High and stable CO$_2$ capture capacity of natural limestone at Ca-looping conditions by heat pretreatment and recarbonation synergy

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Abstract

The Ca-looping (CaL) process, based on the multicyclic carbonation/calcination of limestone derived CaO, has emerged recently as a potentially economically advantageous technology to achieve sustainable postcombustion and precombustion CO\textsubscript{2} capture efficiencies. Yet, a drawback that hinders the efficiency of the CaL process is the drastic drop of limestone capture capacity as the number of carbonation/calcination cycles is increased. Precalcination of limestone at high temperatures for a prolonged period of time has been proposed as a potential technique to reactivate the sorbent, which is however precluded by regeneration temperatures above 850°C and low CO\textsubscript{2} concentrations in the carbonator to be found in the practical situation. Under these conditions, heat pretreatment leads to a stable yet very small CaO conversion. On the other hand, the introduction of a recarbonation stage between the ordinary carbonation and calcination stages has been shown to decelerate the rate of sorbent activity decay even though this favorable effect is not noticeable up to a number of above 10-15 cycles.

The present manuscript demonstrates that the synergetic action of heat pretreatment and recarbonation yields a high and stable value for the multicyclic conversion of limestone derived CaO. It is foreseen that recarbonation of heat pretreated limestone would lead to a reduction of process costs especially in the case of precombustion applications. Even though sorbent purging will always be needed because of ash accumulation and sulphation in postcombustion CO\textsubscript{2} capture applications, the stable and high multicyclic CaO conversion achieved by the combination of these techniques would make it necessary to a lesser extent.
I. INTRODUCTION

The carbonation reaction of CaO at high temperature constitutes the basis for emerging technologies in precombustion and postcombustion CO$_2$ capture applications [1–3]. Normally, CaO particles react in a fluidized bed reactor (carbonator) with CO$_2$ present at low concentrations in the inlet gas stream at atmospheric pressure. Partially carbonated particles are then circulated into a second fluidized bed reactor (calciner) where a pure stream of CO$_2$ ready for transport and storage is produced and the sorbent is regenerated for its use in a new cycle. By taking into account the tradeoff between the reaction equilibrium driving force and the reaction kinetics, the optimal carbonation temperature is around 650°C whereas calcination must be carried out at temperatures above 850°C to assure complete decarbonation in the CO$_2$ rich atmosphere of the calciner [4].

Carbonation of CaO particles proceeds along two well differentiated phases as demonstrated by multicyclic thermogravimetric analysis (TGA) tests. The reaction takes place by means of a kinetically-driven mechanism in a first fast carbonation phase, which ends after a 30-50 nm CaCO$_3$ layer thickness is developed on the surface of the solid [5]. Carbonation is then controlled by diffusion of CO$_2$ in the solid, which is a much slower process [5, 6]. Given the constrain imposed by short residence times in practical applications, most of carbonation in the Ca-looping (CaL) technology would take place in the fast phase, which depends essentially on the CaO skeleton porosity. A main drawback of the CaL technology is that sintering of the CaO skeleton regenerated during the calcination stage causes a progressive loss of conversion in the fast phase as carbonation/calcination cycles build up [5, 6]. This requires a continuous purge of the spent sorbent in the process that must be counterbalanced by fresh limestone, which increases further the demand of heat at the calciner [7, 8].

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A current direction of research to improve the regenerability of natural limestones is the formulation of synthetic CaO-based sorbents [9, 10]. Nonetheless, taking into account the interplay between sorbent cost and multicyclic conversion improvement [7, 11], the low cost and wide availability of natural limestone ensures that it is still the most suitable candidate as CaO precursor to ensure the industrial competitiveness of the CaL technology. Other strategies have been explored to mitigate the loss of limestone multicyclic activity such as hydration to reactivate the sorbent [1, 12], heat pretreatment [1, 13, 14] and recarbonation [15, 16]. Manovic and Anthony [14] proposed heat pretreatment as a suitable technique to improve the CaO activity during multicyclic carbonation/calcination. TGA tests demonstrated that some natural limestones actually exhibited an increase of conversion with the cycle number if they had been pre-subjected to long periods of isothermal heating at high temperatures. Heat pretreatment is a well known process used for hardening a crystalline solid just by creating structural dislocations caused by thermal stresses. In addition, the increase of structural defects density would lead to an enhancement of solid-state diffusion [17]. A careful analysis of the thermograms derived from TGA tests shows indeed that reactivation of thermally pretreated limestones is essentially due to the enhancement of carbonation in the solid-state diffusion phase [18–20]. When the carbonated sorbent is regenerated at moderate calcination temperatures the porosity of the resulting CaO skeleton is enhanced, which leads to a promotion of fast carbonation in the subsequent cycle. However, most of early TGA studies were carried out isothermally (at temperatures in the range 750-850°C) by switching the gas between an inert gas for calcination and a gas mixture containing a high CO₂ partial pressure for carbonation as corresponds to conditions in practice [13, 14, 21–25]. More recent tests show that calcination temperatures above 850°C are sufficiently high to prevent reactivation of heat pretreated sorbents carbonated under low CO₂ partial pressure.
Looping-calcination temperatures above 850°C lead to stable yet very low values of conversion for heat treated limestones [18, 27] whereas the minimum target value for the calcination temperature to ensure full decarbonation of the partially carbonated solids under practical constraints such as high CO₂ partial pressure (50 - 70 kPa) and short residence times (2 - 3 min) in the calciner [28] is around 870°C [4].

A feasible new CaL concept using low-cost natural limestone consists of the introduction of a recarbonation stage under pure CO₂ (available from the calciner) and at high temperature (800°C) in between the carbonation and calcination stages [16]. According to this method, the partially carbonated CaO particles would be circulated before calcination to a recarbonator reactor wherein further carbonation would be intensified. TGA tests demonstrate that the residual conversion of limestone is increased by cyclic recarbonation, which would reduce the fresh sorbent make-up flow required and the heat demand in the calciner thus lowering the overall cost of the CaL capture process [16]. Recarbonation in pure CO₂ was firstly suggested in [15] for reactivation as evidenced from results derived using a batch fluidized bed combustor. Nevertheless, thermogravimetric analysis (TGA) tests earlier reported in [15] failed to demonstrate reactivation, which is consistent with TGA results recently reported in [16] showing that reactivation is only noticeable after about 15-20 cycles (see Fig. 3b of [16]). In the present manuscript we propose a modification of recarbonation as reactivation technique by combining it with heat pretreatment. As will be shown, the combination of both techniques leads synergetically to a further enhancement of the multicyclic CaO conversion, which reaches a high and stable value from the 2nd cycle.
II. MATERIALS AND METHODS

High purity natural limestone supplied to us by Segura S.L. (Matagallar quarry, Pedrería, Spain) has been used in our tests as CaO precursor (CaCO$_3$ 99.62%, SiO$_2$ < 0.05%, Al$_2$O$_3$ < 0.05%, MgO 0.24%, Na$_2$O 0.08%). Heat pretreatment was performed by subjecting the material to isothermal heating at 950°C for 12 h in dry air. Carbonation/calcination multicyclic tests were carried out in a Q5000IR TG analyzer (TA Instruments). This equipment is provided with an infrared furnace heated with halogen lamps and with a high sensitivity balance (<0.1 μg) characterized by a minimum baseline dynamic drift (<10 μg). The use of an infrared halogen furnace in our TGA runs allowed us for heating/cooling the sample very quickly (300°C min$^{-1}$), which serves to minimize the duration of the transitional periods thus allowing to test the multicyclic conversion of the sorbent at conditions close to CaL realistic conditions. As a general procedure, a sorbent sample (around 10 mg) was firstly subjected in-situ to a linear heating program (20°/min) up to 850°C in air prior to cycling. Benchmark conditions of subsequent carbonation/calcination (c/c) cycles consisted of carbonation at 650°C (85% air/15% CO$_2$ vol/vol) and calcination at 850°C (air), both stages for 5 minutes. Carbonation/recarbonation/calcination (c/r/c) cycles were performed by subjecting the sample to a 3 min recarbonation stage (10% air/90% CO$_2$ vol/vol) at 800°C in between the carbonation and calcination stages.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows examples of thermograms obtained from multicyclic c/r/c tests carried out on raw and heat pretreated limestone samples. As may be seen, heat pretreatment leads to a relatively higher and more stable weight% gain of the sorbent along the carbonation
stages of the cycles. The weight% evolution for the pretreated sorbent in the two first cycles is shown in detail in Fig. 2. Carbonation of the heat pretreated CaO skeleton in the first cycle is seen to exhibit two main distinctive features. As reported in previous works [27], the pretreated sorbent activity in the kinetically driven fast phase (phase I in Fig. 2) is very low while diffusive carbonation is relatively intense. On the other hand, we observe that carbonation in the diffusion-controlled recarbonation stage is remarkably enhanced. After calcination, the sorbent activity in the fast carbonation phase of the 2nd cycle is markedly promoted (see Fig. 2). As a result, CaO conversion at the end of the carbonation phase is increased from just $X_1 \approx 0.12$ in the 1st cycle up to $X_2 \approx 0.37$ in the 2nd cycle. The multicyclic conversion remains practically stable around this value for the following c/r/c cycles (up to 100 cycles were performed). In contrast, the c/r/c cycled raw limestone still shows a decay with the cycle number which is especially noticeable in the first 10 cycles. Data of multicyclic conversion are plotted in Fig. 3 for the raw and pretreated limestones subjected to c/c and c/r/c tests (data reported elsewhere by Arias et al. [16] are also plotted for comparison). As shown in [16], our results indicate that introducing an intermediate recarbonation stage serves to mitigate the rate of conversion decay exhibited by the raw limestone subjected to ordinary c/c cycles even though the improvement is not remarkable up to a number of above 10 - 15 cycles.

We noticed that the heat pretreated sample had a great tendency to hydrate and carbonate just in contact with ambient atmosphere as seen in the XRD patterns depicted in Fig. 4 showing that CaO had almost completely converted overnight into Ca(OH)$_2$ and CaCO$_3$. The weight drops observed in the TGA test during the initial linear heating period of an overnight pretreated sample as due to dehydration (at about 400°C) and decarbonation (at about 600°C) indicated that it consisted of a 77.3%wt of Ca(OH)$_2$, 17.7%wt of CaCO$_3$ and...
just 4\%wt was left of CaO. Multicyclic c/r/c conversion data for this sample are also plotted
in Fig. 3. The results show that overnight pre-hydration/carbonation yields a remarkable
reactivation in the 2nd cycle. Conversion reaches in subsequent cycles values well above
those obtained for the raw and soon after pretreated sorbents. Yet, the sorbent activity is
decreased with the cycle number and, after about 30 cycles, it becomes somewhat smaller
than the stable value of conversion exhibited by the soon after pretreated sample.

The enhancement of conversion for the raw limestone is even more marked in the exper-
iments performed in our work than in those reported by Arias et al. [16], which might be
explained by the higher CO\textsubscript{2} vol\% that we use in the carbonation stage (15\% in our tests
vs. 10\% in [16]) and the lower calcination temperature (850°C in our tests vs. 900°C in
[16]). A lower CO\textsubscript{2} vol\% would lead to a smaller conversion [2] since most of carbonation
occurring in the kinetically driven phase conforms to a first order kinetic law being pro-
portional to the difference between the actual CO\textsubscript{2} concentration and the equilibrium CO\textsubscript{2}
concentration (\(\approx\)1\% at 650°C and atmospheric pressure). On the other hand, calcining at a
higher temperature would promote further sintering of the regenerated CaO skeleton thus
hampering fast conversion in the next cycle. As may be seen, the data reported in [16]
exhibit an appreciable scatter as compared to ours, which might be due to vibrations caused
by the vertical displacement of the two-zones furnace used in their specially designed TG
analyzer (originally reported in [29]) to allow for a rapid change of temperature between
cycles resembling practical conditions. In our tests, this requirement is helped by infrared
heating, which allows for quick transitional periods between stages.

In order to assess whether the combination of heat pretreatment and recarbonation would
lead to a reduction of the cost of CO\textsubscript{2} avoided in practice several parameters involved have
to be considered, namely the improvement of the maximum average capture capacity of
the CaO solid population \( (X_{\text{ave}} \), depending on the increment of residual conversion), the sorbent purge flow \( (f \) defined as the percentage of sorbent leaving the process), and the CaO/CO\(_2\) molar ratio \( (R) \). A systematic procedure to carry out this study is detailed in [7].

The applicability of postcombustion CaL technology in coal-fired power plants is critically determined by the irreversible formation of CaSO\(_4\) due to the presence of SO\(_2\) in the flue gas (a simulated flue gas of 0.45% SO\(_2\) is shown to lead to a significant drop of the CO\(_2\) capture capacity just after 2-3 cycles in multicyclic TGA tests [30]). Since CaO with low carbonation activity still has a strong sulphation capability, a feasible strategy is to use purged sorbent with low carbonation activity for the capture of SO\(_2\) from the flue gas before it enters the carbonator [31, 32]. Arias et al. [16] estimated that the residual conversion of c/r/c cycled raw limestone is sufficiently high as to reduce the amount of purged CaO to the amount usable for SO\(_2\) capture thus minimizing the quantity of CaO going to waste. This estimation was made using a residual conversion \( X_r \) between 0.15 and 0.2 obtained from their multicyclic c/r/c experiments on raw limestone (as compared to about 0.07-0.08 for limestones subjected to ordinary c/c cycles [29]). Taking into account the percentage of residual conversion improvement attained for heat pretreated limestone subjected to c/r/c cycles, this same amount of purge flow could be kept (as needed to de-sulfurize the flue gas) while reducing the CaO/CO\(_2\) molar ratio, which would allow to downsize the system thus cutting down further the cost of the process. The influence of \( X_{\text{ave}} \) on the CO\(_2\) avoided cost can be estimated from the industrial scale simulation of the CaL process integrated with a power plant reported in [7]. CO\(_2\) avoided cost data inferred from this simulation are graphically presented versus sorbent price and depending on \( X_{\text{ave}} \). Figure 5 reproduces the results originally reported in [7] for values of \( X_{\text{ave}} = 32\% \) and 67\%, low CaO/CO\(_2\) molar ratio \( (R = 1.5) \) and different values of purge flow in the calciner (1\% and 2.5\%). Following the
procedure described in [7] and using our multicyclic conversion results, it may be estimated

\[ X_{\text{ave}} \sim 40\% \] for the c/r/c raw limestone and \[ X_{\text{ave}} \sim 60\% \] for the c/r/c heat pretreated limestone. According to Fig. 5, the roughly similar increase of \( X_{\text{ave}} \) due to the combination of heat pretreatment and recarbonation would bring about a significant reduction of the cost of CO\(_2\) avoided for incremental sorbent costs up to around 40 €/ton as compared to 5 €/ton for raw limestone (using a purge flow of 2.5%). A decrease of the purge flow down to 1% would allow the incremental sorbent cost to be further increased up to 90 €/ton while still achieving a reduction of the cost of CO\(_2\) avoided. The possibility of increasing sorbent cost while still keeping the cost of CO\(_2\) avoided low by means of c/r/c cycling would make it interesting to investigate the behavior of synthetic sorbents showing reactivation when subjected to c/c cycles similarly to heat pretreated limestone. A significant example is the case of CaO/mayenite polycrystalline composites, which exhibit reactivation when subjected to c/c cycles even under severe calcination conditions [33]. Arguably, solid-state diffusion of CO\(_2\) in these composites is enhanced across the interface between CaO and mayenite crystallites, which would presumably lead to a high and stable value of CaO conversion when the sorbent is subjected to c/r/c cycles as seen in our work for heat pretreated limestone.

The minimum amount of fresh limestone make-up flow which is required to reach a sustained high level of CO\(_2\) post-combustion capture efficiency has been assessed in a very recently work [34] in order to have an accurate estimation on the effect of CaSO\(_4\) and inert solids accumulation. The study allows quantifying the reduction of limestone make-up flow \( F_0 \) (relative to the CO\(_2\) molar flow that enters the carbonator \( F_{CO2} \)) as a function of the reactivation level achieved in a c/r/c process configuration. According to the simulation results, a 90%CO\(_2\) capture efficiency would be reached for a ratio \( F_0/F_{CO2} = 0.08 \) if the residual sorbent conversion is increased up to \( X_r = 0.12 \) whereas this ratio is reduced to
The achievement of a high residual conversion by introducing an intermediate recarbonation stage can be thus expected to have a notable impact on the efficiency of CO₂ post-combustion capture (even though the costs related to the recarbonation reactor should be also considered). Combining heat pretreatment and recarbonation would be thus a useful strategy to be explored in order to notably minimize the limestone make-up flow required. In particular, heat pretreatment/recarbonation of limestone would be specially attractive for post-combustion applications allowing for a low percentage of purge flow as in the case of high quality coal (with low sulfur and ash content). On the other hand, the efficiency of precombustion applications (such as steam methane reforming enhanced via pre-combustion CO₂ capture [35]) would be neatly benefitted from a stable and highly active sorbent since in these applications the gas to be processed is SO₂ free and purging due to sulphation is not required.

To further investigate the role of the recarbonation stage additional tests were carried out in our work by alternating c/r/c and c/c cycles. The thermograms plotted in Fig. 6a are retrieved from tests in which the samples were subjected to a 1st c/r/c cycle followed by 10 c/c cycles and 11 c/r/c cycles. As seen before, it may be observed that carbonation during the 1st recarbonation stage is enhanced for the heat pretreated sorbent, which yields reactivation in the carbonation stage of the 2nd cycle. In contrast, carbonation in the recarbonation stage of the 1st cycle is not significant for the raw sorbent. If the recarbonation stage is eliminated in subsequent cycles, the conversion of both the heat pretreated and raw sorbents exhibit a similar characteristic decay with the cycle number. By reintroducing the recarbonation stage in 12th cycle both sorbents are markedly reactivated. Note that although reactivation in the pretreated sorbent is more noticeable, carbonation in the recarbonation stage becomes appreciable also for the raw sorbent. This might be attributed to thermal
stresses to which the sorbent is subjected in the precedent c/c cycles lowering its resistance to diffusion. Ceramic materials usually experience internal failure when subjected to a sudden change in temperature (thermal shock) or repeated cycling between two temperatures (thermal fatigue) depending on the rates of heating/cooling and material thermomechanical properties [36]. If the material is quickly heated/cooled and its thermal conductivity is low (as it is the case of ceramics in general) it experiences intense tensile/compressive stress that may lead to rupture. Thermal stresses can be further accentuated by the occurrence of exothermical/endothermical reactions such as calcination/carbonation. SEM micrographs of raw limestone previously subjected to 40 c/c cycles (reported in [37]) show indeed cracks in the CaO crystalline structure, which are characteristic of brittle fracture in ceramics. Cracking of the crystal structure would facilitate CO$_2$ diffusion through the solid [38] thus intensifying diffusion controlled carbonation in the recarbonation stage.

Data of conversion at the end of the carbonation stage obtained from our mixed c/c - c/r/c tests are plotted in Fig. 6b, where data from full c/r/c cycling tests are replicated for comparison. After the 1st c/r/c cycle, conversion of the raw and pretreated samples is almost identical along the successive c/c cycles. When recarbonation is again introduced in the 12th cycle both samples exhibit a notable reactivation reaching values of conversion above those obtained for the fully c/r/c cycled sorbents. The relative increase of conversion is markedly important in the case of the heat pretreated sorbent but it becomes also remarkable for the raw sorbent, which can be a consequence of the enhancement of diffusion in the recarbonation stage of the 12th cycle caused by thermal stresses suffered during c/c previous cycling as discussed above. Thermal strains would be more intense for c/c cycling, which subjects the sorbent to higher temperature gradients as compared to c/r/c cycles. Hence, a practical recommendation for raw sorbent reactivation using c/r/c cycles would be to
subject it to recarbonation only when its activity is decreased below a critical value and thermal fatigue along the precedent c/c cycles allows for enhanced diffusion. As can be seen in Fig. 6b, conversion turns again to decay with the cycle number if the recarbonation stage is eliminated. This stage must be thus maintained to keep conversion at a high level.

Finally, it must be remarked that in TGA tests originally carried out to validate the novel CaL technology (based in c/r/c cycling [16]) the calcination atmosphere was air. In our work, we have employed similar calcination conditions to firstly reproduce the observed beneficial effect of recarbonation on the multicyclic behavior of a natural nonpretreated limestone and later on assess the influence of heat pretreatment. Nevertheless, it must be reminded that calcination is carried out in practice in a CO$_2$ rich environment (in fact the calciner is proposed as a source of CO$_2$ for the recarbonator [16]). Carbonation/calcination TGA tests [39] have shown that that the presence of CO$_2$ at high concentration in the calciner may have a great impact on the c/c multicyclic behavior of natural limestone. However, technical limitations prevent TGA tests from closely mimicking CaL conditions since the sorbent partially carbonated is prone to suffer further carbonation when the partial CO$_2$ pressure is increased for calcination until the temperature reaches a sufficiently high value to reverse the reaction towards decarbonation [39]. Thus, it would be difficult to further quantify the effect of a purposely introduced recarbonation stage. To this end, it would be desirable to have an accurate determination of the CO$_2$ concentration and temperature evolution in the transition between carbonation and calcination to be expected at practice, which can be determinant on the sorbent behavior. Ideally, the change of temperature in TGA multicyclic tests should be quick in order to better mimic the practical process wherein the sorbent is circulated between the carbonator and the calciner at high gas velocity. This critical issue will be the subject of a future work under preparation.
IV. CONCLUSIONS

To summarize, the work reported in this paper shows that the synergetic combination of heat pretreatment and recarbonation gives rise to a stable and high value of (limestone derived) CaO conversion in the carbonation stage of multicyclic carbonation/recarbonation/calcination tests. Our work evidences that solid-state diffusion is markedly enhanced during recarbonation of the heat pretreated limestone, which gives rise to a thermally stable CaO skeleton after decarbonation. This sorbent exhibits an almost constant value of conversion from the 2nd cycle substantially higher than the residual conversion of nonpretreated limestone, which is foreseen to allow reducing costs of the CaL technology. Nonetheless, it must be stressed that in our thermogravimetric analysis (as in previous works reported to validate the novel CaL concept based on recarbonation) the sorbent was cyclicly regenerated in air whereas the CO₂ partial pressure in the calciner is expected to be high in the practical application. Since calcination under high CO₂ partial pressure is expected to yield a pronounced intensification of sorbent sintering further tests should be performed wherein the calcination atmosphere in practice is more accurately mimicked in order to better assess the effect of recarbonation on the multicyclic sorbent behavior as well as the expectedly beneficial influence of heat pretreatment.

V. REFERENCES


FIG. 1. Time evolution of sorbent weight % during 50 carbonation/recarbonation/calcination cycles from the TGA multicyclic test for soon after heat treated and raw limestones. The dashed lines are drawn joining the points at the end of the carbonation stage of each cycle.
FIG. 2. Time evolution of weight % during the two first carbonation/recarbonation/calcination cycles from the TGA multicyclic test for soon after heat treated limestone. Fast (I) and diffusion controlled (II) carbonation during the carbonation stages are indicated.
FIG. 3. Conversion at the end of the carbonation stage as a function of the cycle number for raw and heat treated limestones. Results from ordinary carbonation/calcination cycles and carbonation/recarbonation/calcination cycles are plotted (carbonation under 15% CO$_2$ at 650°C and calcination in air at 850°C both stages for 5 min; recarbonation under 90% CO$_2$ for 3 min). Conversion data reported by Arias et al. [16] are reproduced for comparison (carbonation under 10% CO$_2$ at 650°C and calcination in air at 900°C both stages for 5 min; recarbonation under pure CO$_2$ for 3 min).
FIG. 4. XRD patterns of soon after (top) and overnight (bottom) heat treated (950°C for 12 h in air) samples.
FIG. 5. CO₂ avoided cost estimated from the simulation of the capture process integrated with a power plant as a function of sorbent price for different values of the purge flow in the calciner and low CaO/CO₂ molar ratio ($R = 1.5$). The figure shows the effect of increasing the maximum average capture capacity of the CaO solid population ($X_{\text{ave}}$). Adaptation of Fig. 8 originally reported in [7].
FIG. 6. a) Time evolution of sorbent weight % during a 1st carbonation/recarbonation/calcination cycle followed by 10 carbonation/calcination cycles and 11 carbonation/recarbonation/calcination cycles from the TGA multicyclic tests for heat treated and raw limestones. Evolution of temperature (right axis) is also shown. b) Conversion at the end of the carbonation stage as a function of the cycle number for raw and heat treated limestones obtained from these tests. Conversion values obtained from c/r/c multicyclic tests (shown in Fig. 3) are plotted for comparison.