



# SFERA II

Solar Facilities for the European Research Area

Contract n° GA 312643

## SFERA II Project

### Solar Facilities for the European Research Area

<i>Document Title</i>	Deliverable N. D15.9 Survey on chemical storage applications for CSP
<i>Revision</i>	n.a.
<i>Diffusion date</i>	n.a.
<i>WP</i>	WP15
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<i>Verification</i>	n.a.

Project co-funded by the European Commission within the Seventh Framework Programme (2007-2013)		
Dissemination Level		
<b>PU</b>	Public	<b>X</b>
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	

#### For EC Approval

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SFERA II Project:

Start date 1 January 2014

End date 31 December 2017

WP15 Task 15.3, Task leader ENEA



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## INTRODUCTION

Solar energy is an abundant and unlimited resource, but its discontinuous nature represents nowadays a barrier to a large diffusion of this technology. Currently, energy dispatchability, that is, the ability to modulate the production of electricity according to the consumption, is a major challenge for the success of solar technology and, as a consequence, one of the active field in research. To date, significant progress has been made in the development of sensible heat thermal storage systems, that ensure the damping of solar fluctuations due to adverse weather conditions and allow the use of the accumulated heat overnight. These systems are for short term periods as they guarantee only a few hours of compensation. A bigger challenge is represented by the realization of long-term storage systems that would allow both to solve the problem of dispatchability of the solar energy and to maximize the capacity factor, aligning the seasonal production capacities of the concentrating solar power (CSP).

Chemical storage is a technology where the solar heat is used to carry out a reaction, or a series of reaction (charging phase); then, the obtained product is reacted when the solar radiation is not available, by an exothermic process, so making usable the solar heat previously stored (discharging phase). In this respect two main methods are applied: in a former one a reversible process is used, in general employing inorganic oxides, hydroxides or salts: the endothermic reaction is performed during the charging phase, and the exothermic one to discharge the energy stored. In another configuration a “solar fuel” is produced by means of the solar heat: hydrogen (by reforming, pyrolysis or thermochemical cycles), organic fuels, and so on. In that case the discharging phase is the combustion of the fuels.

In principle, the strong point of the methods is the possibility of a seasonal storage. A chemical can be produced during the summer and used over the rest of the year.

The present report, related to the subtask T15.3.5, describes and discusses the state of the art of this technology. The document is divided into the following sections:

- Review of solar thermal heat storage systems and comparison with the chemical storage
- Thermochemical storage: metal hydrides
- Thermochemical storage: hydroxides
- Thermochemical storage: Carbonates
- Thermochemical storage: Oxydes
- Chemisorption for chemical storage systems
- Solar driven hydrogen production
- Solar powered biomass upgrading



## COMPARISON BETWEEN SOLAR HEAT STORAGE SYSTEMS

Given the discontinuity of the solar irradiation, the diffusion of concentrating solar plants (CSP) is related to the possibility to store the solar thermal energy. A storage system is necessary both to compensate radiation fluctuations, due to atmospheric conditions, and to separate the phase when solar heat is gathered from the actual use of the accumulated energy. In this way it is possible to size a CSP in order to allow a continuous energy production over the year, irrespectively of seasonal or daily fluctuations of the solar radiation.

Actually, the real advantage of a CSP system with respect to a photovoltaic plant is the possibility to store great amounts of heat, while the accumulation of significant quantities of electric energy, by batteries, seems more costly and problematic.

The thermal energy can be stored by thermophysical or thermochemical technologies. In the former case, the heat is accumulated by increasing the temperature of a material (sensible heat storage) or by producing a phase change (latent heat systems). In the latter configuration, the solar energy is used to perform an endothermic chemical reaction.

In general, a thermal storage system (TES) is characterized by the following parameters:

- The density of storage, that is the quantity of thermal energy stored per mass (or volume) unit
- The efficiency of the storage, that is the ratio between the heat actually extracted during the discharging phase and the energy stored during the charging process
- The stability over the thermal or reaction cycles of the employed materials, and the heat losses of the systems

### SENSIBLE HEAT STORAGE

In a sensible heat storage system, the thermal energy is accumulated by increasing the temperature of a selected material, without any phase change.

The stored heat (Q) can be calculated as following:

$$Q = m \int_{T_i}^{T_f} C_p dT$$

where m is the mass of the storage medium,  $C_p$  its specific heat (in J/K Kgr) and  $T_i$  and  $T_f$  are, respectively, the initial and final temperature in the charging phase.

The storage materials can be solids, liquids or gases. Liquids present good specific heat values and thermal exchange properties, their restriction being a limited chemical stability. Water can be used below 100°C, while at higher temperatures thermal oils, molten salts and liquid metals can be adopted [1]. Oils can be generally used up to 300 °C, or 400 °C under pressure with an inert gas; they are costly, flammable, toxic and pollutant [2]. Molten salts and liquid metals can be employed above 300 °C, and especially the former materials have been extensively investigated in the last years [3][4].

Solid materials are more thermally stable and generally less costly, but their specific heat can be lower than the one of liquid mediums and, besides, an intermediate fluid is



necessary to ensure a proper heat transfer with the working fluid in a power block. A combination of liquid and solid materials can have interesting and cost effective features [5]. Table 1 summarizes the characteristics of several types of liquid and solids mediums [6].

**Table 1: Characteristics of some heat storage materials (HSM) used as sensible heat storage medium**

Medium	Type	T operating range (°C)	Specific Heat (J/Kg K)	Notes
Water	Liquid medium	0-374	4190	To be pressurized above 100 °C
Therminol 66	Oil	9-343	2100	To be used under inert at high temperatures
Hitec®	Molten salt	150-430	1550	NaNO <sub>3</sub> /KNO <sub>3</sub> /NaNO <sub>2</sub> of 7/53/40 wt%
“Solar Salt”	Molten salt	270-600	1550	NaNO <sub>3</sub> /KNO <sub>3</sub> 60/40 wt%
Sodium	Liquid metal	125-760	1300	High flammable with oxygen and water
Aluminium	Solid metal	<660	896	
Concrete	Solid		1130	
Potassium chloride	Solid Salt		670	
Aluminium oxide	Oxide		840	

## LATENT HEAT STORAGE

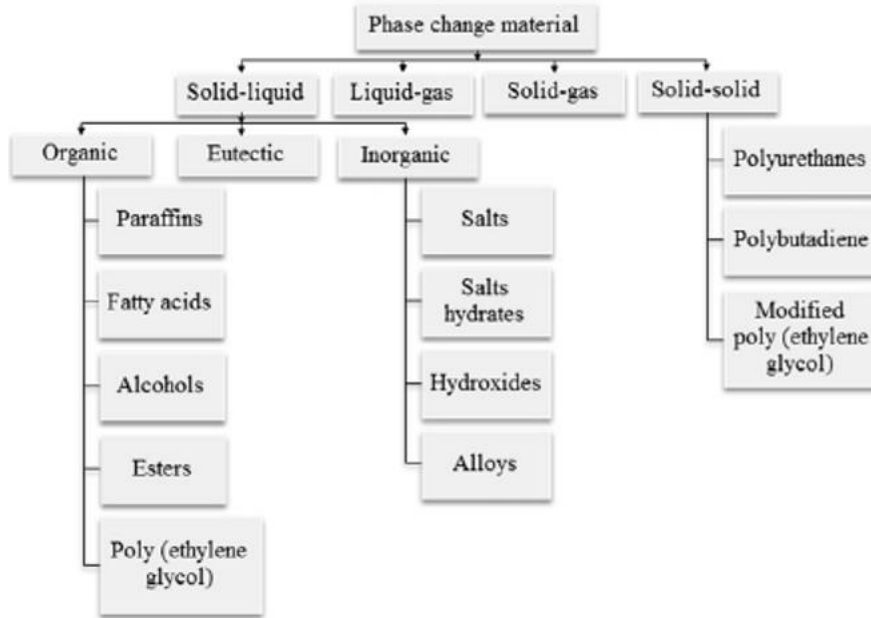
In a latent heat storage (LHS) system, the thermal energy is accumulated by a phase change in the selected medium (PCM). The stored energy (Q) is calculated as following:

$$Q = m \lambda$$

Where m is the mass of the PCM and  $\lambda$  the latent heat, in J/Kg.

In general, given the high energy density and a limited change in volume (10% or less [7]), solid/liquid transitions are employed.

The most used PCMs are eutectic mixtures of salts, also hydrates at low temperatures [8][9], however also other materials have been proposed, including organics [10], and eutectic metal alloys [11] as summarized in Fig. 1 [10].



**Fig. 1 Classifications of PCMs, from [10]**

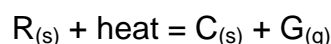
The key characteristics required to a good PCM are [10][12]: cost effectiveness, commercial availability, high energy density and thermal conductivity, volume change as limited as possible, non toxicity and flammability.

The main issues with this technology are the material stability under thermal cycles and the design of proper heat exchangers.

## CHEMICAL STORAGE

In thermochemical storage (TCS) the solar heat is stored as chemical energy by proper chemical reactions. The characteristics necessary for a good TCS system are [13][14]: high reaction enthalpy and quantitative reversibility (in case a reversible reaction is employed), no or limited secondary reactions, good reaction kinetics, low temperature difference between charging and discharging phases, cost effectiveness, limited or absent toxicity.

If a reversible reaction is used as TCS, it is also necessary to employ a heat transfer fluid (HTF) in order to ensure the heat transfer from the reaction to a power block working fluid [15]. In general, solid/gas decomposition processes are considered, given their high reaction enthalpy. Considering a generic reaction:



the requested heat ( $Q$ ) during the charging phase depends on the mol reacted ( $n_r$ ) and the reaction enthalpy:

$$Q = n_r \Delta H_{\text{reaz}}$$



In the discharging phase, in order to recover the stored energy, C and G are reacted together and the produced heat transferred to a proper HTF. The solids species can be virtually stored at room temperature, while the produced gas should be pressurized or liquefied.

This technology can in principle be used as seasonal thermal storage. The discharging temperature can be selected choosing an appropriate reversible reaction.

Some examples of solid/gas TCS systems are reported in table 2 [14][15][16][17].

**Table 2. TCS solid/gas systems**

Reaction	T <sub>eq</sub> (1 bar)	ΔH <sub>reaz</sub> (Kj/mol of reagent)
$\text{NH}_4\text{Cl} \rightleftharpoons \text{NH}_3 + \text{HCl}$	618	176.15
$\text{NH}_4\text{Br} \rightleftharpoons \text{NH}_3 + \text{HBr}$	677	188.32
$\text{MgH}_2 \rightleftharpoons \text{Mg} + \text{H}_2$	280	75
$\text{CaH}_2 \rightleftharpoons \text{Ca} + \text{H}_2$	250	181
$\text{NaMgH}_3 \rightleftharpoons \text{NaH} + \text{Mg} + \text{H}_2$	380	86
$\text{Ca(OH)}_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}$	479	109
$\text{Mg(OH)}_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O}$	258	84
$\text{MgCO}_3 \rightleftharpoons \text{MgO} + \text{CO}_2$	397	96
$\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$	837	178
$2\text{Co}_3\text{O}_4 \rightleftharpoons 6\text{CoO} + \text{O}_2$	890	195
$6\text{Mn}_2\text{O}_3 \rightleftharpoons 4\text{Mn}_3\text{O}_4 + \text{O}_2$	1000	31.9

## COMPARISON BETWEEN STORAGE SYSTEMS: FINAL REMARKS

The systems based on sensible heat storage are currently the most investigated and used. Their advantage is the manageability of the storage configuration, also considering the heat exchange characteristics. The main drawback is a low energy density, around 50 kWh/m<sup>3</sup>, that leads to the necessity to use large amounts of storage materials. In turn, that causes high costs, significant heat losses and possible temperature fluctuations during the discharging phase.

Latent heat storage is more convenient with respect to the energy density, that can reach values around 100 kWh/m<sup>3</sup>. Moreover, the temperature value during the discharging phase is practically constant. The disadvantage is a low actual thermal conductivity, which leads to the necessity to employ properly designed and costly heat exchange systems.

Chemical storage presents three main advantages with respect to the other storage technologies:

- High energy density, up to 500 kWh/m<sup>3</sup>
- Negligible heat losses, considering the possibility to store the reaction products at low temperatures
- Possibility to perform a long period (seasonal) storage

The last point is the more relevant for the LCA technology, given the best efficiency of sensible heat storage to manage daily and short term heat fluctuations. A limit of LCA configurations is the relative complexity of the storage systems, with the necessity to select

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a proper heat transfer fluid in case a reversible reaction is used. In that case, also the stability of the materials over the charging/discharging cycles is an important point to be taken into account.





## CHEMICAL STORAGE: METAL HYDRIDES

The reversible reactions involving metal hydrides have extensively been investigated for hydrogen storage. Since the 90s they have also been considered for thermal storage purposes. Actually, those reactions present high enthalpy, high stability (if reactants and products are kept under inert conditions) over the charging discharging phases (up to 1000 cycles) [14][18].

However, they present the following limitations [16]:

- High corrosive properties
- Necessity to a costly storage system for H<sub>2</sub>
- Low reaction velocity, which leads to the necessity to add catalyst materials, such as transition metals
- Sintering problems, that can be sorted out by using additives (Fe, for instance)
- Necessity to operate at high pressures, typically up to or above 100 bar

The alloys based on Mg are the most investigated, given their cost effectiveness, high enthalpy reaction and good reversibility. They operate at 590°C during charging and 510 °C in discharging (hydrogenation) with an energy storage density of 234 GJ/m<sup>3</sup>[19].

Calcium hydride can be operated at atmospheric pressure [20] and 3 Ton of that medium can guarantee 18 hours of thermal storage [20]. Another interesting system, to be applied at low pressure, is TiH<sub>1.72</sub> [21].

Table 3 resumes the features of some selected hydrides based systems.

**Table 3. Features of some hydrides based chemical storage systems, from [21]**

Hydride	T (°C) (discharging- charging)	Operating P (bar)	ΔH <sub>reaz</sub> (Kj/mol reactant)	Theoretical H <sub>2</sub> loading (KgH <sub>2</sub> /KgMH)	Bulk density (Kg/m <sup>3</sup> )	Cost (€/Kg)
MgH <sub>2</sub>	300-500	10-200	75	7.6	870	2.9
Mg <sub>2</sub> FeH <sub>6</sub>	350-550	10-200	77	5.5	1300	1.9
NaMgH <sub>3</sub>	400-600	10-80	88	4.0	1000	4.2
LiH	950-1150	0.1-1.5	190	12.6	500	70.0
TH <sub>1.72</sub>	650-950	0.5-10	142	3.5	1600	12.0
CaH <sub>2</sub>	900-1100	0.1-1.5	171	5.0	890	6.0
NaH	400-600	0.5-70	130	4.2	750	4.0



## CHEMICAL STORAGE: METAL HYDROXIDES

The most studied hydroxide/oxide couples are the Mg and Ca OH<sup>-</sup>/O systems. The latter, which operates in the interval 400-700°C, is considered one of the most chemical storage system since the 80s [22]. In fact, it presents very interesting characteristics:

- Cost effectiveness (50 €/ton [23])
- High reaction kinetics and stability [24], tested also in lab [25] and pilot scale plants [26]. Those tests confirmed the presence of high conversions (77-96%) until over 100 cycles. Kinetics models have been developed and validated [24][27].

The drawback is the sintering of the oxide/hydroxide particles, due to the small size of the granules ( $d_{50} \sim 5\mu\text{m}$ ), the low thermal conductivity (0.1– 0.4W/mK) and gas permeability. Moreover, the volumetric expansion of the particles during hydroxide formation limits the use of the medium as pellets. Therefore, the scientific research is currently focused on technical solution for overcoming those problems.

Theoretical studies have been carried out about the employment of fixed bed reactors, with direct or indirect contact with a heat transfer fluid. A direct concept reactor presents advantages regarding the heat exchange properties, but high pressure drops need to be considered operating with small size powders[25][26][28][29][30].

The sintering of the particles can be avoided by the insertion of additives, such as silica nanoparticles [31]. On the other hand, although the worsening of the heat exchange features, an indirect reactor concept seems preferable and more practical for large scale plants. That configuration has been tested on a relevant scale of 10kWth with 25Kg of material [26] and a kinetics model has been validated [32].

More recently, fluidized bed reactors have been investigated, in order to obtain good heat exchange properties, along with a reduction of sintering phenomena [33].



## CHEMICAL STORAGE: METAL CARBONATES

Calcium and magnesium carbonate are the materials potentially feasible for chemical storage applications, given their decomposition temperature is in a range compatible with the temperature of CSP plants [34][35].

Magnesium carbonate is not currently considered, presumably for the poor kinetics of the carbonation reaction. Anyway, literature data are available concerning the carbonate decomposition [36][37] and the reaction between magnesium oxide (supported and not supported) and carbon dioxide [38][39][40].

On the other hand, calcium carbonate is considered one of the most performing material for chemical storage, given the following characteristics [41]:

- High storage energy density: 3.26 GJ/m<sup>3</sup>
- Decomposition temperature between 700 and 1000 °C, with a CO<sub>2</sub> partial pressure from zero to 10 bar
- Cost effectiveness
- Non toxicity of reagents and products
- No secondary reactions
- Reaction products easy to separate

The main drawback is the poor stability under charging/discharging cycles. In particular, the carbonation reaction presents conversions that decrease during the cycles, and a drastic drop in the discharging reaction efficiency is noted just after 20 cycles [42], afterwards the carbonation capacity remains at a constant, but low value, around 7.5-8%, for further 500 cycles [43].

The main reason for that behaviour is the sintering of the material, and the pores occlusion due to the fact that the carbonate presents twice a molar volume than the oxide.

To improve the system performance, a thermal pre-treatment of the carbonate has been proposed [44][45], or a previous hydration with steam [46][47]. The results seem promising, but the experimental tests have been carried out by calcining with nitrogen, therefore not considering possible effect of carbon dioxide on the material sintering[48].

As an alternative, new synthetic CO<sub>2</sub> sorbents have been synthesized and described. Some examples are: calcium carbonate precipitated (which presents a high active surface)[49], mixed oxides (Ca<sub>0.9</sub>M<sub>0.1</sub>O<sub>x</sub> where M=Cu,Cr,Co,Mn) [50], calcium oxide doped with cesium [51], oxides derived from calcium lignosulfonate [52], CaO supported on CaTiO<sub>3</sub> [41] or on calcium aluminate (Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>)[53][54][55]. The last solution seems very interesting, in fact, a supported calcium oxide medium presents a CO<sub>2</sub> adsorption of 0.374 gCO<sub>2</sub>/g-sorbent after 35 cycles di carbonation/calcination [53] and 0.264 gCO<sub>2</sub>/g-sorbent over 45 cycles [56].



## CHEMICAL STORAGE: METAL OXIDES

The redox reactions presented by some transition metals are extensively investigated in order to employ these reversible processes for chemical storage purposes.

This type of system presents high storage energy density and a wide temperature range (600-1000 °C) for the charging/discharging operations. Moreover, air can be directly used both as product/reactant (by means of oxygen) and heat transfer fluid, so avoiding the necessity to design closed cycles.

Numerous oxide couples have been proposed in the scientific literature at this aim [57], below are summarized the most interesting systems.

The configuration BaO<sub>2</sub>/BaO was studied in the past, but it is no longer considered given the material toxicity, an incomplete conversion during oxidation (discharging) [58] and poor chemical stability [59].

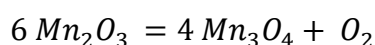
Cobalt oxide is in general considered one of the most interesting chemical storage medium. Actually, the Co<sub>3</sub>O<sub>4</sub>/CoO couple is stable over 100 cycles [60] and the reaction energy density is quite high (about 400 J/g[61]).

The system has been well characterized with respect to the kinetics of both direct and inverse reactions [60][62], and a temperature interval between 800 and 100 °C has been determined as the most feasible.

In order to increase the stability of the microstructure, the effect of the addition of Fe<sub>2</sub>O<sub>3</sub>, in a percentage around 10%, has been reported [63].

Several reactor configurations have been proposed, with the aim of a long period heat storage, using CSP plants. Fixed bed reactors have been discarded [14], because they are not economic feasible. The investigations have been focused on rotary kiln type reactors, with direct solar irradiation [57][64][65][66], or on hybrid systems, where both chemical and sensible heat storage are employed[67]. The latter technology is concerned with the use of honeycomb like receivers [67][68], made of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, cordierite, SiC or ceramic foams[69] coated with cobalt oxide. Up to 100 charging/discharging tests have been carried out with that configurations, and the results shown a very good material stability[67][68][69][70].

Regarding the manganese oxide, the following reaction has been studied:



compared with the system with cobalt oxide, that couple can be considered less feasible, for the following reasons:

- a slower oxidation kinetics
- a lower storage energy density (110J/g against 500J/g with the Co<sub>3</sub>O<sub>4</sub>[71])
- The discharging phase can be carried out at lower temperatures in the range 500-650 °C (920-1000°C for the charging/reduction step)[70][71]

On the other hand, the system seems chemically stable, and has been tested up to 10 cycles [72].



## CHEMICAL STORAGE BY REVERSIBLE REACTIONS: RESUME

The following tables (4 and 5) summarize the characteristics, advantages and disadvantages of some of the chemical storage systems discussed above.

**Table 4. Thermophysical properties of some chemical storage systems**

Storage type	Reaction	T <sub>charging</sub> (°C)	T <sub>discharging</sub> (°C)	T <sub>eq</sub> (1 bar) (°C)	ΔH <sub>reaz</sub> (Kj)	ΔG <sub>reaz</sub> (Kj)	Energy density (Gj/m <sup>3</sup> )
Hydroxides	$Ca(OH)_2 \rightleftharpoons CaO + H_2O$	550	450	505	104.4	65.9	1.6
Carbonates	$CaCO_3 \rightleftharpoons CaO + CO_2$	850-950	550-700	896	178	130.4	2.5
	$MgCO_3 \rightleftharpoons MgO + CO_2$	510-750	na	395	125	48.3	2.0
	$CaCO_3/CaO/Ca_{12}Al_{14}O_{33}$	850-950	750	896	178	130.4	-
Oxides	$2BaO_2 \rightleftharpoons 2 BaO + O_2$	650-850	450-580	844	77	na	1.2
	$2Co_3O_4 \rightleftharpoons 6CoO + O_2$	915-920	835-850	891	354.6	262.8	1.1
	$6Mn_2O_3 \rightleftharpoons 4Mn_3O_4 + O_2$	920-1000	500-650	1000	202.8	153.8	1.2

**Table 5. Advantages and disadvantages of some chemical storage systems**

Storage system	Advantages	Disadvantages
$Ca(OH)_2 \rightleftharpoons CaO + H_2O$	Low cost and good availability Reagents and products are not toxic No secondary reactions No need of catalysts Chemical stability (over more than 100 cycles)	Low thermal conductivity ( $\approx 0.1 + 0.4$ W/K m) Sintering problems High change of the molar volume during hydration ( $\approx 95\%$ )
$CaCO_3 \rightleftharpoons CaO + CO_2$	High enthalpy of reaction Low cost and good availability Reagents and products are not toxic No secondary reactions No need of catalysts Good thermal conductivity ( $\approx 4 + 5$ W/K m)	Poor chemical stability and reproducibility Particles agglomeration Necessity of additives (Ti) Strong dependence of the calcination kinetics on the $CO_2$ partial pressure
$MgCO_3 \rightleftharpoons MgO + CO_2$	Low cost and good availability Reagents and products are not toxic	Little data available for the $CO_2$ sorption reaction
$CaCO_3/CaO/Ca_{12}Al_{14}O_{33}$	Reagents and products are not toxic No secondary reactions Chemical stability (over more than 1000 cycles)	Synthetic material
$2BaO_2 \rightleftharpoons 2 BaO + O_2$	Air can be used as HTF No secondary reactions Possibility to operate in open cycles	High toxicity Non quantitative reactions (direct and back reaction) Not stable (high decrease in efficiency even after the first cycle)
$2Co_3O_4 \rightleftharpoons 6CoO + O_2$	High enthalpy of reaction (with respect to other oxide based systems) Air can be used as HTF No subproducts Possibility to operate in open cycles Good stability (over $\approx 500$ cycles)	Toxic Reagents are costly
$6Mn_2O_3 \rightleftharpoons 4Mn_3O_4 + O_2$	Air can be used as HTF Possibility to operate in open cycles	Very high operating temperatures (near 1000 °C) Few experimental data available



## CHEMISORPTION FOR CHEMICAL STORAGE SYSTEMS

Also chemisorption methods can be employed to store and release solar heat. In general, these processes involve the adsorption/desorption of ammonia or crystallization water. The reaction enthalpies are decent, around 30-60 KJ/mol, but the operating temperature is low, in a range between 20 and 200 °C [73][74]. Table 6 summarizes the equilibrium temperature of some chemisorption based systems.

**Table 6. Equilibrium temperature for some chemisorption storage systems**

Chemisorption storage system	T <sub>eq</sub> (1 bar) (°C)
$\text{CaCl}_2 \cdot 8\text{NH}_3(\text{s}) \rightleftharpoons \text{CaCl}_2 \cdot 4\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	32
$\text{NH}_4\text{Cl} \cdot 3\text{NH}_3(\text{l}) \rightleftharpoons \text{NH}_4\text{Cl}(\text{s}) + 3\text{NH}_3(\text{g})$	47
$\text{MnCl}_2 \cdot 6\text{NH}_3(\text{s}) \rightleftharpoons \text{MnCl}_2 \cdot 2\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	91
$\text{MgCl}_2 \cdot 6\text{NH}_3(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot 2\text{NH}_3(\text{s}) + 4\text{NH}_3(\text{g})$	135
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{MgSO}_4(\text{s}) + 7\text{H}_2\text{O}(\text{g})$	122
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}(\text{g})$	115
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{MgCl}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}(\text{g})$	150



## SOLAR DRIVEN HYDROGEN PRODUCTION

The use of solar energy for hydrogen production can also be seen as an application of chemical storage. In this case the solar power is stored as the hydrogen heat of combustion.

Given the depletion of the fossil fuels, and the problems related with the carbon dioxide contribution to greenhouse effect, hydrogen has been proposed as a feasible energy vector[75].

Two main paths have been proposed for solar driven hydrogen production:

- Water splitting thermochemical cycles, where the H<sub>2</sub>O molecule is decomposed into hydrogen and oxygen by a series of chemical reactions
- Solar assisted hydrogen production from reactions between organics and water: typically by reforming. In this case the solar energy is used to provide the heat for the endothermic reactions involved. It is noteworthy that, if biomasses are used, no new carbon dioxide is produced.

In this case the charging phase consists of the whole process of hydrogen production, which will be eventually stored and used, for instance in fuel cells, in the discharging step. A detailed description of these fields is beyond the purpose of this report, further information can be found in the cited scientific literature.

## HYDROGEN PRODUCTION FROM WATER SPLITTING

Hydrogen can be produced by electrolysis, which can be fed with energy from a photovoltaic plant [76].

As far as concentrating solar power is concerned, a thermal hydrogen production can be considered. A direct water thermal splitting would require very high temperatures (above 2500 °C), and the necessity to use very resistant materials and to manage hydrogen and oxygen under these conditions. For these reasons, it is more convenient to split the water molecule indirectly, by a series of chemical reactions, as quantitative as possible [77].

As an example, one of the most investigated thermochemical cycle is the so called "sulfur iodine" [78][79]. The reactions involved are shown below:



Several thermochemical cycles have been proposed and tested [80], and they can be divided into two main categories: processes where sulfur based compounds are used and, with higher temperature levels, methods involving metal oxides. The following table summarizes the most commonly employed solar driven thermochemical cycles[77][78][79][81][82][83]. The so called "Westinghouse" cycle is an example of a hybrid cycle, that is a process presenting an electrochemical step.





**Table 7. Resume of solar driven thermochemical cycles**

Cycle	Reactions involved	Reference
Sulfur-Iodine	$2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$ (25÷120°C) $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$ (850°C) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ (200÷ 700°C)	78,79
“Westinghouse” cycle	$\text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{SO}_4$ (25-100°C, by electrolysis) $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \frac{1}{2}\text{O}_2$ (850°C)	81
Zinc oxide cycle	$\text{Zn} + \text{H}_2\text{O} \rightarrow \text{ZnO} + \text{H}_2$ (450 °C) $\text{ZnO} \rightarrow \text{Zn} + \frac{1}{2}\text{O}_2$ (≈2000°C)	77
UT-3 Cycle	$\text{CaBr}_2 + \text{H}_2\text{O} \rightarrow \text{CaO} + 2\text{HBr}$ (760 °C) $\text{CaO} + \text{Br}_2 \rightarrow \text{Br}_2 + \frac{1}{2}\text{O}_2$ (572 °C) $\text{Fe}_3\text{O}_4 + 8\text{HBr} \rightarrow 3\text{FeBr}_2 + 4\text{H}_2\text{O} + \text{Br}_2$ (220 °C) $3\text{FeBr}_2(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightarrow \text{Fe}_3\text{O}_4(\text{s}) + 6\text{HBr}(\text{g}) + \text{H}_2(\text{g})$ (560 °C)	82
Mixed Ferrites Cycle	$2\text{MnFe}_2\text{O}_4 + 3\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 6\text{Na}(\text{Mn}1/3\text{Fe}2/3)\text{O}_2 + 3 \text{CO}_2 + \text{H}_2$ (≈ 800°C) $6\text{Na}(\text{Mn}1/3\text{Fe}2/3)\text{O}_2 + 3 \text{CO}_2 \rightarrow 2\text{MnFe}_2\text{O}_4 + 3\text{Na}_2\text{CO}_3 + \frac{1}{2}\text{O}_2$ (≈ 600°C)	83

An interesting variation of sulfur based water splitting processes can be obtained by storing, and eventually burning, sulfur as solar fuel at high temperatures, as described below[84].



### SOLAR ASSISTED HYDROGEN PRODUCTION FROM ORGANIC SPECIES

Another alternative route is to use the solar for providing the reaction enthalpy to endothermic processes where organic molecules are involved. A typical example is methane steam reforming, a well-known industrial process for hydrogen production; hydrocarbons, from natural gases or other sources, can as well undergo the same reactions, and also dry reforming (with CO<sub>2</sub>) can be considered[85][86]; in this way hydrogen can produced and used, in fuel cells as an instance, or the fuel is partially converted and “enriched” with hydrogen[87].

As a variation, methane, or other hydrocarbons can be decomposed by pyrolysis into carbon and hydrogen [88][89] so avoiding the necessity to separate the produced carbon dioxide.

Also the upgrading of biomass materials can be performed using solar driven reactors [90][91], which can be considered an alternative technique with respect to biological treatments.

Not only the biomasses, but also products derived from them can be reacted with water in order to obtain hydrogen and, in general, more valuable or, at least, more environmental friendly products, for instance oils from biomass pyrolysis[92] and bioethanol[93].

Another interesting field research is the upgrading of the glycerine obtained from biomass materials after a transesterification process. At this aim, given the lack of information in the scientific literature, an experimental campaign was carried out at ENEA laboratories, in order to show the potential feasibility of the method, to point out the interest of further investigations, and to complete the available data on the valorisation of biomass derivate products. By using the same catalysts employed for ethanol reforming [93], glycerine and water were reacted at low-intermediate temperatures, and the results are summarized





below (gas composition analysed by a microGC 4900 varian equipped with two columns: a molecular sieve one (5A 10 m), and a poraplot Q (10 m)).

**Table 8. Results of glycerine steam reforming**

T (°C)	Composition of the produced gas (% v/v)							Final water (%wt)	Final glycerine (%wt)	Final secondary products (wt%)
	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	ethylene	ethane	other			
400	55.1	28.2	6.9	1.2	0.0	0.1	8.5	51.3	12	37
375	59.3	26.4	6.7	0.9	0.0	0.1	6.7	47.8	17	35
425	53.3	31.3	5.5	1.6	0.0	0.1	8.2	51.7	24	24
450	51.3	34.3	3.6	2.1	0.0	0.1	8.6	61.6	14	24
425	46.7	37.3	2.1	3.6	0.0	0.2	10.1	68.9	16	15
425	50.8	34.8	2.8	2.3	0.0	0.1	9.3	57.5	25	17

The results show a good hydrogen production, along with hydrocarbons, and good conversions. The secondary products were analysed by GC/MS (GC Agilent 7890 equipped with MS quadrupole 5973N, column CP-Sil 8CB, 30 m) and several oxygenated species were identified; the possible use or further upgrading of these chemicals has to be discussed.



## CONCLUSIONS

The present report is concerned with a review about the most important chemical storage technology currently under investigation for CSP plants.

To summarize, two different approaches can be considered:

- The use of reversible reactions, involving oxides, hydroxides or carbonates, where the exothermic process is fed by solar energy (charging phase) and the exothermic one is used to obtain heat when the solar irradiation is not available (discharging phase). Since these kind of techniques are specific for CSP plants, most of this deliverable was dedicated to discuss their characteristics. In general, it can be stated that the use of the couple calcium oxide/hydroxide is nowadays the most mature technology, but, the systems involving calcium carbonate/oxide and cobalt oxides are definitely very promising, and could lead to storage systems presenting manageable chemicals and high energy densities.
- A second method is to employ the solar power to carry out an exothermic reaction where hydrogen or other fuels are produced. In this case the discharging phase is performed by using the fuel previously obtained. In principle, any reforming or thermolysis method can be powered with solar energy, and, as a consequence, the scientific literature on the topic is quite wide. The coupling of industrial production processes, which are generally designed for continuous reactors, with CSP plants could be problematic, given the discontinuity of the solar source and the difficult to employ reliable backup systems especially at high temperatures.

In both cases the main advantage, with respect to sensible or latent heat storage systems, is the possibility of seasonal storage, where, for example, the reactant to be discharged is produced and accumulated in sites with high solar irradiation, and eventually transported to the user.



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