

Thermochemical energy storage by consecutive reactions for higher efficient concentrated solar power plants (CSP): proof of concept

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Abstract

Concentrated solar power plants (CSP) combined with thermal energy storage (TES) offers the benefit to provide continuous electricity production by renewable energy feed. There are several TES technologies to be implemented, being the thermochemical energy storage the less studied and the most attractive since its volumetric energy density is 5 and 10 times higher than latent and sensible TES, respectively. Thermochemical energy storage technology is based on reversible chemical reactions, also named thermochemical materials (TCM). One of the main challenges of TCM is to achieve a proper reversibility of the reactions, which in practical conditions leads to lower efficiencies than the theoretically expected. A new concept based on changing from reversible TCM reactions towards TCM consecutive reactions aims to eliminate reversibility problems and therefore improve the overall efficiency. Consecutive TCM reactions can either be based in one cycle, where reactants are needed to feed the reaction, or two coupled cycles which offer the possibility to work without any extra mass reactants input. The plausibility of the implementation of both concepts in CSP is detailed in this paper and case studies are described for each one.

Keywords: *Thermal Energy Storage (TES); Thermochemical materials (TCM); High temperature; Concentrated Solar Power plant (CSP); Consecutive reactions*

1. Introduction

The fact of taking profit from renewable energies, like solar energy, and turning to sustainable and competitive energy systems is in agreement with the current world wide directives and H2020 [1]. The general target is focused on reducing fossil fuel consumption for electricity production, heating, and cooling in order to decrease CO₂ emissions and thus support climate change goals. Regarding electricity production, concentrated solar power (CSP) plants are attractive alternative technologies. CSP technologies generate electricity by concentrating the solar radiation beam onto a small area, where a heat transfer fluid (HTF) is heated up and this

40 energy is ultimately transferred to the steam. Electricity is then generated by an electric
41 generator which is driven by a steam turbine with the efficiency limited by the Carnot cycle [2].

42

43 Today, several countries such as USA or Spain have developed commercial CSP plants [3,4]
44 which are using different technologies to concentrate the solar beam. Nowadays, four CSP
45 technologies are represented at pilot and commercial scale: parabolic-trough collectors (PTCs),
46 linear Fresnel reflector (LFR) systems, power towers or central receiver systems (CRS), and
47 dish/engine systems (DE). All existing plants imitate parabolic geometries with large surface
48 area for the mirrors [4].

49

50 Energy production is restricted when sun shines, therefore, a system that allows storing solar
51 heat is required. In case of not having problems with sun shine, a producer company might
52 want to store the energy as a function of the price of kWh on the market (to increase company
53 benefits). For this purpose a thermal energy storage system (TES) is essential. TES is becoming
54 particularly important for electricity storage in combination with concentrating solar power
55 (CSP) plants where solar heat can be stored for electricity production when sunlight is not
56 available [5,6].

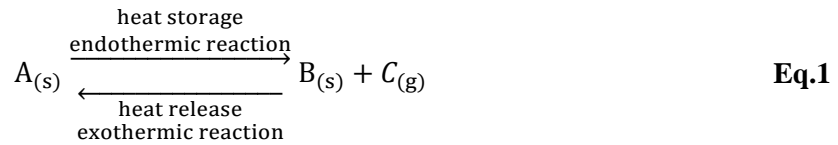
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58 Proposed mechanisms to store thermal energy are based on different physical or chemical
59 principles: sensible heat (molten salts, solid particle materials, etc.), latent heat by means of
60 phase change materials (PCM), and thermochemical heat storage (TCS) using thermochemical
61 materials (TCM) [7-13]. Nowadays, the use of molten salts is the most viable alternative for
62 TES coming from solar heat to supply intermittent power demand. Nevertheless, molten salts
63 cannot provide a temperature or an energy density as high as the TCS due to the mechanism
64 itself. From a theoretical point of view the use TCS is a challenge that can provide higher
65 storage of energy for longer periods and operate at higher temperatures compared to the other
66 mentioned systems. Consequently, implementing TCS technology would allow increase
67 efficiency of a CSP plant [5,6]. This topic has experienced a remarkable increased perception in
68 the last few years and thus several studies are being published. For instance, modeling of redox
69 reactions where the model is shown to track complex trends in measured non-stoichiometry
70 data, specific heat capacity, and global heats of reaction with respect to changes in T and p_{O_2}
71 [14], novel concepts based coupling a CSP-CaL process and CO_2 power cycle [15], cascade
72 thermochemical storage with internal condensation [16], algorithm for searching potential
73 thermochemical energy storage for a wide temperature range (25-1000 °C) [17], etc.

74

75 Actually, TCS for CSP is based on reversible reactions with high enthalpy of reaction but these
76 reactions presented low efficiency and poor reversibility. The trend is to use heterogeneous

77 reactions (solid-gas) to facilitate the removal and transport of the gases involved in the reaction.
78 Redox systems based on oxide pairs, i.e. Mn_3O_4/Mn_2O_3 [12,13] are the most used to achieve the
79 requirements and maintain material stability. The storage mechanism can be defined as depicted
80 in equation 1:



82
83 During the charging process (endothermic reaction), solar thermal energy is used to move the
84 reaction from the solid reactant (A) (sometimes together with a gas reactant) to products B(
85 solid) and C (gas). During this step, the TCM is absorbing the heat concentrated at the solar
86 receiver. The storage process consists on keeping B and C products separated. In order to
87 discharge the system (exothermic reaction), the former solid product, B, is placed in contact
88 with the gas C, to react and thus release the chemical reactions energy between the product
89 stored.

90
91 The problem that is seen from the TCS systems prototypes is that the reaction must be
92 reversible and this premise is not being fully achieved. This implies that the chemical
93 conversion and reversibility of the reaction [18,19] is not fulfilled and therefore the storage
94 capacity differs from the expected. This makes difficult to find a TCM that can be adjusted to
95 the theoretical model and in all, it will be difficult to implement TCS systems with the
96 established premises.

97
98 The main objective of this paper is to demonstrate the feasibility of a new concept of a CSP
99 plant with solar central receiver reactors technology implementing thermochemical materials.
100 This concept overcomes the drawback of the poor reversibility and low efficiencies in high
101 temperature storage by changing from the reversible reactions towards TCM consecutive
102 reactions. To illustrate this, two case studies are shown, one for a one cycle of TCM consecutive
103 reactions and another for two coupled cycles of TCM consecutive reactions.

104

105 **2. Consecutive TCM reactions**

106

107 Two different concepts, one based on one cycle and the other based on two coupled cycles of
108 consecutive TCM reaction were developed [20,21] and are presented in this section.

109

110

111 **2.1. One cycle TCM consecutive reaction, a case study Zn + CO₂**

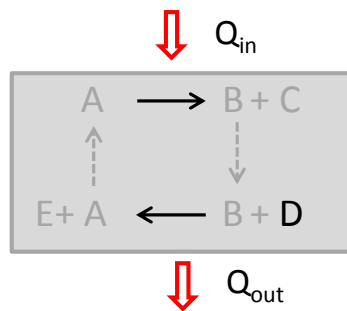
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113 2.1.1. Presentation of the concept

114

115 The general concept of one cycle of TCM consecutive reactions is depicted in Figure 1. The
116 initial solid A is transformed into another solid B and a gas C, this last solid reacts with another
117 gas D, giving the initial solid A and a gas E. The consecutive reaction can be running being the
118 only input the gas D in the second reaction.

119



120

121

Figure 1. Simplified scheme of the consecutive reactions concept: one cycle.

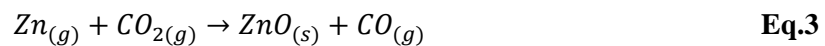
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123 2.1.2. Case study: chemical basis

124

125 As an example of this concept, the ZnO/Zn cycle is considered. The first step is the endothermic
126 thermal reduction ($\Delta H_{298K} = 350.85 \text{ kJ}\cdot\text{mol}^{-1}$) of zinc oxide and can be referred as the solar step
127 (**eq. 2**). The second step, the non-solar step (**eq. 3**), is the exothermic reduction ($\Delta H_{298K} = -67.87$
128 $\text{kJ}\cdot\text{mol}^{-1}$) of CO₂ with zinc to generate CO and ZnO [22,23].

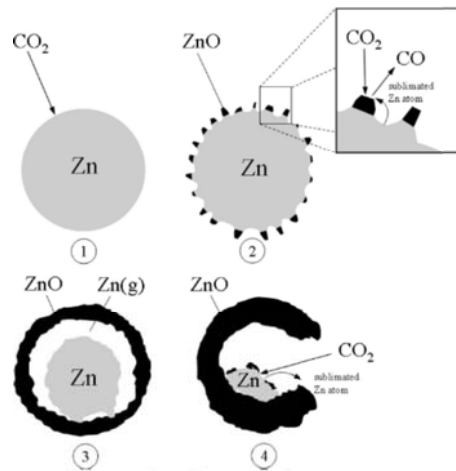
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131 The thermal reduction of ZnO can be performed at 1627-1727°C [24,25] at 1 bar and inert
132 atmosphere (N₂ or Ar). After this thermal reduction, zinc is obtained in gas form (T_b=912°C)
133 [26]. Afterwards, in the non-solar step, the produced Zn gas reacts with CO₂ giving the initial
134 oxide (solid) and CO. This second reaction may be performed at temperatures below ZnO
135 thermal decomposition. However, it presents a high resistance due to the formation of an oxide
136 layer which slows the reaction (Figure 2) which drops the chemical conversion [23]. This
137 phenomenon can determine the working temperature, because at temperatures lower than 912°C
138 it has a low rate and conversion, but above 912°C it would work in the gas phase. Some studies

142 that perform CO₂ splitting using liquid Zn achieved less than 50% of Zn conversion at 500°C
 143 [22,23,27,28]. Having a phase change can facilitate the reduction of the thermal reduction
 144 temperature through decreasing the system pressure.



143
 144 **Figure 2. Scheme of CO₂ splitting mechanism [23].**

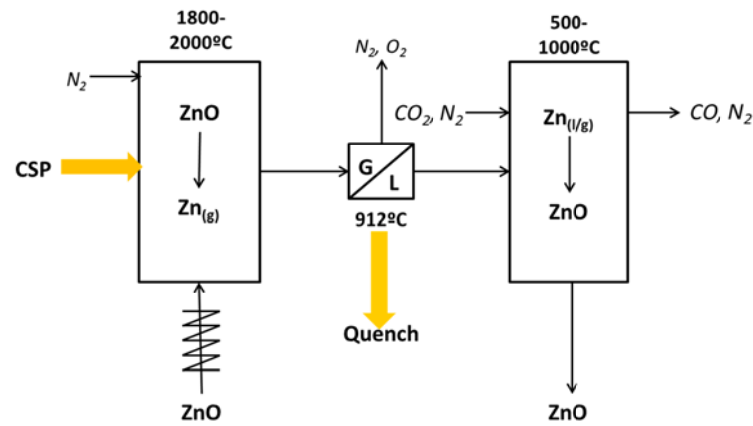
145
 150 Table 1 shows the enthalpy of each reaction of the thermochemical heat storage system. The
 151 optimal working temperature (T_w) and the maximum chemical efficiency (X) calculated in
 152 bibliography or estimated have been taken into account. Therefore, three values of enthalpy are
 153 shown at 25°C, at optimum T_w and, at optimum T_w taking into account the maximum chemical
 154 efficiency.

151
 153 **Table 1. Enthalpy of reaction at different conditions (1 atm), working temperature (T_w), and maximum**
 154 **chemical efficiency (X).**

Reaction	T_w (°C)	X (%)	ΔH_{298K} (kJ/kg)	ΔH_T (kJ/kg)	$\Delta H_{T,X}$ (kJ/kg)
$ZnO_{(s)} \rightarrow Zn_{(g)} + \frac{1}{2}O_{2(g)}$	1700	95	2072	2631	2769
$Zn_{(g)} + CO_{2(g)} \rightarrow ZnO_{(s)} + CO_{(g)}$	1000	95	-400	-272	-258

154
 155
 156 2.1.3. Engineering diagram and plant application

157
 163 Figure 3 shows a possible engineering scheme of the ZnO/Zn system implemented in a CSP
 164 plant. Therefore the proposed configuration is to perform Eq. 2 in a direct (closed) rotary kiln
 165 [29,30], and then to separate the Zn from the O₂ in a condenser (at T below 912°C) and finally
 166 reaction following Eq. 3 is performed in an indirect or non-solar fluidized bed reactor. The main
 167 drawback of this system is the phase change of Zn, which determines the phase that the Zn will
 168 be during the CO₂ splitting.



165

166

Figure 3. Scheme of the single cycle based in ZnO/Zn consecutive reactions.

167

174 An interesting point is to use the heat generated in the condenser to preheat the Zn before
 175 entering the fluidized bed. The reaction kinetics will be higher, but the most important point is
 176 to prevent the oxide layer formation. With this concept it can be considered a cycle of
 177 consecutive reactions with three steps, where it is not necessary to store Zn. Another aspect to
 178 take into account is that reaction shown in the Eq. 3 is exothermic, and thus preheating of
 179 CO₂/CO/N₂ mixture (rich in CO₂) may not be required. Therefore, this is why a reactor without
 180 receiver is proposed.

175

182 Advantages of this specific one cycle of consecutive TCM reactions is the low cost of ZnO, well
 183 know thermal decomposition of ZnO in a solar receiver/reactor, only needs one receiver, can
 184 operate at 1 bar, easy to separate gases, it allows heat storage and also CO₂ capture. On the
 185 contrary, as disadvantages there are the phase change of Zn, maintenance can be complicated by
 186 Zn condensation, requires temperatures higher than 1000 °C, presumed low absorptivity (white
 187 material), thermodynamic constraints (low solar-to-chemical efficiency for solar step, higher
 188 than other cycles, i.e. Fe₃O₄/FeO), and CO generation.

183

186 It is important to highlight that CO/CO₂ is released/consumed because the example is based on a
 187 specific reactions being a case study to show the concept, but other reactions with other pair of
 188 gases can be found for each application.

187

188

189

190

191

192

192 **2.2. Two coupled cycles of consecutive TCM reactions, a case study BaS/BaSO₄ +**
193 **Mn₃O₄/Mn₂O₃**

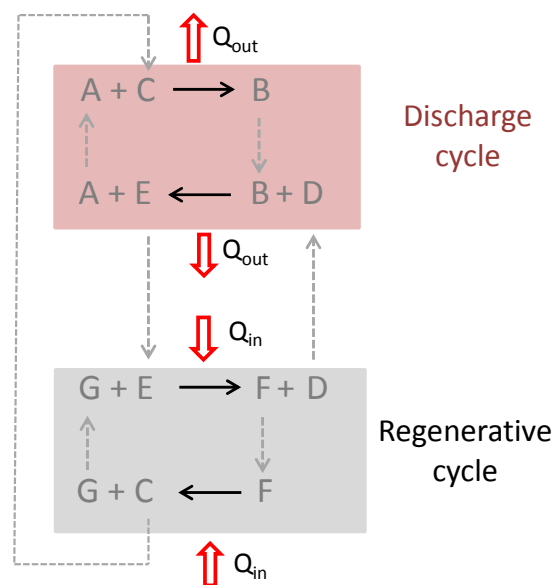
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195 2.2.1. General concept

196

197 Since the main drawback of the one cycle TCM consecutive reactions is the need of a reactant
198 input, a new concept is presented where this reactant is produced in a second coupled cycle to
199 close completely the system by generating and regenerating within the reaction all the products
200 and reactants. The general concept of two coupled cycles TCM consecutive reactions is drawn
201 in Figure 4.

202



203

204

Figure 4. Simplified scheme of the consecutive reactions concept: two cycles.

205

206 This approach of storing the TCM and not the solar heat, can be very similar to those proposed
207 for obtaining solar fuels, fuel for fuel cells or via water or CO₂ splitting (WS and CS,
208 respectively) [27, 42-48]. However, the difference is that the material is used for WS and/or CS
209 to produce a chemical to store (H₂, CO₂), and further perform another process such as Fischer-
210 Tropsch which allows benefiting solar heat. Instead, in the proposed system, the material is
211 directly stored with the function of storing heat.

212

213 In conclusion, a TCS system based in four consecutive reactions divided in two-loops. One of
214 them is exothermic and the other is endothermic, so it can be considered the discharge cycle as
215 the discharge process and the regenerative cycle as the charge cycle; in energy terms.

216

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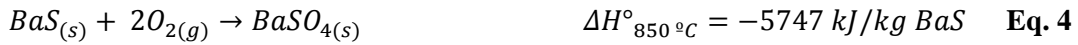
218 2.1.2. Case study: chemical basis

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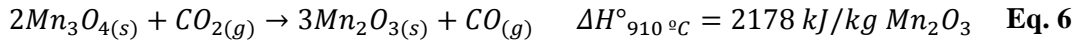
220 It consists in a discharging cycle and a regenerative cycle. The concept is divided into a main
221 cycle (discharge cycle) which is focused to release heat. The other cycle (regenerative) is
222 focused to close the system. Consequently total enthalpy of the system should be zero, and if
223 discharge cycle is exothermic, regenerative cycle must be endothermic. In this particular
224 concept the involved gases are O₂ and CO/CO₂. This system of gases and the reactions involved
225 are interesting to check in deep, in particular the thermodynamic data, conditions of work (P,T)
226 used in many industrial processes. An example of a thermochemical storage concept based on
227 two coupled cycles of consecutive reactions is BaS/BaSO₄ coupled to Mn₃O₄/Mn₂O₃ and shown
228 in Eq 4- Eq 7 and drawn in Figure 5.

229

Discharge cycle



Regenerative cycle



230

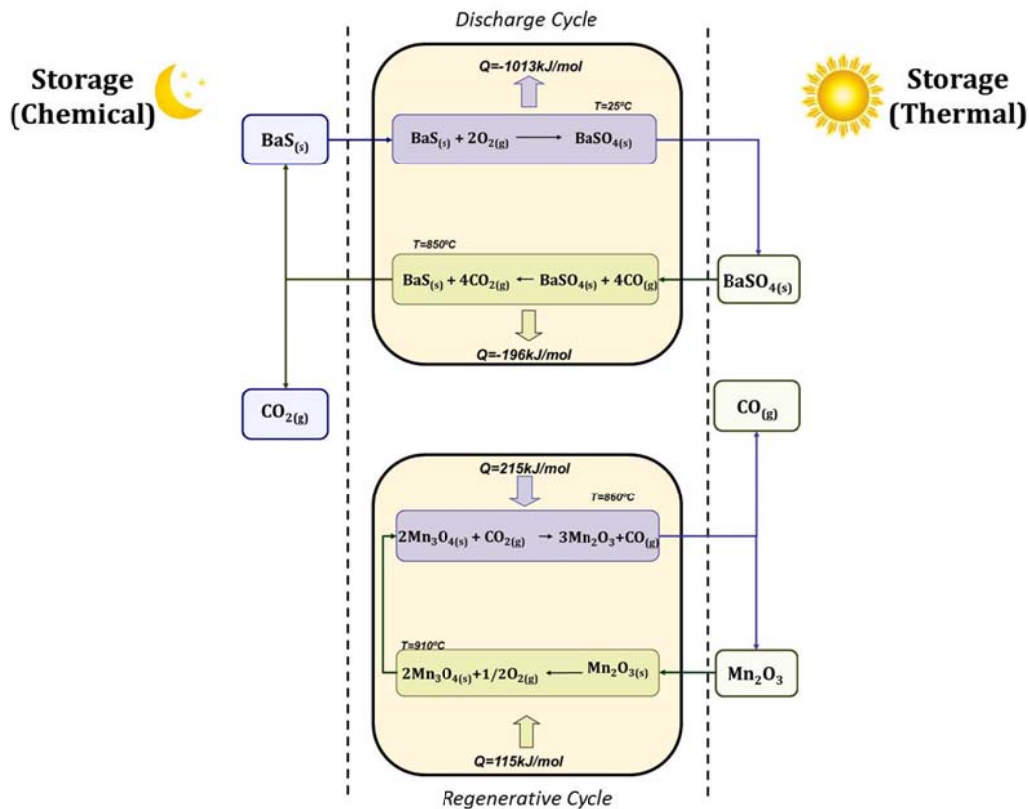
231 As it can be seen, the system consists in four intertwined reactions, but, based on the first
232 reaction (Eq. 4) [31-35]. A second charge reaction (Eq. 5) is necessary to recover BaS,
233 obtaining a closed cycle for TCM. However, to perform the discharge cycle and to maintain the
234 TCS system closed, a second cycle (regenerative cycle) is needed to regenerate/recover the
235 product gases involved in the reactions. A third reaction (Eq. 6) regenerates CO₂ produced in
236 the second reaction, and at the same time, produces CO for BaSO₄ reduction. The last reaction
237 (Eq. 7) serves to close the regenerative cycle for the part of the solid, and at the same time to
238 release O₂ that is needed in the BaS oxidation (Eq. 5).

239

240 Unlike the TCM system concept [36-38, 39-41], in which the system store solar heat is
241 considered, in this novel concept, solar heat is used to achieve the required temperature and the
242 thermal energy for the desired TCM reaction. Therefore, the proposed system store chemical
243 compounds capable to release thermal energy.

244

251 Another difference with conventional TCM systems is that there is not a pure charge reaction.
 252 Equation 4, where BaSO₄ is reduced, could be considered as charging step, but is an exothermic
 253 reaction, and at the same time is the reaction for recovery the BaS. On the other hand, there are
 254 two endothermic reactions (Eq. 6 and 7), but these are not directly involved on the discharge
 255 reaction. Therefore, the system is divided into a main cycle (discharge cycle) which releases
 256 heat and the other cycle (regenerative) closes the system (see Figure 5).
 252



253
 254 **Figure 5. Scheme of the novel two coupled cycles of TCM consecutive reactions based on BaS oxidation.**

255
 256 **a. Discharge cycle**

257
 263 The material used in the discharge cycle is the Barite (mineral of BaSO₄) which can be reduced
 264 with CO at temperatures between 800-1000°C to obtain BaS [31,49-58]. Furthermore, BaS can
 265 be oxidized by O₂ (or air) at temperatures above 25-1400 °C [26,31- 35]. Both reactions (Eq. 4
 266 and 5) are exothermic, and BaSO₄ and BaS are also stable at temperatures higher than 1400 °C,
 267 with melting point of 1580 °C and 2229 °C, respectively [26, 59]. For this reason, a discharge
 268 cycle based on BaS/BaSO₄ is a good candidate for a TCS system in a CSP plant.

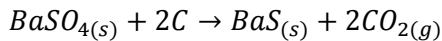
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 266 Since barite is the industrial precursor of BaS [51,56] there are not many studies of BaS
 267 industrial combustion. However, the literature reveals that the BaS oxidation reaction is highly

266 exothermic ($\Delta_r H^0 = -1013.20$ kJ/mol, -5963.75 kJ/kg_{BaS}) [26,31-33]. Furthermore, it is well
267 known that sulphur (S²⁻) oxidation has high reaction kinetics, and even become spontaneous
268 [60-62]. This, added to the working temperature (800-1000 °C) in a CSP plant suggests that
269 oxidation of BaS will be a fast reaction.

270

271 For barite reduction there is literature available regarding the process on an industrial scale,
272 however it is presented as a carbothermic reaction [51,53-56] (Eq. 8):

273



Eq. 8

274

275 Nevertheless, at temperatures higher than 800 °C carbothermal reduction is similar to equation 5
276 [50], because the CO reduction mechanism is stabilized due to the Boudouard reaction
277 equilibrium at working temperatures [52][63]. In this manner, it works in solid-gas reactions
278 that is easier to operate and, at the same time, CO is easier than C to recover in a regenerative
279 cycle.

280

281 Another advantage of the BaS/BaSO₄ consecutive reactions in front other possible cycles as
282 MS/MSO₄ (where M is a metal) is that BaSO₄ is one of the most thermal and water stable
283 [26,31,60,64]. Thermal stability of BaSO₄ is only exceeded by alkali sulfates, but on the other
284 hand, alkali sulphides have very low water stability. Sulphides of some transition metals such as
285 Fe, are more stable in water than BaS [26,65], but their sulfates have poor thermal stability.
286 Besides the high thermal stability and relatively high stability in water of the BaS/BaSO₄ redox
287 pair suggests stability in the presence of CO₂ gas [51]. This means that the carbonation of the
288 barium salt could be minimized during the BaSO₄ reduction (Eq. 5) unlike what might happen
289 with other metal sulfates. For that reason, the most attractive MS/MSO₄ redox pair for discharge
290 cycle is BaS/BaSO₄.

291

292 Furthermore, there are some studies that evaluate the cyclability using carbothermal reduction
293 of BaS [51]. Another indication which suggests the feasibility/viability of these reactions is the
294 high melting temperature of BaSO₄ and BaS in comparison with the working temperature,
295 which hinders particle sintering. On the other hand, minimization of coarsing will depend, in
296 part, on the particle size distribution and the particle shape [66,67] .

297

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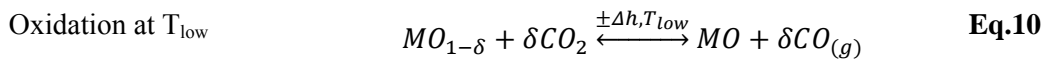
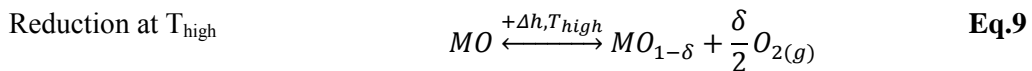
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b. Regenerative cycle

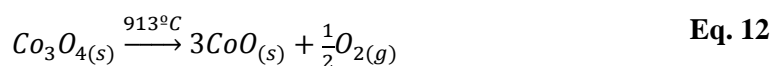
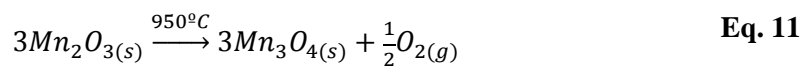
As CO/CO₂ is used as a reducer/oxidizer gas, the aim of the regenerative cycle is to recover CO from the produced CO₂ in equation 5 to be reused as a reactive in the discharge cycle. Therefore, the regenerative cycle is an important part of the proposed TCS system. Due to the nature of the cycle, which reactions are endothermic, those reactions should be performed in a solar reactor/receiver located in the central tower. Paradoxically, the regenerative cycle requires solar thermal energy but not for storing thermal energy. Absorbed heat in the solar reactor/receiver is not stored as heat; rather it will serve to store CO.

CO₂ is a very stable gas, so it is not usually considered an oxidizing gas although at elevated temperatures can be reduced and oxidize a reduced metal (or reduced metal oxide). The reaction mechanism is used to WS and CS, where a reduced metal is used as a reaction support (not as catalyst). Usually the used support is a cheaper reduced metal oxide such as iron oxide (FeO/Fe₃O₄) [22,23,28,43,68,69]; ceria oxides (CeO) [68,70]; or metals such as Zn [22,23,43,68,71]; Sn [46,47,71].

Equations 9 and 10 show the CS mechanism based on the thermal stability of the metal oxide. At a given temperature it favours the reduced or oxidized form. The reduced form always will be more thermally stable, so the reduction reactions will always be at higher temperature than the oxidation reaction. Every metal oxide redox pair has a specific temperature for thermal reduction; consequently, it could control the process by temperature control. On the other hand, the reduction reaction always requires thermal energy (endothermic reaction), but in the case of the metal oxidation (CS) reaction could be exothermic or endothermic, depending of material enthalpy formation:



Due to the disproportionation temperature or because it may experiment a phase change in the temperature range, initially, none of the mentioned metal oxides is suitable for the system. Therefore the best options could be other redox pairs like Mn₂O₃/Mn₃O₄ and Co₃O₄/CoO which disproportionation temperature is in the range of the working temperature and have no phase change (Eq. 11 and 12) [40,41, 72-76]:



333

334 According to the Ellingham-Richarson diagram [32,77], Mn₃O₄ or CoO can reduce CO₂
 335 performing Eq. 10. Although the reaction is thermodynamically feasible, the tolerance of the
 336 metal oxides to CO₂/CO mixture should be considered. There could be a small fraction of CO
 337 changing direction in Eq. 10, and that would affect the reactor design and the purity of CO
 338 (mixture CO₂/CO rich in CO) obtained.

339

340 Manganese (Mn) cobalt (Co), and iron (Fe) are very similar elements, since they are very close
 341 on the periodic table and have very similar electron configuration [60,78]. Except for the
 342 different disproportionation temperature between each redox pairs, that is given by the better
 343 ability of Fe to stabilize the iron oxides. Consequently, the expected behaviour for the two redox
 344 pairs should be similar to FeO/Fe₃O₄, with good kinetics and cyclability of the redox pair. On
 345 the other hand, use of doping agents, such as iron or nickel, can vary the disproportionation
 346 temperature [40,41,74,75,79,80].

347

348 Studies indicate that Co can be oxidized/reduced from 30 cycles [[56]] and up to 100 cycles
 349 without reactivity loss [81]. This ensures the ability of cobalt to be reduced by thermal
 350 disproportionation, along with presumption of good oxidation with CO₂, cobalt becomes a good
 351 candidate. Similarly to cobalt, other studies have shown the same behaviour with manganese
 352 [40,41]. Although manganese cyclability is not as good as that of cobalt, some studies [67]
 353 suggest that it is possible to improve its cyclability.

354

355 As the oxidation temperature of the metal oxide is lower than that of the disproportionation, this
 356 means that it can work below 1000⁰C, complying with the first premise of the concept.
 357 Furthermore, the re-oxidation mechanism usually is controlled by oxygen diffusion inside the
 358 particle [67,81]. Although there is a maximum temperature which cannot be overcome, this will
 359 not have an important role in the kinetics. To improve kinetics it is essential to control the
 360 morphology and particle size of the metal oxide, and also to have a controlled atmosphere. To
 361 ensure morphology, minimizing sintering and maintaining surface/volume ratio, it may be
 362 advisable to decrease the disproportionation temperature.

363

364 Finally, considering the economic aspects, manganese is considered the best alternative for the
 365 regenerative cycle. Particularly, manganese has a cost approximately ten times lower than
 366 cobalt.

367 2.2.3. Case study: engineering and implementation

368

369 Following the presented case study (2.2.2) and according to the patent submitted [17] the results
 370 of mass and energy balances and the plant diagram of this concept are presented in this section.

371 To know how much potential and the viability of this concept, mass and heat balances for whole
 372 cycle of BaSO₄/BaS coupled to Mn₃O₄/Mn₂O₃ cycle are provided. First of all, BaSO₄/BaS
 373 balances are shown taking into account Eq. 4 and 5 (see Table 2, note that a basis of 100 kg of
 374 BaSO₄ in solid state is taken for the balances). Then, operating modes during day and night for
 375 BaSO₄/BaS cycle are detailed and afterwards the balances of the regenerative cycle (see Table
 376 3) and the diagram of the whole concept are provided.

377

378 **Table 2. Mass balance of BaSO₄/BaS cycle**

Reaction	1BaSO ₄ (s)	+	4CO (g)	→	1BaS (s)	+	4CO ₂ (g)
Mass (kg)	100.00		48.00		72.57		75.43
Molar mass (kg/kmol)	233.34		28.00		169.34		44.00
Moles (kmol)	0.43		1.71		0.43		1.71
Reaction	1BaS (s)	+	2 O ₂ (g)	→	1BaSO ₄ (s)		
Mass (kg)	72.57		27.43		100.00		
Molar mass (kg/kmol)	169.34		32.00		233.34		
Moles (kmol)	0.43		0.86		0.43		

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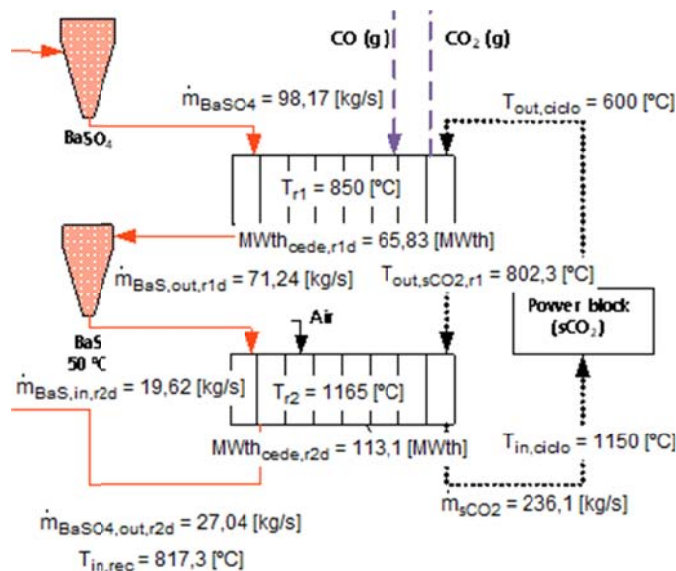
380 The total energy released from both reactions for full conversion (X=1) conditions is: -6680
 381 kJ/kg of BaS (Eq. 4 and 5). However, this level of conversion is rarely reached by a chemical
 382 reaction and therefore 60% is commonly used as level of conversion (conservative value). Then,
 383 the total energy available for heating up the power block fluid would be -4008 kJ/kg of BaS.

384

386 a) Day / charging mode

387 Day operation cycle works as follows (see also Figure 6):

- 389 - The reduction of BaSO₄ to BaS takes place at 850°C thus it is needed the BaSO₄
- 390 receiver to rise the temperature of the BaSO₄ up to 850°C;
- 391 - The BaSO₄ enters into the reduction reactor at 850°C and it is reduced to BaS in contact
- 392 with CO coming from the regenerative cycle;
- 393 - The reduction reaction gives 933KJ/kg of BaS. This heat is used to heat up the cold
- 394 sCO₂ in the reduction reactor – generator from 600°C to 802.3°C
- 395 - The BaS stream coming out of the reduction reactor goes to the hot storage tank and in
- 396 parallel to the oxidation reactor:
 - 396 o BaS is stored in a silo to be oxidized in discharge mode;
 - 398 o BaS is oxidized in the oxidation reactor with Air giving 5747KJ/kg BaS. This
 - 399 heat is used to rise the temperature of the sCO₂ stream up to 1150°C
- 400 - The BaSO₄ coming out of the oxidation reactor is sent to the BaSO₄ receiver to be
- 401 heated up again to 850°C to restart the cycle.



402

403 Figure 6. Operation mode during day (conversion reaction 99%)

404

405 **b) Night / discharge mode**

406 Night cycle mode works as follows (see Figure 7):

- 409 - The BaS stored in the hot tank enters to the oxidation reactor and it is oxidized with Air
- 410 giving 5747KJ/kg of BaS. This heat is used to bring the cold sCO₂ stream from 600°C
- 411 to 1150°C;
- 410 - The BaSO₄ outlet is stored in the cold tank at about 817°C.
- 411 - The day after this BaSO₄ would be again reduced and stored as BaS in the hot tank.

413 By this process the discharge could be performed only with an air inlet in the oxidation reactor

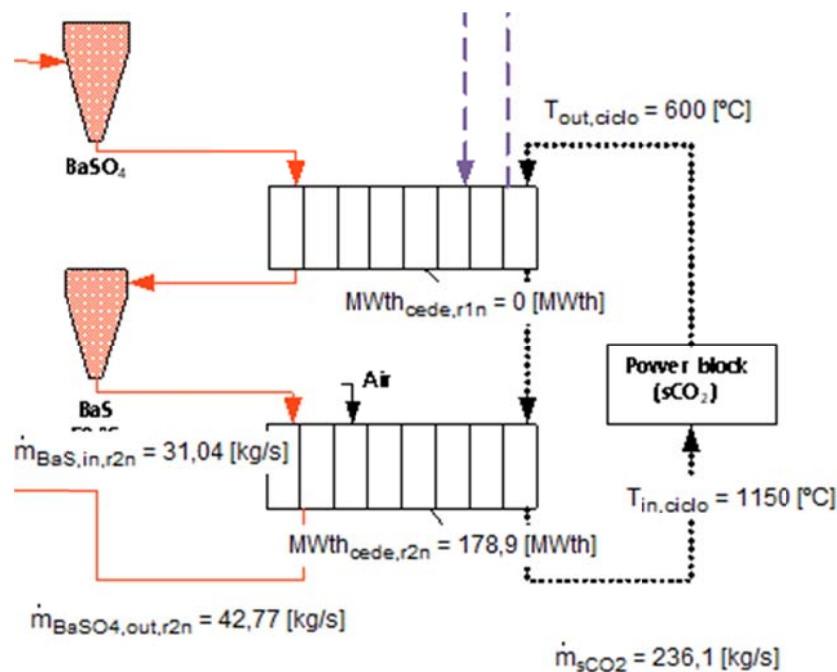
414 avoiding the need of storing CO/CO₂.

416 If it was desired to be able to use both reactors in discharge mode a big storage system of

417 CO/CO₂ or at least of the reactants of the regenerative cycle should be implemented avoiding

418 the needs of storing solid particles of BaS and BaSO₄.

417



418

419 Figure 7. Operation mode at night (conversion reaction 99%)

420

420 **c) Regenerative cycle Mn_2O_3 - Mn_3O_4**

421 The mass balance of the regenerative cycle following Eq. 6 and 7 is shown in Table 3, whereas
 422 in Figure 8 the diagram of the whole concept implementation is drawn.

423 **Table 3. Mass balance of Mn_2O_3 / Mn_3O_4**

Reaction	$2Mn_3O_4$ (s)	+	$1CO_2$ (g)	→	$3Mn_2O_3$ (s)	+	$1CO$ (g)
Mass (kg)	784.50		75.43		811.93		48.00
Molar mass (kg/kmol)	228.82		44.00		157.88		28.00
Moles (kmol)	3.43		1.71		5.14		1.71
Reaction	$3Mn_2O_3$ (s)	→	$2Mn_3O_4$ (s)	+	$0.5O_2$ (g)		
Mass (kg)	811.93		784.50		27.4		
Molar mass (kg/kmol)	157.88		228.82		32.00		
Moles (kmol)	5.14		3.43		0.86		

424

425 The regenerative cycle, used for regenerating the CO for reducing $BaSO_4$, is composed for two
 426 endothermic reactions which need absorbing 2222 kJ/kg of Mn_2O_3 for a full conversion reaction
 427 (see Eq. 6 and 7). For these reactions, it has also considered a chemical conversion of 60% and
 428 as consequence the total energy absorbed per kg of Mn_2O_3 is higher than for a full chemical
 429 conversion. So, this energy increases until 3703 kJ/kg of Mn_2O_3 for 60% of conversion.

430 The net energy value, released on $BaSO_4$ / BaS cycle and absorbed on Mn_2O_3 / Mn_3O_4 cycle,
 431 should be interpreted as kJ per kg of BaS . According to the mass balance (see Table 2 and 3),
 432 for producing 72.57 kg of BaS , the system needs 811.93 kg of Mn_2O_3 , and thus the net energy
 433 balance is 37165 kJ per kg of BaS for a 60% of chemical conversion.

434

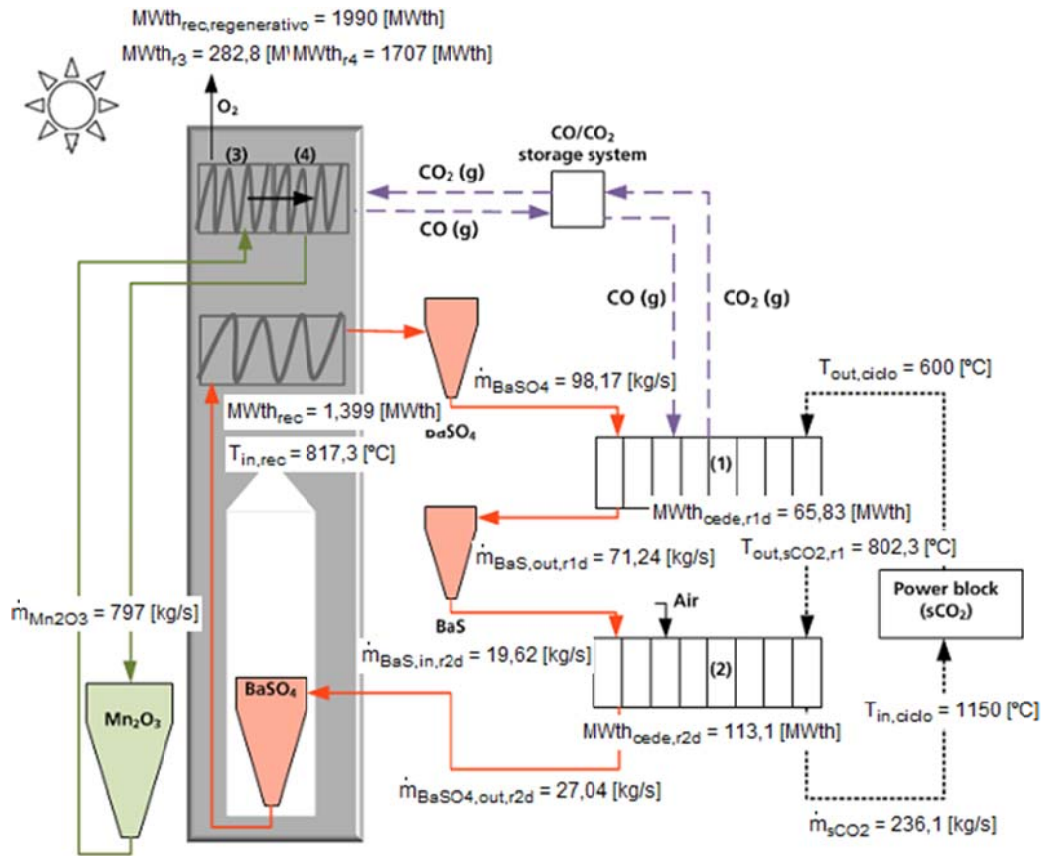


Figure 8. Plant diagram of the two coupled cycles of consecutive TCM reactions.

3. Conclusions

Concentrated solar power plants are potential technologies to increase the share of renewables and to reduce CO₂ emissions and therefore contribute positively to Earth environment. Although there are some hybrids CSP, usually their primary energy is solar energy, to finally produce electricity. These technologies operate when the renewable energy is available and consequently to operate in continuous thermal energy storage (TES) should be considered. The R&D of TCM as TES materials implemented in CSP, specifically for solar central receiver reactors, is now focused on looking for efficient reversible chemical reactions, and heat exchangers/reactors design. Regarding both, to increase the overall reactor efficiency, a new concept based on consecutive reactions TCM is presented.

Consecutive TCM reactions concepts have been detailed; first the one cycle concept which is based on two reactions, where the main product from the first reaction, in solid state, reacts with a gas (CO₂) to give again the reactive, solid, of the first reaction. Then the process can restart again, being CO₂ the only external input. Whereas the second concept, based on two coupled

454 cycles, is born with the idea of coupling another cycle of consecutive reaction to need o extra
455 input of reactants.

456

457 Therefore, the proposed system store chemical compounds capable to release thermal energy.
458 By changing from reversible endothermic/exothermic reactions towards consecutive reactions a
459 higher chemical reaction conversion can be achieved and this would also contribute in a better
460 material stability, leading to a longer material life time and thus longer operational plant
461 periods.

462

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464

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473

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