Effect of Steam Injection during Carbonation on the Multicyclic Performance of Limestone (CaCO₃) under Different Calcium Looping Conditions: A Comparative Study

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ABSTRACT: This study explores the effect of steam addition during carbonation on the multicyclic performance of limestone under calcium looping conditions compatible with (i) CO₂ capture from postcombustion gases (CCS) and with (ii) thermochemical energy storage (TCES). Steam injection has been proposed to improve the CO₂ uptake capacity of CaO-based sorbents when the calcination and carbonation loops are carried out in CCS conditions: at moderate carbonation temperatures (∼650 °C) under low CO₂ concentration (typically ∼15% at atmospheric pressure). However, the recent proposal of calcium-looping as a TCES system for integration into concentrated solar power (CSP) plants has aroused interest in higher carbonation temperatures (∼800–850 °C) in pure CO₂. Here, we show that steam benefits the multicyclic behavior in the milder conditions required for CCS. However, at the more aggressive conditions required in TCES, steam essentially has a neutral net effect as the CO₂ uptake promoted by the reduced CO₂ partial pressure but also is offset by the substantial steam-promoted mineralization in the high temperature range. Finally, we also demonstrate that the carbonation rate depends exclusively on the partial pressure of CO₂, regardless of the diluting gas employed.

KEYWORDS: Concentrated solar power, CO₂ capture, Thermochemical energy storage, Calcium looping, Steam

1. INTRODUCTION

Climate change has evinced the need to mitigate CO₂ emissions from fossil fuel combustion in power plants. The development of efficient CO₂ capture technologies and the global deployment of renewable energy are keys to overcoming this challenge. The progress of renewable energies goes parallel with the development of efficient energy storage systems to avoid issues related to the intrinsic intermittency of natural energy sources, such as solar. With regards to this latter energy source, several systems have been proposed, including the use of molten salts and liquid metal oxides.1,2

In recent years, the calcium looping (CaL) process has aroused a great deal of interest as a potential avenue for reducing carbon emissions from postcombustion gases.3 The CaL-based technology relies on the reversible carbonation/calcination reaction of CaO/CaCO₃:4

\[
\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 \quad \Delta H = 178 \text{ kJ/mol} \tag{1}
\]

In the scheme proposed for carbon capture and storage (CCS), carbonation of CaO is conducted at around 650 °C, with a low CO₂ concentration (∼15% vol as typical in postcombustion gases). To complete the cycle, after carbonation, CaCO₃ particles are driven to the calciner reactor, where calcination is carried out at around 950 °C in a CO₂ rich atmosphere (typically 70% vol).5 Then, CO₂
CO2 atmosphere. High carbonation temperatures in CO2 (around 850 °C) maximize by carrying out carbonation at high temperatures under demand. Afterward, the regenerated (carbonation) that provides the heat needed for power brought back together to drive the exothermic reverse reaction separately. When the power supply is required, they are brought together for the thermochemical energy storage of concentrated solar power (CSP). The CaL-CSP technology presents certain advantages as compared to current commercial storage systems24 \footnote{Coppola et al.} \footnote{Dong et al.} \footnote{Arcenegui et al.} \footnote{Linden et al.} \footnote{Li et al.} \footnote{Manovic and Anthony} \footnote{Homsy et al.} \footnote{Champagne et al.} \footnote{Kavosh et al.} \footnote{Li et al.}. It has been demonstrated that the presence of steam accelerates CaCO3 calcination. Some authors attribute this effect to an increase in the heat transfer coefficient due to the higher thermal conductivity of steam as compared to N2.}

### Table 1. Selected Literature on the Influence of Steam on the Capture Performance of CaO-Based Sorbents

| authors (ref) | temperature (°C) | atmosphere | conclusions |
|--------------|-----------------|------------|-------------|
| Coppola et al.\textsuperscript{32} | Car: 650 | Car: 15% CO₂, 10% steam, balanced by air | steam enhances sorbent reactivity |
| Donat et al.\textsuperscript{31} | Cal: 940 | Cal: 70% CO₂, balanced by air | steam enhances sorbent reactivity |
| Champagne et al.\textsuperscript{34} | Cal: either 875 or 925 | Car: 15% CO₂, balanced by N₂, 0–20% steam | steam enhances sorbent reactivity |
| Homsy et al.\textsuperscript{35} | Car: 650 | Car: 12% CO₂ and 10% steam, balanced by N₂ | Steam negatively influences the capture performance of marble-derived CaO |
| Manovic and Anthony\textsuperscript{36} | Car: From 350 to 800 | Car: 20% CO₂ and 0–20% steam, balanced by N₂ | steam enhances sorbent reactivity |
| Li et al.\textsuperscript{37} | Car: From 400 to 700 | Car: 15% CO₂ and 2–20% steam, balanced by N₂ | steam enhances sorbent reactivity |
| Kavosh et al.\textsuperscript{38} | Car: 650 | Car: 15% CO₂, 4% O₂ and 6–20% steam, balanced by N₂ | steam enhances sorbent reactivity |
| Li et al.\textsuperscript{43} | Car: 650 | Car: 33% steam balanced by CO₂ | steam enhances sorbent reactivity |
| Arcenegui et al.\textsuperscript{52} | Car: 850 | Car: 100% CO₂ | steam enhances sorbent reactivity |
| Linden et al.\textsuperscript{35} | Cal: 800 | Car: 100% N₂ | steam enhances sorbent reactivity |
| Dong et al.\textsuperscript{54} | Cal: 900 | Cal: 100% N₂ | steam enhances sorbent reactivity |

released in calcination is stored, whereas the regenerated CaO is used in a new cycle.

Recently, the CaL-based technology has also been proposed for the thermochemical energy storage of concentrated solar power (CSP).\textsuperscript{8} The CaL-CSP technology presents certain advantages as compared to current commercial storage technologies based on sensible heat storage in molten salts. These include long-term energy storage and high energy densities (∼3.2 GJ/m³).\textsuperscript{7} Besides, natural CaO precursors such as limestone or dolomite are abundant, nontoxic, and cheap, which would facilitate the commercial deployment of the CaL-CSP technology.\textsuperscript{8–12}

In the general scheme proposed for CaL-CSP, solar radiation is used to drive the endothermic decomposition of CaCO₃ (calcination), as originally proposed by Flamant et al.\textsuperscript{13} The products of the reaction, CaO and CO₂, are stored separately. When the power supply is required, they are brought back together to drive the exothermic reverse reaction (carbonation) that provides the heat needed for power production under demand. Afterward, the regenerated CaCO₃ is again ready for a new calcination cycle.

In the CaL-CSP integration, heat to power efficiency is maximized by carrying out carbonation at high temperatures (around 850 °C), which may be quickly achieved in a pure CO₂ atmosphere.\textsuperscript{14} High carbonation temperatures in CO₂ ensure not only fast carbonation in short residence times but also allow for higher exergy efficiencies.

A main caveat of the CaL-based technologies is the progressive loss of the CaO carbonation reactivity, essentially due to intense sintering at high temperatures and further promoted in a CO₂-rich atmosphere.\textsuperscript{16,17} In order to preserve activity and mitigate CaO and CaCO₃ sintering, mild calcination conditions are preferred, at around 750 °C in an inert gas.\textsuperscript{14,18,19} A further limiting mechanism evidenced mainly for particle sizes above ~50 μm is pore plugging; carbonation at high temperatures under high CO₂ partial pressure leads to the rapid formation of a thick CaCO₃ layer on the CaO surface which blocks the pores and impedes CO₂ from reaching the CaO unreacted core.\textsuperscript{20–22} Significant CaO deactivation eventually requires the removal of the spent sorbent to be replaced by fresh CaO precursor, thereby decreasing the efficiency and increasing the cost of these technologies.\textsuperscript{23} Therefore, much effort has been devoted to developing strategies for preventing the loss in CaO reactivity. Most methods rely on thermal and chemical pretreatments\textsuperscript{24–28} or even CaO modification using refractory additives.\textsuperscript{29–31}

The influence of high-temperature steam on CaO reactivity has been amply studied in conditions compatible with CaL-CCS,\textsuperscript{32–41} as the combustion flue gases contain steam in 5–10% volume content for coal combustion, and up to 20% for oxy-fuel combustion.\textsuperscript{33,34,36} As a summary, Table 1 contains a selection of works exploring the influence of steam on the capture performance of CaO-based sorbents.
Other authors have reported a catalytic effect of steam.45–49 Giammara and Lefferts observed a decrease in the apparent activation energy and attributed the acceleratory effect of steam to the formation of hydrogen carbonate ions as intermediates.50 Alternatively, faster calcination has been ascribed to steam-induced changes in crystal growth and surface reactivity.51 In any case, it has been proposed the acceleratory effect of steam injection can be used to lower the temperature needed to fully calcine the CaCO₃ in the short residence time required in practice, which would lead to important energy savings. Moreover, attaining full calcination at lower temperatures would alleviate any sintering-induced deactivation thus improving multicyclic performance.39,42−44,52

An open question remains on the overall impact of steam on the multicyclic performance of CaO-based sorbents. It is widely acknowledged that steam substantially promotes sintering,16,55 but the implication of this effect on CaO carbonation is still controversial. Thus, while several authors have reported that steam addition offers negligible or even negative influence on CO₂ carrying capacity, 26,57 other researchers have otherwise observed a beneficial effect.33,34,36,37,53,54,58 Furthermore, Donat et al. observed that the addition of steam enhances multicyclic activity regardless of whether steam is injected during calcination, carbonation, or in both stages.33 In the latter cases, the improvement is attributed to the synergistic action of different mechanisms.34 Thus, the enhanced particle sintering during calcination in the presence of steam gives rise to a CaO structure with large pores (≈1 μm), which are less susceptible to pore plugging, thereby favoring the subsequent carbonation stage.39,52 On the other hand, as Manovic and Arias observed, steam has no influence on the carbonation rate during the initial fast reaction-controlled regime, but it strongly promotes the rate of conversion during the subsequent slow diffusion-controlled regime.36,59 Thus, the benefit of steam on CaO reactivity is explained mainly by an enhancement of the solid-state diffusion through the carbonate layer.33,36,60,61 Li et al. pointed out that enhanced carbonation might be attributed to the formation of OH⁻ ions after H₂O dissociation.37 As a consequence of the enhanced solid-state diffusion, the microstructure of CaCO₃ formed during carbonation in the presence of steam lacks nanosized porosity.36 Nonetheless, Homzy et al. has recently pointed out that this effect is by no means universal to all CaO-based sorbents but would ultimately depend on the calcium precursor’s microstructure.35

On the other hand, it is generally agreed that CaO hydration to obtain Ca(OH)₂ can be used to enhance the extension of carbonation. As Ca(OH)₂ is more reactive toward CO₂ than CaO, some authors have suggested the transient formation of Ca(OH)₂ as the reason behind the improvement of conversion.57,62 However, while reasonable at intermediate temperatures, it is debatable that such mechanism remains at temperatures over 500 °C, when the formation of Ca(OH)₂ is no longer thermodynamically favored. In such cases, the enhanced carbonation should be attributed to steam-enhanced solid-state diffusion in the presence of steam.33,36

As it can be observed in Table 1, to this date, most experiments with steam were carried out in conditions relevant for CCS, in environments with low CO₂ concentration (10−30%) and carbonation temperatures around 600 °C.33,34 These conditions are substantially different than those used in the CaL-CSP integration, where calcination is conducted at ∼750 °C in pure N₂ and carbonation is carried out at ∼850 °C in 100% CO₂. The effect of steam addition during calcination has been previously studied in these latter conditions,52 but the role of steam when it is injected during carbonation remains to be revealed. Understanding the influence of steam on both stages is key to finding the operating conditions that may lead to significant improvement of the multicyclic CaL performance.

In the present work, we study the effect of injecting steam during the carbonation stage on the multicyclic performance of limestone when cycled under conditions relevant for CaL-CSP, involving high temperature and 100% CO₂ in the carbonation stage, and compare the results with those obtained in multicyclic tests conducted with steam under CCS conditions.

2. EXPERIMENTAL SECTION

The limestone tested in this work (ESKAL 60) was provided by KSL Staubtechnik GmbH (Germany) with a particle size distribution (PSD) obtained by aerodynamic classification. Figure 1 shows a SEM micrograph of ESKAL 60 and its PSD. The micrograph was taken using a scanning electron microscope HITACHI S4800, while PSD was determined by laser diffractometry as described in ref 63. As may be seen, the sample shows a PSD that peaks around 60 μm. It is well-known that particles’ size can strongly condition calcination and carbonation kinetics, as well as the multicyclic performance.64

Figure 2 depicts the experimental setup used. The multicyclic tests were carried out in a thermogravimetric analyzer (TGA) Linseis STA PT 1600 customized for steam injection. To generate steam, water was injected in a vaporizer using a water flow controller (WFC) Bronkhorst Liqui-Flow L13 V12 that allows control of the flow with an accuracy of 1%. Nitrogen was employed to pressurize the water tank and as a purge gas. Steam was mixed with the carrier gas in the vaporizer. The mixture was then injected into the furnace through a heated line kept at 165 °C to avoid condensation. The gas flow rate was controlled using mass flow controllers (MFCs) El-Flow/
Bronkhorst. Depending on the target conditions, the carrier gas was N2, CO2, or a mixture of both.

The CaL-CSP multicyclic tests were devised to imitate reaction conditions relevant in a CaL-CSP operation. Experiments started with a heating ramp of 20 °C/min from room temperature up to the target calcination temperature (730 °C). Calcination lasted 10 min and was carried out in pure N2. After calcination, the sample was again increased at a heating rate of 20 °C/min up to the target carbonation temperature: either 800, 830, or 850 °C in different tests. The carbonation reaction was carried out in 5 min long stages conducted under mixtures of either H2O/CO2 or N2/CO2. Different values of CO2 partial pressure were tested. At the end of the carbonation stage, steam (or N2) was removed from the furnace and the temperature was decreased down to 730 °C under CO2. At this temperature, CO2 was replaced by N2 to start a new calcination stage, and the cycle was repeated 20 times.

In the CaL-CCS experiments, calcinations were carried out for 10 min at 900 °C under a 60% CO2/40% N2 vol/vol atmosphere. Carbonation was carried out at 650 °C for 5 min under 15% CO2, using either 0% or 10% steam balanced up to 100% with N2. Heating and cooling rates were the same as for CaL-CSP experiments. All the tests were carried out at an absolute pressure of 1 bar.

Scanning electron microscopy (SEM) Hitachi S4800 was used to analyze the impact of sintering on the surface of the particles when the sample was subjected to different conditions. Before SEM, the samples were gold-coated utilizing an Emitech K550 Telstar sputter-coating machine (30 s, 30 mA).

Ssurf surface area and pore size distribution of CaO after one cycle, carried out in different atmospheric compositions, was determined by N2 physisorption analysis. In order to minimize measuring errors, a sample of 1 g was cycled in a tubular furnace in conditions that mimicked those used in the multicyclic experiments conducted in the TGA. In these experiments, the sample was first heated at 10 °C/min up to 730 °C, and the temperature was maintained constant for 30 min to carry out calcination in N2. Then, the temperature was raised at 10 °C/min up to 850 °C and kept constant for 10 min and the atmosphere changed to conduct the carbonation reaction. Three atmospheres were employed: 29% N2/71% CO2, 29% steam/71% CO2, and 100% CO2, with a flow rate of 80 cm3. Water was injected into the tubular furnace through a peristaltic pump. Once carbonation was completed, the temperature was decreased down to 730 °C and the sample was calcined again in N2 for 30 min. Before the physisorption analysis, the samples were degassed at 350 °C for 2 h.

3. RESULTS AND DISCUSSION

3.1. Influence of Steam Injection during Carbonation on Multicyclic Performance in CaL-CSP Conditions. Figure 3 shows the time evolution of effective conversion Xeff attained during the 1st and the 19th cycles measured in TGA tests carried out under CaL-CSP conditions. Carbonation was performed at 850 °C with a steam partial pressure of 3%. Qualitatively similar profiles were obtained for the different CO2/H2O ratios tested. Effective conversion is defined as the quotient between the mass of CaO converted to CaCO3 and the total mass of the sample m, which includes inert solids if present:

\[
X_{eff}(t) = \frac{(m_{CaO}(t) - m)W_{CaO}}{mW_{CO2}}
\]

being \(m_{CaO}(t)\) the sample mass at time \(t\), and \(W_{CaO}\) and \(W_{CO2}\) the molar masses of CaO and CO2, respectively.

As expected, effective conversion decreases progressively with the cycle number arguably due to the sintering of the surface phugging carbonate layer. Two different phases can be observed as carbonation proceeds. In the first stage, carbonation occurs rapidly at the CaO particles’ surface. This reaction-controlled phase is followed by a significantly slower phase in which CO2 diffuses through the CaCO3 layer built upon the CaO surface during the prior stage.

Contrarily to what occurs in CaL-CCS conditions, when slow but non-negligible carbonation takes place during this second stage, at the high temperatures in the CO2-rich atmosphere used in CaL-CSP, the formation of the blocking layer impedes any relevant carbonation during the diffusive stage. Thus, as may be seen in Figure 3, most of the reaction occurs during the reaction-controlled fast phase.

Figure 4 compares data of conversion attained at the end of the carbonation stage as a function of the cycle number for experiments in which the carbonation step is carried out in different gas mixtures. Multicycle CaO conversion has been calculated using eq 2 and considering the mass converted at the deactivation constant, and \(X_i\) is the conversion at the first cycle. Fitting curves are represented as solid lines in Figure 4. The best-fitting parameters are collected in Table 2.

![Figure 2. Schematic illustration of the experimental setup.](https://example.com/image2)

![Figure 3. Time evolution of temperature and effective conversion during the 1st and the 19th cycles measured in experiments carried out under CaL-CSP conditions. Carbonation was conducted at 850 °C with a steam partial pressure of 3%.](https://example.com/image3)
Since the material is expected to be cycled many times, the most relevant parameter for practical purposes is the residual conversion. No significant influence of steam amount is observed in these experiments on the residual conversion values, which are similar regardless of the steam/CO₂ ratio employed. Nevertheless, the deactivation constant increases with the amount of steam, which might indicate that steam promotes the rate of sintering.16,69

Figure 5 illustrates the influence of the carbonation temperature in the presence of steam. It includes data on the CaO multicyclic conversion obtained from experiments carried out at diverse carbonation temperatures for a fixed atmosphere composition (3% H₂O/97% CO₂). The best-fitting parameters of eq 3 to these data are shown in Table 3. While modest, a slight improvement of the multicyclic conversion is observed when carbonation temperature is reduced.

It should be taken into account that the injection of steam has a dilution effect, reducing the percent CO₂ in the atmosphere, thereby modifying the thermodynamic equilibrium temperature. Since carbonation is carried out at high temperatures close to equilibrium a slight change of the CO₂ volume percent may have a relevant influence on both the reaction kinetics and on the morphology of the arising CaCO₃ particles.70 Therefore, to better assess the role of steam during carbonation, multicyclic tests were carried out using N₂/CO₂ gas mixtures instead, keeping the same CO₂ concentrations used in the previous H₂O/CO₂ gas mixtures. Experimental results are depicted in Figure 6. The values of residual conversion and deactivation constant corresponding to these experiments are collected in Table 3. In contrast to what was observed with steam, the dilution of CO₂ with N₂ noticeably improves the multicyclic performance of the sample. Residual conversion values derived from the experiments under N₂/CO₂ are consistently higher than values observed in the corresponding H₂O/CO₂ mixtures.

Data plotted in Figure 6 indicate that diluting CO₂ with N₂ has a positive impact on the multicyclic performance.

| temperature (°C) | Xₜ | k   | R²  |
|------------------|----|-----|-----|
| 800              | 0.18 ± 0.01 | 0.39 ± 0.02 | 0.998 |
| 830              | 0.14 ± 0.01 | 0.33 ± 0.01 | 0.999 |
| 850              | 0.14 ± 0.01 | 0.34 ± 0.02 | 0.998 |

Figure 6. Multicyclic conversion obtained from tests in which carbonation was carried out at 850 °C, in atmospheres that contained different CO₂/N₂ gas mixtures as indicated. Solid lines correspond to the best fit of eq 3 to the experimental data.

Table 2. Best-Fitting Parameters of Equation 3 to Multicycle CaO Conversion Data (Figures 4 and 6), Corresponding to Multicyclic Experiments Run Using a Carbonation Temperature of 850 °C under Different Gas Mixtures

| carbonation atmosphere | H₂O     | N₂      |
|------------------------|---------|---------|
| 100% CO₂               | 0.15 ± 0.01 | 0.15 ± 0.01 |
| 97% CO₂                | 0.14 ± 0.01 | 0.16 ± 0.01 |
| 90% CO₂                | 0.15 ± 0.01 | 0.21 ± 0.01 |
| 71% CO₂                | 0.18 ± 0.01 | 0.31 ± 0.01 |

The carbonation atmosphere is balanced up to 100% with either H₂O or N₂ as indicated in the first row.
reduction in the proportion of CO₂ in the sample environment alleviates the sintering-induced deactivation. However, when dilution is done in steam no positive influence on the multicycle activity is observed. This could be explained by the mineralizing effect of steam, which at such high temperatures accelerates the loss of reactivity, and adversely compensates for the positive effect of the dilution. The impact of H₂O on CaCO₃ is observed in Figure 7, which shows two SEM micrographs taken after the first carbonation conducted with a) 0% H₂O and b) 29% H₂O. c) Pore size distribution and BET surface measurements of CaO after one cycle carbonating in different atmosphere compositions: 100% CO₂, 29% H₂O/71% CO₂, and 29% N₂/71% CO₂.

Figure 7. SEM micrograph taken after the first carbonation conducted with a) 0% H₂O and b) 29% H₂O. c) Pore size distribution and BET surface measurements of CaO after one cycle carbonating in different atmosphere compositions: 100% CO₂, 29% H₂O/71% CO₂, and 29% N₂/71% CO₂.

Figure 8. Equilibrium temperature as a function of the CO₂ partial pressure. Indicated as colored points are the points corresponding to the values of partial pressures of CO₂ used in our experiments.

Figure 9 shows the time evolution of effective conversion during the first carbonation at 850 °C as well as its derivative, dXeff/dt, under different gas mixtures. As expected, the rate of carbonation decreases with decreasing CO₂ partial pressure. The maximum reaction rate is approximately the same regardless of the used gas to dilute the CO₂. Thus, carbonation kinetics during the fast kinetic-controlled stage is not influenced by steam but depends exclusively on the partial pressure of CO₂.

3.2. Influence of Steam Injection during Carbonation on Multicyclic Performance in Cal-CCS Conditions.

At first sight, the results presented in the previous section contrast with several previous studies reporting that the use of steam during either carbonation or calcination (or in both) enhances the CaL multicyclic activity of limestone derived CaO. However, previous studies were all performed under reaction conditions compatible with Cal-CCS, involving carbonation under relatively low temperature and low CO₂ concentration, while the tests presented above involve carbonation at high temperature and high CO₂ concentration.

\[
T_{\text{eq}} = -\frac{\alpha}{\ln(p_{\text{CO}_2}/A)}
\]

where \(A = 4.083 \times 10^7 \text{ atm, } \alpha = 20 \, 474 \text{ K, and } p_{\text{CO}_2}\) is given in atm. This equation is plotted in Figure 8. As the CO₂ partial pressure is decreased by the addition of steam or N₂, the equilibrium temperature approaches the target carbonation temperature used in the multicyclic tests under CaL-CSP conditions (\(T = 850 \, \text{°C}\)), resulting in slower carbonation kinetics, as proven in Figure 9.
Under these conditions, the results depicted in Figure 4 show that steam injection during carbonation does not improve the multicyclic performance. Indeed, the effect of steam appears to be even detrimental if we compare the values of residual conversion when CO$_2$ is diluted with steam with those in which CO$_2$ is diluted with N$_2$ at the same CO$_2$ concentration (Table 2). This could be explained by the high carbonation temperatures and high CO$_2$ concentration values employed for carbonation in CaL-CSP as compared to the conditions used in CaL-CCS. Under such harsh conditions, particle sintering is substantially promoted. Moreover, as a mineralizer agent, the presence of H$_2$O further promotes grain growth and particle sintering.$^{16}$ The adverse effect of H$_2$O during carbonation at high temperature is also upheld by the results shown in Figure 5 and data collected in Table 3, indicating that the residual conversion decreases with the carbonation temperature.

To further investigate this apparent contradiction, multicyclic tests under CaL-CCS conditions, in which steam was added in the carbonation stage, were also conducted to check whether steam enhances in these conditions the multicycle performance as reported in the literature thereby reinforcing our results. In these experiments, we replicated the experimental conditions employed by Donat et al.$^{33}$ The results here obtained, shown in Figure 10, are very similar to those reported by Donat et al, even though their experimental setup differ from ours; they utilized a bubbling fluidized bed (BFB) reactor instead of a TGA apparatus. The fact that the improvement typically reported in CCS conditions was replicated in our multicycle tests confirms that steam’s addition during carbonation is indeed beneficial for CaL-CCS but neutral under CaL-CSP conditions. This contrast may be ascribed to the different carbonation conditions regarding temperature and CO$_2$ partial pressure.

Time evolution of conversion during the fifth cycle, obtained in our work from the experiments conducted in CaL-CCS conditions, is depicted in Figure 11. Albeit, during carbonation, the positive influence is observed on both the reaction-controlled and the diffusion-controlled phases, the improvement is more pronounced in the latter as it has been previously reported by Manovic et al.$^{36}$ Arguably, the improvement can be attributed to an enhancement in the diffusion of CO$_2$ through the CaCO$_3$ blocking layer formed during the reaction-controlled stage, favored by the steam. Conversely, as shown in

Figure 9. Time evolution of effective conversion and its derivative during carbonation in atmospheres of different gas mixtures for the first cycle.

Figure 10. Multicyclic conversion data obtained from tests conducted under CaL-CCS conditions with steam addition during carbonation (red open circles) and with no steam (black open squares).

Figure 11. Time evolution of effective conversion during carbonation at the fifth cycle from tests carried out in CaL-CCS conditions.
4. CONCLUSION

The results reported in this work show that the effect of steam injection during carbonation on the multicycle activity of limestone-derived CaO strongly depends on the conditions used for carbonation. In agreement with previous results reported in the literature, we found that steam enhances the CaO multicycle activity under carbonation conditions suitable for CO₂ capture from postcombustion gases (CaL-CCS); moderate temperatures (~600 °C) under an atmosphere with low CO₂ concentration. Under such conditions, steam significantly enhances the conversion during the diffusion-controlled stage, which accounts for a large share of the total conversion attained. Arguably, the presence of steam favors solid-state diffusion of the CO₂ across the CaCO₃ layer built upon the CaO particles in the reaction-controlled phase of carbonation. Conversely, when the carbonation reaction is carried out at high temperatures (over 800 °C) in a CO₂-rich atmosphere, overall, the addition of steam does not alter the multicyclic performance. The slight benefit gained by the effective dilution of CO₂ by the addition of steam is offset by the mineralizing effect of steam, which noticeably promotes particle sintering, harming CaO reactivity and probably the diffusion of CO₂ toward the inner unreacted core of the particles. The influence of steam on carbonation kinetics is also different at temperatures over 800 °C in CO₂-rich atmospheres. Under such conditions, the fraction of CaO converted during the diffusion-controlled phase becomes negligible and it is not improved by steam. Finally, the results herein show that that carbonation kinetics are essentially governed by the partial pressure of CO₂, as similar reaction rates are observed regardless of whether the CO₂ is diluted in steam or N₂.

However, the CaL-CSP integration for thermochemical storage of solar energy benefits from the rapid and extensive carbonation attained at high temperatures in CO₂ Therefore, since steam is beneficial when injected during calcination but not during carbonation, any application of steam to CaL-CSP should be constrained to the calcination stage.

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Notes

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