses 125,000 MT of nitrate salt and has a storage capacity of 6 hours.

The Department of Energy's (DOE) Solar Energy Technology Office introduced its SunShot Initiative in February 2011 to help make solar energy more affordable and make solar energy plants competitive with today's fossil fuel plants. Specifically, it is exploring price reductions for solar technologies by about 75% between 2010 and 2020. Under SunShot the installed system price by 2020 for CSP solar systems is being targeted at about $3.60/W. To achieve this goal, the SunShot projected targets for CSP systems from 2015 through 2020 all require significant TES capacity with the ultimate 2020 SunShot CSP Target estimating a need for 14 hours TES capacity (3).

There are three main methods for providing TES for CSP systems – sensible heat, latent heat and thermochemical energy storage. Table 1 shows examples of each of these three TES methods along with typical thermal energy storage capacities. From Table 1 (4) it can be seen that thermochemical energy storage systems offer energy densities considerably higher than other methods. Another advantage of thermochemical energy storage systems is that since they utilize reversible reactions and store energy in chemical products, the energy that is stored can be stored indefinitely without incurring thermal losses. For CSP to be successful three major improvement areas for TES system are needed: 1) lowering their costs, 2) reducing their full charging time to less than 6 hours and 3) increasing their temperature of

operation to improve the CSP overall production efficiency. Metal hydride-based TES systems have the ability to enable all of these improvements.

Table 1. Thermal Energy Storage Examples

Type of thermal energy storage (TES)	Example of TES material	Total heat storage capacity (kJ/kg)
Sensible heat	Molten salt mixtures	153
Latent heat / phase change materials	$NaNO_3$	282
Thermochemical	Oxidation of Co_3O_4	1055

The purpose of this paper is to report on our initial research aimed at evaluating a metal hydride-based TES system for use with a CSP system. Preliminary calculations indicate that existing metal hydride TES systems can approach $15-$25/kWh. Because of their very high thermal capacity (approximately 15-20 times that of current molten salt systems), the size of the overall TES systems along with its associated BOP can be substantially reduced leading to additional capital cost savings. Metal hydride TES systems can also be made to be self-regulating, thereby simplifying their design and lowering not only their capital but their operating costs as well.

A unique approach that was previously applied to hydrogen storage for mobile applications (5) was applied to this work and is presented in this paper. The approach makes use of the hierarchal modeling methodology developed by the Savannah River National Laboratory (SRNL) (6,7). This approach combines our modeling experience with the extensive material knowledge and expertise at both SRNL and Curtin University (CU) to efficiently screen promising metal hydride candidate materials and then select the best candidates for more thorough evaluation through focused experiments and more detailed models.

Metal Hydride Materials and Systems

Metal hydrides for vehicle applications have demonstrated charging rates in minutes and tens of minutes as opposed to hours. This coupled with high heats of reaction allow metal hydride TES systems to produce very high thermal power rates. A major objective of this work is to evaluate some of the new metal hydride materials that have recently become available. Metal hydride systems have been attracting recent interest for TES applications. Metal hydride reactions are highly reversible, compact, environmentally-safe and operate over a wide range of operating temperatures [8]. Table 2 shows the energy storage capacity and approximate operating temperature range for several high temperature metal hydride materials. Some of the materials in Table 2, such as magnesium and magnesium-iron have been well studied over the years for a variety of energy storage applications including solar thermal storage. Others, such as sodium magnesium hydride ($NaMgH_3$), have only recently begun to be investigated.

Table 2. Energy Storage Density and Operating Temperature Range for Several Metal Hydride Materials.

Material	Energy Storage Density	Operating Range
CaH_2	**4934 kJ/kg**	**950 - 1100°C**
LiH	**8397 kJ/kg**	**850 - 1000°C**
TiH_2	**1900 – 2842 kJ/kg**	**600 - 900°C**
$NaMgH_3$	**1721 – 2881 kJ/kg**	**400 - 650°C**
Mg_2FeH_6	**2090 kJ/kg**	**400 - 600°C**
MgH_2	**2814 kJ/kg**	**350 - 500°C**

In the past, only a small number of metal hydride TES systems have been considered (9-14). One of the issues has been the availability of suitable high capacity metal hydride materials. While a few prototype metal hydride TES systems have been demonstrated (12-14) using magnesium and magnesium-iron as the high temperature materials, the choices for a suitable low temperature material have been limited.

Recent DOE and other national and international efforts to seek better solutions for onboard hydrogen storage systems for fuel cell vehicles has led to the discovery of numerous new metal hydride material (15-16). Many of these materials and system designs that were developed are finding their way into a variety of other applications including stationary, backup and portable power systems. CSP systems, specifically, have a unique opportunity to take advantages of much of what has been learned over the past several years in hydrogen storage materials and systems and apply that knowledge and expertise to the development of the next state-of-the-art CSP TES systems.

Metal Hydride TES CSP System Description

The solar plant, shown in Figure 1, is comprised of a solar capturing and concentrating section, a TES section (based on the metal hydride system concept), and a power plant (based on a steam cycle). For the current analysis a steam power plant has been assumed as the baseline power system; however the same metal hydride (MH) based storage system can be adopted with other power plants, with only a few minor variations.

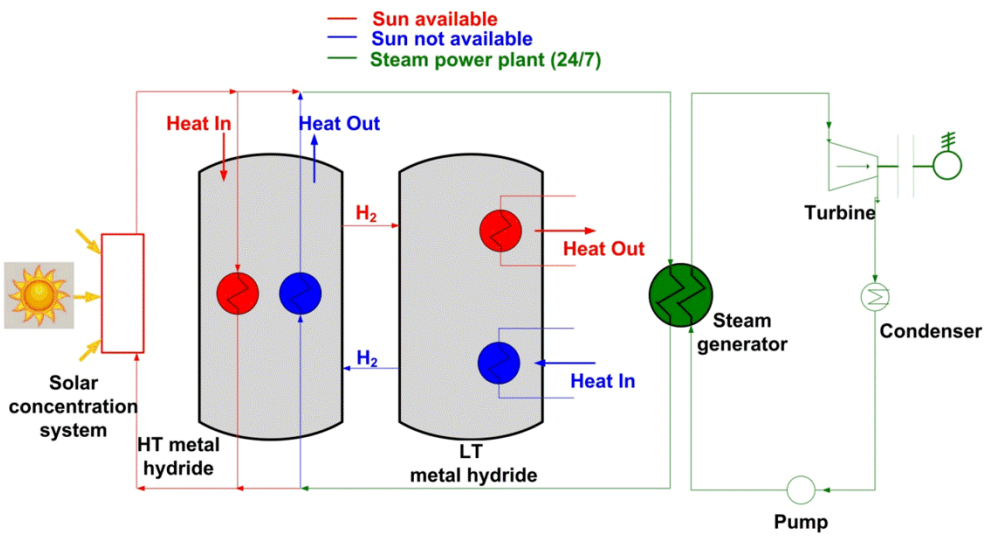

Figure 1: CSP plant, which is comprised of the Solar Concentration system, the TES system (constituted by HT Metal Hydride and LT Metal Hydride materials) and Power Plant system

The power plant works 24/7. The TES system stores and releases the needed thermal power to assure continuous operation of the power section. The storage system shown in Figure 1 is comprised of two metal hydride materials operating at different temperatures and its conceptual behavior is described below.

During the day when the sun provides the heat to the power plant, the available surplus solar power is stored in the TES. The high temperature (HT) metal hydride (MH) stores the high temperature heat, releasing hydrogen (endothermic process) to the low temperature (LT) metal hydride (MH) which works at low temperature. The LTMH tank absorbs hydrogen (exothermic process) and releases low temperature heat (Heat Out) which is extracted from the TES system. During the night or times when additional thermal energy is required to run the power plant, the process is reversed. Hydrogen flows from the LTMH and it is absorbed by the HTMH providing the needed high temperature heat to the steam generator. The higher energy density that can be provided by the use of metal hydride systems have been shown to have a mass energy density on the order of 15-20 times higher than molten salts-based TES systems (4).

Modeling and Analysis Approach

The analysis approach that was used here for this work makes use of the Hierarchical Modeling System, developed by SRNL (6). The Hierarchical Modeling System is a novel approach to the evaluation and design of general hydrogen systems in that it first uses screening models to quickly identify viable systems prior to applying detailed models that provide an accurate depiction of system behavior. The system consists of kinetics, geometric and heat exchange screening models. The screening models are used to quickly determine whether the storage media, storage system component designs, and the overall storage system configurations meet the performance criteria. If so, they are analyzed with more detailed two- and three-dimensional models that couple the transport equations with chemical kinetics. This approach was found not only to save time and effort by eliminating unneeded calculations but also help guide parallel experimental efforts. This paper will only focus on the results of the screening models with an overview on future modeling and experimental activities.

A techno-economic model was developed to screen and compare the most promising metal hydride materials-based TES systems, which have the potential of achieving the targets indicated below in Table 3. The tool can also be utilized to define the properties of an ideal metal hydride material-based TES which can meet all the targets, in the event that none of the currently available MH materials can meet all of the DOE targets. More details on the equations, assumptions and structure of the screening model in this analysis can be found in Reference (17).

Table 3. DOE Technical Targets for CSP TES systems (3)

- TES operating temperatures higher than 600 °C to assure high efficiencies of the power plant,
- TES volumetric energy density greater than 25 kWhth/m^3,
- TES exergetic efficiency higher than 95%, and
- TES specific cost lower than 15 $/kWhth.

The physical and thermodynamic properties for more than a dozen potential metal hydride candidates for a TES system were evaluated from the current literature (17, 8). The practical operating temperature of each material, the material's reaction enthalpy, theoretical hydrogen capacity and approximate raw material cost were all collected and used for the screening and system models discussed below in this paper. In turn, the results of the screening models were used to help guide the experimental portion of our program to focus our investigations on the specific material property data that most needed to be measured and collected.

The best HTMH material candidates are those with: 1) high reaction enthalpy, 2) high working temperatures; 3) high theoretical weight capacity, which determines the HTMH material cost; and 4) low raw material cost, in order to reduce the system cost. The best LTMH materials to be coupled with the HTMH are those with: 1) low reaction enthalpy,; 2) low working temperature; 3) high theoretical capacity, which determines the LTMH material cost; and 4) low raw material cost, in order to reduce the LTMH system cost.

A preliminary screening analysis was made on raw materials costs. This eliminated several lithium-, potassium- and zirconium-based high temperature materials as well as vanadium- and nickel-based low temperature materials. Only the HTMH materials that had the potential to meet or approach the targets were selected to be paired with suitable LTMH materials. The materials (HTMH and LTMH) were paired based on their properties (especially operating pressure) in order to avoid compression/expansion requirements to be included in the system. As a consequence, only a few HTMH-LTMH paired TES systems were down selected as possible final candidates. The selected TES systems were examined and the techno-economic analysis was carried out, based on a typical baseline power plant with the parameters shown in Table 4.

Table 4: Baseline Power Plant Parameters

CSP plant parameters
Wel (avg. power plant annual capacity) = 100 MW
PCF (plant capacity factor) = 63%
η_{PP} (power plant efficiency) = 45%
Δt_s (thermal storage time) = 13 h

The CSP plant characteristic values shown in Table 4 were assumed based on some of the DOE projected values for solar plants from 2015 to 2020 (3). For this screening analysis a shell and tube heat exchanger system was used with the metal hydride material in the shell and the heat transfer fluid flowing through the tubes. This design has been used in many previous metal hydride applications [18,19] and served as a good starting point for this analysis. More information on the specific assumptions used in the analysis can be found in Reference (17).

Comparison of Modeling Results to DOE Targets

TES Operating Temperature and Volumetric Energy Density

The results of the screening analysis for several high temperature metal hydride (HTMH) materials are reported below with respect to their typical operating temperatures and their expected system volumetric energy densities, respectively. Figure 2 reveals that several candidate HTMH materials like Ti, Li and Na easily exceeded the DOE 600°C target and several others had typical operating temperatures at or near the target. With respect to volumetric energy density results obtained showed that all of the HTMH material easily exceeded the 25 kWhth/m^3 targets normally associated with molten salt TES systems. The minimum volumetric energy density is for NaH material, resulting in a value of approximately 500 kWhth/m^3. Even when the HTMH and LTMH system volumes are combined a high volumetric energy density TES systems can be easily achieved with metal hydrides.

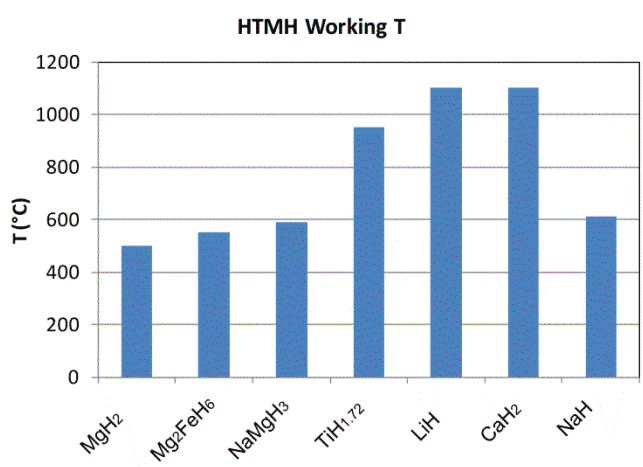

Figure 2: HTMH materials typical operating temperatures

Based on the operating temperatures and on the other properties of the materials reported in the literature (17, 8), three HTMH materials were downselected as potential materials capable of meeting the targets. The first material is the $NaMgH_3$ that shows temperature close to the target of 600 °C. The other two selected material are $TiH_{1.72}$ and CaH_2 which show very high operating temperatures, beyond the target.

The downselected HTMH materials need to be coupled with corresponding suitable LTMH materials. Among the LTMH materials (8, 4), two materials were selected as potential candidates based on the raw material price. These materials are: NaAlH4 (referred to as Sodium Aluminum Hydride, SAH) and TiFe material. The first material needs to operate at pressure on the order of at least 10-20 bar, due to its kinetics limitations. The second LTMH material can work at lower pressures and temperatures. Thus, based on the operating conditions of the three downselected HTMH materials, the following three possible TES systems were downselected as possible candidates to meet the targets: 1) NaMgH3 – SAH; 2) TiH1.72 – TiFe; 3) CaH2 – TiFe. Figure 3 shows the operation of a high pressure operating system (namely NaMgH3 –SAH system) working at pressures on the order of 20-40 bar. Figure 4 shows the operation of a lower pressure system (namely TiH1.72 – TiFe) working at pressures on the order of 1-3 bar. Equilibrium profiles are reported in the Figures based on the data reported in References (17, 20), with pressure values plotted on y axis and temperature values on x axis. When solar power is available (Sun available) hydrogen is moved from HTMH to LTMH material, with HTMH material storing the high temperature thermal power. During the night or when solar power is not available the hydrogen previously stored in the LTMH material is moved back to the HTMH material. The exothermic reaction occurring inside the HTMH material allows high temperature power to be released and used to drive the power plant.

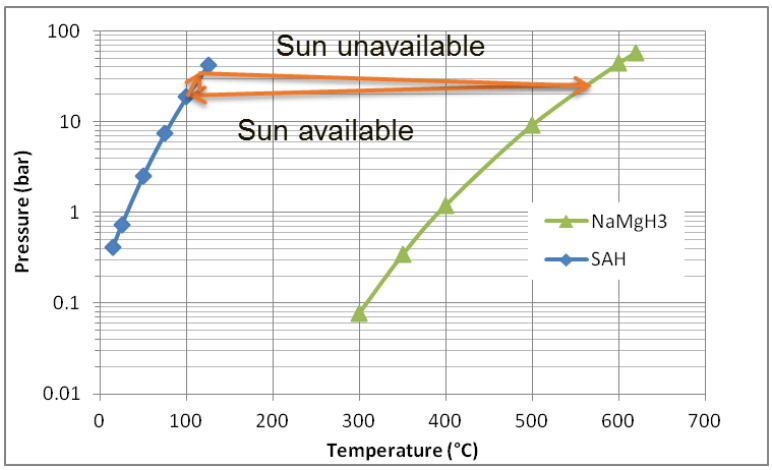

Figure 3: Operating diagram for high pressure MH-based TES system. NaMgH3 is the HTMH material, coupled with corresponding LTMH, SAH, operating at pressures on the order of 20-40 bar

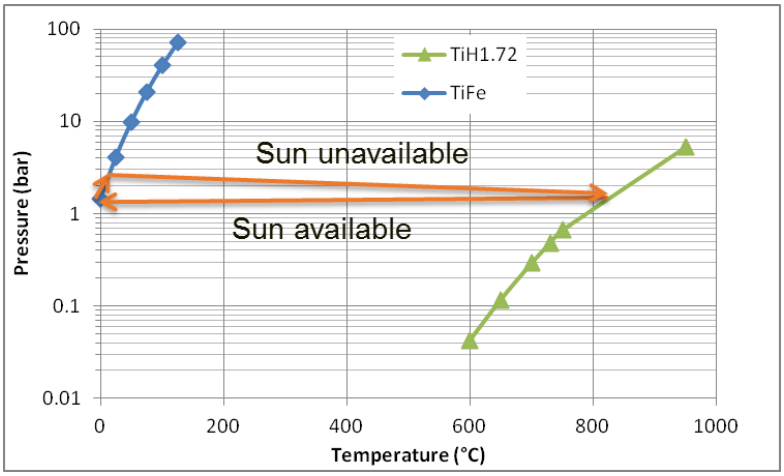

Figure 4: Operating diagram for low pressure MH-based TES system. TiH1.72 is the HTMH material, coupled with corresponding LTMH, TiFe material, operating at pressures on the order of 1-3 bar

TES Cost

One of the main objectives of the techno-economic analysis for the TES system is the evaluation of the system installed cost compared to the economic target. The specific installed cost of the TES system has been assessed including the cost of the metal hydride materials, the cost of the heat transfer system, and the cost of the pressure vessel and associated piping. Additional terms were added to the raw material cost to account for all the additional manufacturing, work and handling needed to locate the metal hydride inside the vessels. The cost of the MH material and the amount of MH material required, depends on several factors. These factors include the amount of hydrogen that needs to be stored (i.e. moved from the HTMH to the LTMH and vice versa), the MH material's heat of reaction needed to absorb and desorb the hydrogen as well as specific plant parameters like the amount of TES required, the power plant capacity factor and the power plant efficiency etc.

To evaluate the cost of the heat transfer system, preliminary assumptions were made regarding the technology adopted. Due to the screening purpose of the model, the shell and tube heat exchanger concept was assumed as the baseline heat transfer system. . The MH vessels were modeled as a series of structures comprising cylindrical tubes, with the heat transfer fluid flowing inside them, surrounded by the MH material. The heat exchanger cost was evaluated as a function of working conditions (pressure), vessel material (SS is the baseline material) and the size of the heat exchanger (heat transfer area, diameter and length). To evaluate the size of the pressure vessel an additional 25% of void volume was included to allow the expansion/contraction of the MH material during charging and discharging process, based on previous experiences (18).

Estimates were made to include installed component costs, based on the size of the heat exchangers and on previous experience gained with small scale stationary applications (18).

The system costs associated with the down selected TES systems are shown below in Figure 5.

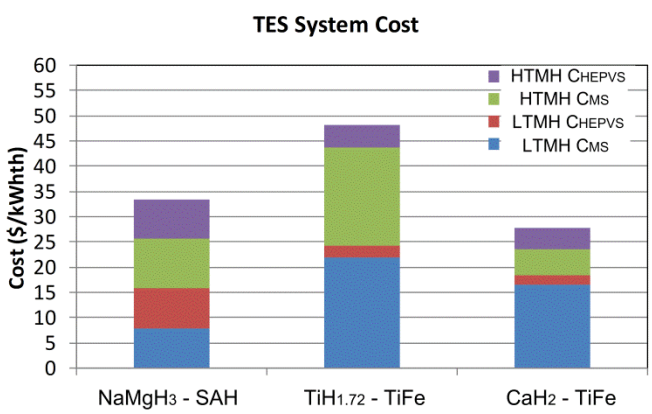

Figure 5: *TES system specific installed cost (where: Cms = metal hydride material specific installed cost in $/kWhth and Chepvs = heat transfer and pressure vessel system specific installed cost in $/kWhth)*

The pairs with the lowest costs are those with SAH as the LTMH material or those with CaH_2 as the HTMH material. This is due to the low material specific cost and the good thermochemical properties of these materials. For the $NaMgH_3$-SAH pair, approximately the same contribution to the specific cost is due to the HTMH system and the LTMH system. The influence of the heat exchanger and pressure vessel cost is also significant for both the MH materials mainly due to the high operating pressure and to the intrinsic characteristics of the two MH's.

The low pressure material pairs, which use Ti-based LTMH materials, show a significant influence of the LTMH material cost on the overall system cost due to the expensive price of this material based on Ti. Regarding the $TiH_{1.72}$-TiFe couple, the influence of the HTMH and LTMH system costs on the overall system cost is approximately the same, because of the comparable weight capacity of the two materials and of the similar specific material costs. The largest part of the cost for this system is due to the materials (both HT and LT).

TES exergetic efficiency

Another TES system target is related to its performance in terms of exergetic efficiency. Because of their good reversibility many metal hydride systems and some of the thermochemical thermal energy storage systems are often considered to have high energy and exergetic efficiencies. The exergetic efficiency of the three downselected systems have been assessed based on the efficiency definition given in Reference (20). The approach reported in Reference (20) compares the exergetic behavior of the TES during night (or when solar power is not directly available) and during the day (or when solar power is directly available) comparing their exergetic efficiency. More details can be found in Reference (17) with detailed assessment for all the systems. The first system ($NaMgH_3$ based system) shows exergetic efficiencies on the order of 82% at operating temperatures of 550 °C. The $TiH_{1.72}$ based system shows exergetic efficiencies on the order of 95% at approximately 730 °C, while the CaH_2 material based system can reach efficiencies of about 95% at temperatures of about 850 °C.

In general, the higher operating temperature materials have the highest exergetic efficiencies, typically between 90 to 95%. The lower operating temperature materials have lower exergetic efficiencies, typically between 70 to 85%. Their exergetic efficiency values can be higher at lower operating temperatures but at the expense of decreased power plant efficiency.

Future Work

Based on the results obtained from the screening analysis, some of today's MH-based TES systems show the potential to meet many of the DOE targets, even exceeding some of them. In comparison with molten salts, which represent the current baseline TES technology, the MH system shows specific installed costs on the same order of those for molten salt (21). The MH technology can also achieve high exergetic efficiency and high volumetric capacity, meeting exceeding the corresponding DOE targets. However the ultimate TES system needs to meet all the DOE targets in order to be part of a CSP plant system which can achieve the ultimate economic target represented by the electricity production cost equal to 0.06 $/kWh [3]. Presently none of the systems included in the current screening analysis shows a cost lower than the target. Starting from the three selected MH based storage systems, the following possible future material and system development directions have been proposed and preliminary results obtained at SRNL, in conjunction with Curtin University, are here reported..

Regarding the first system (NaMgH3 – SAH) several analyses have been carried out at Curtin University proposing modifications of the NaMgH3 material. In particular, one of the main activities is related to the inclusion of F as constitutive component. The results of the analysis can be found in Reference (22). Compared to the other Mg-based material, the F-NaMgH3 material shows higher operating temperatures (about 600 °C), higher reaction enthalpy (about 97 kJ/molH2). This results in a lower amount of hydrogen

to be stored in the TES (about 14% less than NaMgH3 material). This also results in a reduction of the mass of the LTMH material needed to store the hydrogen. SRNL is also working on possible modifications of the coupled LTMH (namely SAH). Particular attention is being paid on inclusion of additional Al in the compound along with Expanded Natural Graphite (ENG) inside the compound. Preliminary cycling results of these materials are reported in the Figure 8. The figure shows a comparison of the weight capacity among 1) the original SAH material doped with TiCl3, 2) the material with additional Al included (10 wt%) and 3) the material with Al and ENG included. The third material shows very stable performance after around 500 cycles. The addition of Al and ENG in the material also results in an improvement of the thermal properties (thermal conductivity) of the material, leading to a reduction of the heat transfer system cost as well.

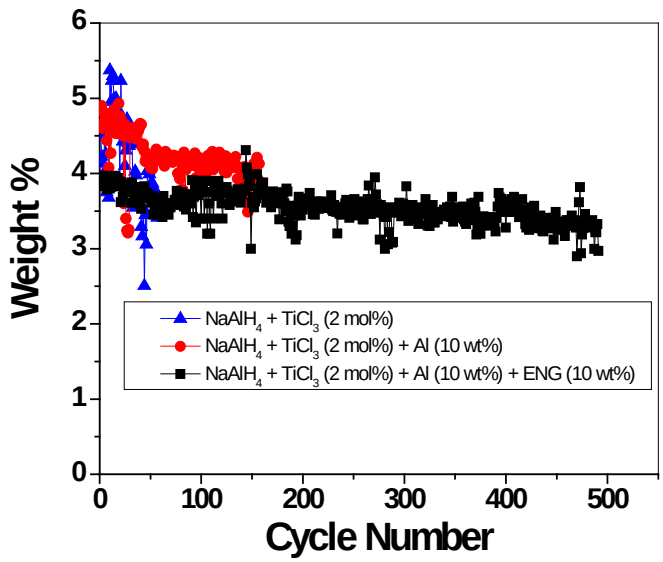

Figure 8: Weight capacity of the SAH materials (experiments carried out at 120 °C and 90 bar)

For the Ti/Ti-Fe system, the material cost (both HTMH and LTMH) represents the most influential parameter on the system cost, suggesting that material modifications must be a high priority in the future development for this type of TES system. Several HTMH material modifications are being evaluated at SRNL such as adding additional elements to the hydride to increase the operating pressure as well as lowering the material cost. Possible inclusion of Al in the system is being considered. Previous studies available in literature demonstrate the feasibility of this approach. This will have two important consequences. First, the cost of the HTMH material decreases depending on the amount of Al included. Second, the pressure of the HTMH system increases with Al addition in the material. This results in possible coupling of this material with higher pressure LTMH materials (namely SAH based LTMH) that show a lower cost than TiFe based LTMH material.

Results obtained for the Ca/Ti-Fe system show that this system has the potential to achieve the economic target considering possible LTMH material modifications which can reduce the cost of the material and the amount of hydrogen to be stored. In addition, possible HTMH material modifications are also being studied, with the aim of increasing the operating pressure, which could result in a lower installed cost, similar to what was described for the Ti/Ti-Fe system.

Summary and Conclusions

A screening analysis of potential candidate MH-based TES systems for large scale CSP plants was carried out to select the most promising (existing) metal hydrides. To do that a simplified techno-economic system model was developed to evaluate the performance of the system in terms of specific cost and the exergetic efficiency. The model can be applied to different metal hydride-based systems, under different operating conditions, accounting for different heat transfer solutions as well. Three preliminary systems were selected for future consideration based on their potential of achieving the DOE targets and their actual material pairing compatibility.

- $NaMgH_3$ (or NaH or Mg_2FeH_6) – SAH
- $TiH_{1.72}$ – TiFe
- CaH_2 – TiFe

The first system, based on an Mg-family material (e.g. Mg-Fe or Na-Mg materials) or NaH material coupled with SAH material, works well for high pressures and low temperature (approximately 500-550°C) applications. The second system, based on the coupling of Ti-based HTMH material with Ti-Fe based LTMH material, works well at low pressure and high temperatures on the order of 700 °C. The third system, based on the coupling between Ca-based HTMH material and Ti-Fe LTMH material, works well at low pressure and very high temperatures (on the order of 800-1000°C) for high efficiency power plants, resulting in potentially very low CSP system costs. Currently none of the selected systems can completely meet the DOE economic target for TES systems.

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