DE GRUYTER DOI 10.1515/green-2013-0011 — Green 2013; 3(2): 113–123

Review

M. Felderhoff*, R. Urbanczyk and S. Peil

Thermochemical Heat Storage for High Temperature Applications – A Review

Abstract: Heat storage for high temperature applications can be performed by several heat storage techniques. Very promising heat storage methods are based on thermochemical gas solid reactions. Most known systems are metal oxide/steam (metal hydroxides), carbon dioxide (metal carbonates), and metal/hydrogen (metal hydrides) systems. These heat storage materials posses high gravimetric and volumetric heat storage densities and because of separation of the reaction products and their storage in different locations heat losses can be avoided. The reported volumetric heat storage densities are 615, 1340 and 1513 [kWh m^{-3}] for calcium hydroxide $Ca(OH)_2$, calcium carbonate $CaCO_3$ and magnesium iron hydride Mg_2FeH_6 respectively. Additional demands for gas storage decrease the heat storage density, but metal hydride systems can use available hydrogen storage possibilities for example caverns, pipelines and chemical plants.

Keywords: heat storage, thermochemical, metal hydrides, metal hydroxides, metal carbonates

PACS® (2010). 88.80.F-

***Corresponding author: M. Felderhoff:** Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim/Ruhr, Germany. E-mail: felderhoff@mpi-muelheim.mpg.de
R. Urbanczyk, S. Peil: Institut für Energie- und Umwelttechnik e.V., Bliersheimer Str. 58-60, 47229 Duisburg, Germany

1 Introduction

The increased production of electricity from renewable sources (wind, sun, water) makes a continuous and reliable electricity supply more difficult, because of fluctuating amounts of wind and/or sun power and to a lesser extent of waterpower. To overcome these problems flexible power stations (e.g. combined-cycle power plants) and energy storage systems must be developed and constructed. Possibilities for the storage of electricity are, amongst others, big battery systems, power-to-gas conversion (methanation) or pumped-storage power plants. All these different systems are currently under investigation or construction. Contrary to most of the electricity produced from re-newables, carbon-based power plants (oil, gas, coal) produce electricity and heat. This heat is useable for industrial processes or in urban heating networks or it is released in the environment as exhaust heat. The electricity feed act in Germany and other European countries demands a preferred feeding of electricity produced from renewables into the grid, with the consequences that conventional power plants must reduce their production. This leads to unbalanced electricity in the grid and lowered amounts of heat, especially for industrial processes. This gap must be closed in near future with new developed efficient heat storage systems [1, 2].

Reversible thermochemical reactions are appropriate for thermal energy storage because of their high energy densities compared to the sensible or latent heat storage systems. During the thermochemical heat storage a thermochemical material is converted under the addition of heat into two other components. Both of them can be stored separately. By recombining the components the original thermochemical material is produced, releasing the same amount of heat which was previously stored (Equation 1).

$$\text{A-B} \quad \underset{\substack{\text{heat release}\\ \text{exothermic reaction}}}{\overset{\substack{\text{heat storage}\\ \text{endothermic reaction}}}{\rightleftarrows}} \quad \text{A} + \text{B} \qquad \text{(Eq. 1)}$$

The advantages and disadvantages of the three possible concepts for the storage of thermal energy were proposed by [3] and are listed in Table 1.1.

The energy densities and operational temperatures for different heat storage materials can be found in Table 1.2. The heat storage Q of the sensible heat storage materials like water, rock, concrete and salt (nitrate salt-sensible heat) depend on both the available temperature difference

Table 1.1: Advantages and disadvantages of the three different kinds of thermal energy storage concepts

heat storage	sensible heat	latent heat	thermochemical heat
capacity	weak	weak	large
restitution	variable temperature	constant temperature	variable temperature
insulation	required	required	not required
energy losses	large in long term	fair in long term	low (losses in sensible heat)
working temperature	low	low	high
life	long	limited	high
environmental impact	nil	nil	sometimes hazardous
transportability	little distances	little distances	long distances
technology	simple	simple	complex

Table 1.2: Energy densities and temperature data of different heat storage materials

Material	Gravimertic energy density [kWh kg⁻¹]	Volumetric energy density [kWh m⁻³]	Temperature change [K]	Temperature [°C]
Water	0.093	93	80	$t_{1bar} < 100$
Sand rock [4]	0.035	60	100	$t_{hot} = 300$
Reinforced concrete [4]	0.045	100	200	$t_{hot} = 400$
Nitrate salts (sensible) [4]	0.134	250	300	$t_{hot} = 565$
Nitrate salts (KNO_3-latent) [4]	0.074	155		$t_{melting} = 333$
$CaO + H_2O \rightleftharpoons Ca(OH)_2$ [5]	0.336	615		$t_{1atm} = 527$
$CaO + CO_2 \rightleftharpoons CaCO_3$ [5]	0.6	1340		$t_{1atm} = 890$
$Mg + H_2 \rightleftharpoons MgH_2$ [6]	0.78	1110		$t_{range} = 350–450$
$2Mg + Fe + 3H_2 \rightleftharpoons Mg_2FeH_6$ [6]	0.55	1513		$t_{range} = 450–550$

ΔT between the heat source and the sink, and on the mass m of the material (Formula 1).

$$Q = m \cdot c \cdot \Delta T \tag{1}$$

The storable heat of the latent heat storage (KNO_3-heat of fusion) and the thermochemical systems ($Ca(OH)_2$, $CaCO_3$, hydrides) depend only on the mass as variable (Formula 2). The signs $\Delta^R H$, c and $\tilde{M}$ describe the heat of fusion or reaction enthalpy, specific heat capacity and molar weight of the compound respectively.

$$Q = m \cdot \frac{\Delta^R H}{\tilde{M}} \tag{2}$$

If chemical reactions for heat storage are considered, the heat of reaction should be taken into account for comparison reasons. Under equilibrium state conditions the change of the Gibbs free energy $\Delta^R G$ (Formula 3) is 0.

$$\Delta^R G = \Delta^R H - T \cdot \Delta^R S \tag{3}$$

This means that the reaction enthalpy $\Delta^R H$ is equal to the expression $T\Delta^R S$, where $\Delta^R S$ is the entropy change of the reaction and T is the temperature. Entropy changes are high if solid-gas reactions occur. These systems are dominated through the entropy rise from the solid to the gaseous state. Gas-solid reactions are outstandingly suitable for the storage of heat, because of the easy separation of the released gas during the heat absorption. The released gases can be stored under the equilibrium pressure of the system (closed system), under pressure conditions, in large underground gas caverns or sometimes in liquefied form.

Thermochemical gas-solid reactions are suitable as short-term and long-term heat storage systems. Important for short-term heat storage applications is a good kinetics of the absorption and desorption of the gaseous compound, combined with good heat conductivity of the reaction bed. After the separation of both compounds during the heat storage process, the whole reaction energy is trapped in the system and can be used at any time without energy losses (long-term storage conditions).

In the following sections three interesting systems for high-temperature heat storage are presented and described in more detail. None of them is commercially available, but they are being intensively investigated for several high temperature applications.

2 Metal hydrides

Metal hydrides are materials that are produced from a metal, or a metal alloy and hydrogen gas. They are useful for the storage of hydrogen in the solid state. In reversible metal hydride systems, the absorption of hydrogen gas is combined with the release of heat. The same amount of heat must be added to the metal hydride system for the decomposition and release of hydrogen. The high heat amount and the stability over thousands of cycles (closed systems) turn metal hydrides into ideal candidates for different heat storage applications, depending on the thermodynamic properties of the metal hydrides system [6, 7]. Important data for selected metal hydrides useful for heat storage applications can be found in Table 2.1. Hydrogen gas in this application is used only as a working medium during heat storage and heat release. Hydrogen is proposed as a secondary energy carrier in a future hydrogen economy. Metal hydrides for heat storage can link the electricity and heat production with excess energy storage and distribution of hydrogen in future energy systems.

Table 2.1: Selected physical data of metal hydrides for heat storage applications

	H_2-content [wt.%]	$\Delta^R H$ [kJ mol^{-1} H_2]	heat storage density [kWh kg^{-1}]	equilibrium temperature at 1 bar [°C]
MgH_2	7.7	75	0.78	280 [8]
$NaMgH_3$*	4.0	86	0.47	380 [9]
Mg_2FeH_6	5.5	77	0.55	320 [8]
Mg_2NiH_4	3.6	62	0.31	250 [8]
CaH_2	4.8	181	1.19	950 [7]

* calculated for the reaction $NaMgH_3 \rightleftarrows NaH + Mg + H_2$

Metal hydride systems for heat storage can be constructed as closed systems with an intermediate storage of hydrogen under the dissociation pressure of the metal hydride given by the working temperature. In this case, the complete system is self-regulated and the status of the system depends only on the heat in- or output into the metal hydride bed.

Huge amounts of hydrogen for heat storage applications can be stored for example in salt caverns, available hydrogen pressure reservoirs or hydrogen gas pipelines or it can be exchanged with plants dealing with hydrogen e.g. refineries (Part A in Figure 2.1). Salt caverns for hydrogen storage already exist in Texas USA or in Teesside UK. In combination with a second metal hydride for the hydrogen uptake and release near room temperature (low tem-

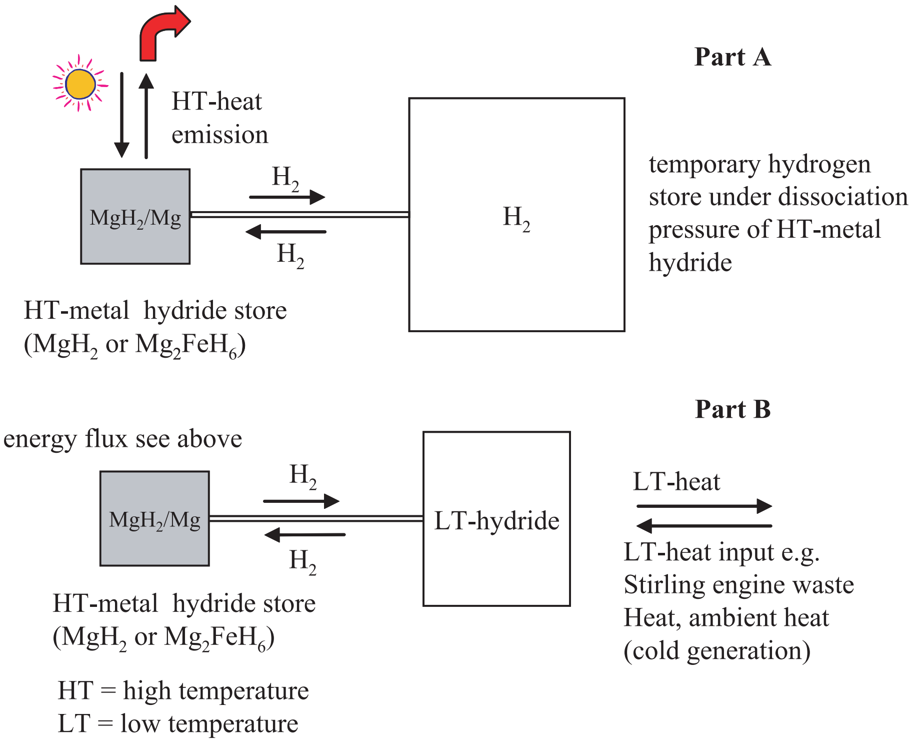

Fig. 2.1: Heat storage based on metal hydride/hydrogen system [6].

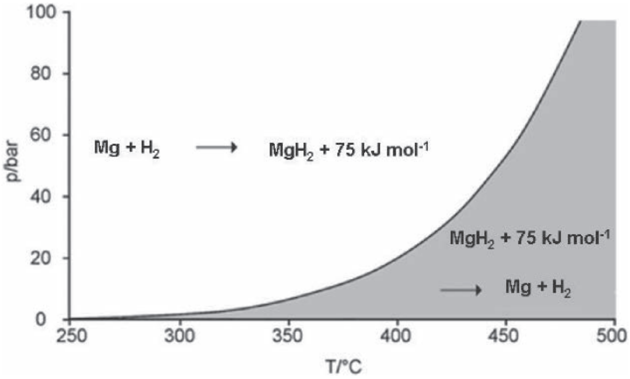

Fig. 2.2: Equilibrium pressure of MgH_2 depending on the temperature [6].

perature (LT)-hydride) the volume for the intermediate storage of hydrogen gas is drastically reduced (Part B in Figure 2.1).

Magnesium hydride has been regarded as a possible heat storage material over the last thirty years [10, 11]. It is a well-studied metal hydride compound with a working temperature around 400 °C. The reaction enthalpy is 75 kJ mol^{-1} resulting in a heat storage capacity around 0.8 kWh_{th} kg^{-1}. MgH_2 decomposes in a single reaction step into Mg-metal releasing one mol of H_2 (Equation 2).

$$MgH_2 + 75\ \mathrm{kJ\ mol^{-1}} \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} Mg + H_2 \qquad \text{(Eq. 2)}$$

The hydrogen gas can be stored in a pressure tank under the equilibrium pressure of MgH_2.

Figure 2.2 shows the equilibrium pressure of MgH_2 depending on the temperature. The equilibrium pressure of MgH_2 at 350 °C is 10 bar and 20 bar at 400 °C. If the pressure is lower than the equilibrium pressure at the given temperature (grey area in Figure 2.2) MgH_2 decomposes until the pressure inside the closed system reaches 10 bar at 350 °C or 20 bar at 400 °C. At pressures higher than the equilibrium pressure Mg-metal can be hydrogenated (white area in Figure 2.2). With the selection of the backpressure in the closed system and the overall volume of the system the heat release and storage can be cycled in small temperature ranges or at one temperature if the volume of the hydrogen reservoir is “endless”. Under heat storage conditions MgH_2 decomposes e.g. at 400 °C until the pressure inside the system reaches 20 bar (equilibrium conditions). If the temperature is not increased the decomposition comes to an end. Heat release is combined with a reduction of the temperature in the metal hydride bed. This means that the pressure inside the system is now higher compared to the equilibrium pressure at the lower temperature, consequently Mg-metal is hydrogenated and heat is released from this reaction. With a backpressure of 10 bar, the lowest temperature for the released heat is 350 °C. As mentioned before, the temperature range of heat release and storage can be reduced if the backpressure and the volume of the hydrogen reservoir are adapted to the amount of produced or absorbed hydrogen gas and the working temperature of the heat storage system.

The production of directly generated superheated steam from the thermochemical MgH_2/Mg heat storage system was shown several years ago [12]. With an amount of 14.5 kg Mg-powder the system has the ability to produce 10 kWh of heat, mostly on the same temperature level.

Magnesium is a ubiquitous element and therefore relatively low in price. Because of its high hydrogen storage amount (7.7 wt.%) it is under commercialization for the storage of hydrogen. With the addition of different transition metals (Ni, Ti) or transition metal oxides the kinetic of hydrogenation and dehydrogenation can be extremely accelerated.

Another lightweight metal hydride, suggested as a possible heat storage material is $NaMgH_3$. The overall hydrogen amount is 6 wt.%. The material can be prepared in a simple ball milling process from NaH and MgH_2 or it is produced through hydrogenation from the pure metal Na and Mg or from a mixture of one metal and one metal hydride. The decomposition/hydrogenation proceeds in two steps. The first decomposition produces Mg-metal and sodium hydride. An amount of 4 wt.% hydrogen is released during this step. Additional 2 wt.% of H_2 are released in the second step from the mixture of NaH + Mg.

$$NaMgH_3 + 86\ \mathrm{kJ\ mol^{-1}} \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} NaH + Mg + H_2 \qquad \text{(Eq. 3)}$$

$$NaH + Mg \rightleftarrows Na + Mg + 1/2\ H_2 \qquad \text{(Eq. 4)}$$

The reaction enthalpy for the first step is 86 kJ mol^{-1} H_2, slightly higher compared to pure MgH_2 with a Δ^RH of 75 kJ mol^{-1} H_2. At 410 °C the hydrogen dissociation pressure is only 2 bar and at 500 °C around 11 bar [9]. The high reaction enthalpy in combination with a flat pressure plateau and negligible hysteresis (Figure 2.3) makes $NaMgH_3$ a potential and interesting material for heat storage in solar and other heat applications. Since long-term behavior of the material is unknown, this compound is currently under ongoing investigation.

An interesting material for heat storage useable at higher temperatures than MgH_2 is Mg_2FeH_6 with a gravi-

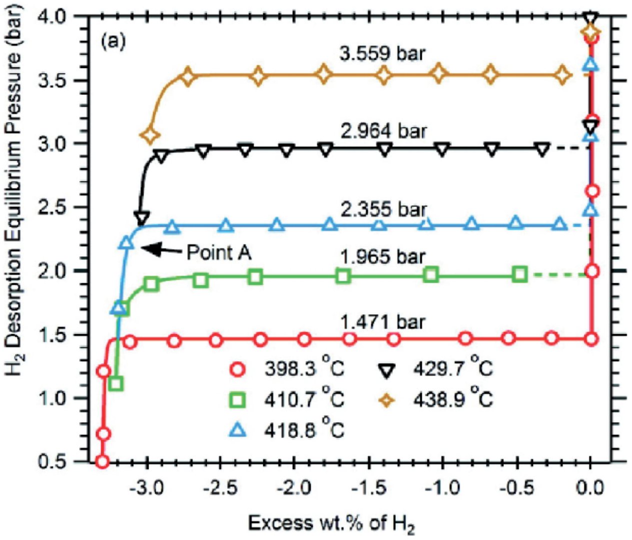

Fig. 2.3: Pressure concentration isotherms of $NaMgH_3$ at different temperatures. Reprinted with permission from [9]. Copyright (2011) American Chemical Society.

metric hydrogen content of 5.5 wt.%. It can be easily prepared from stoichiometric mixtures of Mg and Fe powders at 450 °C and at hydrogen pressures between 20–120 bar. During the reversible hydrogenation/dehydrogenation process, the Mg_2FeH_6 produces two moles of Mg, one mole of iron and releases 3 moles of hydrogen (Equation 5). Magnesium and iron are completely immiscible to each other and do not produce any kind of alloy or intermetallic compound over the whole concentration range. Therefore, a complete separation into two metallic phases is observed during every decomposition process.

$$Mg_2FeH_6 + 77\ \mathrm{kJ\ mol^{-1}} \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} 2\,Mg + Fe + 3\,H_2 \qquad \text{(Eq. 5)}$$

Mg_2FeH_6 shows a somewhat higher reaction enthalpy $\Delta^R H$ compared to MgH_2 (77 kJ mol^{-1} H_2 vs. 75 kJ mol^{-1} H_2) resulting in a lower dissociation pressures at the same temperature. The hydrogen dissociation pressure is e.g. 66 bar at 500 °C for Mg_2FeH_6 and 100 bar for MgH_2. The material shows excellent cycle stability under severe conditions without any capacity loss. In a cycling test over 50 cycles at temperatures of 510 °C (hydrogenation) and 590 °C (dehydrogenation) and in a pressure range between 138–149 bar H_2 a constant hydrogen amount of 5.1–5.2 wt.% is observed without any degradation [13] (Figure 2.4). Under these pressure conditions, heat can be delivered at temperatures between 550–556 °C.

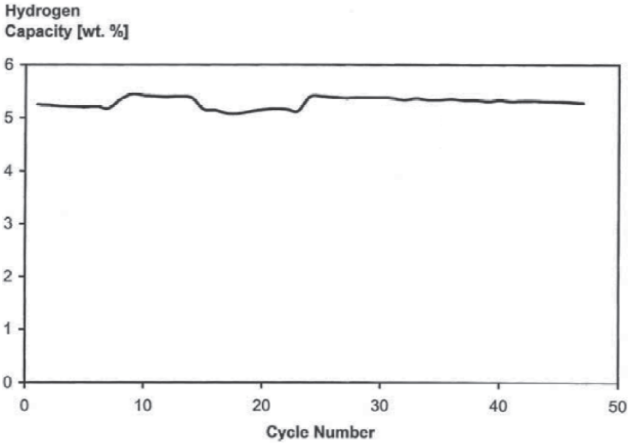

Fig. 2.4: Hydrogen storage capacity of Mg_2FeH_6. Cycling conditions: hydrogenation/dehydrogenation 510/590 °C, 138–139 bar. Reprinted from [13], with permission from Elsevier.

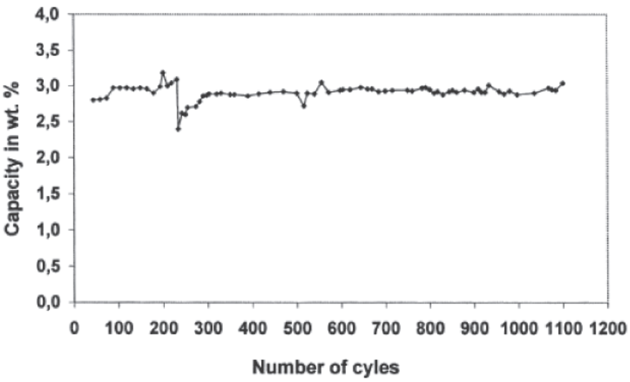

Fig. 2.5: Cyclic stability of Mg_2Ni. Cycling conditions: hydrogenation/dehydrogenation 230/330 °C, 0.4–2.8 bar, 3 h for one cycle. Reprinted from [14], with permission from International Assoc of Hydrogen Energy.

The experimentally realized heat storage densities without any optimization is 0.54 $kWh_{th}\ kg^{-1}$ based on the weight and 0.65 $kWh_{th}\ dm^{-3}$ based on the volume.

In contrast to Mg and Fe, magnesium and nickel produce an intermetallic compound Mg_2Ni. The corresponding metal hydride, Mg_2NiH_4, is also suitable for heat storage applications with a theoretical hydrogen amount of 3.6 wt.% [14]. During the decomposition of Mg_2NiH_4 the compound Mg_2Ni is produced and 2 mol of H_2 are released (Equation 6).

$$Mg_2NiH_4 + 62\ \mathrm{kJ\ mol^{-1}} \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} Mg_2Ni + 2\,H_2 \qquad \text{(Eq. 6)}$$

The reaction enthalpy $\Delta^R H$ is only 62 kJ mol^{-1} H_2 [14], lower than for MgH_2 and Mg_2FeH_6. Mg_2NiH_4 can be used for heat storage application in a temperature range 230–330 °C and shows good cyclic stability over thousands of cycles

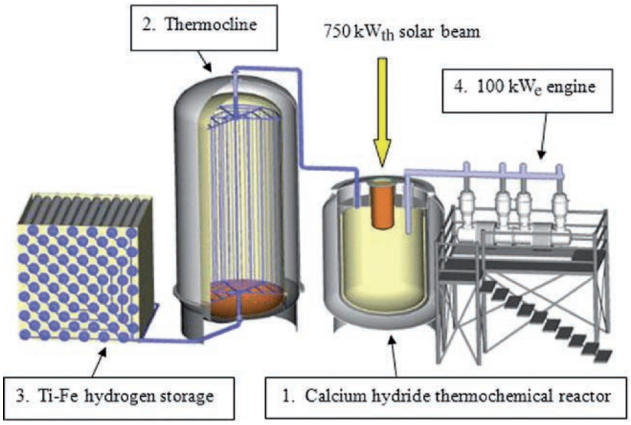

Fig. 2.6: Conceptual 100 kW$_{el}$ calcium hydride reactor with thermocline heat storage and TiFe-hydride hydrogen storage, © [2012] IEEE. Reprinted, with permission, from [7].

(Figure 2.5). Under conditions of the long term cycling test a heat density of 0.25 kWh$_{th}$ kg^{-1} is observed.

A possible metal hydride system operating at very high temperatures around 900 °C is CaH_2. The reaction enthalpy of CaH_2 is $\Delta^R H$ is 181 kJ mol^{-1} H_2 resulting in 1.19 kWh$_{th}$ kg^{-1}, which is much higher compared to MgH_2. Like Mg-metal, calcium belongs to the alkaline earth metals and forms a similar metal hydride compound. Starting from CaH_2 it decomposes into Ca metal and releases one mol of hydrogen (Equation 7).

$$\mathrm{CaH_2 + 181\ kJ\ mol^{-1}} \quad \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} \quad \mathrm{Ca + H_2} \qquad \text{(Eq. 7)}$$

CaH_2 is currently under investigation as a heat storage compound for concentrated solar power systems. The Australian company EMC Solar has developed a concept for a CST (concentrated solar tower) plant with a CaH_2-heat storage system and a Stirling engine with a continuous output of 100 kW$_{el}$ (Figure 2.6) [7]. The released hydrogen during the energy storage process is stored in Ti-Fe-hydride, a low temperature metal hydride with a working temperature around 20 °C. Calculated for an 18 h storage capacity an amount of 3 tons of Ca is required. The principal functionality of the CaH_2-storage system was shown for a 50 kg CaH_2 test reactor.

3 Metal hydroxides

Hydroxides for heat storage purposes result usually by reaction of water (steam) and metal oxides, preferable from the alkaline and alkaline earth metals. Decomposition reactions with hydroxides of the first alkaline group like LiOH, NaOH, KOH, RbOH or CsOH, all of them in liquid state, are described in the following equation (Equation 8):

$$\mathrm{2\,MeOH} \quad \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} \quad \mathrm{Me_2O + H_2O} \qquad \text{(Eq. 8)}$$

Me = Li, Na, K, Rb, Cs

Only LiOH is pointed out as a good storage material for solar heat storage. The alkaline earth metal hydroxides like $Mg(OH)_2$, $Ca(OH)_2$, $Sr(OH)_2$ or $Ba(OH)_2$ have been considered as heat storage materials [15].

$$\mathrm{Me(OH)_2} \quad \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} \quad \mathrm{MeO + H_2O} \qquad \text{(Eq. 9)}$$

Me = Mg, Ca, Sr, Ba

Beside of them also $Cu(OH)_2$ was proposed as a candidate for storage of thermal energy [3]. However, mainly the hydroxides $Ca(OH)_2$ and $Mg(OH)_2$ were investigated theoretically and experimentally. The thermodynamics ($T_{eq,1\ bar}$, reaction enthalpy $\Delta^R H_{298K}$ and reaction entropy $\Delta^R S_{298K}$) and operational data ($T_{exothermic}$, $T_{endothermic}$) for these both hydroxides are given in Table 3.1.

The data shown in Table 3.1 for the metal hydroxides $Ca(OH)_2$ and $Mg(OH)_2$ are based on systems with evaporated water (steam). The operational temperatures $T_{exothermic}$ and $T_{endothermic}$ describe required temperatures for discharging or recharging the heat storage system.

In highly superheated steam, MgO is inactive and reaction rates decrease with enhance of temperature. Below 230 °C MgO reacts with steam, if it is superheated only in the range of 35–75 K [5]. These characteristics were not observed for $Ca(OH)_2$. As emphasized in Figure 3.1 the reaction enthalpy of $Mg(OH)_2$ changes much more in depen-

Table 3.1: Temperatures, enthalpies and entropies for $Ca(OH)_2$ and $Mg(OH)_2$ [3].

Reaction	$T_{eq,1bar}$ [K]	$T_{exothermic}$ [K]	$T_{endothermic}$ [K]	$\Delta^R H_{298K}$ [kJ mol^{-1}]	$\Delta^R S_{298K}$ [J mol^{-1} K^{-1}]
$CaO_{(s)} + H_2O_{(g)} \rightleftharpoons Ca(OH)_{2(s)}$	752	675	800	109.2	145.2
$MgO_{(s)} + H_2O_{(g)} \rightleftharpoons Mg(OH)_{2(s)}$	531	450	550	81.2	152.8

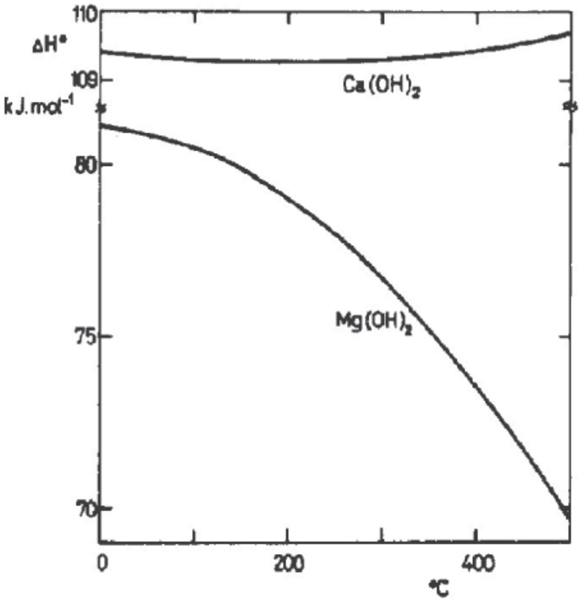

Fig. 3.1: Enthalpy of dehydration reaction in dependence on temperature for $Ca(OH)_2$ and $Mg(OH)_2$, reprinted from [16], with permission from Elsevier.

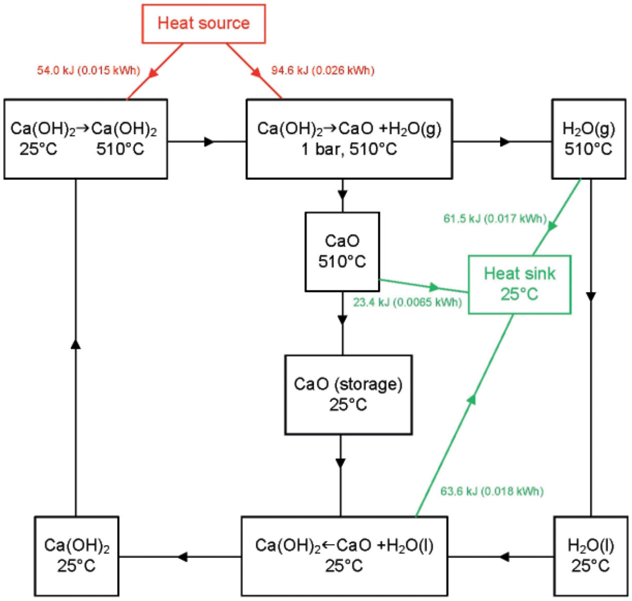

Fig. 3.2: Heat storage cycle of $Ca(OH)_2$ system with separately stored products CaO and H_2O at ambient temperature [17].

dence on the temperature up to 500 °C compared to the reaction enthalpy of $Ca(OH)_2$ [16].

The capacity degradation of $Mg(OH)_2$ system was reported to be quite high. In one investigation the capacity dropped from 95% to 60–70% after 40 cycles (in total 500 cycles), whereas the capacity of $Ca(OH)_2$ was stable at 95% (211 cycles) [5]. Also energy losses, if condensation/evaporation energy is considered, are higher for $Mg(OH)_2$ (1/2 of the total energy) than for $Ca(OH)_2$ (1/3 of the total energy) [5]. Due to the above mentioned reasons and the lower material costs for $Ca(OH)_2$ compared to $Mg(OH)_2$, calcium hydroxide is much more attractive for heat storage applications. Theoretical and practical heat storage densities of $Ca(OH)_2$ in relation to the volume are 615 $kWh_{th}\ m^{-3}$ and 246 $kWh_{th}\ m^{-3}$ respectively [3, 5].

A heat storage cycle based on $Ca(OH)_2$, with the exchanged thermal energies is shown in Figure 3.2 [17]. Each value of the transported heat is related to one mol H_2O stored as a liquid, which reacts when heat is desired (in Figure 3.2 during the night or wintertime) with solid CaO at ambient temperature. It is pointed out, that also sensible heat is needed to cool down the products or for heating of $Ca(OH)_2$ in the heat storage reaction at 510 °C.

The temperature of solid CaO can rise as high as 535 °C, when the reaction with water (CaO sphere in water flow at 2 $m\ s^{-1}$, 30 °C) takes place [18]. The evolved thermal energy is used then for water evaporation and superheating, and therefore partially uses of the released heat for the phase change of water decreases the available heat. So the reaction enthalpy for the $Ca(OH)_2$ system is $\Delta^R H_{298K} = 73.7\ kJ\ mol^{-1}$ if liquid water is considered [5] in comparison to 109.2 $kJ\ mol^{-1}$ (see Table 3.1) if there is another heat source for the phase change and if steam is already available. It would be advantageously if CaO could be operated within an industrial application, which is able to exchange steam for some purposes, such as power generation using steam turbines. When liquid water is stored, also the heat of condensation has to be consumed by an appropriate cooling device. In this case, it would be an energetic advantage, if any application is available which can consume the superheated low pressure steam (e.g. 5 bar at 589 °C [1]).

Recent investigations at DLR Germany have shown new results for material data of $Ca(OH)_2$ and CaO regarding heat capacity, reaction enthalpy and kinetics [19]. In laboratory experiments $Ca(OH)_2$ was tested with partial pressures of H_2O up to 0.956 bar and also 100 cycling tests were carried out without any significant losses of conversion ability. The equilibrium partial pressure of 1 bar was achieved at 505 °C and the estimated reaction enthalpy was 104.4 $kJ\ mol^{-1}$. In the past, equilibrium pressures up to 50 bar at 800 °C (94 $kJ\ mol^{-1}$ reaction enthalpy) were reported [20] and experiments with melted material at 1000 bar were published [21]. However one problem for the operation of $Ca(OH)_2$ reactors is the tendency towards agglomeration of the material particles and the low permeability of the packed bed. The drawback of permeability seems to be solved in optimized reactors, when steam flows through the reactor [22], but agglomeration is still a problem [23]. Other demerits of metal hydroxides used as materials for heat storage applications are their poor heat transport characteristics [24] (thermal conductivity of $Ca(OH)_2$ is in the range of 0.6 $W\ m^{-1} K^{-1}$ [25]), possible crystallization after dehydration [26] and sintering at higher temperatures [27]. The reaction kinetics are enhanced and the decomposition temperature of $Ca(OH)_2$ is decreased, when dopants like $Ni(OH)_2$, $Zn(OH)_2$ or $Al(OH)_3$ are used [28]. Also additives like Zn, Al and Cu were tested as admixtures to $Ca(OH)_2$ and prepared to pellets [29]. These additives can significantly increase the reaction rate with Al as the most advantageous one. However pelletized $Ca(OH)_2$ shrinks after dehydration and because of volume expansion during rehydration, cracks are generated, so the shape of the pellets after several cycles can vanish and the pellets are destroyed.

As mentioned above the thermal conductivity of calcium hydroxide is very low and therefore improvements in this field are necessary. The insertion of copper fins in the packed bed were investigated and showed very good enhancement of heat transfer characteristics [17]. Heat transport can be improved, if fluidization of the material particle can be achieved [1], which is currently under investigation. It is worthy to mention, that also combined $Ca(OH)_2$-$CaCO_3$ systems were investigated [30]. In this case instead of carbonation of CaO, $Ca(OH)_2$ reacts with CO_2 to $CaCO_3$. In this case the carbonation of calcium hydroxide takes place at lower temperatures compared to the carbonation of CaO, with higher conversion rates and positive effects concerning material aging.

The heat storage systems on the basis of metal hydroxides can be operated in such a way, that the heat transport can be realized directly or indirectly as pointed out for $Ca(OH)_2$ in [1]. In the former case steam and inert fluid is entering the reactor charged with CaO, when heat demand occurs. The inertial fluid transports the heat to the heat demand, which is produced from the reaction of steam and calcium oxide. In the opposite case, when heat should be stored, a thermal energy carrying inertial fluid at appropriate temperature enters the reactor. Than the heat is stored during the decomposition of the metal hydroxide and the mixture of both fluids (inertial fluid and the steam) escape the vessel. This direct heat exchange is more effective compared to a transport with an additional heat exchanger installed in the heat storage reactor. In the later case, the heat storage system can be used as a closed system. After the separation of CaO and steam, the storage of both products is desired [1] or the steam can be exchanged for some other purposes without storage. For a closed heat storage system, when additional storage volume for condensed steam is needed, a volumetric heat capacity of 364 $kWh_{th}\ m^{-3}$ can be achieved, whereas in an open system a volumetric heat capacity of 462 $kWh_{th}\ m^{-3}$ was reported [1]. Beside the DLR system for heat storage based on $Ca(OH)_2$ there are only few known constructed heat storage systems [25].

4 Metal carbonates

Metal carbonates are further potential candidates for high-temperature heat-storage systems. The decomposition reactions of metal carbonates provide similar possibilities of heat-storage to the hydroxides.

Among the carbonates, $CaCO_3$ has been considered as the most promising heat-storage material [31]. Depending on the manageable CO_2-pressure, a $CaCO_3$ based system appears to be suitable for high-temperature heat-storage above 700 °C [32]. The construction of a heat storage system with metal carbonates follows the same logic as applied to the metal hydrides with an intermediate storage of CO_2. The necessary pressure for liquefaction of CO_2 at room temperature is around 60 bar. Storage of CO_2 under these conditions reduces the volume for the intermediate gas storage significantly.

$$CaCO_3 + 167\ kJ\ mol^{-1} \quad \underset{\text{heat recovery}}{\overset{\text{heat storage}}{\rightleftarrows}} \quad CaO + CO_2 \qquad \text{(Eq. 10)}$$

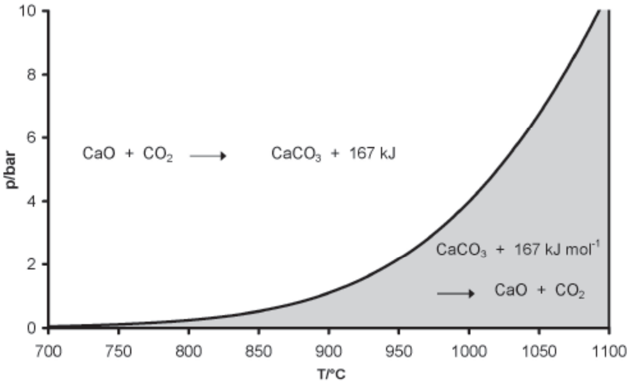

Fig. 4.1: Equilibrium decomposition pressure of the system $CaCO_3$/CaO/CO_2 depending on the temperature for [33].

The process described by the above equation is also known as the calcination of limestone to produce the widely used chemical compound quicklime.

The equilibrium temperature at 1 bar of CO_2 is 896 °C, reaction enthalpy at 1 bar is $\Delta^R H = 167\ \mathrm{kJ\ mol^{-1}}$, and the storage capacity of the solid is 0.6 $\mathrm{kWh_{th}\ kg^{-1}}$. Assuming a porosity of 50% – the volumetric storage capacity is 670 $\mathrm{kWh_{th}\ m^{-3}}$. Taking into account the volumes of the tanks of a complete heat storage system, the volumetric storage density amounts to 113 $\mathrm{kWh_{th}\ m^{-3}}$ [34].

$CaCO_3$ is one of the most abundant compounds on earth and is found frequently in geologic settings. The pure calcium carbonate minerals are calcite, aragonite and vaterite. The majority of $CaCO_3$ used in industrial processes is extracted by mining or quarrying. Pure $CaCO_3$ can be prepared from burnt lime by adding water to give a solution of $Ca(OH)_2$ and passing CO_2 through the solution to precipitate $CaCO_3$.

In the heat storage process, the carbonate is decomposed to CO_2 and metal oxide. The reversible reaction leads to the release of the reaction enthalpy by absorbing the CO_2. The output temperature of the reactor can be controlled by adapting the CO_2-pressure: If the CO_2-pressure during the carbonation-process is higher than the CO_2-pressure during the decarbonation-process, then the carbonation-reaction will take place at higher temperatures than the temperatures where the decomposition of $CaCO_3$ had occurred [31].

Regarding the working pressures it is found, that for the heat storage process, e.g. the decarbonation of $CaCO_3$, the pressure of CO_2 has to be below half of the equilibrium-pressure of CO_2 in order to obtain usable reaction rates [35].

In comparison to the hydroxides differences result due to higher decomposition temperatures and higher storage capacities. Furthermore, the desorbed CO_2 has to be stored in an adequate way, e.g. as a liquid by mechanical compressing is. This leads to parasitic losses of energy [5].

Alternative methods for storing the CO_2 are
- absorbing the CO_2 on other metal oxides or
- adsorbing the CO_2 on appropriate adsorbents.

For the discharge of the high temperature heat the stored CO_2 has to be released thermally at a lower temperature level in order to react with the calcium oxide.

Such systems can be build up as chemical heat pumps (CHP). E.g., a $CaO/CO_2 + PbO/CO_2$ – system has been investigated as CHP with the capability to store heat at 900 °C (decarbonation of $CaCO_3$) and to release heat up to 997 °C (carbonation of CaO). The heat storage capacity of this CHP-system was evaluated to 0.22–0.25 $\mathrm{kWh_{th}\ kg^{-1}}$ [36, 37, 38].

The system CaO/CO_2 has been investigated as a promising possibility for high-temperature heat-storage since a long time. It had been found, that the decarbonation-carbonation cycle of $CaCO_3$ in the form of a powder with particle sizes around 10 μm is not wholly reversible. Furthermore, there is also a continuous loss of reversibility with increasing number of reaction-cycles, which is explained mainly by a decrease of the surface area of CaO by sintering of the particles. It has also been shown, that the reaction-cycle using significantly smaller CaO-particles (10 nm), where the reaction of CO_2 with CaO is not diffusion-controlled, can be made almost wholly reversible [39].

Further enhancements of the long-term stability could be achieved by introducing an inert framework, e.g. of $CaTiO_3$, in the CaO-reactant [40].

Until now, the practical application of the experimental and theoretical investigations concerning $CaCO_3$ as heat storage material in field-scale is not performed.

5 Conclusion

The intermediate storage of heat will become an important point in future energy systems to compensate the fluctuating production of electricity and heat from renewable and carbon based power plants. In comparison to other heat storage systems, thermochemical reactions can store much larger amounts of heat on different high temperature levels. In thermochemical gas-solid reactions with H_2O, H_2 or CO_2 as gaseous compounds all gases are only working media and not consumed or burned during the heat storage and heat release. Thermochemical heat storage systems are self-regulated and the status of the system depends only on the in- and output of energy. Metal hydrides, metal hydroxides and metal carbonates are important systems currently under intensive investigation. Indeed, such systems have already been investigated in the past, but now they attract new attention for the storage of heat in solar thermal power plants or as intermediate storage of heat in conventional power plants. Most of the described systems were not tested on a technical scale until now. Scientific and engineering challenges (e.g. heat conductivity, kinetics) must be solved in the next years, before these systems can be successfully implemented in new developed energy systems based on renewable production. They have the potential to become an important part for sustainable and ecological handling of energy.

Received: March 4, 2013. Accepted: April 29, 2013.

References

[1] Kerskes H, Bertsch F, Mette B, Wörner A, Schaube F. Thermochemische Energiespeicher. Chem Ing Tech. 2011; 83 (11): 2014–26.

[2] Kato Y. Chemical Energy Conversion Technologies for Efficient Energy Use, In Thermal Energy Storage for Sustainable Energy Consumption, Ed. H.Ö. Paksoy, Springer Netherlands 2007, 377–91.

[3] Garg HP, Mullick SC, Bhargava AK. Chemical Energy Storage, In Solar Thermal Energy Storage, D. Reidel Publishing Company Holland 1985, 292–427.

[4] Gil A, Medrano M, Martorell I, Lazaro A, Dolado P, Zalba B, Cabeza LF. State of the art on high temperature thermal energy storage for power generation. Part 1-Concepts, materials and modellization. Renew Sust Energ Rev. 2010; 14 (1): 31–55.

[5] Ervin G. Solar Heat Storage Using Chemical Reactions. J Solid State Chem. 1977; 22 (1); 51–61.

[6] Felderhoff M, Bogdanović B. High temperature metal hydrides as heat storage materials for solar and related applications. Int J Mol Sci. 2009; 10: 325–44.

[7] Harries DN, Paskevicius M, Sheppard DA, Price TEC, Buckley CE. Concentrating Solar Thermal Heat Storage Using Metal Hydrides. Proc. IEEE. 2012; 100: 539–49.

[8] Yvon K, Metal Hydrides, In: Hydrogen as a Future Energy Carrier, Ed. A. Züttel, A. Borgschulte and L. Schlapbach, 2008 WILEY_VCH Verlag GmbH&Co. KGaA, Weinheim, 195–203.

[9] Sheppard DA, Paskevicius M, Buckley CE. Thermodynamics of hydrogen desorption from $NaMgH_3$ and its application as a solar heat stoarge medium. Chem Mat. 2011; 23: 4298–300.

[10] Bogdanović B, Ritter A, Spliethoff B. Active MgH_2-Mg systems for reversible chemical energy storage. Angew Chem Int Ed. 1990; 29 (3): 223–34.

[11] Bogdanović B, Hartwig Th, Spliethoff B. The development, testing and optimization of energy-storage materials based on the MgH_2-Mg System. Int J Hydrogen Energy 1993; 18 (7): 575–89.

[12] Bogdanović B, Ritter A, Spliethoff B, Straßburger K. A process steam-generator based on the high-temperature magnesium hydride magnesium heat-storage system. Int J Hydrogen Energy 1995; 20 (10): 811–22.

[13] Bogdanović B, Reiser A, Schlichte K, Spliethoff B, Tesche B. Thermodynamics and dynamics of the Mg-Fe-H system and its potential for thermochemical thermal energy storage. J Alloys Compd. 2002; 345: 77–89.

[14] Reiser A, Bogdanović B, Schlichte K. The application of Mg-based metal-hydrides as heat energy storage systems. Int J Hydrogen Energy. 2000; 25 (5): 425–30.

[15] Wentworth WE, Chen E. Simple thermal decomposition reactions for storage of solar thermal energy. Sol Energy. 1976; 18 (3): 205–14.

[16] Hartman M, Trnka O, Svoboda K, Kocurek J. Decomposition kinetics of alkaline-earth hydroxides and surface area of their calcines. Chem Eng Sci. 1994; 49 (8): 1209–16.

[17] Kanzawa A, Arai Y. Thermal energy storage by the chemical reaction augmentation of heat transfer and thermal decomposition in the $CaO/Ca(OH)_2$ powder. Sol Energy. 1981; 27 (4): 289–94.

[18] Dutta S, Shirai T. Experimental investigation on a fast and exothermic solid-liquid reaction system. Chem Eng Sci. 1980; 35 (1–2): 209–16.

[19] Schaube F, Koch L, Wörner A, Müller-Steinhagen H. A thermodynamic and kinetic study of the de- and rehydration of $Ca(OH)_2$ at high H_2O partial pressures for thermo-chemical heat storage. Thermochim Acta. 2012; 538: 9–20.

[20] Samms JAC, Evans BE. Thermal dissociation of $Ca(OH)_2$ at elevated pressures. J Appl Chem. 1968; Vol. 18 (1): 5–8.

[21] Wyllie PJ, Tuttle OF. Melting of portlandite in the system CaO-H_2O. J Am Ceram Soc. 1959; 42 (9): 448–9.

[22] Roßkopf C, Linder M, Wörner A. Optimierung der Reaktionsbetteigenschaften für thermochemische Energiespeicher. Chem Ing Tech. 2012; 84 (8): 1244.

[23] Schaube F, Kohzer A, Schütz J, Wörner A, Müller-Steinhagen H. De- and rehydration of $Ca(OH)_2$ in a reactor with direct heat transfer for thermo-chemical heat storage. Part A: Experimental results. Chem Eng Res. 2013; 91 (5): 856–64.

[24] Schmidt EW. Reversible chemische Reaktionen zur Wärmespeicherung. VDI-Berichte NR. 288, 1977.

[25] Fujii I, Tsuchiya K, Higano M, Yamada J. Studies of an energy storage system by use of the reversible chemical reaction: $CaO + H_2O \rightleftarrows Ca(OH)_2$. Sol Energy. 1985; 34 (4–5): 367–77.

[26] Anderson PJ, Horlock RF. Thermal decomposition of magnesium hydroxide. Trans Faraday Soc. 1962; 58: 1993–2004.

[27] Borgwardt RW. Sintering of nascent calcium oxide. Chem Eng Sci. 1989; 44 (1): 53–60.

[28] Murthy MS, Raghavendrachar P, Sriram SV. Thermal decomposition of doped calcium hydroxide for chemical energy storage. Sol Energy. 1986; 36 (1): 53–62.

[29] Fujii I, Ishino M, Akiyama S, Murthy MS, Rajanandam KS. Behavior of $Ca(OH)_2/CaO$ pellet under dehydration and hydration. Sol Energy. 1994; 53 (4): 329–41.

[30] Criado JM, Macias M, Macias-Machín A. Analysis of the system CaO-CO_2-H_2O for storage of solar thermal energy. Sol Energy; 1992, 49 (2): 83–6.

[31] Kyaw K, Matsuda H, Hasatani M. Applicability of carbonation/decarbonation reactions to high-temperature. Thermal energy storage and temperature upgrading. J Chem Eng Jpn. 1996; 29 (1): 119–25.

[32] Barker R. The reactivity of calcium oxide Towards carbon dioxide and its use for energy storage. J Appl. Chem Biotechnol 1974; 24: 221–7.

[33] Lide DR (ed.) CRC Handbook of Chemistry and Physics (86th ed.). Boca Raton (FL). CRC Press. ISBN 0-8493-0486-5

[34] Schaube F, Wörner A, Tamme R. High temperature heat storage for concentrated solar power using gas-solid reactions. J Sol Energy Eng. 2011; 133: 031006-1–031006-7.

[35] Kubota M, Kyaw K, Watanabe F, Matsuda H, Hasatani H. Study of decarbonation of $CaCO_3$ for high temperature thermal energy storage. J Chem Eng Jpn. 2000; 33 (5): 797–800.

[36] Kato Y, Yamada M, Kanie T, Yoshizawa Y. Calcium oxide/carbon dioxide reactivity in a packed bed reactor of a chemical heat pump for high-temperature gas reactors. Nucl Eng Des. 2001; 210: 1–8.

[37] Wongsuwan W, Kumar S, Neveu P, Meunier F. A review of chemical heat pump technology and applications. Appl Therm Eng. 2001; 21: 1489–519.
[38] Kato Y, Harada N, Yoshizawa Y. Kinetic feasibility of a chemical heat pump for heat utilization of high-temperature processes. Appl Therm Eng. 1999; 19: 239–54.
[39] Barker R. The reactivity of calcium oxide Towards carbon dioxide and its use for energy storage. J Appl. Chem Biotechnol 1974; 24: 221–7.
[40] Aihara M, Nagai T, Matsushita J, Negishi Y, Ohya H. Development of porous solid reactant for thermal-energy storage and temperature upgrade using carbonation/de-carbonation reaction. Appl Energy. 2001; 69: 225–38.

The Authors

Dr. Michael Felderhoff studied at the University of Essen, where he completed his Ph.D in 1993 in organic chemistry. After spending two additional years in Essen, he did postdoctoral studies at the Universities of Tübingen and Osnabrück working in the fields of radical chemistry and electrochromic materials. Since 1999 he is a member of the hydrogen storage group at the MPI für Kohlenforschung, responsible for the development of new metal hydrides for hydrogen and heat storage applications.

Robert Urbanczyk studied Mechanical engineering at the Universität GH Essen in Germany with the specialisation Energy science and graduated in February 2000. Afterwards he worked until 2007 at the meanwhile founded Universität Duisburg–Essen in research and academia field and supervised projects concerned with fuel cells and synthesis gas production and utilisation for fuel cells. Since April 2007 he works at the Institut für Energe- und Umwelttechnik e.V. (IUTA) in Duisburg Germany, where he develops hydrogen and heat storage systems based on metal hydrides.

Dr. Stefan Peil was born in 1958. After the study of chemistry at the Philipps-Universität Marburg and his doctoral thesis in physical chemistry there, he worked as a post-doc at the Alfred-Wegener-Institut für Polar- und Meeresforschung in Bremerhaven in the area of atmospheric chemistry. Since January 2000 he works at the Institut für Energie- und Umwelttechnik e.V. (IUTA) in Duisburg. His research areas are energy conversion and energy storage.