Carbonation of Limestone Derived CaO for Thermochemical Energy Storage: From Kinetics to Process Integration in Concentrating Solar Plants

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ABSTRACT: Thermochemical energy storage (TCES) is considered as a promising technology to accomplish high energy storage efficiency in concentrating solar power (CSP) plants. Among the various possibilities, the calcium-looping (CaL) process, based on the reversible calcination–carbonation of CaCO3 stands as a main candidate due to the high energy density achievable and the extremely low price, nontoxicity, and wide availability of natural CaO precursors such as limestone. The CaL process is already widely studied for CO2 capture in fossil fuel power plants or to enhance H2 production from methane reforming. Either one of these applications requires particular reaction conditions to which the sorbent performance (reaction kinetics and multicycle conversion) is extremely sensitive. Therefore, specific models based on the conditions of any particular application are needed. To get a grip on the optimum conditions for the carbonation of limestone derived CaO in the CaL-CSP integration, in the present work is pursued a multidisciplinary approach that combines theoretical modeling on reaction kinetics, lab-scale experimental tests at relevant CaL conditions for TCES, process modeling, and simulations. A new analytic equation to estimate the carbonation reaction rate as a function of CO2 partial pressure and temperature is proposed and validated with experimental data. Using the kinetics analysis, a carbonator model is proposed to assess the average carbonation degree of the solids. After that, the carbonator model is incorporated into an overall process integration scheme to address the optimum operation conditions from thermodynamic and kinetics considerations. Results from process simulations show that the highest efficiencies for the CaL-CSP integration are achieved at carbonator absolute pressures of ~3.5–4 bar, which leads to an overall plant efficiency (net electric power to net solar thermal power) around 41% when carbonation is carried out at 950 °C under pure CO2.

KEYWORDS: Calcium looping, Carbonation kinetics, CSP, Energy storage, Limestone

INTRODUCTION

The main challenge to increase the share of renewable energy in the global energy mix is dispatchability. Regarding this issue, concentrating solar power (CSP) shows several advantages over solar photovoltaic (PV) and wind due to the relatively low cost and feasible integration of thermal energy storage technologies in large-scale facilities compared to battery storage.1–3 Thus, thermal energy storage (TES) in CSP plants has gained attention in the last years as demonstrated by the current data on commercial CSP facilities. A 42% of commercial CSP plants in operation incorporate TES systems while this percentage rises up to 83% for those planned and under development.4

Most commercial TES systems are based on sensible heat storage by means of molten salts, which allows plant operation for up to 15 h in the absence of direct solar irradiation. However, molten salt based systems have several drawbacks that penalize the performance of CSP plants. On one hand, the maximum working temperature is limited to ~600 °C to avoid salt degradation, which reduces the power cycle efficiency.5 On the other, there is a minimum working temperature of ~200 °C to avoid salt solidification,6 which demands a significant amount of energy to keep the molten salts from solidifying when the plant is out of operation. Thus, annual efficiencies for CSP plants with tower technology are currently found in the range 14–18%7 with a power cycle efficiency usually lower than 38%.8 Salt corrosiveness is also a serious issue that requires the use of expensive highly resistant materials for transport and storage.8,9

Thermochemical energy storage (TCES) is a promising alternative to TES to overcome these drawbacks in addition to providing other advantages such as the possibility to store energy in the long term and a relatively higher energy density.10,11 Among the diverse TCES systems proposed, the CaCO3/CaO

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system based on the cyclic calcination/carbonation of CaCO₃ (calcium-looping)

\[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \quad \Delta H^0_f = 178 \text{ kJ/mol} \]  

stands as a promising alternative for its high energy density and the extremely low price, non-toxicity, and wide availability of natural CaO precursors such as limestone or dolomite. Thus, the calcium-looping (CaL) process shows a theoretical energy density around 3–4 GJ/m³ depending on storage temperatures and pressure and the multicycle performance of the Ca-based materials employed. In the case of commercial CSP plants with tower technology based on a two tank molten salts system, the energy density is just around 0.4 GJ/m³.2,12

The CaL process is initiated by CaCO₃ decomposition in the calciner to produce CaO and CO₂, which are stored separately. When energy is needed, CaO and CO₂ are brought together in a separate reactor to release the stored energy by means of the exothermic carbonation reaction. Before being considered as a potential TCES system in the late 1970s,18–20 the use of CaO-based materials was already used for CO₂ capture to enhance H₂ production from methane reforming as early as 1933.21 More recently, the CaL process has been widely studied for post-combustion CO₂ capture (PCC) in fossil power plants where it has recently been successfully demonstrated at the 1–2 MWth pilot scale.22–26

The microscopic reversibility principle determines that for the overall reaction to reach equilibrium \( \theta = \theta_{eq} \), the rate of any process in each elementary step must be equal to the rate of its reverse process \( r_1 = r_2 \). The microscopic reversibility principle has been successfully applied to the kinetics description of a number of reversible processes such as the dehydrogenation/hydrogenation of MgH₂.45

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Let us consider an ideally flat surface of a CaO solid where carbonation proceeds in a gas environment at a given temperature and CO₂ partial pressure \( P \). Arguably, the overall carbonation mechanism consists of two stages as usually observed in heterogeneous gas/solid reactions.42 In the first stage, CO₂ molecules become physically adsorbed on the CaO surface after which a chemical reaction stage yields CaCO₃:

**Stage I CO₂ adsorption**

\[ \text{CaO} + L + \text{CO}_2 \xrightarrow{k_1} \text{CaO} + L(\text{CO}_2) \]

**Stage II Chemical reaction**

\[ \text{CaO} + L(\text{CO}_2) \xrightarrow{k_2} \text{CaCO}_3 + L \]

Here L represents the active site wherein physical adsorption of a CO₂ molecule takes place before the chemical reaction occurs, \( k_1 \) are the reaction rate constants, \( \theta \) is the fraction of active empty sites, and \( 1 - \theta \) is the fraction of active sites filled with adsorbed CO₂ molecules.

According to the pseudosteady state hypothesis, the rate of increase of the fraction of active sites filled with CO₂ by adsorption must balance the rate of decrease of filled active sites by chemical reaction in order not to have a net accumulation of reactive intermediates. Thus, the rates of adsorption \( r_s \) and chemical reaction \( r_c \):

\[
\begin{align*}
   r_s &= k_1 \theta P - k_2 d (1 - \theta) \\
   r_c &= k_2 (1 - \theta) - k_2 \theta
\end{align*}
\]

must balance out \( r_s = r_c \), which yields

\[
\theta = \frac{k_2 + k_d}{k_P + k_d + k_1 + k_2}
\]

The microscopic reversibility principle determines that for the overall reaction to reach equilibrium \( \theta = \theta_{eq} \), the rate of any process in each elementary step must be equal to the rate of its reverse process \( r_1 = r_2 \). The microscopic reversibility principle has been successfully applied to the kinetics description of a number of reversible processes such as the dehydrogenation/hydrogenation of MgH₂.45

This principle leads to

\[
\begin{align*}
   k_P \theta_{eq} P &= k_d (1 - \theta_{eq}) \\
   k_2 (1 - \theta_{eq}) &= k_1 \theta_{eq}
\end{align*}
\]

leads to

\[
\begin{align*}
   k_1 \theta_{eq} P &= k_d (1 - \theta_{eq}) \quad \Rightarrow \quad P_{eq(\text{atm})} = \frac{k_1}{k_2 k_d}
\end{align*}
\]
Assuming, as in most gas–solid heterogeneous reactions,\(^{32}\) that the rate-limiting step is the chemical reaction stage \((k_1, k_2 \ll k_P, k_d)\) it is
\[
\theta \approx \frac{k_d}{k_d + k_P}
\]
\[
r \approx r_2 = k_2(1 - \theta) - k_1 \theta
\]
Rearranging, we arrive at
\[
r \approx a_2e^{-E_2/RT} \left( \frac{P}{P_{eq}} - 1 \right) \left[ \frac{1}{P_{eq}} + e^{\Delta S_r^0/R - \Delta H_r^0/RT} \right]
\]
where \(E_2\) is the carbonation activation energy, \(a_2\) is a pre-exponential factor, and \(R\) the gas constant \((k_2 = a_2 e^{-E_2/RT})\). The Van’t Hoff equation\(^ {42}\) has been used for the equilibrium constant \(K_r = k_r/k_d = e^{-\Delta G_0^0/RT}\) being \(\Delta G_0^0 = \Delta H_0^0 - T \Delta S_0^0\) the standard free energy change of carbonation.

Using eq 5, we obtain
\[
P_{eq(atm)} = \frac{1}{K_r K_a} = e^{-(\Delta S_0^0 + \Delta S_0^0)/R} (\Delta H_0^0 + \Delta H_0^0)/RT
\]
where the Van’t Hoff equation has been used for the equilibrium constant \(K_a = k_a/k_d = e^{-\Delta G_0^0/RT}\), with \(\Delta G_0^0 = \Delta H_0^0 - T \Delta S_0^0\) the standard free energy change of adsorption. On the other hand, from thermochemical data,\(^ {46-48}\) the following is inferred:
\[
P_{eq} = Ae^{-\alpha T
\]
where \(A = 4.083 \times 10^7\) atm, \(\alpha = 20474\) K, which from eq 7 yields \(\Delta S_0^0 + \Delta S_0^0 = -146\) J/mol-K and \(\Delta H_0^0 + \Delta H_0^0 = -170\) kJ/mol. On the other hand, the sum of the standard enthalpy change of adsorption \(\Delta H_0^0\) and carbonation \(\Delta H_0^0\) is the standard enthalpy change of the overall reaction: \(\Delta H_0^0 + \Delta H_0^0 = -178\) kJ/mol as independently determined from the difference between the standard enthalpies of formation of the final product \((\text{CaCO}_3(s))\) and initial reactants \((\text{CO}_2(g)\) and \(\text{CaO}(s))\). Likewise, it is \(\Delta S_0^0 = \Delta S_0^0 + \Delta S_0^0 = -160\) J/mol-K. As should be expected, these independently determined values are similar to those derived from comparison of eqs 7 and 8.

The standard entropy change of adsorption \(\Delta S_0^0\) may be obtained from the difference between the standard entropy of adsorbed \(\text{CO}_2\) \((S_0^0)\) and the standard entropy of \(\text{CO}_2\) in the gas phase \((S_0^0 = 238\) J/mol-K for \(\text{CO}_2\)). According to Campbell and Sellers,\(^ {49}\) the standard entropy of adsorbed molecules on single crystal surfaces can be well fitted (up to \(S_0^0 = 60\)R) to the universal law \(S_0^0 = 0.75S_0^0 - 3.3R\). Thus, it is \(\Delta S_0^0 = S_0^0 - S_0^0 = -92\) J/mol-K. On the other hand, using \(\Delta H_0^0 = -20\) kJ/mol as a typical value\(^ {50}\) in eq 7, it is
\[
\frac{P}{P_{eq}} + e^{\Delta S_0^0/R - \Delta H_0^0/RT}
\]
\[
= e^{\Delta S_0^0/R - \Delta H_0^0/RT} (1 + P e^{\Delta S_0^0/R - \Delta H_0^0/RT})
\]
\[
\approx e^{\Delta S_0^0/R - \Delta H_0^0/RT}
\]
for the typical range of carbonation temperatures and \(\text{CO}_2\) partial pressures \((P e^{\Delta S_0^0/R} e^{\Delta H_0^0/RT} \ll 1)\), which leads to (eq 6):
\[
r \approx a_2e^{\Delta S_0^0/R} e^{-\Delta H_0^0/RT} \left( \frac{P}{P_{eq}} - 1 \right)
\]
where it has been used \(\Delta H_0^0 = E_2 - E_1\) with \(E_1\) the activation energy for chemical decomposition. Using, as estimated above, \(\Delta S_0^0 = -92\) J/mol-K and \(\Delta S_0^0 + \Delta S_0^0 = -160\) J/mol-K, the standard entropy change of carbonation is \(\Delta S_0^0 = -68\) J/mol-K whereas the activation energy for chemical decomposition is similar to the total reaction enthalpy change as measured experimentally: \(^ {51}\) \(E_1 \approx 180\) kJ/mol.

Note that for \(\frac{P}{P_{eq}} \approx 1\) and using eq 7:
\[
r \approx a_2e^{\Delta S_0^0/R} e^{-\Delta H_0^0/RT} P
\]
where \(\Delta H_0^0 = E_0 - E_0\), being \(E_0\) the activation energy for adsorption and the activation energy for adsorption \(E_0\) is assumed to be negligible.

### EXPERIMENTAL RESULTS ON THE CARBONATION KINETICS

In this work, thermogravimetric analysis (TGA) tests have been carried out to analyze experimentally the carbonation reaction kinetics depending on the reaction temperatures under pure \(\text{CO}_2\) and high temperature as relevant conditions in the CaL-CSP integration for TCES. Natural limestone of high purity (99.6 wt % \(\text{CaCO}_3\)) was used in the tests, which were carried out by employing two different thermogravimetric analyzers (TA Q600 and Setaram LABSYS evo). In all the tests, a small sample mass (10 mg) was employed to minimize mass/heat transfer undesired effects. The limestone samples were calcined at 750 °C under pure \(\text{N}_2\) for 5 min after which the temperature was increased to the target carbonation temperature and pure \(\text{CO}_2\) at atmospheric pressure was introduced for carbonation to proceed.

Results for the time evolution of \(\text{CaO}\) conversion during carbonation at different temperatures are shown in Figure 1. As can be seen, \(\text{CaO}\) conversion is hindered as the carbonation temperature approaches the equilibrium temperature (\(T \sim 895\) °C under pure \(\text{CO}_2\) at atmospheric pressure). As the reaction evolves, the carbonation rate is determined as a function of conversion degree \(X\), and reaction temperature \(T\) and pressure \(P\) (eq 12). Note that the conversion degree \(X\), which is usually employed to note the conversion of \(\text{CaO}\) during carbonation, is equivalent to the term \(\alpha\) usually employed in kinetics studies.

![Figure 1](image-url)
Atmospheric Pressure and Several Carbonation Temperatures

The assumed kinetic model, and in any case, it leads to the real value of energy, obtained from the analysis of isothermal data, is independent of the assumptions.52 Our experimental results on the time evolution of conversion (Figure 1) showed the typical sigmoidal shape of autocatalytic processes and are well fitted by a Prout–Tompkins model function \( f(X) = X(1 - X)^n \) modified by introducing a conversion limit \( X_0 \) which is the CaO conversion at the end of the reaction controlled phase (after which carbonation becomes controlled by solid-state diffusion of CO\(_2\) across the CaCO\(_3\) layer built up on the CaO surface). Thus

\[
\frac{dX}{dt} = f(X)r(T, P)
\]

where \( f(X) \) is a mechanistic-rate function that takes into account solids’ heterogeneities.52 Experimental results on the time evolution of conversion (Figure 1) showed the typical sigmoidal shape of autocatalytic processes and are well fitted by a Prout–Tompkins model function \( f(X) = X(1 - X)^n \) modified by introducing a conversion limit \( X_0 \) which is the CaO conversion at the end of the reaction controlled phase (after which carbonation becomes controlled by solid-state diffusion of CO\(_2\) across the CaCO\(_3\) layer built up on the CaO surface). Thus

\[
\frac{dX}{dt} = X \left(1 - \frac{X}{X_K}\right) r(T, P) \leftrightarrow X(t) = \frac{X_0}{1 + e^{-kr(t-t_0)}}
\]  (13)

Equation 13 fits quite satisfactorily to our experimental data on CaO conversion (Figure 1), which allows us to derive experimental values for the reaction rate at different temperatures \( r(T, P) \). Best-fitting parameters are shown in Table 1. Reaction rates obtained in this way are compared to the theoretically predicted values (eq 6) in Figure 2. It should be noted that while the modified Prout–Tompkins model used here provided a good fitting to experimental data, it has been shown in the literature that the kinetics parameters, i.e., activation energy, obtained from the analysis of isothermal data, is independent of the assumed kinetic model, and in any case, it leads to the real value of the activation energy.54

As may be seen in Figure 2a, a rather good agreement can be found between experiments and theory (eq 6) by only adjusting the prefactor \( a_1 \) as a free parameter in the theoretical curve. Interestingly, data obtained using different commercial thermal analysis instruments with quite different experimental setups could be nicely fitted by eq 6. In view of these results, and even though technical limitations prevented us from carrying out carbonation experiments at pressures greater than atmospheric, we will use eq 6 and its approximate limit (eq 10) to estimate the reaction rate under CO\(_2\) at pressurized conditions (predicted curves are shown in Figure 2b).

Table 2 summarizes the values used for the reaction enthalpies, entropies, and activation energies, as discussed in the previous section, that will be employed for the theoretical reaction rate in the modeling analysis ahead.

As seen in Figure 2b, there is a temperature at which the carbonation rate reaches a maximum and above which it rapidly decreases as the equilibrium temperature is approached. This same trend was already predicted by Kyaw et al.41 The temperature at which the reaction rate is maximum is a relevant input for the CaL cycle assessment. The CaL process applied to postcombustion CO\(_2\) capture involves carbonation under low CO\(_2\) partial pressure (around 0.15 bar for coal fired power plants) whereas calcination is carried out under high CO\(_2\) concentration at temperatures around 950 °C. These harsh calcination conditions lead to a severe decay of CaO conversion in short residence times with the number of cycles due to progressive sintering of the regenerated CaO and the consequent drop of available surface area for carbonation in the fast reaction controlled stage.55 Thus, conversion of limestone derived CaO in short residence times (of a few minutes) decays significantly after just a few cycles at CaL conditions for CO\(_2\).

### Table 1. Best Fitting Parameters of Equation 13 to Experimental Data on CaO Conversion for Carbonation under CO\(_2\) at Atmospheric Pressure and Several Carbonation Temperatures

<table>
<thead>
<tr>
<th>( X(t) = \frac{X_0}{1 + e^{-kr(t-t_0)}} )</th>
<th>Carbonation Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>( X_K )</td>
<td>( T = 865 ^\circ C )</td>
</tr>
<tr>
<td>( X_K )</td>
<td>0.691</td>
</tr>
<tr>
<td>( r ) (1/min)</td>
<td>0.798</td>
</tr>
<tr>
<td>( t_0 ) (min)</td>
<td>34.330</td>
</tr>
</tbody>
</table>

### CARBONATOR MODEL

**TGA Data Analysis.** The behavior of CaO conversion \( X \) along multiple calcination/carbonation cycles is a critical input for the CaL cycle assessment. The CaL process applied to postcombustion CO\(_2\) capture involves carbonation under low CO\(_2\) partial pressure (around 0.15 bar for coal fired power plants) whereas calcination is carried out under high CO\(_2\) concentration at temperatures around 950 °C. These harsh calcination conditions lead to a severe decay of CaO conversion in short residence times with the number of cycles due to progressive sintering of the regenerated CaO and the consequent drop of available surface area for carbonation in the fast reaction controlled stage.55 Thus, conversion of limestone derived CaO in short residence times (of a few minutes) decays significantly after just a few cycles at CaL conditions for CO\(_2\).
capture and converges toward a residual value of just around $0.07 - 0.08$. Moreover, part of the CaO is irreversibly sulfated or deactivated by ashes. A number of methods to enhance the multicycle CaO conversion have been reported in the last years, such as the formulation of synthetic sorbents, thermal pretreatment, and using steam or helium in either the calcination or carbonation reactors.

However, CaL conditions for TCES in CSP do not need to be identical to those employed for CO2 capture. In previously proposed CaL-CSP integration schemes carbonation is carried out under a pure CO2 atmosphere whereas calcination can be carried out under low CO2 partial pressure, which leads to a different multicycle behavior. Moreover, SO2 and ashes are not present in the reactors. Thus, the residual conversion of limestone derived CaO can be as large as 0.5 for carbonation under 100% CO2 atmosphere and calcination at 725 °C in absence of CO2 for residence times in both stages of 5 min and using limestone particles smaller than 45 μm. Carbonation under these conditions is limited by pore plugging, which leads to a significant loss of activity for typical particle sizes to be employed in circulating fluidized beds (>100 μm). Thus, pore plugging causes a drop of the residual conversion of limestone derived CaO to just about $X_r = 0.2$ for particles larger than about 45 μm. Nevertheless, it has been reported that pore plugging does not limit carbonation for large enough dolomite particles (>∼100 μm) reaching a residual effective conversion of about 0.4.

Figure 5 shows thermogravimetric experimental data (see refs 35 and 37 for further details) on the multicycle conversion of limestone derived CaO for several carbonation/calcination conditions for postcombustion CO2 capture (PCC) and thermochemical energy storage of CSP. Testing conditions are shown in Table 3. The lines are the best fit curves from eq 14 to data. Best fitting parameters are shown in the legend.

$$\frac{X_n}{X_i} = \frac{1}{k(N - 1) + \left(1 - \frac{X_i}{X_r}\right)^t}$$

where $X_i$ is CaO conversion in the first cycle, $k$ is the deactivation rate constant, and $X_r$ is the residual CaO conversion.
which would be reached asymptotically after a very large number of cycles (as would occur in commercial CaL plants).

As shown in Figure 5, a higher CaO deactivation occurs for postcombustion CO2 capture (PCC) conditions compared to CaL-CSP conditions. Thus, after 20 cycles, CaO conversion drops to 0.1 whereas under CaL-CSP3 conditions (calcination at 950 °C) conversion after 20 cycles remains at 0.18. A similar value of the residual value, which is also dependent on process conditions.

Multicycle CaO Conversion Data Plotted in Figure 5

According to previous TGA studies, after calcination at 725 °C, most of the carbonation in short residence times on the regeneration layer and characterized by a much lower reaction rate. According to previous TGA studies, after calcination at 725 °C, most of the carbonation in short residence times on the regenerated CaO skeleton occurs in the fast stage due to the high CO2 concentration and carbonation temperature, which promote the reaction kinetics. Thus, carbonation in the diffusion-controlled phase is neglected in this model, and therefore, $X_i = X_C$.

Accordingly, the present carbonator model assumes that carbonation occurs at a given rate until it reaches the maximum carbonation allowed in the fast carbonation stage, after which the particles remain inactive. Thus, only a fraction of particles, $f_x$, are active in the carbonator with the capacity to react in the fast reaction controlled stage:

$$f_x = (1 - e^{-t_0/\tau})$$

where $t_0$ is the fast carbonation stage time and $\tau$ is the average residence time of CaO solids in the carbonator:

$$\tau = \frac{N_C}{F_R}$$

where $F_R$ is the flow rate of makeup fresh limestone introduced to the system in order to mitigate CaO deactivation. If this fresh material is not introduced into the system, the maximum conversion after many cycles would be just the residual CaO conversion ($X_{\text{max,ave}} \approx X_r$).

As is well-known from previous works, carbonation takes place through two differentiated stages, a first fast stage in which the reaction occurs on the free surface of CaO particles (see reaction mechanism in the Carbonation Kinetics section) and a second stage, that takes place once a carbonate layer has been formed on the particles’ surface, controlled by counter-current diffusion of CO$_2$ and O$_2$ across the CaCO$_3$ product layer and characterized by a much lower reaction rate. By means of a mass balance, the maximum average conversion of the CaO particles in the carbonator can be expressed as

$$X_{\text{max,ave}} = \sum_{N=1}^{N=\infty} \phi_N X_N$$

Here $X_N$ is the average CaO conversion at cycle $N$ and $\phi_N$ is the fraction of solids that are cycled $N$ times.

$$\phi_N = \frac{N_1 N_{R}}{(N_1 + N_{R})^N}$$

Table 3. TGA Test Conditions Corresponding to Measured Multicycle CaO Conversion Data Plotted in Figure 5

<table>
<thead>
<tr>
<th>reference</th>
<th>particle size</th>
<th>gas calciner–carbonator</th>
<th>temperature calciner–carbonator</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSP 1</td>
<td>&gt;45 μm</td>
<td>He–CO$_2$</td>
<td>725–850 °C</td>
</tr>
<tr>
<td>CSP 2</td>
<td>&lt;45 μm</td>
<td>He–CO$_2$</td>
<td>725–850 °C</td>
</tr>
<tr>
<td>CSP 3</td>
<td>&gt;45 μm</td>
<td>CO$_2$–CO$_2$</td>
<td>950–850 °C</td>
</tr>
<tr>
<td>PCC</td>
<td>&gt;45 μm</td>
<td>CO$_2$–N$_2$/CO$_2$ (15% v/v)</td>
<td>950–650 °C</td>
</tr>
</tbody>
</table>

Figure 6. Carbonator model flow diagram.
Considering a perfect mixing model, the average conversion of the particles leaving the carbonator \(X\) can be calculated using the followed equations:

\[
X = \frac{\int_{0}^{t_{t}} r_{av} \left( \frac{t}{T_{r}} \right) e^{-t_{r}/\tau} dt}{1 - e^{-t_{f}/\tau}} = \frac{f_{f}}{\ln \left( \frac{1}{1-f_{f}} \right)}
\]

(19)

\[
f_{\text{carb}} = \frac{X}{X_{\text{max,ave}}}
\]

(20)

\[
E_{\text{CO2}} = \frac{F_{\text{r}}}{F_{\text{CO2}}} = \frac{N_{\text{carb}} f_{\text{ave}}}{F_{\text{CO2}}}
\]

(21)

where \(f_{\text{carb}}\) is the average carbonation level in the carbonator and \(r_{av}\) is the average reaction rate in the fast carbonation stage, which is calculated from the kinetics model theoretical prediction (eq 10).

The carbonator model allows us to carry out a sensitivity analysis to assess the effect of pressure, temperature and solids inventory in the carbonator on the average carbonation level \(f_{\text{carb}}\). Results are shown in Figure 7.

As can be seen in Figure 7, the average carbonation level \(f_{\text{carb}}\) is enhanced by increasing the carbonator pressure due to faster reaction kinetics (Figure 2b). After a few of seconds in the carbonator, most of the CaO reaches the maximum conversion (according to eq 13) due to the very fast kinetics achieved in these CaL conditions. This is basically because of the high amount of CO\(_2\) entering the carbonator (which exceeds the stoichiometric amount in order to use the effluent excess as heat carrier). According to the kinetics model, by increasing the carbonator temperature, the average carbonation level is slightly enhanced up to the temperature \(T_{(\text{max})}\)—Figure 3—is reached from which kinetics is penalized with the consequent curtailment of the average carbonation level. As shown in Figure 7, this effect is mitigated when the carbonator pressure is increased, which is beneficial in practice since working at higher carbonator temperatures will promote the power cycle efficiency. Next section analyses the CSP-CaL integration efficiency as a function of carbonator temperature and pressure in order to select the best conditions based on both experimental data and the theoretical reaction kinetics study.

**CSP-CaL Plant.** This section is devoted to a detailed analysis on the CSP-CaL integrated plant for TCES. As main novelties regarding previous works\(^{12,70}\) new CaL conditions, TGA experimental data and the carbonator model above-described will be introduced in the analysis. Calculations have been performed using the commercial software Aspen Plus\textsuperscript{TM}.

The CSP-CaL plant (see Figure 8) works as follows: Direct solar irradiation is used to preheat the streams entering the calciner up to the reaction temperature to carry out the calcination reaction. Calcination occurs under helium atmosphere which allows reducing the calcination temperature to 725 \(^\circ\text{C}\)\(^{33}\) in short residence times to simulate conditions as tested in the Carbonation Kinetics section using limestone as a CaO precursor. Note that the proposed scheme (Figure 8) is a closed cycle in which any stream must be fed continuously to the plant. This is relevant for the recycling of helium in the system, which is a rare and expensive gas. Several solar calciner reactors have been already proposed in the literature.\(^{71-74}\) By calcination under an He atmosphere, a reduction of the calcination temperature would lead to an increase in the solar receiver efficiency as a consequence of the lower radiative losses. Full calcination is assumed in our model.\(^{4,75}\) After calcination, the CaO stream (\(\text{g1 in Figure 8}\) is separated from the He-CO\(_2\) stream by means of a cyclone. The He-CO\(_2\) stream is passed through a separation system based on membranes. A detailed study on the membrane system is out of the scope of this work and an ideal separation is assumed. However, it may be noted that commercial H\(_2\)/CO\(_2\) separation membranes are available, and since He molecule is similar to H\(_2\), the He/CO\(_2\) separation system could take advantage of H\(_2\)/CO\(_2\) currently commercial technologies. The He stream (\(\text{g1-2}\) is recirculated into the calciner while the pure CO\(_2\) stream (\(\text{g1-2}\) is passed through a heat recovery steam generator (HRSG) to use its high temperature as a previous step to be stored or used in the power cycle. Since heat input to the steam power cycle is moderate, a simple superheated steam cycle without reheat stages and moderate live steam conditions are assumed. Thus, the steam cycle is modeled by considering a condensing pressure of 0.075 bar, an evaporation pressure of 45 bar and a superheated steam temperature of 400 \(^\circ\text{C}\).

On the carbonator side of the plant, a CaO stream from the storage vessel (\(\text{g2}\) reacts with the CO\(_2\) stream coming either from storage (\(\text{g7b}\) or the calciner side (\(\text{g3}\) according to the carbonation reaction at atmospheric pressure (carbonation at higher pressure will be also considered ahead). The CO\(_2\) entering the carbonator (\(\text{g9-2}\) exceeds the stoichiometric amount

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**Figure 7.** Carbonator model results. Average carbonation level \(f_{\text{carb}}\) for several carbonation conditions \((P, T)\). \(T_{\text{(max)}}\) is the temperature at which the reaction rate reaches a maximum (Figure 3).
needed for carbonation. The CO₂ in excess that exits the carbonator acts as heat carrier to produce electrical power by means of a CO₂ closed Brayton cycle wherein a heat exchanger HXG is used as a recuperator.

Different operations in “sun” and “night” modes are simulated. A solar multiple (SM) equal to 3 is assumed for the system design and, for simplicity, the day is considered as composed by 8 sun h, which constantly provides 100 MWth to the calciner, and of 16 night h. Thus, in the “sun” operating mode, the CO₂ mass flow entering the carbonator side (g₃ or g₇b) is 1/3 the amount produced in the calciner (g₁). Accordingly, the plant efficiency is determined as a weighted average of the performances in sun and night modes (eq 22). Although it is out of the scope of the present work, an additional analysis to consider real solar irradiance as well as off-design conditions would be required for further assessing equipment sizing and costs. Moreover, other plant operation modes could be considered as a function of solar irradiation, electricity prices, filling level of storage tanks, etc. On the other hand, more detailed study on the different operation modes would be useful to estimate the penalty associated with daily start-up/shut-down of the plant. In this regard, lower start-up/shut-down penalties than in commercial CSP plants are expected since the system is designed to achieve a full working hours capacity. Note that efficiency in this model considers the heat input to the calciner and disregards the thermal efficiency of the solar receiver whose design and modeling is beyond the scope of this work. Concerning solids transport, a power consumption of 20 MJ/ton is assumed. Thus, the global plant efficiency will be given by

\[
\eta = \frac{\int_{24h} W_{\text{net}} \, dt}{\int_{24h} Q_{\text{input}} \, dt} = \frac{W_{\text{net, sun}} \Delta t_{\text{sun}} + W_{\text{net, night}}(24 - \Delta t_{\text{sun}})}{Q_{\text{input}} \Delta t_{\text{sun}}} \quad (22)
\]

where \(W_{\text{net}}\) is the net electrical power produced by the system and \(Q_{\text{input}}\) is the solar power input in the calciner. The electric power produced is computed for the sun mode (\(W_{\text{net, sun}}\)) and the night mode (\(W_{\text{net, night}}\)).

Several assumptions have been made to model the CSP-CaL plant, which are summarized in Table 4.

**CSP-CaL Integration Model Results.** The proposed CSP-CaL integration model has been simulated considering in the base case that the carbonator works at 850 °C/1 bar and with a solids inventory of 105 kmol, which allows to achieve a 95% of average carbonation level (\(f_{\text{carb}}\)) in the carbonator (Figure 7). An important benefit of working at atmospheric pressure in the carbonator is that high temperature lock hoppers for solids pressurization are not necessary. On the other hand, hermetic machines and heat exchangers must be employed. Tables 5 and 6 show the main streams and energy balance results. The energy balance for the CSP-CaL integration shows an overall daily efficiency of 38% (Table 6). Since the main turbine (M-TURB) has been selected to work at constant power production, a higher net power output is achieved during the night mode compared to the sun mode. This is because the high-pressure CO₂ storage compressor (HPS-COMP) and auxiliaries’ consumptions are not fully compensated by the steam turbine production in the sun mode. As shown in Table 6, main heat rejections to the ambient occur in the steam condenser (COND) and in the CO₂ cycle precooler (COOLER-3) while the main power consumption is caused by the CO₂ compressor in the carbonator side (M-COMP).

The CSP-CaL integration performance has been analyzed as a function of the pressure ratio (PR) defined as the ratio of the carbonator pressure (1 bar) to the turbine outlet pressure. On one hand, by increasing the pressure ratio the power production in the CO₂ power cycle is enhanced, which increases the global cycle efficiency. On the other hand, by increasing PR, the temperature of the CO₂ exiting the turbine is lowered and a
higher amount of energy is recovered in the recuperator (HXG), which translates into a higher amount of carbonation energy needed to bring the reactants to carbonation conditions. The effect of increasing the PR on the overall plant efficiency is illustrated in Figure 9.

As can be seen in Figure 9, a higher overall efficiency is calculated as the carbonation temperature is increased at a given value of PR. Thus, the benefits of increasing the carbonation temperature above \( T_{\text{calc}} \sim 728 ^\circ \text{C} \) (at which the reaction rate is maximum for atmospheric carbonation as shown in Figure 2b) compensates the penalty caused by the reduction of the reaction speed which yields a lower carbonation level and therefore a lower CaO conversion (X).

The temperature limit imposed by the thermodynamic equilibrium (eq 8) for carbonation under pure CO\(_2\) at atmospheric pressure is 895 °C (Figure 3). Thus, the carbonator pressure must be increased over atmospheric pressure to further increase the carbonator temperature above 895 °C. This would enhance the power plant efficiency (higher temperature at turbine inlet) as well as the carbonation kinetics (as shown in Figure 2a and Figure 7). The CSP-CaL integration (Figure 8) is also valid when the carbonator is operated under over atmospheric pressure. For that purpose, the only modification needed is that the

Table 4. Main Assumptions in the CSP-CaL Model

<table>
<thead>
<tr>
<th>group/component</th>
<th>parameter</th>
<th>turbomachinery</th>
<th>intercooling/ reheating stages and temperatures</th>
<th>mechanical-electric efficiencies</th>
<th>isentropic efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>main CO(_2) turbine (M-TURB)</td>
<td>0.9</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>main CO(_2) compressor (M-COMP)</td>
<td>0.87</td>
<td>0.98</td>
<td>2/40 °C</td>
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<td></td>
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<tr>
<td>high pressure storage turbine (HPS-TURB)</td>
<td>0.8</td>
<td>0.96</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>high pressure storage compressor (HPS-COMP)</td>
<td>0.8</td>
<td>0.96</td>
<td>5/40 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>steam turbine (ST)</td>
<td>0.75</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>component</td>
<td>parameter</td>
<td>heat exchangers</td>
<td>minimum temperature difference</td>
<td>pressure drops</td>
<td>0.8% of heat released(^{[36]})</td>
</tr>
<tr>
<td>coolers</td>
<td></td>
<td>HXG (both sides)</td>
<td>15 °C</td>
<td>1%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HRSG (hot side)</td>
<td>15 °C</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HRSG (cold side)</td>
<td>15 °C</td>
<td>3%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>solid-gas HX (both sides)</td>
<td>15 °C</td>
<td>11%</td>
<td></td>
</tr>
<tr>
<td>component</td>
<td>parameter</td>
<td>various</td>
<td>efficiency</td>
<td>heat input</td>
<td>heat losses</td>
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<tr>
<td>calciner</td>
<td></td>
<td></td>
<td>1</td>
<td>100 MWt</td>
<td>1% of heat transferred</td>
</tr>
<tr>
<td>carbonator</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>storage vessels</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Table 5. Main Stream Data for the CSP-CaL Integration (Base Case)

<table>
<thead>
<tr>
<th>ID</th>
<th>( P ) (bar)</th>
<th>( T ) (°C)</th>
<th>( m ) (kg/s)</th>
<th>ID</th>
<th>( P ) (bar)</th>
<th>( T ) (°C)</th>
<th>( m ) (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>1.00</td>
<td>850</td>
<td>29.13</td>
<td>g4</td>
<td>1.14</td>
<td>44.43</td>
<td>14.69</td>
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<tr>
<td>s1-1</td>
<td>0.97</td>
<td>703.17</td>
<td>29.13</td>
<td>g5</td>
<td>7.57</td>
<td>123.63</td>
<td>14.69</td>
</tr>
<tr>
<td>s1-2</td>
<td>0.94</td>
<td>588.83</td>
<td>29.13</td>
<td>g5-2</td>
<td>7.5</td>
<td>25</td>
<td>14.69</td>
</tr>
<tr>
<td>s2</td>
<td>0.94</td>
<td>588.83</td>
<td>87.37</td>
<td>g6</td>
<td>74.25</td>
<td>130</td>
<td>7.34</td>
</tr>
<tr>
<td>c1</td>
<td>1.00</td>
<td>725</td>
<td>65.39</td>
<td>g7</td>
<td>1.14</td>
<td>21.92</td>
<td>7.34</td>
</tr>
<tr>
<td>c2</td>
<td>1.00</td>
<td>725</td>
<td>21.79</td>
<td>g8</td>
<td>1.14</td>
<td>72.10</td>
<td>134.62</td>
</tr>
<tr>
<td>r1</td>
<td>0.074</td>
<td>40.13</td>
<td>5.27</td>
<td>g8-1</td>
<td>1.14</td>
<td>72.10</td>
<td>134.62</td>
</tr>
<tr>
<td>r2</td>
<td>45.00</td>
<td>40.53</td>
<td>5.27</td>
<td>g8-2</td>
<td>1.10</td>
<td>535.06</td>
<td>134.62</td>
</tr>
<tr>
<td>v3</td>
<td>40.00</td>
<td>40.00</td>
<td>5.27</td>
<td>g9</td>
<td>1</td>
<td>679.56</td>
<td>134.62</td>
</tr>
<tr>
<td>v4</td>
<td>0.075</td>
<td>40.31</td>
<td>5.27</td>
<td>g9-1</td>
<td>1</td>
<td>675.41</td>
<td>134.62</td>
</tr>
<tr>
<td>r1</td>
<td>1.00</td>
<td>725</td>
<td>440.58</td>
<td>g9-2</td>
<td>1.05</td>
<td>703.17</td>
<td>134.62</td>
</tr>
<tr>
<td>g1</td>
<td>1.00</td>
<td>725</td>
<td>22.03</td>
<td>g10</td>
<td>1.00</td>
<td>850</td>
<td>133.82</td>
</tr>
<tr>
<td>g1-1</td>
<td>1.00</td>
<td>725</td>
<td>418.55</td>
<td>g11</td>
<td>0.33</td>
<td>694.56</td>
<td>133.82</td>
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<tr>
<td>g1-2</td>
<td>1.00</td>
<td>725</td>
<td>22.03</td>
<td>g12</td>
<td>0.32</td>
<td>87.30</td>
<td>133.82</td>
</tr>
<tr>
<td>g2</td>
<td>0.97</td>
<td>58.99</td>
<td>22.03</td>
<td>g13</td>
<td>0.31</td>
<td>40</td>
<td>133.82</td>
</tr>
<tr>
<td>g3</td>
<td>1.14</td>
<td>44.43</td>
<td>7.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CO₂ stream coming from the calciner (g3 stream in Figure 8) in the day mode is passed through the main CO₂ compressor (M-COMP) up to reach the carbonator pressure (including the exchangers would not be necessary. Figure 10 shows the overall carbonation conditions. Therefore, hermetic machines and heat exchangers would not be necessary. Figure 10 shows the overall plant efficiency as a function of pressure ratio (PR).

CSP-CaL efficiency for the pressurized carbonator case. Except for the carbonator conditions (P, T), the rest of the parameters are the same as in the base case.

By comparing Figures 9 and 10 it is appreciated that the overall plant efficiency is significantly enhanced by increasing the carbonator temperature, which is facilitated when the carbonator works under pressurized conditions. In this way, overall plant efficiencies above 41% are achievable. Note that in the case of T_{carb} = 1000 °C the carbonator pressure must be higher than 4.21 bar due to thermodynamic equilibrium constraints.

Carbonator Presizing. At this point an important issue regarding the carbonator size must be addressed. The carbonator in the application of the CaL technology for post-combustion CO₂ capture (PCC) is characterized by a very large size (volume ~ 18 m³/MWe; solids inventory ~ 1300 kg/MWe⁷⁷), which significantly increases capital and operating costs (CAPEX and OPEX).⁷⁸,⁷⁹ Previous works have shown that the sizes of the carbonator and calciner play an important role on increasing the cost of the PCC technology. In contrast, the carbonator size in the application of the CaL technology for TCES in CSP would be remarkably reduced as evidenced by stream data (Table 5). Table 7 shows the carbonator reactor presizing for the case proposed in our study. Since gas and solids mass flow rates in the CSP-CaL case are relatively small, the cross-section surface area of the carbonator reactor (A ~ 21 m² for the pressurized carbonator case) is small as compared to the typical size of the carbonator in the PCC-CaL application (A ~ 175 m²) assuming the same superficial velocity for the fluidized bed to be operated in a circulation regime. Likewise, the carbonator height, which can be estimated from the ratio a H/D ~ 3⁷⁷ is much smaller in the CSP-CaL technology as compared to the PCC-CaL application.

The minimum amount of solids inventory needed can be estimated to achieve a 95% of average carbonation level in the carbonator while carbonation kinetics can be inferred from the Carbonation Kinetics section of this manuscript. As shown in Table 7, a solids inventory of ~128–234 kg/MWe is needed, which is significantly lower than in the case of the PCC-CaL application (~1300 kg/MWe). A direct consequence of a reduction in solids inventory in the carbonator, is a significant reduction of fan power consumption to ensure fluidization conditions. As would be expected, the base case requires a larger carbonator size as compared with the pressurized carbonator configuration. The atmospheric pressure carbonator in the base case involves a larger amount of CO₂ volume entering the reactor as well as a much smaller in the CSP-CaL technology as compared to the PCC-CaL application.

Table 7. Carbonator Reactor Properties in the CSP-CaL Integration (Base Case)

<table>
<thead>
<tr>
<th>parameter</th>
<th>base case (P_{carb} = 1 bar)</th>
<th>pressurized carbonation (P_{carb} = 3 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor type</td>
<td>CFB</td>
<td>CFB</td>
</tr>
<tr>
<td>μ₀ (m/s)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>particle size (μm)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>A (m²)</td>
<td>62.12</td>
<td>21.36</td>
</tr>
<tr>
<td>D (m)</td>
<td>8.89</td>
<td>5.21</td>
</tr>
<tr>
<td>W//A (kg/m²)</td>
<td>128.78</td>
<td>234.08</td>
</tr>
<tr>
<td>H (m)</td>
<td>36.67</td>
<td>15.64</td>
</tr>
</tbody>
</table>

CONCLUSIONS

This paper analyzes the carbonation of limestone derived CaO in the CaL process as for thermochemical energy storage in CSP plants. Since the carbonation behavior (kinetics and
multicyclic CaO conversion) is highly dependent on the CaL conditions, which vary according to the type of application, a theoretical reaction kinetics study has been carried out to analyze the effect of the particular CaL carbonation conditions to be used in the CSP-CaL integration, which involve carbonation under high CO_2 partial pressure at high temperature. The reaction kinetics study is supported by TGA tests performed under these specific conditions. As a result, a new expression to estimate the carbonation conversion rate as a function of the carbonator pressure and temperature has been derived. A carbonator model based on the kinetics study is used to estimate the average carbonation level after a long number of cycles as would occur at industrial scale. Accordingly, the carbonation rate is enhanced with the carbonator temperature up to reach a maximum, from which a further increase of temperature is detrimental as the thermodynamic equilibrium temperature is approached. On the other hand, an increase in the carbonator pressure promotes significantly the conversion rate and therefore the average carbonation level in short residence times. Thus, an increase of the carbonator pressure yields an improved performance not only from a reaction kinetics perspective but also because a higher carbonator pressure allows for a higher carbonator temperature, which enhances the power cycle efficiency when stored energy is released. The CSP-CaL integration model explored in this work, which is based on power production by means of a closed CO_2 Brayton cycle, shows that the overall plant efficiency is significantly promoted as the carbonator temperature is increased. Thus, optimum carbonator pressures are in the range of 3.5–4 bar, which allow carbonator operation temperatures of 950 °C to yield global efficiencies of about 41%. As a final comment, it is remarkable that a fundamental understanding of physicochemical processes at the molecular level helped us tackle the industrial process with an extra degree of confidence.

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Notes
The authors declare no competing financial interest.

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■ NOTATION

$A$ = carbonator cross-section, m$^2$
$D$ = carbonator diameter, m
$E_i$ = activation energy for chemical decomposition, kJ/mol
$f_i$ = fraction of CaO that reacts in the carbonator in the fast stage

$F_{\text{ave}}$ = average carbonation level
$F_i$ = molar flow rate of component $i$, kmol/s
$F_{\text{CaCO}_3}$ = CaCO$_3$ molar flow rate
$F_{\text{CaCO}_3,\text{crb}}$ = CaCO$_3$ molar flow rate (carbonator side)
$F_{\text{CaO,crb}}$ = molar flow rate of unreacted CaO (carbonator side)
$F_{\text{CO}_2}$ = CO$_2$ molar flow rate at calciner outlet
$F_{\text{CO}_2,\text{crb}}$ = CO$_2$ molar flow rate at carbonator outlet
$F_0$ = mole flow rate of fresh makeup limestone, kmol/h
$F_X$ = mole flow rate of CO$_2$ in flue gas entering the carbonator, kmol/h
$F_{\text{rec}}$ = recirculating mole flow rate (carbonator side)
$F_{\text{rec,c}}$ = recirculating mole flow rate (calciner side)
$h_i$ = enthalpy, kJ/kmol
$H$ = carbonator height, m
$in$ = mass flow rate, kg/s
$N$ = cycle number
$N_{\text{Ca}}$ = mol of Ca in the carbonator, mol
$P$ = pressure, bar
$P_{\text{abs}}$ = absolute carbonator pressure, bar
$P_{\text{eq}}$ = CO$_2$ partial pressure at equilibrium, bar
$PR$ = pressure ratio
$Q_{\text{input}}$ = solar power input
$r$ = reaction rate, s$^{-1}$
$r_{\text{ave}}$ = average reaction rate, s$^{-1}$
$SM$ = solar multiple
$t$ = time, s
$T$ = temperature, °C
$T_{\text{calciner}}$ = calciner temperature, °C
$T_{\text{carb}}$ = carbonator temperature, °C
$T_{\text{eq}}$ = equilibrium temperature, °C
$t_{\text{st}}$ = fast carbonation stage time, s
$\mu_0$ = mean superficial velocity in the CFB riser, m/s
$V_{\text{CO}_2}$ = CO$_2$ volume flow rate, m$^3$/s
$W$ = solid inventory in the carbonator per MW of a typical power plant, kg
$W_{\text{net}}$ = average electrical power, MWe
$W_{\text{net,night}}$ = net electrical power for the night mode, MWe
$W_{\text{SET,summer}}$ = net electrical power for the sun mode, MWe
$W_{\text{COMP}}$ = power produced by the main CO$_2$ turbine, MWe
$W_{\text{M-TURB}}$ = power consumed by the main CO$_2$ compressor, MWe
$W_{\text{HPS-TURB}}$ = power produced by the high-pressure CO$_2$ turbine, MWe
$W_{\text{HPS-COMP}}$ = power consumption of high pressure intercooled CO$_2$ compressor for the storage system, MWe
$W_{\text{F}}$ = power produced in the steam turbine cycle, MWe
$W_{\text{a}}$ = power consumed in the steam turbine cycle, MWe
$W_{\text{PSOLCAR}}$ = power consumptions for solids transport in the calciner side, MWe
$W_{\text{POLSOLCAR}}$ = power consumptions for solids transport in the carbonator side, MWe
$W_{\text{AUXPOWCA}}$ = auxiliary power consumptions in the calciner side, MWe
$W_{\text{AUXPOWCR}}$ = auxiliary power consumptions in the carbonator side, MWe
$X$ = average CaO conversion
$X_{\text{ave}}$ = average conversion of the sorbent
$X_{\text{ave,crb}}$ = maximum average conversion of the sorbent
$X_{\text{c}}$ = CaO conversion in the fast carbonation stage
$X_N$ = CaO conversion at the N cycle
$X_r$ = residual CaO conversion
$\Delta P$ = pressure drop at carbonator, bar

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\[ \Delta S^f = \text{carbonation entropy change, J/(mol·K)} \]
\[ \Delta H_{\text{run}} = \text{reaction enthalpy at the reactor temperature, kJ/mol} \]
\[ \Delta P = \text{pressure drop at carbonator, bar} \]
\[ \Delta S^f = \text{carbonation entropy change, J/(mol·K)} \]
\[ \Delta H_{\text{run}} = \text{average daytime period, h} \]
\[ \Delta H(T_{\text{react}}) = \text{reaction enthalpy at the reactor temperature, kJ/mol} \]
\[ \Delta f^p = \text{standard enthalpy of reaction, kJ/mol} \]
\[ \eta = \text{overall net efficiency} \]
\[ \kappa = \text{deactivation constant rate} \]
\[ \tau = \text{average residence time in the carbonator, s} \]
\[ \phi_{\text{cyclic}} = \text{fraction of solids cycled N times} \]

REFERENCES


(34) Valverde, J. M.; Medina, S. Limestone Calcination under Calcium-Looping Conditions for CO₂ Capture and Thermochromic...


References

