Supporting information

Surface area measurements

200-300 mg of each sample was degassed at 300 ˚C for 2h under N_2 flow followed by a six point N_2 adsorption carried out at p/p_0 of 1 to 5 using a Nova® 2200 analyzer. The surface area was determined by the Nova® 2200 analyzer software using the B.E.T. method.[78] The degassing conditions were chosen based on the conditions used in earlier work for similar materials.[79,80] A six point adsorption is the recommended standard setting for determining surface area using the B.E.T. method according to the analyzer manufacturer. All surface area measurements are given in $m^2\ g^{-1}$.

TGA

Raw data

Fig. 16 show the raw TGA data for the $Ca(OH)_2$ experiment and the blank experiment.

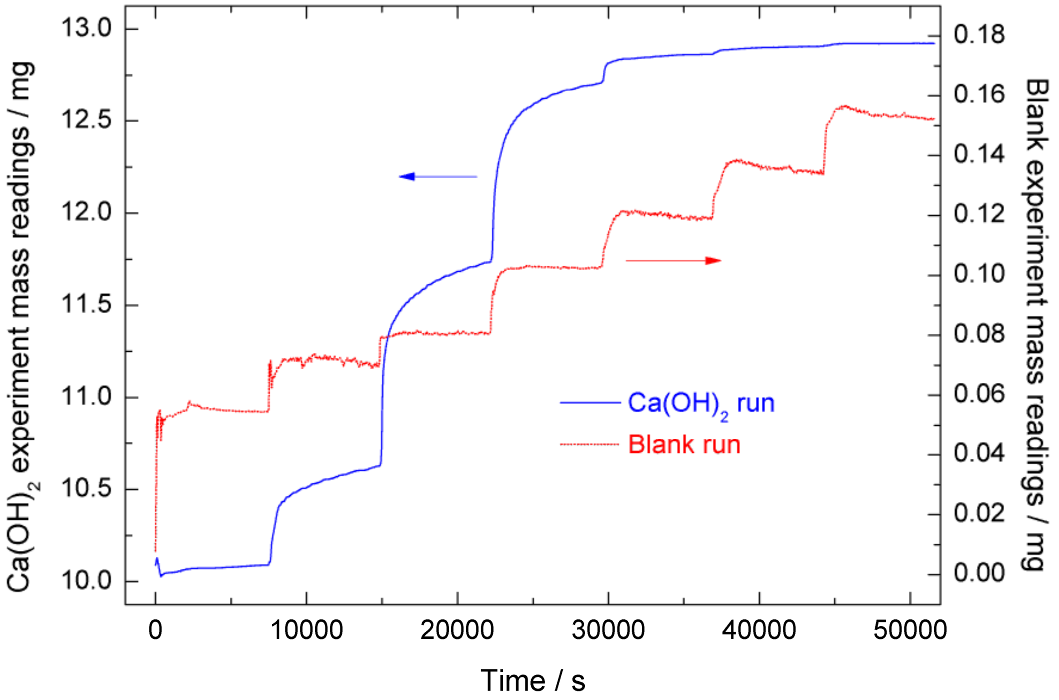

Figure 16. TGA raw data from the $Ca(OH)_2$ experiment and the blank experiment.

Decomposition of $Ca(OH)_2$

Decomposition of $Ca(OH)_2$ in N_2 was carried out by heating to 100, 200, 300, 400, 500, 600 and 700 ˚C with a 10 min temperature hold at each temperature and a ramp of 40 ˚C min^{-1}. The starting mass was 10 mg. Note that Rietveld refinement had revealed that the $Ca(OH)_2$ contained 3 wt% $CaCO_3$. Assuming this sample composition, the sample mass was converted to conversion to CaO (Fig. 17). Conversion began at 400 ˚C and reached 40% after 10 min. With a temperature increase to 500 ˚C the conversion rate increased and reached 80%. Complete conversion was reached at 700 ˚C. Note that the hold time here was 10 min and during the carbonation experiments the hold time was 2h. Therefore the decomposition of the $Ca(OH)_2$ can be expected to be much higher at the end of the each hold during the carbonation experiments. However the extent of the decomposition at any given time could not be accurately determined using the TGA setup and subsequently an assumption had to be made. Based on the data presented here, the more accurate assumption is that of complete decomposition.

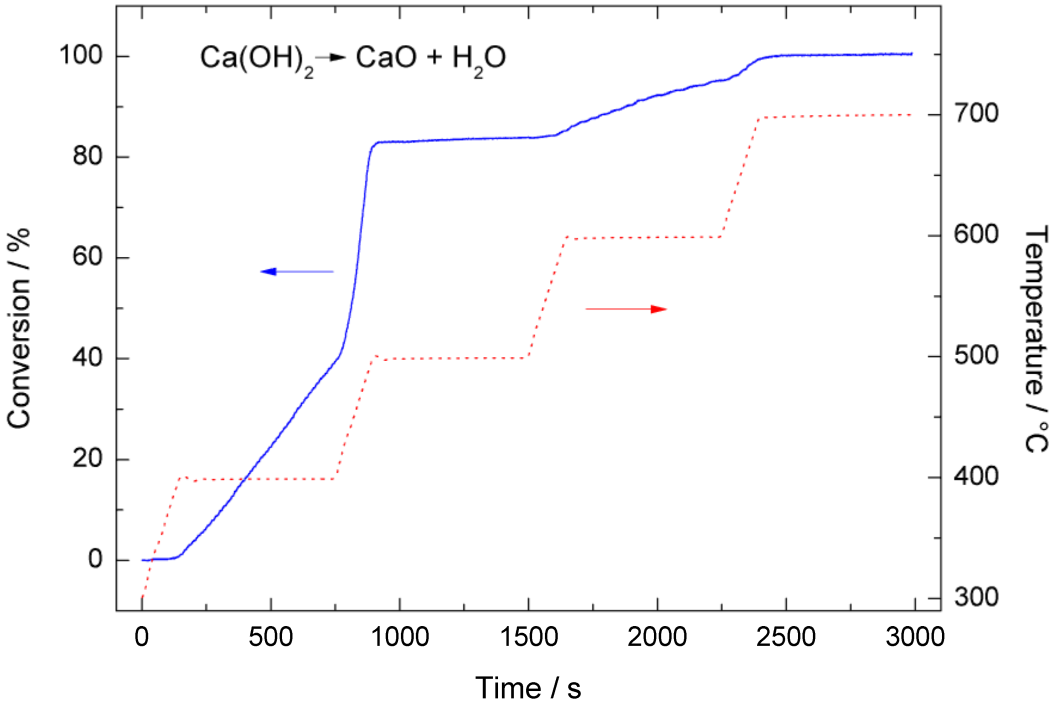

Figure 17. $Ca(OH)_2$ decomposition in the TGA system.

Details of XRD calibration

The XRD data, along with the model generated by the Rietveld refinement and residual for the XRD calibration with samples of known composition is shown in Fig. 18 to 22.

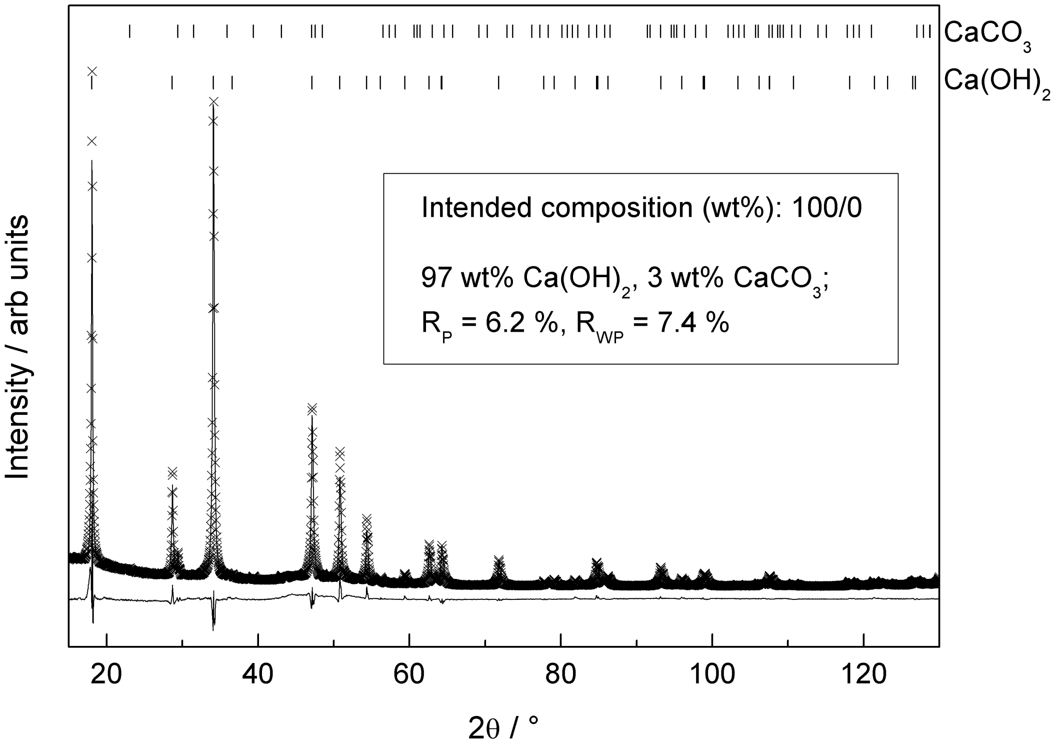

Figure 18. XRD spectra of a mixture of $Ca(OH)_2$ and $CaCO_3$ with an intended composition of 100 wt% $Ca(OH)_2$ and 0 wt% $CaCO_3$. Crosses = raw data, upper solid line = refinement model, lower solid line = residual. Insert showing phase composition (in wt.%), residual (R_P) and weighted residual (R_{WP}). Vertical lines show the expected positions of diffraction peaks for $Ca(OH)_2$ and $CaCO_3$.

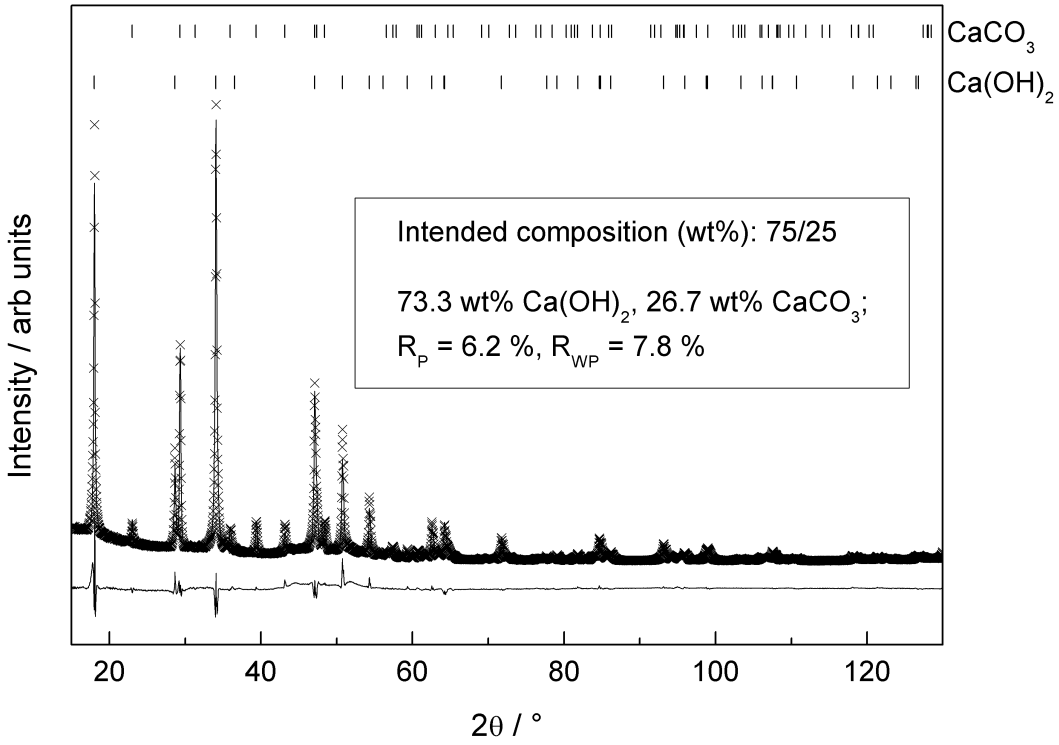

Figure 19. As for Fig. 18 with an intended composition of 75 wt% $Ca(OH)_2$ and 25 wt% $CaCO_3$.

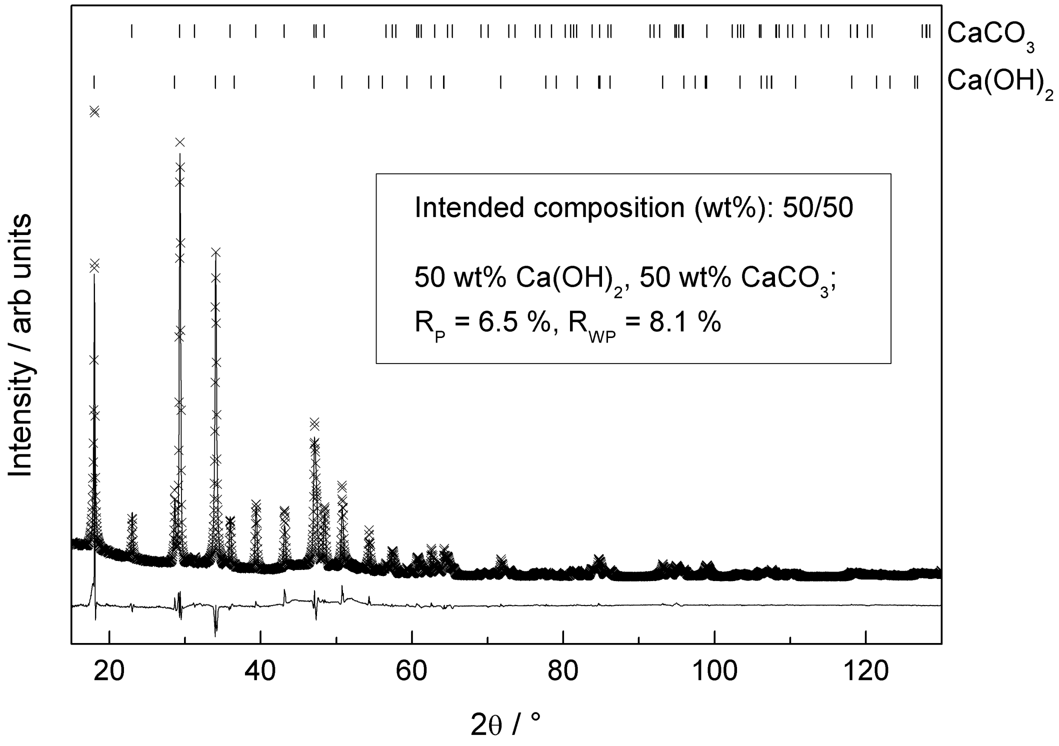

Figure 20. As for Fig. 18 with an intended composition of 50 wt% $Ca(OH)_2$ and 50 wt% $CaCO_3$.

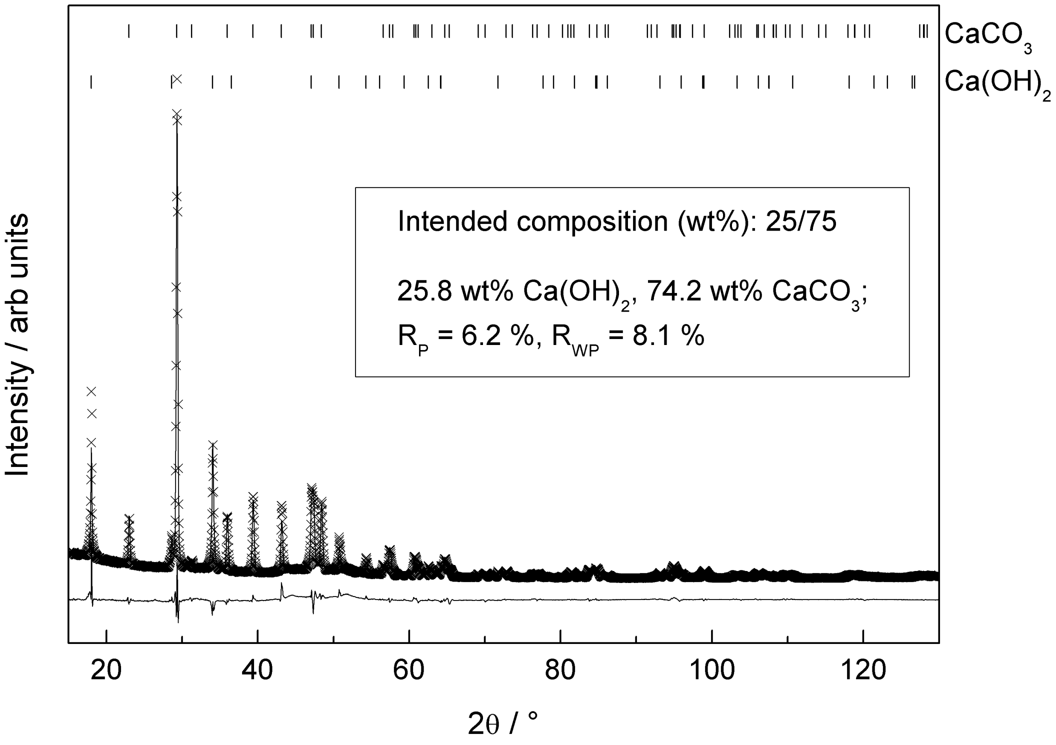

Figure 21. As for Fig. 18 with an intended composition of 25 wt% $Ca(OH)_2$ and 75 wt% $CaCO_3$.

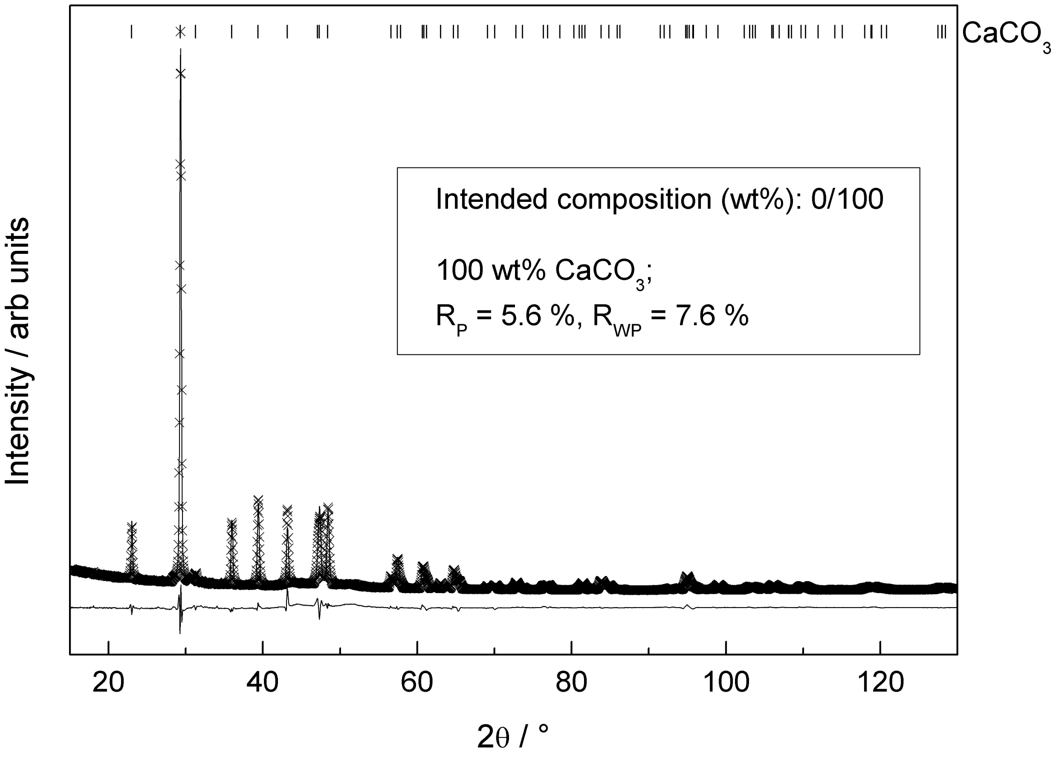

Figure 22. As for Fig. 18 with an intended composition of 0 wt% $Ca(OH)_2$ and 100 wt% $CaCO_3$.

$Ca(OH)_2$ phase peak broadening in partially hydrated CaO

The $Ca(OH)_2$ phase displayed a change in broadening with an increase in temperature during CO_2 capture. The highest intensity $Ca(OH)_2$ peak (at 2θ 34.1 ˚) is shown in Fig. 23 while the others are left out for clarity. The CaO peak at 2θ 32.2 ˚ is shown as a reference. Note that the peak broadening for the CaO phase is much smaller than for the $Ca(OH)_2$ phase. As the temperature was increased, this broadening was reduced and the peaks became sharper. Simultaneously, there was no change in peak broadening for the CaO phase. Above 300 ˚C the intensity of the $Ca(OH)_2$ peaks were reduced while the intensity of the CaO peaks remained stable.

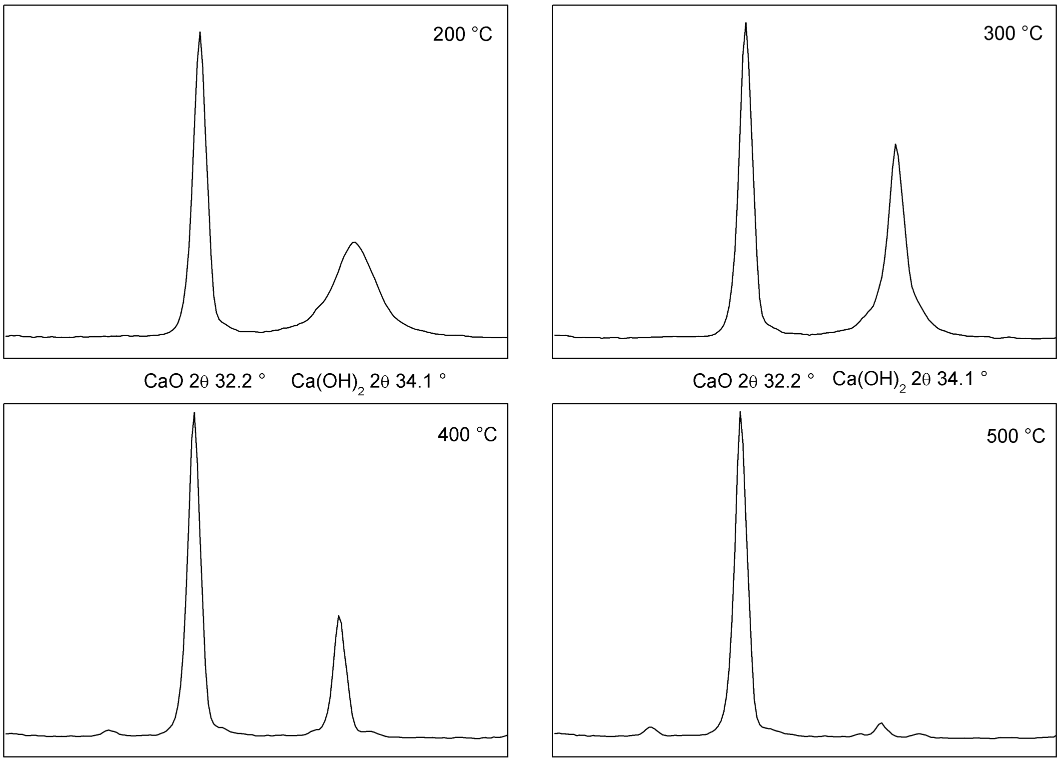

Figure 23. XRD spectra at 2θ 30-35 ˚ at temperatures of 200-500 ˚C displaying the broadening of the $Ca(OH)_2$ peak at 2θ 34.1 ˚ during CO_2 capture using partially hydrated CaO.

$CaCO_3$ microstrain during CO_2 capture of CaO

Microstrain was observed in the $CaCO_3$ phase during CO_2 capture using the pure CaO material (Section 2.1). This microstrain was originally 0.4% when the $CaCO_3$ phase was first observed in the material at 300 ˚C and was then reduced as the temperature was increased to reach zero at 600 ˚C (Fig. 24).

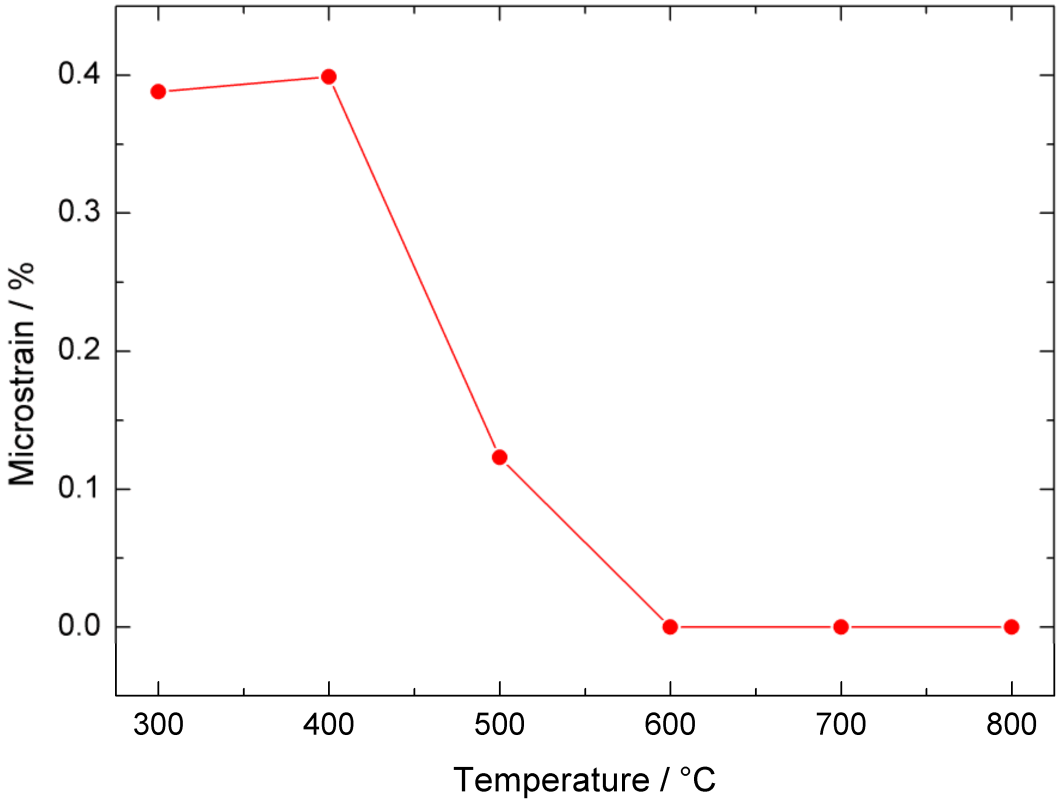

Figure 24. Microstrain in the $CaCO_3$ phase during CO_2 capture using the CaO material investigated in Section 2.1.

Note on the *in situ* XRD methodology

As outlined in Section 5, 12 scans were carried out at each temperature and a refinement was carried out on a sum of all 12 scans. This was done because a total scan time of 2h was needed to collect enough data to ensure a high quality refinement. However, given that the sample was converted over time a 2 h scan could not be used. Fig. 25 shows the results of scans nr 1, 6 and 12 collected for CaO at 500 ˚C. A close up of the scan range 2θ 46-50 ˚ revealed an increase in the intensity for two peaks corresponding to the calcite phase from scan 1 to 12 which incurred a minor error.

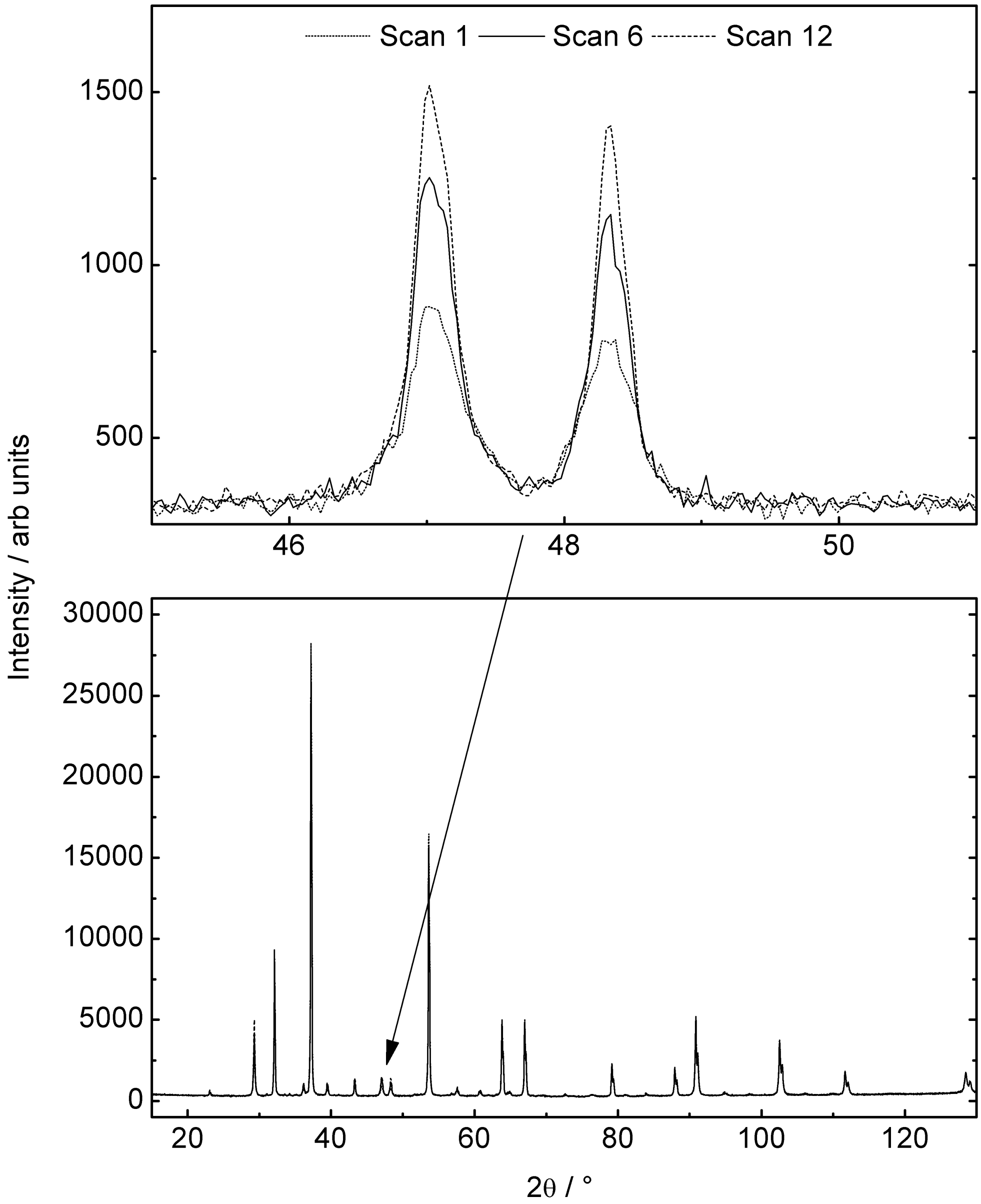

Figure 25. Details of individual scans (1, 6 and 12) during carbonation of CaO at 500 ˚C.

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