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

Luisa F. Cabeza¹*, Aran Solé¹, Xavier Fontanet¹, Camila Barreneche¹, 2, Aleix Jové³, Manuel Gallas³, Cristina Prieto³, A. Inés Fernández²

¹GREA Innovació Concurrent, Universitat de Lleida, Lleida, Spain. Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain.
²DIOPMA Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Barcelona, Spain. Martí i Franqués 1-11, 08028 Barcelona, Spain
³Abengoa Research, C/Energía Solar 1, 41012 Seville, Spain

*Corresponding author e-mail: lcabeza@diei.udl.cat

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

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

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

Proposed mechanisms to store thermal energy are based on different physical or chemical
principles: sensible heat (molten salts, solid particle materials, etc.), latent heat by means of
phase change materials (PCM), and thermochemical heat storage (TCS) using thermochemical
materials (TCM) [7-13]. Nowadays, the use of molten salts is the most viable alternative for
TES coming from solar heat to supply intermittent power demand. Nevertheless, molten salts
cannot provide a temperature or an energy density as high as the TCS due to the mechanism
itself. From a theoretical point of view the use TCS is a challenge that can provide higher
storage of energy for longer periods and operate at higher temperatures compared to the other
mentioned systems. Consequently, implementing TCS technology would allow increase
efficiency of a CSP plant [5,6]. This topic has experienced a remarkable increased perception in
the last few years and thus several studies are being published. For instance, modeling of redox
reactions where the model is shown to track complex trends in measured non-stoichiometry
data, specific heat capacity, and global heats of reaction with respect to changes in T and \( p_{O2} \)
[14], novel concepts based coupling a CSP-CaL process and \( CO_2 \) power cycle [15], cascade
thermochemical storage with internal condensation [16], algorithm for searching potential
thermochemical energy storage for a wide temperature range (25-1000 ºC) [17], etc.

Actually, TCS for CSP is based on reversible reactions with high enthalpy of reaction but these
reactions presented low efficiency and poor reversibility. The trend is to use heterogeneous
reactions (solid-gas) to facilitate the removal and transport of the gases involved in the reaction. Redox systems based on oxide pairs, i.e. Mn$_3$O$_4$/Mn$_2$O$_3$ [12,13] are the most used to achieve the requirements and maintain material stability. The storage mechanism can be defined as depicted in equation 1:

$$A(s) \xrightarrow{\text{heat storage} \text{ endothermic reaction}} B(s) + C(g)$$  \hspace{1cm} \text{Eq.1}

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

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

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

2. Consecutive TCM reactions

Two different concepts, one based on one cycle and the other based on two coupled cycles of consecutive TCM reaction were developed [20,21] and are presented in this section.
2.1. One cycle TCM consecutive reaction, a case study Zn + CO₂

2.1.1. Presentation of the concept

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

![Diagram of the consecutive reactions concept: one cycle.](image)

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

2.1.2. Case study: chemical basis

As an example of this concept, the ZnO/Zn cycle is considered. The first step is the endothermic thermal reduction ($\Delta H_{298K} = 350.85$ kJ·mol$^{-1}$) of zinc oxide and can be referred as the solar step (eq. 2). The second step, the non-solar step (eq. 3), is the exothermic reduction ($\Delta H_{298K} = -67.87$ kJ·mol$^{-1}$) of CO$_2$ with zinc to generate CO and ZnO [22,23].

\[
\begin{align*}
\text{ZnO} & \rightarrow \text{Zn} + \frac{1}{2} \text{O}_2 \\
\text{Zn} + \text{CO}_2 & \rightarrow \text{ZnO} + \text{CO}
\end{align*}
\]

**Eq.2**

**Eq.3**

The thermal reduction of ZnO can be performed at 1627-1727°C [24,25] at 1 bar and inert atmosphere (N$_2$ or Ar). After this thermal reduction, zinc is obtained in gas form ($T_b=912^\circ$C) [26]. Afterwards, in the non-solar step, the produced Zn gas reacts with CO$_2$ giving the initial oxide (solid) and CO. This second reaction may be performed at temperatures below ZnO thermal decomposition. However, it presents a high resistance due to the formation of an oxide layer which slows the reaction (Figure 2) which drops the chemical conversion [23]. This phenomenon can determine the working temperature, because at temperatures lower than 912°C it has a low rate and conversion, but above 912°C it would work in the gas phase. Some studies...
that perform CO$_2$ splitting using liquid Zn achieved less than 50% of Zn conversion at 500°C [22,23,27,28]. Having a phase change can facilitate the reduction of the thermal reduction temperature through decreasing the system pressure.

![Diagram of CO$_2$ splitting mechanism](image)

**Figure 2. Scheme of CO$_2$ splitting mechanism [23].**

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

| Reaction | $T_w$ (°C) | $X$ (%) | $\Delta H_{298K}$ (kJ/kg) | $\Delta H_T$ (kJ/kg) | $\Delta H_{T,X}$ (kJ/kg) |
|----------|------------|---------|--------------------------|---------------------|-------------------------|
| ZnO$_{(s)}$ → Zn$_{(g)}$ + $\frac{1}{2}$O$_2$(g) | 1700 | 95 | 2072 | 2631 | 2769 |
| Zn$_{(g)}$ + CO$_2$(g) → ZnO$_{(s)}$ + CO$_{(g)}$ | 1000 | 95 | -400 | -272 | -258 |

2.1.3. Engineering diagram and plant application

Figure 3 shows a possible engineering scheme of the ZnO/Zn system implemented in a CSP plant. Therefore the proposed configuration is to perform Eq. 2 in a direct (closed) rotary kiln [29,30], and then to separate the Zn from the O$_2$ in a condenser (at T below 912°C) and finally reaction following Eq. 3 is performed in an indirect or non-solar fluidized bed reactor. The main drawback of this system is the phase change of Zn, which determines the phase that the Zn will be during the CO$_2$ splitting.
An interesting point is to use the heat generated in the condenser to preheat the Zn before entering the fluidized bed. The reaction kinetics will be higher, but the most important point is to prevent the oxide layer formation. With this concept it can be considered a cycle of consecutive reactions with three steps, where it is not necessary to store Zn. Another aspect to take into account is that reaction shown in the Eq. 3 is exothermic, and thus preheating of CO₂/CO/N₂ mixture (rich in CO₂) may not be required. Therefore, this is why a reactor without receiver is proposed.

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

It is important to highlight that CO/CO₂ is released/consumed because the example is based on a specific reactions being a case study to show the concept, but other reactions with other pair of gases can be found for each application.
2.2. Two coupled cycles of consecutive TCM reactions, a case study BaS/BaSO₄ + Mn₃O₄/Mn₂O₃

2.2.1. General concept

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

![Simplified scheme of the consecutive reactions concept: two cycles.](image)

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

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

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

**Discharge cycle**

\[
\begin{align*}
BaS(s) + 2O_2(g) & \rightarrow BaSO_4(s) \quad \Delta H^\circ_{850 \, ^\circ C} = -5747 \, kJ/kg \, BaS \quad \text{Eq. 4} \\
BaSO_4(s) + 4CO(g) & \rightarrow BaS(s) + 4CO_2(g) \quad \Delta H^\circ_{850 \, ^\circ C} = -933 \, kJ/kg \, BaS \quad \text{Eq. 5}
\end{align*}
\]

**Regenerative cycle**

\[
\begin{align*}
2Mn_3O_4(s) + CO_2(g) & \rightarrow 3Mn_2O_3(s) + CO(g) \quad \Delta H^\circ_{910 \, ^\circ C} = 2178 \, kJ/kg \, Mn_2O_3 \quad \text{Eq. 6} \\
3Mn_2O_3(s) & \rightarrow 3Mn_3O_4(s) + \frac{1}{2}O_2(g) \quad \Delta H^\circ_{910 \, ^\circ C} = 397 \, kJ/kg \, Mn_2O_3 \quad \text{Eq. 7}
\end{align*}
\]

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

Unlike the TCM system concept [36-38, 39-41], in which the system store solar heat is considered, in this novel concept, solar heat is used to achieve the required temperature and the thermal energy for the desired TCM reaction. Therefore, the proposed system store chemical compounds capable to release thermal energy.
Another difference with conventional TCM systems is that there is not a pure charge reaction. Equation 4, where \( \text{BaSO}_4 \) is reduced, could be considered as charging step, but is an exothermic reaction, and at the same time is the reaction for recovery the \( \text{BaS} \). On the other hand, there are two endothermic reactions (Eq. 6 and 7), but these are not directly involved on the discharge reaction. Therefore, the system is divided into a main cycle (discharge cycle) which releases heat and the other cycle (regenerative) closes the system (see Figure 5).

![Figure 5](image)

**Figure 5.** Scheme of the novel two coupled cycles of TCM consecutive reactions based on \( \text{BaS} \) oxidation.

### a. Discharge cycle

The material used in the discharge cycle is the Barite (mineral of \( \text{BaSO}_4 \)) which can be reduced with \( \text{CO} \) at temperatures between 800-1000°C to obtain \( \text{BaS} \) [31,49-58]. Furthermore, \( \text{BaS} \) can be oxidized by \( \text{O}_2 \) (or air) at temperatures above 25-1400 °C [26,31- 35]. Both reactions (Eq. 4 and 5) are exothermic, and \( \text{BaSO}_4 \) and \( \text{BaS} \) are also stable at temperatures higher than 1400 °C, with melting point of 1580 °C and 2229 °C, respectively [26, 59]. For this reason, a discharge cycle based on \( \text{BaS}/\text{BaSO}_4 \) is a good candidate for a TCS system in a CSP plant.

Since barite is the industrial precursor of \( \text{BaS} \) [51,56] there are not many studies of \( \text{BaS} \) industrial combustion. However, the literature reveals that the \( \text{BaS} \) oxidation reaction is highly
exothermic ($\Delta_{r}H^0 = -1013.20 \text{ kJ/mol, } -5963.75 \text{ kJ/kg}_{\text{BaS}}$) [26,31-33]. Furthermore, it is well known that sulphur ($S^{2-}$) oxidation has high reaction kinetics, and even become spontaneous [60-62]. This, added to the working temperature (800-1000 °C) in a CSP plant suggests that oxidation of BaS will be a fast reaction.

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

$$BaSO_4(s) + 2C \rightarrow BaS(s) + 2CO_2(g) \quad \text{Eq. 8}$$

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

Another advantage of the BaS/BaSO$_4$ consecutive reactions in front other possible cycles as MS/MSO$_4$ (where M is a metal) is that BaSO$_4$ is one of the most thermal and water stable [26,31,60,64]. Thermal stability of BaSO$_4$ is only exceeded by alkali sulfates, but on the other hand, alkali sulphides have very low water stability. Sulphides of some transition metals such as Fe, are more stable in water than BaS [26,65], but their sulfates have poor thermal stability. Besides the high thermal stability and relatively high stability in water of the BaS/BaSO$_4$ redox pair suggests stability in the presence of CO$_2$ gas [51]. This means that the carbonation of the barium salt could be minimized during the BaSO$_4$ reduction (Eq. 5) unlike what might happen with other metal sulfates. For that reason, the most attractive MS/MSO$_4$ redox pair for discharge cycle is BaS/BaSO$_4$.

Furthermore, there are some studies that evaluate the cyclability using carbothermal reduction of BaS [51]. Another indication which suggests the feasibility/viability of these reactions is the high melting temperature of BaSO$_4$ and BaS in comparison with the working temperature, which hinders particle sintering. On the other hand, minimization of coarsing will depend, in part, on the particle size distribution and the particle shape [66,67].
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:

\[
\text{Reduction at } T_{\text{high}}: \quad MO \xrightarrow{\Delta h,T_{\text{high}}} MO_{1-\delta} + \frac{\delta}{2} O_2(g) \quad \text{Eq.9}
\]

\[
\text{Oxidation at } T_{\text{low}}: \quad MO_{1-\delta} + \delta CO_2 \xrightarrow{\pm \Delta h,T_{\text{low}}} MO + \delta CO(g) \quad \text{Eq.10}
\]

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]:

\[
\text{Eq.11}
\]

\[
\text{Eq.12}
\]
According to the Ellingham-Richarson diagram [32,77], Mn$_3$O$_4$ or CoO can reduce CO$_2$ performing Eq. 10. Although the reaction is thermodynamically feasible, the tolerance of the metal oxides to CO$_2$/CO mixture should be considered. There could be a small fraction of CO changing direction in Eq. 10, and that would affect the reactor design and the purity of CO (mixture CO$_2$/CO rich in CO) obtained.

Manganese (Mn), cobalt (Co), and iron (Fe) are very similar elements, since they are very close on the periodic table and have very similar electron configuration [60,78]. Except for the different disproportionation temperature between each redox pairs, that is given by the better ability of Fe to stabilize the iron oxides. Consequently, the expected behaviour for the two redox pairs should be similar to FeO/Fe$_3$O$_4$, with good kinetics and cyclability of the redox pair. On the other hand, use of doping agents, such as iron or nickel, can vary the disproportionation temperature [40,41,74,75,79,80].

Studies indicate that Co can be oxidized/reduced from 30 cycles [56] and up to 100 cycles without reactivity loss [81]. This ensures the ability of cobalt to be reduced by thermal disproportionation, along with presumption of good oxidation with CO$_2$, cobalt becomes a good candidate. Similarly to cobalt, other studies have shown the same behaviour with manganese [40,41]. Although manganese cyclability is not as good as that of cobalt, some studies [67] suggest that it is possible to improve its cyclability.

As the oxidation temperature of the metal oxide is lower than that of the disproportionation, this means that it can work below 1000$^\circ$C, complying with the first premise of the concept. Furthermore, the re-oxidation mechanism usually is controlled by oxygen diffusion inside the particle [67,81]. Although there is a maximum temperature which cannot be overcome, this will not have an important role in the kinetics. To improve kinetics it is essential to control the morphology and particle size of the metal oxide, and also to have a controlled atmosphere. To ensure morphology, minimizing sintering and maintaining surface/volume ratio, it may be advisable to decrease the disproportionation temperature.

Finally, considering the economic aspects, manganese is considered the best alternative for the regenerative cycle. Particularly, manganese has a cost approximately ten times lower than cobalt.
Following the presented case study (2.2.2) and according to the patent submitted [17] the results of mass and energy balances and the plant diagram of this concept are presented in this section. To know how much potential and the viability of this concept, mass and heat balances for whole cycle of BaSO₄/BaS coupled to Mn₃O₄/Mn₂O₃ cycle are provided. First of all, BaSO₄/BaS balances are shown taking into account Eq. 4 and 5 (see Table 2, note that a basis of 100 kg of BaSO₄ in solid state is taken for the balances). Then, operating modes during day and night for BaSO₄/BaS cycle are detailed and afterwards the balances of the regenerative cycle (see Table 3) and the diagram of the whole concept are provided.

### Table 2. Mass balance of BaSO₄/BaS cycle

| Reaction | 1BaSO₄ (s) + 4CO (g) → 1BaS (s) + 4CO₂ (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 O₂ (g) → 1BaSO₄ (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 |

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

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

- The reduction of BaSO₄ to BaS takes place at 850°C thus it is needed the BaSO₄ receiver to rise the temperature of the BaSO₄ up to 850°C;

- The BaSO₄ enters into the reduction reactor at 850°C and it is reduced to BaS in contact with CO coming from the regenerative cycle;

- The reduction reaction gives 933KJ/kg of BaS. This heat is used to heat up the cold sCO₂ in the reduction reactor – generator from 600°C to 802.3°C

- The BaS stream coming out of the reduction reactor goes to the hot storage tank and in parallel to the oxidation reactor:
  - BaS is stored in a silo to be oxidized in discharge mode;
  - BaS is oxidized in the oxidation reactor with Air giving 5747KJ/kg BaS. This heat is used to rise the temperature of the sCO₂ stream up to 1150°C

- The BaSO₄ coming out of the oxidation reactor is sent to the BaSO₄ receiver to be heated up again to 850°C to restart the cycle.

Figure 6. Operation mode during day (conversion reaction 99%)
b) **Night / discharge mode**

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

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

By this process the discharge could be performed only with an air inlet in the oxidation reactor avoiding the need of storing CO/CO₂.

If it was desired to be able to use both reactors in discharge mode a big storage system of CO/CO₂ or at least of the reactants of the regenerative cycle should be implemented avoiding the needs of storing solid particles of BaS and BaSO₄.

![Figure 7. Operation mode at night (conversion reaction 99%)](image-url)
c) **Regenerative cycle Mn$_2$O$_3$-Mn$_3$O$_4$**

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

### Table 3. Mass balance of Mn$_2$O$_3$/Mn$_3$O$_4$

| Reaction | 2Mn$_3$O$_4$ (s) | + | 1CO$_2$ (g) | → | 3Mn$_2$O$_3$ (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$_2$O$_3$ (s) | → | 2Mn$_3$O$_4$ (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            |

The regenerative cycle, used for regenerating the CO for reducing BaSO$_4$, is composed for two endothermic reactions which need absorbing 2222 kJ/kg of Mn$_2$O$_3$ for a full conversion reaction (see Eq. 6 and 7). For these reactions, it has also considered a chemical conversion of 60% and as consequence the total energy absorbed per kg of Mn$_2$O$_3$ is higher than for a full chemical conversion. So, this energy increases until 3703 kJ/kg of Mn$_2$O$_3$ for 60% of conversion.

The net energy value, released on BaSO$_4$/BaS cycle and absorbed on Mn$_2$O$_3$/Mn$_3$O$_4$ cycle, should be interpreted as kJ per kg of BaS. According to the mass balance (see Table 2 and 3), for producing 72.57 kg of BaS, the system needs 811.93 kg of Mn$_2$O$_3$, and thus the net energy balance is 37165 kJ per kg of BaS for a 60% of chemical conversion.
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
cycles, is born with the idea of coupling another cycle of consecutive reaction to need o extra input of reactants.

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

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