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Theoretical Investigation of Solar Energy High Temperature Heat Storage Technology Based on Metal Hydrides

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ABSTRACT

A solar energy storage system based on metal hydrides was proposed in this paper. The numerical simulation of processes of energy storage and thermal release were carried out. The dynamic behavior of heat and mass transfer in the metal hydride energy system were reported. Some factors which influence the whole system performance were discussed. The paper also made an economic analysis of the system, the results proved that the large amounts of metal hydride materials and the configurations of metal hydrides energy storage system involve a critical situation from an economical point of view. Then further analysis, particularly regarding the performance optimization and new plant arrangement of the metal hydrides energy storage system, has to be developed in order to attain the economical feasibility of the proposal.

1. INTRODUCTION

Nowadays, carbon dioxide is responsible for more than 50% of the man-made greenhouse effect, making it the most important contributor to climate change. It is produced mainly by the burning of fossil fuels. Because of the time lapse between emissions and their effects, the full consequences of developing climate change are still to emerge over the coming decades, bringing increased danger to the stability of the world’s economy and lifestyle (Gil et al., 2010). Solar thermal power generation is one of the promising ways to use the renewable energy instead of the fossil fuel. Solar thermal power plants produce electricity in the same way as other conventional power plants, but using solar radiation as energy input. This energy can be transformed to high-temperature steam, to drive a turbine or a motor engine. Usually the major components of a solar thermal power system include solar collector, storage units, conversion devices (such as engine or turbine), loads, auxiliary (supplemental) energy supplies, and control systems. In all of the components, thermal energy storage (TES) is a key component, because TES systems have the potential of increasing the effective use of thermal energy equipment and of facilitating large-scale switching. They are normally useful for correcting the mismatch between the supply and demand of energy. However, it is also less developed. Only a few plants in the world have tested high temperature TES systems. The optimum capacity of a TES system depends on the expectation on the process, degree of reliability, the manner in which auxiliary energy is supplied, and an economic analysis weighing the relative use of solar and auxiliary energy. Therefore, the scientific evaluation of the solar energy storage technology is crucial in the development of the solar thermal power production.

There are mainly two types of TES systems, sensible storage systems and latent storage systems. As the temperature of a substance increases, its energy content also increases. The energy released (or absorbed) by a material as its temperature is reduced (or increased) is called sensible heat. On the other hand, the energy required to convert a solid material in a liquid material, or a liquid material in a gas (phase change of a material) is called heat of fusion at the melting point (solid to liquid) and heat of vaporization (liquid to gas), respectively. Latent heat is associated with these changes of phase. The other category of storing heat is through the use of reversible...
endothermic chemical reactions. Chemical heat is associated to these reversible chemical reactions where heat is needed to dissociate a chemical product. All this heat (or almost all) will be recuperated later, when synthesis reaction takes place. A complete storage process involves at least three steps: charging, storing and discharging. In practical systems, some of the steps may occur simultaneously, and each step can happen more than once in each storage cycle. In the concept of chemical reactive storage, the energy is stored in the form of heat of chemical reactions which are often of larger magnitude than the sensible and the latent heat storage. Chemical energy storage is very attractive due to high energy storage densities, high reaction temperature attainable by solar concentrators suitable for power production, fast reaction rates, low energy losses, in principle, an unlimited life and easy transportability. In the range of chemical energy storage technology, the application of metal hydrides attracts more and more researchers’ attention because of its excellent characteristics such as compact, environmentally safe, energy efficient and offer wide operating temperature ranges (Yang et al. 2008). A specific advantage of these systems is that by varying the alloy composition, the pressure-temperature characteristics can be adjusted to suit various heating and cooling requirements. The purpose of the present paper is to carry out a theoretical analysis of the solar energy storage process based on metal hydrides.

In the investigation, a solar energy storage system was proposed. The configuration and working principles were introduced. Numerical simulation of processes of energy storage and thermal release was carried out, and the results of the calculation were discussed in detail. The dynamic behavior of heat and mass transfer in the metal hydride energy system was reported. Some factors which influence the whole system performance were discussed. The paper also made an economic analysis of the system. The results proved that the large amounts of metal hydride and the configuration of MHHP system involve a critical situation from an economical point of view. Then further analysis, particularly regarding the performance optimization and new plant configurations of the MHHP system, has to be developed in order to attain the economical feasibility of the proposal.

2. WORKING PRINCIPLES OF THE SYSTEM

The system presented in this paper includes two major parts: solar energy power generation system and metal hydrides energy storage system (as shown in Fig. 1). The solar energy power generation system exploits the temperature difference between solar energy and condensed water to operate as a Rankine cycle system in day time. A working fluid is evaporated by solar energy in the heat exchanger through the heat transfer fluid circulating in the system, the resulting vapor drives a turbine. The vapor is then condensed at the turbine outlet by cooling water with the ambient temperature. Pumps send the condensed working fluid to the heat exchanger to begin the cycle again.

Figure 1: Schematic diagram of solar energy storage system based on metal hydrides

The concept of metal hydride energy storage systems is based on cyclic operations of hydriding and
dehydriding reactions between two coupled metal hydride containers. The metal hydride containers are reactors combined with heat exchangers, filled with metal hydride, which allow us to transfer the heat of hydriding and dehydriding reaction between the metal hydrides and the heating/cooling fluids. The hydride formation reaction is exothermic and, consequently, cooling is necessary for the hydriding reaction, while heating is required in the dehydriding reaction. Thus, the mass transfer (hydrogen desorbed from one container and absorbed in the other one) is strongly related to the heat transfer between each container and heat transfer media, which indicate that the operation conditions of metal hydrides heat pump are important influence factors of system working.

Owing to the different properties of each hydr ide, the desorption and simultaneous adsorption of the hydrogen in the coupled containers involves different temperature levels for the supplied heat (to the hydride which desorbs hydrogen) and released heat (from the hydride which absorbs hydrogen). Thus, the system works as a heat temperature transformer, and then, if the hydriding-dehydriding reactions are converted into continuous cyclic operation, it becomes possible to implement kinds of thermally driven energy conversion systems and, particularly, temperature upgrading systems for power generation.

![Figure 2: Energy storage and release cycle](image)

The cyclic operations of a metal hydride system working as an "Energy Storage and Conversion" device are shown schematically in Fig. 2. The hydrogen transfer between points 1 and 2 is the hydrogen regeneration and energy storage process. This exothermic process is cooled by the low temperature source TL at ambient conditions, and metal hydrides MH2 is cooled from state point 2 to 3. While the useful output is realized by hydrogen transfer from point 4 to 1. In this process, the heat is supplied by the medium temperature source such as solar energy hot water, industrial waste heat, etc. The hydrogen will be adsorbed by MH1 at the state point 1 with high temperature TH, and this exothermic reaction process will provide high temperature source for the Rankine cycle in the night time with reference to Fig. 1. In this way, the solar power generation system is fed by continuous high temperature working fluid no matter whether in day or night time.

3. MATHEMATICAL MODEL OF THE SYSTEM

The present investigation has been carried out by two numerical models properly connected. These numerical models allow the performance evaluation of both power generation and energy storage systems. They are properly connected to take into account the increase of the water temperature at the evaporator inlet of the plant produced by the energy storage system and the increase of the pumping power owing to the water circulation in the metal hydride heat exchangers. The numerical model regarding closed-cycle Rankine cycle plants allows the evaluation of the net power of the plant and the efficiency of the Rankine cycle as a function of the water temperature at the evaporator inlet.

3.1 Rankine cycle model

The net power, which is the most important performance parameter of the Rankine plant, is defined as:

\[ P_N = P_T - P_F \]
Where $P_T$ is the gross output power of the turbine, $P_F$ is working fluid pumping power (P3 power as shown in Fig. 1). The gross power $P_T$ can be calculated as follows:

$$P_T = G_F \cdot \Delta h_T \cdot \eta_{elm}$$

(2)

Where $G_F$ is the working fluid flow rate, $\Delta h_T$ is the adiabatic enthalpy drop during the expansion, and $\eta_{elm}$ is the mechanical electrical efficiency of the turbine and of the alternator.

### 3.2 Numerical model of MHHP

For equilibrium pressure of the metal hydrides bed, it can be set as (Askri et al. 2004)

$$P_{eq} = f\left(\frac{H}{M}\right) \exp\left(\frac{\Delta H}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$

(3)

where $f(H/M)$ is the equilibrium pressure at the reference temperature $T_{ref}$. This function $f(H/M)$ is given by fitting the experimental data. In this investigation, the reactor chosen for discussion is a cylindrical configuration. (as shown in Fig. 3)

![Figure 3: Schematic photo of cylindrical configuration of a reactor (Meng et al. 2010)](image)


The mathematical heat and mass transfer model of reactor are depicted as follows. Two dimensional energy equation in cylindrical coordinates becomes:

$$\left(\rho C_p\right)_r = \frac{1}{r} \frac{\partial}{\partial r}\left(r \lambda \frac{\partial T}{\partial r}\right) + \frac{1}{r} \frac{\partial}{\partial z}\left(\lambda \frac{\partial T}{\partial z}\right) - \left(\rho C_p V_s\right) \frac{\partial T}{\partial r} - \left(\rho C_p V_s\right) \frac{\partial T}{\partial z} - \rho (1-\varepsilon) \frac{\Delta H}{M_{H_2}} \frac{\partial x}{\partial t}$$

(4)

$$\left(\rho C_p\right)_t = \varepsilon \left(\rho C_p\right)_s + (1-\varepsilon) \left(\rho C_p\right)_s$$

(5)

$$\lambda_t = \varepsilon \lambda_s + (1-\varepsilon) \lambda_s$$

(6)

The last term of the right-hand side of the energy equation (Eq. (4)) represents the heat release during adsorption ($W/m^3$), which is a function of hydride bed temperature, hydride equilibrium and hydrogen supply pressures, and hydrogen concentration. The generalized reaction kinetic equation (used for wide range of hydrogen adsorbing alloys) for hydrogen adsorption and desorption process are given by (Muthukumar and Ramana, 2008):

$$\frac{\partial x}{\partial t} = \sigma_a \frac{P_g - P_{eq}}{P_{eq}} \left(\frac{1}{x_s} - \frac{1}{x_f}\right) \exp\left(-\frac{E_a}{R_g T}\right)$$

(7)

$$\frac{\partial x}{\partial t} = -\sigma_d \frac{P_g - P_{eq}}{P_{eq}} \left(\frac{1}{x_s} - \frac{1}{x_f}\right) \exp\left(-\frac{E_d}{R_g T}\right)$$

(8)

Where ‘$x$’ is the hydrogen concentration defined as the quantity obtained by dividing the number of hydrogen atoms absorbed by number of metal atoms per mole of alloy (H/M). $\sigma_a$ and $\sigma_d$ is the reactive constant, and $E_a$ and $E_d$ are the activation energy of the reaction.

The continuity equation includes a sink term to take the amount of hydrogen absorption into account and the resulting equation per unit volume (kg/m$^3$ s) is given by:
\[ \frac{\partial \rho_t}{\partial t} + \nabla \cdot (\rho_t \bar{V}) = \Delta \rho (1 - \varepsilon) \frac{dx}{dt} \quad (9) \]

Where \( \varepsilon \) is the porosity of the reactive bed. The gas density \( \rho_g \) is deduced from the perfect gas model:

\[ \rho_g = \frac{P_g M_{H_2}}{R T} \quad (10) \]

The momentum equations are then solved in the porous medium using the classical Darcy law:

\[ \nabla P = -\frac{\mu \bar{V}}{K} \quad (11) \]

Where, the coefficient \( K \) denotes permeability and is a function of the particle size of the metal hydride powder.

3.3 Heat transfer fluid model

Average attainable temperature level of the useful heat is the most important in the present analysis owing to its correlation with the temperature of the Rankine plant working fluid at the turbine inlet, the average outlet temperature of the hot water is evaluated by (Gambini,1994)

\[ T_{fo} = T_{fi} + \left[ T_{ro,zi} - T_{fi} \right] \left[ 1 - \exp \left( -\frac{UA}{m_l C_{pf}} \right) \right] \quad (12) \]

Where \( T_{ro,zi} \) is the temperature of the bed at the interface between the hydride bed and the convective boundary. \( T_{fi} \) and \( T_{fo} \) are the inlet and outlet temperatures of the cooling fluid. \( U \) is overall heat transfer coefficient. \( A \) is the area of heat transfer.

4. PERFORMANCE SIMULATION

4.1 Initial and boundary conditions

In order to simplify the governing equations, the following assumptions are made.

• The gas phase is ideal from thermodynamic point of view.
• The medium is in local thermal equilibrium.
• There is no heat transfer through the porous filter.
• The thermo-physical properties of the hydride bed are independent of temperature and hydrogen pressure.

Initially \((t = 0)\), the bed temperature, hydride equilibrium pressure and hydride density are assumed to be uniform throughout the reactor.

\[ \rho_s(z, r, 0) = \rho_0; \quad T_s(z, r, 0) = T_0; \quad P_s(z, r, 0) = P_0 \quad (13) \]

Along the porous wall:

\[ P_s(z, r, t) = P_r; \quad \frac{\partial T}{\partial r}(z, r, t) = 0 \quad (14) \]

Along the left face, where \( z = 0 \), adiabatic and impervious conditions give:

\[ \frac{\partial T}{\partial z}(0, r, t) = 0; \quad \frac{\partial P}{\partial z}(0, r, t) = 0 \quad (15) \]

Along the right face, where \( z = Z \), adiabatic and impervious conditions give:

\[ \frac{\partial T}{\partial z}(Z, r, t) = 0; \quad \frac{\partial P}{\partial z}(Z, r, t) = 0 \quad (16) \]

4.2 Numerical Solution

The basic operation parameters of system are listed in Table 1. In this study, water is chosen as the working fluid of the Rankine cycle power, and oil is selected as the circulating heat transfer fluid for the solar energy concentrator.

The present analysis is carried out for a cylindrical reactor of 27mm internal diameter, 3mm wall thickness and 450mm length. To maximize the heat storage performance of the metal hydride system within a given temperature range, the equilibrium pressure of the hydride material has to be carefully chosen. If the equilibrium pressure is too low, the heat storage performance would be degraded because of the slow hydrogen gas flow due to the low pressure differential between two metal hydride reactors. If the equilibrium pressure is too high, it would be difficult to recover the hydrogen from the metal hydrides for hydrogen storage through moderate heat source. Based on the
considerations, Mg-MmNi_{4.6}Al_{0.4} was selected for the prototype metal hydride energy storage system. Thermophysical properties of the alloy and various constants used in the mathematical modeling are listed in Table 2.

### Table 1: Operation parameters of the system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher Temperature for MH energy storage (K)</td>
<td>643</td>
</tr>
<tr>
<td>Moderate Temperature for MH energy storage (K)</td>
<td>333</td>
</tr>
<tr>
<td>Low Temperature for MH energy storage (K)</td>
<td>293</td>
</tr>
<tr>
<td>The load of the Rankine power system (kW)</td>
<td>10~12</td>
</tr>
<tr>
<td>Thermal efficiency of the Rankine cycle η(%)</td>
<td>15</td>
</tr>
<tr>
<td>Overall heat transfer coefficient U(W.m^{-2}.K^{-1})</td>
<td>500</td>
</tr>
<tr>
<td>Area of heat exchanger A(m²)</td>
<td>0.5</td>
</tr>
<tr>
<td>Porosity of the reactive bed ε</td>
<td>0.5</td>
</tr>
<tr>
<td>Heat capacity of fluid C_p(kJ.kg^{-1}.K^{-1})</td>
<td>4.186(water);2.5(oil)</td>
</tr>
<tr>
<td>Flow rate of fluid m(_f)(kg.s^{-1})</td>
<td>0.01(water);0.04(oil)</td>
</tr>
</tbody>
</table>

### Table 2: Thermo-physical properties of alloy and constant in this investigation

<table>
<thead>
<tr>
<th>Name (MH)</th>
<th>Density(kg.m^{-3})</th>
<th>Reactive Enthalpy (kJ.mol^{-1}H(_2))</th>
<th>Reactive Entropy (kJ.mol^{-1}H(_2))</th>
<th>σ(_a)(s^{-1})</th>
<th>σ(_d)(s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (MH1)</td>
<td>1738</td>
<td>74.4</td>
<td>0.135</td>
<td>2x10(^5)</td>
<td>5.5 \times 10(^5)</td>
</tr>
<tr>
<td>MmNi(<em>{4.6})Al(</em>{0.4}) (MH2)</td>
<td>8400</td>
<td>28</td>
<td>0.107</td>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

The resulting system of governing equations is discretized using the finite volume method. An alternative direction implicit (ADI) scheme with tri-diagonal matrix algorithm (TDMA) is used for solving the governing equations. Velocity terms are handled using staggered grids to catch the heat transfer across the control volume by convection. Boundary conditions are applied using half control volume method. While applying the boundary condition, the cooling fluid temperature at any iteration is calculated from previous iteration bed temperature. For a given time step, by using Eq. (12) cooling fluid temperature in the axial direction is updated. The variation of hydrogen concentration for energy storage process can be seen in the Fig. 4.

Figure 4 Hydrogen concentration variation for energy storage process

Figure 5 Temperature of heat transfer fluid for energy storage process

Figure 4 shows the reactive rate of alloy Mg is slower than the rate of MmNi\(_{4.6}\)Al\(_{0.4}\). The reason is that the kinetic of hydrogen desorption process of alloy Mg is very slow, and the amount of hydrogen stored in alloy Mg is larger than that stored in alloy MmNi\(_{4.6}\)Al\(_{0.4}\). Figure 5 is variation of heat transfer fluid temperature for energy storage process.
storage process. When the process is started (by opening the valve in the gas line) the pressure in each reactor immediately attains the same value, different from the equilibrium pressures. These differences between the equilibrium pressures of the hydrides and gas pressure may be indicated as the “driving forces” of the process because they represent the major determinants of the mass transfer process (equations (7) and (8)). Owing to these driving forces, a hydrogen flow rate from MH1 to MH2 takes place, which produces an abrupt decrease in the MH1 temperature and an increase in the MH2 temperature (Gambini, 1994). These temperature variations, together with the hydrogen concentration decrease in MH1 and increase in MH2 (as shown in Fig. 4), lead to a decrease in the equilibrium pressure difference, due to simultaneous decrease of $P_{eq1}$ and increase of $P_{eq2}$ (Eq. (3)). Then, both the differences between gas pressures and equilibrium pressures become smaller. These driving force decrease are very fast and they lead to an abrupt decrease of hydrogen flow rate. Then, the temperature of heat transfer fluid through MH1, after initial abrupt decrease, begins to increase and the temperature of heat transfer fluid through MH2, after the initial increase, begins to decrease (as shown in Fig. 5). After this initial abrupt transient behavior, the process slowly proceeds towards its equilibrium conditions until the extinction of hydrogen flow rate, the hydrogen concentrations attain their maximum and minimum values (Fig. 4). Similar trend also can be seen in the thermal release process, as shown in Figs. 6 and 7.

![Figure 6 Hydrogen concentration variation for Thermal release process](image1)

![Figure 7 Temperature of heat transfer fluid for thermal release process](image2)

By the above explanation, it may be pointed out that major determinates of the heat and mass transfer are the driving forces related to the equilibrium pressure differences between two metal hydrides reactive bed. The heat transfer performance of reactor and operational parameters of the heat transfer fluids assume a determinant role in the mass transfer process and, consequently in the overall performance of the metal hydride energy storage system, and the novel reactor developed for heat and mass transfer enhancement is the critical for this kind of high temperature storage technology application.

### 5. ECONOMIC ANALYSIS

Besides the technology feasibility of the proposal, Table 1 allows the evaluation of the cost and size of the MH energy storage system, which are fundamental to evaluate the economical feasibility of the solar power plant. The costs of heat storage systems based on different materials are listed in Table 3.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (K)</th>
<th>Density (kg/m³)</th>
<th>Cost per kg (€/kg)</th>
<th>Energy Density (kWht/m³)</th>
<th>Specific cost (€/kWht)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate salts</td>
<td>643</td>
<td>1870</td>
<td>1.25</td>
<td>77</td>
<td>30</td>
</tr>
<tr>
<td>Molten-Salt</td>
<td>643</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Concrete</td>
<td>643</td>
<td>2200</td>
<td>0.1</td>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>Metal hydrides</td>
<td>643</td>
<td>1738/8400</td>
<td>2</td>
<td>-</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 3 Performance parameters and cost of different heat storage materials

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From Table 3, we can get that the metal hydrides in this study doesn’t take a superiority position to other kinds of heat storage materials in specific cost aspect. This is because the alloy for hydrogen storage (MmNi_{4.6}Al_{0.4}) is very expensive, which indicates that develop new low cost alloy for hydrogen storage is very important. Leaving out details on metal hydride, heat transfer fluid and Rankine cycle specific costs, the foregoing explanation is already enough to deduce a critical economical feasibility of the proposed plant. This might be improved by a proper metal hydride reactor design and operational parameters choice or by the employment of a multistage metal hydride system, which leads to a temperature upgrading certainly greater than the single stage.

6. CONCLUSIONS

A solar power plant coupled with high temperature storage system based on metal hydrides was proposed. The hydride material should be chosen based on equilibrium pressure difference to suit the working temperature demand of the solar power plant. Performance simulation of energy storage and release processes were carried out through numerical calculation, and results show that heat transfer performance of reactor assumes a determinant role in the overall performance of the metal hydride energy storage system. Although the further MH storage performance increase by a proper metal hydride reactor design and operational parameters optimization, the size and cost of the metal hydride system are still very high. Then, further analysis about the application of multistage metal hydride energy system, has to be developed in order to attain the economical feasibility of the proposal.

NOMENCLATURE

<table>
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<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tr>
<td>A</td>
<td>Area of heat exchanger</td>
<td>m²</td>
</tr>
<tr>
<td>C_p</td>
<td>Specific heat</td>
<td>kJ/kg.K</td>
</tr>
<tr>
<td>E</td>
<td>Active energy</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>M</td>
<td>Molecular Weight</td>
<td>g/mol</td>
</tr>
<tr>
<td>m</td>
<td>Mass flow rate</td>
<td>kg/s</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
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</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>x</td>
<td>Hydrogen concentration</td>
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<td>λ</td>
<td>Heat conductivity</td>
<td>w/m.K</td>
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Subscripts

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REFERENCES


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