Conceptual process design of a $\text{CaO}/\text{Ca}(\text{OH})_2$ thermochemical energy storage system using fluidized bed reactors

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ABSTRACT

This paper analyses a thermochemical energy storage process using a $\text{CaO}/\text{Ca}(\text{OH})_2$ chemical loop. A single circulating fluidized bed reactor is proposed to carry out the hydration-dehydration alternating reactions. During the energy discharge step, steam is fed to the reactor and used as a fluidizing gas and as a reactant with the CaO coming from a silo, enabling heat to be recovered at a sufficiently high temperature (around 743 K) from the hydration reaction taking place in the fluidized bed. During the dehydration of $\text{Ca}(\text{OH})_2$ (energy charging step), heat (i.e. from a concentrated solar field) is stored in thermochemical form as CaO by using steam as a fluidizing gas. A basic process integration scheme for a reference case with a power output of 100 MW_t is analysed in this work, by solving the mass and energy balances during charging and discharging steps and by calculating the volume of the silos and characteristic dimensions of the fluidized bed reactor. The effective energy storage densities of the CaO silo is shown to

be over 260 kWh/m³ with reasonable activities of the solids when storing CaO solids in the silo at around 813 K.

Keywords: thermochemical energy storage; calcium oxide; calcium hydroxide; hydration; circulating fluidized bed; concentrated solar power.

1. Introduction

Concentrated solar power (CSP) is a renewable energy technology that obtains its energy input by concentrating solar radiation. This energy is then converted to high temperature steam or another fluid which is used to drive a turbine or engine (for electricity generation). The concentrated solar power can also be directly used for industrial heat processes or in thermochemical processes [1].

The production of electricity from concentrated solar power (CSP) installations has experienced a large increase in recent years and is expected to grow in the mid and long term, as it is already a highly competitive technology in many locations and is expected to contribute substantially to efforts to decarbonize the global energy system [1]. As in the case of other renewable energies, one of the problems with CSP technologies for power generation is that the electricity production profile may not match the electricity demand curves. This problem can be partially overcome by coupling the CSP installations to thermal energy storage systems (TES) [1-3], so that variability in the power output can be managed to some extent independently of the solar power input. There are four main types of TES technologies that are available for CSP plants: sensible heat storage systems (by solid or liquid media, see review by Gil et al.[4]), latent heat storage systems (solid-liquid phase transition is mainly used by existing technologies according to Liu et al.[5]), sorption heat storage (physical or chemical) and heat storage by reversible chemical reactions [1, 4, 6, 7]. The last two methods are

known as thermochemical heat storage. In these systems, the charge stage (low energy demand period, when there is a surplus of thermal power from the solar field) takes place when thermal power is used to drive an endothermic reaction. In the discharge stage (peak energy demand period) the opposite exothermic reaction takes place using the stored products, and heat is released to drive a steam cycle and/or to boost the thermal power input to the steam cycle of the CSP plant. It is generally accepted that chemical sorption processes and other processes based on reversible chemical reactions display the highest potential for energy storage densities [4, 6-11]. Some of the main reaction schemes considered today for thermochemical storage systems were proposed many years ago, but their practical development is still at a very early R&D stage [1, 4, 7].

One of the main lines of research on chemical reactions for energy storage has been focused on the hydration and dehydration of CaO/Ca(OH)₂ [9, 10, 12-18],

which has several theoretical advantages such as its low cost, the non-toxicity of the materials and the high temperatures and the reversibility of the reaction [10, 12-14]. Figure 1 represents the basic CaO hydration Ca(OH)₂ dehydration cycle concept as proposed by Ervin and Rosemary et al. [10, 12, 13, 19] for a concentrated solar power plant, in which heat from the solar plant is used to preheat the calcium hydroxide and decompose it into calcium oxide and water. During the discharge operation, the exothermic reaction takes place and the CaO is re-hydrated releasing useful heat. One of the most interesting characteristics of the CaO/Ca(OH)₂ system is the temperature level at which the heat is released during hydration (723-773 K), since the temperature of the working fluid in the turbine is in the range of 673-873 K [1], so that it could be used to facilitate the thermal integration of the energy storage system with the steam cycle in

the solar field under normal conditions (by supplying a thermal power Q_{OUT} to the steam cycle as indicated in Figure 1). In contrast, high quality heat from the solar field (designated as thermal power input Q_{IN} in Figure 1) must be made available at temperatures above the dehydration temperature during the charge period. Molten salts, oils, saturated or superheated steam have been proposed as heat transport fluids between the solar field and the storage system [20, 21].

In this work we are primarily concerned with the chemical process scheme behind each of the charge/discharge steps represented in Figure 1 and with the reactor characteristics needed to achieve the desired conversions in the solids circulating through the reactor. Fixed beds are usually assumed to be the most suitable reactors for carrying out the hydration and re-hydration steps [22-27]. However, it can be argued that these reactors have serious limitations for this application that may have prevented the development of the process. On the one hand, the modest heat transfer capacity of fixed beds makes the energy charging and discharging steps very difficult because large (and costly) heat transfer surfaces would be required in the fixed beds to enable the hydration/dehydration reactions to match the thermal power ranges (10 to 100s of MW_t) involved in typical large scale energy storage systems. In addition, pressure drop and mass transfer limitations can be a serious drawback in large-scale fixed bed systems of fine particles since they may make it necessary to increase the reaction rates of the solids. In view of these limitations, fluidized bed reactors should be considered as an interesting alternative to CaO/Ca(OH)₂ energy storage systems. Early works in the 70s had already pointed in this direction [10, 12, 13, 19] but to our knowledge, it was only recently, under the EU funded StoRRe project (www.storre.eu) under which this work has been carried out, that a comprehensive effort was made to validate and facilitate the scaling up of the fluidized bed process concept represented in Figure 1.

In this study, a process scheme for a large-scale energy storage system based on the $\text{CaO}/\text{Ca}(\text{OH})_2$ reversible reactions in fluidized beds is analyzed. Mass and heat balances are solved for reasonable conditions and conversions of solids in the reactors when the system is operating in continuous mode during the charge and discharge stages. This allows for an evaluation of the main process performance parameters (solids circulation rates, heat exchange requirements, basic reactor volumes and solids storage silos, energy storage density etc.) and the selection of suitable operating windows for the energy storage system.

2. Description of the process

The chemical process investigated in this work is depicted in the two schemes of Figure 2, which represent the energy discharge (a) and the energy charge mode (b) respectively. Ideally, the cyclic nature of the process should allow the two stages to take place at different times but using the same key components: a single fluidized bed reactor alternating from hydration to dehydration conditions and the two solid storage silos feeding solids continuously to the fluidized bed. The changes between the operating modes (a to b and viceversa) will include dynamic operating conditions, but these are considered to be outside the scope of this preliminary assessment of the process and from this point onwards, steady state will be assumed for each cycle period.

Operation at atmospheric pressure is assumed for simplicity and similarity with existing large scale thermal fluidized bed systems (like CFBCs). This would lead to high volumetric flows of gases through the reactors during hydration and dehydration (see below), and so a circulating fluidized bed design for the reactor is a more natural choice for the reactor design. Bubbling fluidized bed reactors would also be feasible if coarser solid materials could be made available with suitable reactivity and mechanical stability. However, circulating fluidized beds are in principle more suitable for large

scale applications as they can handle the large circulation of solids between silos using standard solid circulation elements (risers, cyclones, stand pipes, loop seals, heat exchangers from fluidizing solids etc.). Not all of these elements are shown in detail in Figure 2 for simplicity.

During the hydration process (Figure 2a), a stream of high temperature solids containing CaO (1) and a flow of steam (2) are fed into the fluidized bed reactor at atmospheric pressure to obtain Ca(OH)_2 . The thermal power released during the discharge step, thanks to the hydration reaction (Q_{OUT} in Figure 2a), is used to produce steam or heat up another fluid (i.e. steam, oil, molten salts) in order to extract heat from the storage system. The heat exchanger located inside the reactor to extract Q_{OUT} can exploit the high heat transfer coefficients typical in fluidized beds ($100\text{-}300 \text{ W/m}^2\text{K}$)[28]. This is a very important advantage respect to fixed bed reactor configurations with similar purposes. Furthermore, the sensible heat contained in the solids leaving the reactor (3) is recovered in a fluidized bed heat exchanger (FBHX) to preheat and fully vaporize the water fed into the reactor (4). The FBHX operates in countercurrent flow to the water-steam flows. This may be achieved by arranging several stages in series or by using elongated fluidized beds such as those proposed by Schwaiger et al. [29] for other solar applications. A small flow of air is used to fluidize the bed under conditions close to minimum fluidization in order to minimize the lateral mixing of solids in the FBHX and to maximize the heat transfer coefficients. Alternatively, other commercial heat exchanger devices could be used for the purpose of cooling the solids arriving from the hydrator reactor. For example, moving bed heat exchangers used to heat up or cool down solids from the silos are already commercially available [30] and are used in large-scale process schemes [31]. After this heat exchange stage, the resulting cold solids stream (5) rich in Ca(OH)_2 , is stored in the silo.

Since the steam will disappear from the gas phase during hydration, a certain excess of steam must be used (stream (6) in Figure 2) to maintain the fluidization conditions at the exit of the riser when the efficiency of the hydration reaction is high. The excess steam will be recycled (7) to the circulating fluidized bed hydrator reactor by means of a fan, after some of the sensible heat it contains has been employed in the FBHX to preheat stream (2), just before it enters the fluidized bed.

Figure 2b describes the dehydration stage, where a continuous flow of solids containing Ca(OH)_2 (8) enters the reactor together with a certain flow of preheated steam (9) as fluidizing agent. As steam is the only fluidizing agent used (no air is introduced into this reactor), equilibrium dictates a minimum dehydration temperature of around 792 K (see equation (2) below). In this work, we have considered steam as the only agent of fluidization in the dehydration stage. Other researchers into CaO/Ca(OH)_2 energy storage systems have proposed the use of air (or even nitrogen) as a gas carrier of the steam [12, 13] generated during the dehydration, to reduce the decomposition temperatures and increase the dehydration rates. However, the introduction of this carrier gas to the reactor comes with serious restrictions for the reactor design. On the one hand, the volumetric flow of gases through the reactor and associated equipment could increase substantially with respect to the hydration stage, compromising the inherent cost advantage of using the same reactor during the hydration and dehydration periods. On the other hand, the 400 ppmv of CO_2 in the air will lead to the carbonation of the sorbent as the equilibrium pressure of CO_2 at dehydration temperatures (around 773 K) is only 130 ppmv. Therefore, in this work we have adopted a design case (see below) where only steam is used as fluidizing agent during dehydration and most of the gas leaving the reactor during dehydration has been generated from the decomposition of Ca(OH)_2 .

As dehydration is the energy storage stage, the thermal power input from the heat transport fluid coming from the solar plant (Q_{IN}) is used in the fluidized bed reactor both to preheat the reactants and to drive the endothermic dehydration reaction. The stream of solids (10) leaving the reactor in this operation mode, which contains mainly CaO, is stored in a silo at the dehydration reaction temperature. Clearly, the energy storage density of the system will increase significantly as a consequence of storing CaO at a high temperature. Furthermore, heat loss from the high temperature CaO silo can be assumed to be negligible considering the low thermal conductivity of CaO and the low surface-to-volume ratio characteristic of large scale silos, as in the case of other large-scale thermal energy storage systems [6].

Finally, as in the hydration process, the gas-solid fluidized bed heat exchanger FBHX is used to preheat the stream of solid reactants (11) with the sensible heat from the steam that leaves the fluidized bed reactor (12) which includes the steam generated during the reaction and the steam used as fluidizing agent (9). After the FBHX, the steam stream (13) is directed to a condenser to be stored as water for use in a new discharge CaO hydration cycle.

3. Case study

In order to analyze the process schemes of Figure 2, the basic design of a particular case has been carried out by solving the mass and energy balances and by incorporating current knowledge on the CaO/Ca(OH)₂ reaction system to the conditions and solid residence times distribution expected in the fluidized bed reactors of Figure 2. Natural CaO particles are known to be friable materials during hydration and dehydration cycles despite the high reversibility of the reaction. A suitable support or binder for the CaO grains needs to be used as those employed in similar thermochemical energy storage loops [32]. Although it is beyond the scope of this work to discuss these materials,

recent reviews on R&D efforts to develop CO₂ sorbents using materials of CaO supported on inorganic, mechanically stable supports or suitable binders [33-35] could also be used as a guide for new materials with suitable fluidizing properties and reactivity.

The choice of temperature for the circulating fluidized bed reactor under hydration or dehydration operation must take into account the information available on equilibrium and kinetics of the hydration and dehydration reactions. Figure 3 represents the equilibrium curve in the temperature interval of interest for this work. As can be seen, predictions from the thermochemical data provided by Barin [36] and Nikulshina [37], differ substantially from those experimentally obtained by Samms and Evans [38], Schaube et al. [14] and Halstead and Moore [39] in the temperature range of interest, even if they appear to be more consistent when wider intervals of temperatures are considered. Using our own experimental results reported elsewhere [40] we have chosen the equation obtained from thermochemical data provided by Barin [36]:

$$P_{eq} = 2.30 \times 10^8 \exp\left[-11607/T\right] \quad (2)$$

where P_{eq} is the equilibrium pressure (kPa) and T is the temperature (K).

Assuming atmospheric steam pressure and using equation (2), the maximum operating temperature is 792 K during hydration. Early kinetic studies on the hydration of CaO particles with steam [10] indicate that hydration is a fast reaction even at temperatures very close to the equilibrium temperature. We have recently confirmed [40] this by measuring the hydration rates of CaO particles under differential conditions, for a suitable particle size range of 0.1-2 mm in a thermogravimetric analyzer. Other authors who have also studied the hydration and dehydration reaction kinetics under diverse conditions [14, 40-46] agree that both reactions rates are relatively fast at the

high temperatures required for thermochemical storage applications. Therefore we have chosen a temperature of 743 K for the hydration step for this reference case, as an interval of around 700-750 K seems reasonable in order to obtain fast reaction rates and high hydration conversions in the reactor. The hydration reaction rates experimentally measured in pure steam at 743 K [40] were consistently higher than $1.3 \times 10^{-2} \text{ s}^{-1}$ (for an average particle size $d_p=0.25\text{mm}$). Therefore, this reaction rate has been adopted for the purpose of the reference reactor design under the conditions selected in this study for the hydration reaction.

We also assume in this reference case that the dehydration stage takes place at a temperature of 813 K, which is just over 20 K higher than the equilibrium temperature of dehydration in pure steam (equation 2) and has been shown to be sufficient to yield reactions rates [40] comparable to those during hydration at 743 K. It should be noted that these are best guess temperatures for the reactors and are not a fully free choice for the operator of the reactor because the temperature in the reactors will move close to equilibrium conditions, fixed at the point where overall heat transfer rates match overall reaction kinetics.

In order to define the magnitude of the solid and steam streams entering the reactors of Figure 2 it is first necessary to solve the mass and heat balances of the process. For this purpose, a reference case is assumed to have a thermal power output of $Q_{\text{OUT}} = 100 \text{ MW}_t$ during the discharge stage. In this work the thermal power output Q_{OUT} is calculated taking into account the hydration reaction power output and the sensible heat requirements of each stream involved in the reaction. The heat balance in the hydrator reactor is as follows:

$$Q_{\text{OUT}} = \dot{m}_{\text{CaHy}} \left(\hat{H}_{743\text{K}} - \hat{H}_X \right) + \dot{Q}_{(1)} + \dot{Q}_{(2)} + \dot{Q}_{(6)} - \dot{Q}_{(3)} + \dot{Q}_{(7)} \quad (3)$$

where for the relevant temperatures in this work the reaction enthalpy associated to equation (1) is $\Delta H_{793K} = 104 \text{ kJ/mol}$.

For the sake of simplicity, adiabatic conditions are assumed throughout the reactor and in all the heat exchange operations. For the heat balance to the hydrator, the total flow of solids (streams (1) and (3) for solids in and out of the reactor respectively) is taken into account, which includes the molar flow of calcium (F_{Ca}) and also a certain fraction of an inert material present in the solids per fraction of Ca (f_{inert}). This inert (i.e. inorganic binder or stable porous support) will be required to ensure the mechanical stability of the $\text{CaO}/\text{Ca}(\text{OH})_2$ particles, as mentioned above. In order to avoid the need to define the inert and its thermal properties at this stage of conceptual design, the heat balance in equation (3) is solved with $f_{inert}=0$ compensating this assumption with relatively modest conversion targets during hydration and dehydration (increment in conversion around 0.6 as discussed below).

In principle, the average Ca conversion of particles at the exit of the hydration reactor could be very high (close to 1, when referred to total free CaO in the material) considering the high hydration conversions obtained in experimental work based on kinetic information obtained at particle level with natural and synthetic CaO materials [10, 14, 40-46]. As indicated above, in the reference conditions chosen for this case (hydration at 743 K and pure steam), the increment in conversion ΔX is calculated taking into account the average conversions (X_{ave}) of hydration and dehydration as:

$$\Delta X = X_{ave \text{ Hy}} - X_{ave \text{ Dehy}} \quad (4)$$

The individual average conversions above can be estimated assuming perfect mixing of the solids in the circulating fluidized bed reactor:

$$X_{ave} = \frac{\int_0^{\infty} X(t) \exp(-t/\bar{\theta}) dt}{\int_0^{\infty} \exp(-t/\bar{\theta}) dt} \quad (5)$$

where $\bar{\theta}$ is the average particle residence time. On the other hand, assuming a shrinking core model [47] during reactions the hydration and dehydration conversion as a function of time $X_{Hy}(t)$ and $X_{Dehy}(t)$ respectively are calculated by means of equations (6a) and (6b):

$$\begin{aligned} X_{Hy} &= 1 - (1 - t k_{Hy})^3 & \text{for } t < t^* \\ X_{Hy} &= 1 & \text{for } t > t^* \end{aligned} \quad (6a)$$

$$\begin{aligned} X_{Dehy} &= t k_{Dehy}^3 & \text{for } t < t^* \\ X_{Dehy} &= 0 & \text{for } t > t^* \end{aligned} \quad (6b)$$

being t^* the time required to achieve the maximum conversion and k_{Hy} and k_{Dehy} the kinetic constants with values of 1.3×10^{-2} and $1.6 \times 10^{-2} \text{ s}^{-1}$ respectively obtained from experimental measurements reported elsewhere [40] for an average particle size of $d_p = 0.25 \text{ mm}$, an atmosphere of pure H_2O at atmospheric pressure and the 743 and 813 K values chosen above.

In order to calculate the time to achieve maximum conversion (t^*), and therefore the conversion of solids at the exit of the reactor, it is necessary to know the fraction of active (non reacted) Ca material in the reactor (f_a), assuming perfect mixing of the solids:

$$f_a = \frac{\int_0^{t^*} \exp(-t/\bar{\theta}) dt}{\int_0^{\infty} \exp(-t/\bar{\theta}) dt} \quad (7)$$

Therefore, the time required to achieve maximum conversion is:

$$t^* = -\ln(1 - f_a) \bar{\theta} \quad (8)$$

Furthermore, in each stage the moles of $\text{Ca}(\text{OH})_2$ that disappear/appear in the solid stream must match the moles of Ca that are reacting in the bed. Therefore the following general mass balance to the reactor can be established:

$$F_{\text{Ca}} \hat{X} = N_{\text{Ca}} f_a \left[dX/dt \right]_{\text{Bed}} \quad (9)$$

where N_{Ca} is the moles of Ca solids present in the bed. For each stage the term dX/dt is given by the reaction kinetics. Using equation (9) and the expressions of dX/dt [40], the individual average conversion for each stage can be written also as:

$$X_{\text{ave}} = 1 - \left[F_{\text{Ca}} \hat{X} / N_{\text{Ca}} f_a \right]^{1/3} \quad (10)$$

where the factor 3 is related to the kinetic expressions [40]. From equation (10) the active fraction of Ca material in the reactor (f_a) can be obtained in each stage, verifying that the average conversions calculated from equation (5) (using equations (6a) and (6b) of hydration and dehydration conversion as function of time respectively) are the same that the ones obtained from equation (10).

The average particle residence time is calculated as a function of the solids inventory (W), the reactor free cross-sectional area for fluidization (A_{free}), (i.e. without counting the area occupied the heat exchanger for $Q_{\text{IN,OUT}}$) and with the total solids flow that enters the reactor in each operation mode, which includes both the total flow of calcium circulating from the silos to the reactor (F_{Ca}) and the moles of inert material present in the solids per mol of Ca (f_{inert}):

$$\tau = W_{\text{bed}} / (F_{\text{Ca}} + f_{\text{inert}} M) \quad (11)$$

It should be noted that the effect of the inert content on the solids is negligible over the residence time of the particles as both the bed inventory and the solids stream arriving at the reactor have similar inert contents. However the overall inventory of

material in the reactor (and ultimately on the reactor volume) is inversely proportional to f_{inert} . Therefore, this is an additional reason for developing materials with a maximum active fraction of $\text{CaO}/\text{Ca}(\text{OH})_2$.

The total solids inventory in a circulating fluidized bed is a complex function of operating conditions inside the reactor, linked to fluid-dynamic properties of the particles and reactor geometry. However, by comparison with commercial systems using CFB with CaO , like circulating fluidized bed combustors, it is possible to anticipate typical inventories of between 100 and 1000 kg/m^2 and a typical range of solids circulation flow rates (G_s) of 0.5-30 $\text{kg}/(\text{m}^2\text{s})$ (as in the case of circulating fluidized bed combustor or Calcium looping reactors employing similar materials [48, 49]).

For the reference case proposed in this work, a conservative value of $\Delta X=0.6$ has been selected to compensate for the choice of $f_{\text{inert}}=0$ to account for the presence of an inert fraction of solids in the material. This increment in conversion as defined in equation (4) allows a first estimation of all the solid and gas streams in Figure 2a and 2b, as indicated in Table 1 and 2.

With respect to the gas velocities in the reactor during the hydration and dehydration steps, an identical reactor cross-section must be assumed all along the riser. This is because during the hydration stage, a large fraction of the gas disappears from the gas phase as the bed height increases, whereas the opposite occurs during the dehydration step. It is therefore impossible to adapt changes in the cross-sectional area in one step without compromising the operation of the other step. Furthermore, general rules and experience acquired from other similar reactor systems using CaO materials (like CFBC) can be followed to estimate minimum reasonable velocities at the exit of the reactor during hydration and at the bottom of the reactor during dehydration [48, 49].

Assuming a maximum gas velocity of 5 m/s during hydration at the inlet of the circulating fluidized bed reactor, a fluidized bed reactor cross-sectional area free for fluidization of 34.4 m² is obtained. The gas velocity will decrease during hydration due to the reaction of the CaO with steam, leading to an exit gas velocity of 1.7 m/s (which means that a 50 % steam excess above the stoichiometric value is used to maintain the solids circulation). In contrast, during the dehydration stage, the gas velocity increases with the height from an inlet gas velocity of 1.7 m/s to 3.9 m/s at the outlet.

The case example solved in the previous paragraph is open to many variations depending, among other factors, on several design parameters affecting the overall system of energy storage into which the CaO/Ca(OH)₂ process of Figure 2 is integrated, for example, when considering different charge and discharge operation times (t_{Dehy} and t_{Hy}).

The required solids inventory in the reactor has been calculated in order to achieve the selected $\Delta X=0.6$ using equations (4) to (10). Figure 4 represents the average hydration and dehydration conversions ($X_{\text{ave Hy}}$ and $X_{\text{ave Dehy}}$ respectively) as well as the increment in conversion ΔX calculated for different values of solids inventories. As can be seen a solids inventory of 443 kg/m² gives $\Delta X=0.6$, which corresponds to an average particle residence time of 120 s for the charge operation mode. During the discharge stage, in order to maintain the same residence time as for the charge stage, the solid inventory required is 373 kg/m². For the hydration and dehydration operations the active fraction of Ca material in the reactor (f_a) is 0.27 and 0.11 respectively. For this reference case, the solid circulation flow rates (G_s) for both hydration and dehydration are around 3.1-3.7 kg/(m²s), values that are in the typical range of other CFBs using similar materials.

In the case of the heat flows, it should be pointed out that for the reference design target of 100 MW_t a thermal power input of 158.7 MW_t (Q_{IN}) is required during the charge mode in order to preheat the reactants to the reaction temperature (46.3 MW_t) and to drive the endothermic dehydration reaction (116.2 MW_t) according to the reference conditions of Table 2. 46.9 MW_t is considered as heat power lost due to the condensation of water during the dehydration stage.

The design of the heat transfer area within the reactor to allow for Q_{IN,OUT} will have to be based on a compromise between the need to operate with minimum average temperature difference (ΔT_{HX}) between the reactor temperature and the temperature of the fluid carrying Q_{IN,OUT} and the need to maintain the heat exchange area (A_{HX}) under reasonable values. For a typical value of heat transfer coefficient in a circulating fluidized bed (h_{CFB}) of 150 W/m²K [28] and an average temperature difference between the heat transport fluid and the bed (ΔT_{HX}) of 30 K a value of A_{HX}=35258m² is obtained. To accommodate this large area in the reactor, waterwalls and a dense packing of tube bundles is needed. This is however a common practice in boiler applications. Future reactor designs will require detailed understanding of heat transfer coefficient and gas and solid flow patterns in such reactor highly packed with tubes, that will largely increase its cross section to accommodate the heat exchanger required for Q_{IN,OUT}.

The hydration-dehydration thermal efficiency of the storage system can be estimated using equation (12):

$$\eta_p = \frac{Q_{OUT}}{Q_{IN}} \cdot \frac{c_{p,Hy}}{c_{p,Dehy}} \cdot 100 \quad (12)$$

Using the numbers and assumptions of the reference case above a maximum net efficiency of 63 % is obtained in the reference conditions chosen for the proposed

process scheme. As noted above this thermal efficiency represents the most pessimistic scenario in which no thermal integration of the storage system is achieved with a solar field except in relation to the heat exchange operations represented as Q_{IN} and Q_{OUT} in Figure 2. In this case, a high level of energy inefficiency is unavoidable due to heat power losses through steam condensation. It should be possible to explore, on a case-by-case basis, more efficient options for integrating the system into a solar field but it is beyond the scope of this conceptual work to analyze such options of thermal integration with the solar field.

As seen from equation (12), the hydration-dehydration thermal efficiency of the storage system considered in this work, only takes into account the ratio Q_{OUT}/Q_{IN} and the operation times under each stage (t_{op}). A more-in-depth evaluation of the full thermal storage system will require considering the parasitics losses associated to the operation of the reactors. If the final use of Q_{OUT} is the generation of electricity the net efficiency for electricity production on Q_{OUT} should not differ from other CSP modern plants (around 25% according to [3]), because the main flow of gases in the proposed system are steam generated from thermal sources (no blowers required) and the negligible flow of gas required to fluidize fine solids in the FBHX.

Finally, by considering the volume of silo required to operate at a reference time of one hour under hydration or dehydration modes, the mass balance leads to 384 m³ of CaO and 457 m³ of Ca(OH)₂ (when assuming a bulk density for the solids of $\rho_s=1000$ kg/m³). In these conditions, the effective energy storage density in this process (ESD_{eff}) can be calculated by means of equation (13):

$$ESD_{eff} = Q_{OUT} \left(\frac{F_{CaHy}}{M_{Hy}} + f_{inert} \right) / \rho_s \quad (13)$$

where the factor 3.6 is introduced in order to give ESD_{eff} in kWh/m^3 . For the reference case proposed in this work $ESD_{eff} = 260 kWh/m^3$.

As a final point, it is interesting to analyze the sensitivity of the main reactor performance variables (ΔX as defined in equation 4) on design reactor variables such as the solid circulation flow rate (G_s), the thermal power input during the charge mode (Q_{IN}), or the required storage volumes per operating hour (V_s). In this analysis, the reactor dimensions, power output and charge-discharge time ratios are maintained as in the previous paragraphs. The result of these simulations is shown in Figure 5. As can be seen, the circulation flow rate increases when ΔX decreases in order to maintain the same Q_{OUT} . The results indicate that low conversions (ΔX just over 0.1) are allowed if the solids circulation rate can be maintained in the reactor close to those of existing large-scale CFBs that use similar solids [48]. This means that solids with modest activities could be allowed in practical designs if combined with large storage volumes (and if much larger solid inventories are allowed in the risers). However, there is an important inefficiency to take into account when operating in these cases with low activity solids as indicated in the right hand side of Figure 5: the thermal power input required during the charge operation (Q_{IN}) increases for reduced hydration conversions, which means that the thermal process efficiency and the energy storage density will also decrease as the hydration conversion decreases. Despite this inefficiency, the possibility of using low activity materials for the energy storage system proposed in this work is a very important advantage of the fluidized bed reactor system. Circulating fluidized bed reactors can handle large flows of solids and the silos of Figure 2 are just large volume storage vessels (where no heat transfer or reaction is taking place). Therefore when the cost of the renewable energy used during dehydration is low and lower overall energy efficiencies are acceptable, modest material properties and hydration conversion

may still provide a good energy storage system. The ability to operate with low hydration conversions would also facilitate low operation and maintenance costs associated with solids, as it is well known that the excessive hydration of CaO materials generates mechanical stress in the particles that leads to fraction and/or attrition [50-52]. This reactor design will be experimentally tested by the authors as part of the ongoing StoRRe project upon which this work has been based.

Conclusions

A thermochemical energy storage process based on CaO/Ca(OH)₂ in a single circulating fluidized bed reactor coupled to large solid storage silos has been studied. The process performance has been evaluated assuming typical operating conditions for the key reactions involved. For the base case proposed, with a maximum thermal output of 100MW_t during hydration, the effective energy storage density is around 260 kWh/m³ and the net process efficiency achieved is 63% with CaO and Ca(OH)₂ storage volumes in the range of 390-460 m³ per operating hour. For a conservative reference case value of increment hydration conversion of $\Delta X=0.6$, a solids inventory in the circulating fluidized bed of around 373-443 kg/m² is required, with average particle residence times of around 120 s and solids circulation flow rates between 3.1-3.7 kg/m²s for a fluidized bed free cross-sectional area for fluidization of 34.4 m².

This conceptual reactor and process design indicates that the proposed process is technically viable. Furthermore, a sensitivity analysis of the process reveals that the process could be also operated with lower solid conversions (at lower energy efficiencies) exploiting the ability of circulating fluidized bed reactors to handle large flows of solids and considering that the silos in this system are just storage vessels where no heat transfer or reaction has to take place.

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Nomenclature

A_{free}	fluidized bed free cross-sectional area for fluidization, m^2
A_{HX}	heat exchange area associated to $Q_{\text{IN,OUT}}$, m^2 dp average particle size, mm
ESD_{eff}	effective energy storage density according to equation (13), kWh/m^3
f_a	fraction of active (non reacted) Ca material in the reactor
F_{Ca}	total flow of calcium circulating from silos to reactor, kmol/s
G_s	solids circulation flow rate, $\text{kg}/\text{m}^2\text{s}$
h_{CFB}	heat transfer coefficient in a circulating fluidized bed, $\text{W}/\text{m}^2\text{K}$
k	kinetic constant, $1/\text{s}$
P_{eq}	equilibrium pressure, kPa
$P_{\text{H}_2\text{O}}$	partial steam pressure, kPa
M	molecular weight, g/mol
m_i	total flow of stream i, kg/s
N_{Ca}	moles of calcium inside the bed, kmol
Q_i	sensible thermal power of stream i, MW_t
Q_{IN}	thermal power input from CSP during charge stage (dehydration reaction), MW_t

Q_{OUT}	thermal power output from the reactor during discharge (hydration reaction), MW_t
t	reaction time, s
t^*	time required to achieve the maximum conversion
t_{op}	operation time, h
X_{ave}	average conversion according to equations (5) and (10)
X	calcium conversion in relation to the total calcium present in the sorbent
f_{inert}	mol of inert material in the sorbent per mol of Ca
T	temperature, K
V_s	solids storage volumes per operating hour, m^3
W	solids inventory in the fluidized bed, kg/m^2
Greek letters	
ΔH	reaction enthalpy, kJ/mol
ΔT_{HX}	minimum average temperature difference between the reactor temperature and the temperature of the fluid carrying $Q_{IN,OUT}$, K
ΔX	increment in conversion according to equation (4)
η_p	hydration-dehydration thermal efficiency of the cycle, %
ρ_s	solids bulk density, kg/m^3
τ	average particle residence time, s
Subscripts	
Hy	hydration

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Figure 1. CaO/Ca(OH)₂ hydration/dehydration energy storage concept

Figure 2. Process scheme proposed in this work during (a) the hydration stage (discharge) and (b) the dehydration stage (charge)

Figure 3. $\text{CaO}/\text{Ca(OH)}_2$ equilibrium, around the proposed operation conditions

Figure 4. Hydration, dehydration average conversions and ΔX as a function of the solids inventory (W) in the fluidized bed

Figure 5. Solids circulation flow rate (G_s), solids storage volumes per operating hour (V_s) and required thermal power input (Q_{IN}) during dehydration as a function of the increment in conversion (ΔX) for a power output of $100 MW_t$ during the discharge stage for a reactor free cross-sectional area for fluidization of $34.4 m^2$

Table 1. Hydration stream specifications for the reference case

Stream N°	(1)	(2)	(3)	(4)	(5)	(6)	(7)
m (kg/s)	106.9	20.1	127.0	20.1	127.0	17.3	17.3
Composition (wt%)							
CaO	90.0		26.5		26.5		
Ca(OH)₂	10.0		73.5		73.5		
H₂O		100		100		100	100
T (K)	813	743	743	373	393	393	743
Q (MW)_l*	55.1	19.1	77.2	6.7	15.6	3.4	16.7

* Specific heat values taken from [53] and [36]. Reference temperature 293K.

Table 2. Dehydration stream specifications for the reference case

Stream N°	(8)	(9)	(10)	(11)	(12)	(13)	(14)
m (kg/s)	127.0	15.8	106.9	127.0	35.9	35.9	35.9
Composition (wt%)							
CaO	26.5		90.0	26.5			
Ca(OH)₂	73.5		10.0	73.5			
H₂O		100			100	100	100
T (K)	597	373	813	393	813	413	373
Q (MW_l)*	50.2	2.5	55.1	18.7	40.0	8.5	9.2

* Specific heat values taken from [53] and [36]. Reference temperature 293K.