## **Electronic Supplementary Information**

# Effect of Molten Sodium Nitrate on the Decomposition Pathways of Hydrated Magnesium Hydroxycarbonate to Magnesium Oxide Probed by *In Situ* Total Scattering

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# 1. TGA/HF coupled with gas analysis (H<sub>2</sub>O, CO<sub>2</sub>)

Species released/decomposed*	HM expected**	HM observed	HM-20NaNO <sub>3</sub> expected**	HM-20NaNO <sub>3</sub> observed
H <sub>2</sub> O	15.4		12.8	
hydroxyl	3.8		3.2	
carbonate	37.6	35.8 (200-550 °C)	31.3	32.2 (200-500 °C)
$H_2O + hydroxyl$	19.2	19.4 (25-500 °C)	16.0	16.0 (25-500°C)
H <sub>2</sub> O + hydroxyl +	56.8	55.0	47.3	48.2

Table S1. Estimated and observed weight losses (%) related to the decomposition steps of hydromagnesite (HM)

\* Release of: H<sub>2</sub>O – water of crystallization, hydroxyl – condensation of hydroxyl groups, carbonate – decomposition of carbonate groups; \*\*expected values according to the chemical composition.

HM-20NaNO<sub>3</sub> releases less  $H_2O$  and  $CO_2$  than unpromoted HM. This is because the material contains NaNO<sub>3</sub>, which lowers the absolute amounts of  $H_2O$  and  $CO_2$  present in the sample.



Figure S1. (a) HF and (b) TGA signals of NaNO<sub>3</sub> upon heating up to 500 °C at 10 °C/min. The peak in the HF signal at 308 °C is related to the melting point of NaNO<sub>3</sub>.

## 2. In situ PDF-XRD analyses

#### Data acqusiton and processing

The X-ray total scattering data were collected at a sample-to-detector distances of ca. 26 cm for PDFs analysis, denoted as  $I(Q)_{26}$ , allowing a  $Q_{max}$  of 22 Å<sup>-1</sup>. Additionally, at the beginning and at the end of the *in situ* experiment, we have collected data at a sample-to-detector distance of ca. 83 cm for Rietveld refinement (i.e. allowing a higher resolution in 20 than in the PDF analysis and a  $Q_{max} = 11$  Å<sup>-1</sup>) denoted as  $I(2\theta)_{83}$  in Figure S2. Azimuthal integration and normalization of the incident beam intensity were performed using the pyFAI software package. The processing of the raw  $I(Q)_{26}$  data was carried out using the PDFgetX3 software allowing us to obtain the background-corrected scattering function I(Q), reduced total scattering structure function F(Q) and the reduced pair distribution function G(r).

The data processing is demonstrated on some exemplary total scattering data ( $HM_{(MgO-308)}$  and  $HM-20NaNO_{3(MgO-308)}$ ) in Figure S3. The PDF data of the CeO<sub>2</sub> standard was used to determine the damping and broadening parameters of the PDF peaks due to the experimental resolution ( $Q_{damp}=0.045$  Å<sup>-1</sup>;  $Q_{broad}=0.026$  Å<sup>-1</sup>). This is shown in Figure S20.



Figure S2. Workflow of the in situ total scattering experiments to obtain the PDF data.



Figure S3. Processing of representative total scattering data ( $HM_{(MgO-308)}$  and  $HM-20NaNO_{3(MgO-308)}$ ): (a) as obtained  $I(Q)_{26}$  without background correction, (b) background-corrected scattering function I(Q), (c) the reduced total scattering structure function F(Q) and (d) the pair distribution function G(r).



Figure S4. (a) Contour plot showing the evolution of the NaNO<sub>3</sub> XRD data (background-corrected I(Q) patterns) upon heating from 40 to 308 °C and isothermal transformation for 10 min at 308 °C. The main Bragg reflections for NaNO<sub>3</sub> (*R-3c* space group) are labelled; (b) the corresponding I(Q) patterns given as stacked plots.



Figure S5. Calculated total and partial PDFs of NaNO3 (R-3c space group, ICSD: 180912).



Figure S6. (a) Evolution of the peak position corresponding to the first Na–O distance in NaNO<sub>3</sub> upon heating as a function of temperature, (b) peak fittings of the PDF data, corresponding to the O–O and Na–O distances for selected data at 40, 240 and 290  $^{\circ}$ C.

Decomposition pathways in HM and HM-20NaNO<sub>3</sub>.



Figure S7. Rietveld refinement of the XRD data of HM measured at 40°C (Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O *P*<sub>2*l*/c</sub> space group, ICSD: 920).



Figure S8. Calculated total and partial PDFs of (a)  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$  (*P21/c* space group, ICSD: 920), (b)  $MgCO_3$  (*R-3c* space group, ICSD: 40117), (c) MgO (*Fm-3m* space group, ICSD: 9863).



Figure S9. The evolution of G(r) of (a) HM and (b) HM-20NaNO<sub>3</sub> in the range of 0–5 Å during thermal decomposition; zoomed in region contains the C–O and Mg–O correlations for (c) HM and (d) HM-20NaNO<sub>3</sub> samples. The arrows describe: Step 1 – release of crystallization water and dehydroxylation, Step 2 – decarbonation.



Figure S10. The evolution of the peak intensities corresponding to termination ripples (ca. 0.8 Å) and the peak at ca. 1.27 Å attributed to the C–O correlation (according to the crystal structure of HM and the corresponding simulated PDF in Figure S8) during heating from 40 to 475 °C for (a) HM and (b) HM-20NaNO<sub>3</sub>. The insets show the fittings at 225 °C. The decrease of the intensity of the peak at ca. 1.27 Å coincides with the decomposition of the carbonates (by TGA and MCR-ALS analyses, Figure 4).



Figure S11. Contour plots showing the evolution of the XRD data (background-corrected I(Q) patterns) during heating from 40 to 475 °C and holding for 15 min at 475 °C for (a) HM and (b) HM-20NaNO<sub>3</sub> (note that the intensity color scale is different in each of the graphs). The corresponding background-corrected I(Q) patterns, shown as stacked plots, for (c) HM and (d) HM-20NaNO<sub>3</sub> samples. The data were plotted in the range that contains the most relevant Bragg peaks.

The decomposition of HM to the final MgO took place through several intermediate stages. At temperatures below 210 °C, HM remained crystalline. The Bragg peaks disappeared at temperatures higher than 225 °C, which is associated with the release of water of crystallization from the structure of HM when correlated with the TGA results (Figure 1). The formation of intermediate amorphous magnesium carbonate (AMC) took place during the release of water of crystallization. No signs of the formation of crystalline components were observed below 435 °C, while the final MgO peaks were detected at temperatures above 435 °C upon decarbonation of the sample.

The presence of NaNO<sub>3</sub> led to considerable changes of the decomposition pathways of HM. The peaks of the crystalline HM were present in the sample at temperatures below 240 °C. In the temperature interval of 240–290 °C, the peaks gradually vanished, showing that the amorphous intermediate was formed and only the peaks corresponding to crystalline NaNO<sub>3</sub> were present in the sample in this temperature region. At a temperature of 305 °C the salt was partially molten (based on PDF results discussed in main text (Figure 2) and the TGA/HF result shown in Figure S1) and the formation of crystalline components was observed (peaks of MgCO<sub>3</sub> and MgO labelled in figure S8). No peaks corresponding to Mg(OH)<sub>2</sub> phase were present in the diffraction patterns.

## 3. Multivariate curve resolution- alternating least squares analysis (MCR-ALS)

## Description of the method

MCR-ALS is a powerful technique for the analysis of large datasets collected during time-resolved *in situ* experiments. It has the potential to separate the constituents of mixtures of unknown components when reference spectra are not available. From a mathematical point of view, the MCR-ALS analysis is described by the equation  $D = C^*S^T + E$ , where D is the initial unresolved mixture, and C (matrix) and S<sup>T</sup> (transpose matrix) are the concentration profiles and the pure spectra of the chemical constituents, respectively. E corresponds to the residuals (not explained by the model) and its value should be as close as possible to the experimental error. Importantly, the eigenvectors (components) obtained via MCR-ALS have a physical meaning. A comprehensive description of the technique and methodology of MCR-ALS is discussed in detail elsewhere.<sup>1-6</sup> In this study, we have applied MCR-ALS to determine the phase changes occurring during the decomposition of HM and HM-20NaNO3. The MCR-ALS decomposition of the data was carried out in the r-range of 0–7 Å. To avoid the ambiguity problem, a combination of data constraints (i.e. concentration profiles satisfy mass balance relations) for the concentration profiles. No constraints were set for the determination of the PDF components.-The quality of MCR-ALS deconvolution can be judged based on several quality indicators, such as the data variance (R) and lack of fit (LOF) and standard deviation of residuals ( $\sigma$ ):

$$R = 100 \sqrt{\frac{\sum_{i,j} d_{ij}^2 - \sum_{i,j} e_{ij}^2}{\sum_{i,j} d_{ij}^2}}}$$
$$LOF (\%) = 100 \sqrt{\frac{\sum_{i,j} e_{ij}^2}{\sum_{i,j} d_{ij}^2}}$$
$$\sigma = \sqrt{\frac{\sum_{i,j} e_{ij}^2}{n_{rows} n_{columns}}}$$

where  $d_{ij}$  is an element of the experimental data matrix and  $e_{ij}$  is the related residual value obtained from the difference between the experimental data and the reproduced data,  $n_{rows}$  and  $n_{column}$  are the number of rows and columns in the D matrix.<sup>2</sup> <sup>6</sup>

#### Initial determination of the number of components

As a first approach to estimate the number of principal components that are present in each *in situ* datasets, we performed a principal component analysis (PCA) using the PrestoPronto software. PCA is a dimension reduction tool for the identification of the number of components in multi-component mixtures. In contrast to MCR-ALS the obtained components have no physical meaning. To estimate the optimal number of meaningful principle components in the system, the so-called scree-plot (plot of the eigenvalues of the principal components versus the number of components considered) was used (Figure 12).<sup>6</sup> Nonetheless, the scree-plots can only provide a qualitative indication of the number of components (ultimately, some additional knowledge of the system obtained through e.g. XRD, TGA and the qualitative description of the PDF is required).

The linear-scale scree-plot obtained for the evolution of HM shows that 3 components are necessary to describe the system (Figure S12a). We observe a change in slope between the  $3^{rd}$  and  $4^{th}$  components. The first 3 components have eigenvalues larger than 1 (Figure S12b), therefore, according to the Kaiser criterion,<sup>7</sup> the initial estimate for the number of components was N = 3 for HM. The scree plots for HM-20NaNO<sub>3</sub> show that this system is more complex than HM (Figure S12d, e). Both the linear scale and logarithmic scale scree-plots show that the addition of a  $4^{th}$  component has a larger influence on the variance in for pure HM. The  $4^{th}$  component has an eigenvalue higher than 1. Thus, following Kaiser criterion the initial estimate for the number of components in HM-20NaNO<sub>3</sub> was N = 4.

According to MCR-ALS user guidelines the prior knowledge of the system under study should be used to corroborate the results of the MCR-ALS. We can correlate the initial estimate of the number of components with the number of magnesium-based phases determined by the initial qualitative assessment of the XRD and PDF data (HM, AMC and MgO for HM; and HM, AMC, crystalline MgCO<sub>3</sub> and MgO for HM-20NaNO<sub>3</sub>). This is in line with the TGA results that suggested a more complex decomposition pathway of HM-20NaNO<sub>3</sub> compared to HM. The selection of the number of components (N = 3 for HM and N = 4 for HM-20NaNO<sub>3</sub>) was further confirmed by MCR-ALS analysis performed for N–1 and N+1 components (vide infra).



Figure S12. PCA analysis: top panel HM, (a) linear and (b) logarithmic scree plots and (c) first 5 principle components obtained; bottom panel HM-20NaNO<sub>3</sub>, (d) linear and (r) logarithmic scree plots and (f) first 6 principle components obtained.

#### **Results of MCR-ALS analysis**

In the case of the HM precursor, the decomposition was finally described by 3 main components (C1, C2 and C3). C1: matches the initial HM PDF and C3: the obtained MgO, while C2 component lacks long-range order and matches well with the PDF acquired at 395 °C. The C2 component is therefore interpreted as AMC (as expected from XRD data).

For the HM-20NaNO<sub>3</sub> sample, 4 components were used. In this case, C1 is assigned to the mixture of crystalline HM and NaNO<sub>3</sub> through comparison with the initial PDF (i.e. data collected at 40°C, HM-20NaNO<sub>3-40</sub>). C2 was attributed to AMC (mixed with and NaNO<sub>3</sub>) as long-range correlations were no longer observed. C3 is attributed to crystalline MgCO<sub>3</sub> by comparing this component and the simulated PDF data for MgCO<sub>3</sub> compound (modelling parameters used are a(MgCO<sub>3</sub>)=4.673 Å; c(MgCO<sub>3</sub>)=15.069 Å; sp<sub>diameter</sub>=8.5 Å; U<sub>iso</sub>(Mg)=0.007 Å<sup>2</sup>; U<sub>iso</sub>(C)=0.004 Å<sup>2</sup>; U<sub>iso</sub>(O)=0.008 Å<sup>2</sup>). The assignment of C3 component to MgCO<sub>3</sub> (with NaNO<sub>3</sub>) is supported by XRD results that showed the presence of MgCO<sub>3</sub> phase (Figure S8). Finally, C4 can be related to crystalline MgO in a mixture with molten NaNO<sub>3</sub> (HM-20NaNO<sub>3(MgO)</sub>). The phase transitions of NaNO<sub>3</sub> were not resolved by this analysis due to a relatively low contribution of NaNO<sub>3</sub> to the total PDF data (Na:Mg molar ratio = 20:100) and the overlapping signal with MgO-based phases. The quality indicators (statistical parameters) of the MCR-ALS analysis are presented in Table S2 and S3 for HM and HM-20NaNO<sub>3</sub>, respectively.



Figure S13. Comparison of components obtained by final MCR-ALS analysis and experimental data of (a) HM collected at 40, 395 and 475 °C (HM40, HM395 and HM475) and (b) HM-20NaNO3 collected at 40, 290 and 475 °C (HM-20NaNO3-40, HM-20NaNO3-290, HM-20NaNO3-475) and simulated MgCO3.

## MCR-ALS results for different number of components (N) and statistical parameters

To estimate the viability of the deconvolution, we performed MCR-ALS analysis using N–1 and N+1 components, where N is the number of components used in the MCR-ALS analyses that are reported in Figures 4 and S13 (i.e. N = 3 for HM and N = 4 for HM-20NaNO<sub>3</sub>). Figure S14a shows the concentration profiles and the component PDFs obtained with 2, 3 and 4 components for HM. When using N = 2, the data does not account for the AMC intermediate. In this case, the component 1 is similar to HM but lacks some features. When adding a 3<sup>rd</sup> component, the statistical parameters show a considerable improvement, i.e. the standard deviation of the residuals (SD) decreases from 0.0304 to 0.0096 and the experimental lack of fit (LOF) from 7.04 % to 2.23 % (Table S2) when increasing the number of components from 2 to 3. Figure S13 shows that the identified components have a physical meaning as previously described (in Results of MCR-ALS analysis section and in Figure 4 of the main manuscript), ascribed to HM, AMC and MgO.When using N = 4, there is some improvement in the statistical parameters, i.e. : the SD decreased to 0.0074 and the LOF reduces to 1.64 % (Table S2). However, the 3<sup>rd</sup> and 4<sup>th</sup> component are very similar (same shape, but different intensity). This indicates that the 3<sup>rd</sup> and 4<sup>th</sup> components represent the same phase in our data (Figure S14f), thus, confirming that the system is well described by 3 components. The residual matrixes of the MCR-ALS analysis are shown in Figure S15 and confirm that the selection of 3 components is justified.

A similar analysis was carried out for HM-20NaNO<sub>3</sub> (Figure S16). When using N = 3, the concentration profile does not describe well the evolution of the phases. Also, the features of PDF components obtained do not represent real phases when compared to the available references. When the 4<sup>th</sup> component was introduced, the SD decreased from 0.0131 to 0.0076 and the LOF from 2.90 % to 1.69 % (Table S3). The introduction of a 5<sup>th</sup> component did not improve the statistical parameters appreciably (slight decrease of the LOF to 1.66 %, while the SD did not vary and was equal to 0.0075). In addition, comparing the features of the components obtained when using 5 components shows that components 1 and 2 (accountable for the mixture of HM and NaNO<sub>3</sub>) are very similar. This implies that introducing the 5<sup>th</sup> component is poorly justified (Figure S16c, f). Similar conclusions can be drawn from the analysis of the residuals (Figure S17c). Therefore, we conclude that a description of the evolution of HM-20NaNO<sub>3</sub> by four components describes the system best.



Figure S14. The results of the MCR-ALS analysis using 2 (a, d), 3 (b, e) and 4 (c, f) components to describe the decomposition of HM.

Table S2. Comparison of the goodness of the MCR-ALS using 2, 3 and 4 component to describe the decomposition of HM

	2 components	3 components	4 components
Standard deviation of residuals	0.0304	0.0096	0.0074
Fitting error (lack of fit, LOF) in % (PCA)	3.16	1.18	1.05
Fitting error (lack of fit, LOF) in %			
(experimental)	7.04	2.23	1.64
% of variance explained	99.5	99.95	99.97



Figure S15 Matrix of residuals of the MCR-ALS analysis using 2 (a), 3 (b), and 4 (c) components to describe the decomposition of HM.



Figure S16. The results of MCR-ALS analysis using 3 (a, d), 4 (b, e) and 5 (c, f) component to describe the decomposition of HM-20NaNO<sub>3</sub>.

Table S3. Comparison of the goodness of MCR-ALS using 3, 4 and 5 components to describe the decomposition of HM-20NaNO3

	3 components	4 components	5 components
Standard deviation of residuals	0.0131	0.0076	0.0075
Fitting error (lack of fit, LOF) in % (PCA)	0.76	0.71	1.42
Fitting error (lack of fit, LOF) in % (experimental)	2.9	1.69	1.66
% of variance explained	99.92	99.97	99.97



Figure S17. Matrix of residuals of the MCR-ALS analysis using 3 (a), 4 (b) and 5 (c) component to describe the decomposition of HM-20NaNO<sub>3</sub>.

## 4. Synthesis of highly crystalline MgCO3 reference for the PDF analysis

The crystalline MgCO<sub>3</sub> reference material was produced via hydrothermal synthesis. The Mg ribbon (Sigma Aldrich,  $\geq$ 99.5%; 0.045 mol), urea (Acros Organics,  $\geq$ 99.5%; 0.050 mol) and 30 mL of deionized water were added to a 45-ml Teflon-lined stainless-steel autoclave. The autoclave was kept in an oven at 160 °C for 48 h. After cooling down to room temperature, a white material was extracted by filtration and thoroughly washed with deionized water and ethanol. The final powder was then dried at 120 °C for 12 h. The XRD data showed that the material is highly crystalline exhibiting a calcite-type structure (*R*-3*c* space group). PDF data were collected as a reference for the analysis at 40°C and 308°C (data at 308°C is shown in Figure S9b).

## 5. Structural characterization of MgO produced from HM and HM-20NaNO3



Figure S18. Results of the Rietveld refinement of the XRD patterns of (a)  $HM_{(MgO-308)}$  and (b)  $HM-20NaNO_{3(MgO-308)}$ . A crystalline MgO structure (*Fm-3m* space group, ICSD: 9863) was applied in the refinement. The data collected in the empty capillary are plotted to show the background signal.

### Peak broadening analysis: microstructure

The average crystallite size of MgO in HM<sub>(MgO-308)</sub> and HM-20NaNO<sub>3(MgO-308)</sub> was determined using peak broadening analysis using the full profile Rietveld refinement (FullProf software package).<sup>8</sup> The instrumental function was determined via the refinement of a CeO<sub>2</sub> standard (Table S4). Since microstrain (due to variations in the lattice parameters across the individual crystallites) can also influence peak broadening, we have modeled the broadening of the Bragg peaks considering the contribution from both crystallite sizes and microstrain. Microstrain and size have a different dependence on the Bragg angle, therefore, it is possible to separate their contributions to the overall peak broadening. Thus, the peak broadening analysis implemented in FullProf provides the average crystallize sizes and microstrain (the details of the line broadening analysis obtained during the refinements in Table S5, S6).<sup>9</sup> We assume isotropic size and strain broadening (i.e. uniform in all crystallographic directions) with Lorentzian and Gaussian breadth for size and microstrain broadening, respectively.

Table S4. Parameters of the instrumental resolution function determined using a  $CeO_2$  standard ( $U_{ins}$ ,  $V_{ins}$  and  $W_{ins}$  are the half-width Caglioti parameters).<sup>9</sup>

$U_{ins}$	$V_{\text{ins}}$	$\mathbf{W}_{\text{ins}}$
0.033385	-0.00149	0.001086

$s=1/d_{hkl}$	$\beta_G$	$\beta_L$	β	h	k	1	20
0.41	5.07	26.13	27.25	1	1	1	4.16
0.47	5.85	26.13	27.70	2	0	0	4.80
0.67	8.28	26.13	29.40	2	2	0	6.79
0.78	9.71	26.13	30.54	3	1	1	7.96
0.82	10.14	26.13	30.90	2	2	2	8.32
0.95	11.71	26.13	32.21	4	0	0	9.61
1.03	12.76	26.13	33.10	3	3	1	10.47
1.06	13.09	26.13	33.38	4	2	0	10.75
1.16	14.34	26.13	34.46	4	2	2	11.78
1.23	15.21	26.13	35.22	3	3	3	12.49
1.23	15.21	26.13	35.22	5	1	1	12.49
1.34	16.55	26.13	36.41	4	4	0	13.60
1.40	17.31	26.13	37.08	5	3	1	14.23
1.42	17.56	26.13	37.30	4	4	2	14.43
1.42	17.56	26.13	37.30	6	0	0	14.43
Average apparent size (nm) 3.8							
Average maximum strain (%) 0.62						2	

Table S5. Results of the peak broadening analysis of the XRD pattern of HM(MgO-308) using FullProf\*

Table S6. Results of the peak broadening analysis of the XRD pattern of HM-20NaNO3(MgO-308) using FullProf \*

s= 1/d <sub>hkl</sub>	$\beta_G$	$\beta_{\rm L}$	β	h	k	1	20
0.41	1.97	9.32	9.81	1	1	1	4.16
0.47	2.27	9.32	9.99	2	0	0	4.81
0.67	3.21	9.32	10.69	2	2	0	6.80
0.79	3.76	9.32	11.14	3	1	1	7.97
0.82	3.93	9.32	11.28	2	2	2	8.33
0.95	4.54	9.32	11.80	4	0	0	9.62
1.03	4.95	9.32	12.15	3	3	1	10.49
1.06	5.08	9.32	12.26	4	2	0	10.76
1.16	5.56	9.32	12.68	4	2	2	11.79
1.23	5.90	9.32	12.98	3	3	3	12.51
1.23	5.90	9.32	12.98	5	1	1	12.51
1.34	6.42	9.32	13.44	4	4	0	13.62
1.40	6.71	9.32	13.71	5	3	1	14.25
1.42	6.81	9.32	13.79	4	4	2	14.45
1.42	6.81	9.32	13.79	6	0	0	14.45
Average apparent size (nm)					10.7		
Average maximum strain (%) 0.24							

\*s=1/d<sub>hkl</sub>: reciprocal distance, Å<sup>-1</sup>;  $\beta_G$ ,  $\beta_L$ ,  $\beta$ : Gaussian, Lorentzian and Total Integral Breadth, Å<sup>-1</sup>; d<sub>hkl</sub>: the distance between hkl planes, Å; h, k, l: Miller indexes, 2 $\theta$ : Bragg position, °.



Figure S19. Comparison of the PDFs of HM<sub>(MgO-308)</sub> and HM-20NaNO<sub>3(MgO-308)</sub> in (a) full r-range 0-60 Å and (b) inset in the short range, between 0-8 Å.



Figure S20. Results of the PDF fitting of the reference CeO<sub>2</sub>:  $Q_{damp}$ =0.045 Å<sup>-1</sup>;  $Q_{broad}$ =0.026 Å<sup>-1</sup>.



Figure S21. Results of the PDF fitting of (a)  $HM_{(MgO-308)}$  and (b)  $HM-20NaNO_{3(MgO-308)}$ ; the fitting of the local structure of (c)  $HM_{(MgO-308)}$  and (d)  $HM-20NaNO_{3(MgO-308)}$ . A crystalline MgO structure (*Fm-3m* space group, ICSD: 9863) was applied in the fitting.

#### 6. PDF analysis of the carbonation of HM(MgO-308) and HM-20NaNO3(MgO-308)



Figure S22. PDFs obtained during CO<sub>2</sub> flow (5 ml/min CO<sub>2</sub>, 308°C, carbonation treatment) of (a) HM<sub>(MgO-308)</sub> and (b) HM-20NaNO<sub>3(MgO-308)</sub>, t<sub>carb</sub> = carbonation time; PDF data is plotted in the range of 0-6 Å.



Figure S23. Linear combination fitting (LCF) of PDF data for (a)  $HM_{(MgO-308)}$  and (b) HM-20NaNO<sub>3(MgO-308)</sub> during carbonation (5 ml/min CO<sub>2</sub>, 308°C).

After thermal treatment in N<sub>2</sub> at 475 °C, the materials were cooled down and held at 308 °C. *In situ* carbonation experiments were performed by switching from a N<sub>2</sub> to a CO<sub>2</sub> flow (5 ml/min) for 30 min. The evolution of the PDFs of both samples are plotted in Figure S13.

To describe the carbonation degree as a function of time under  $CO_2$  flow, linear combination fitting (LCF) analysis was carried out. The PDF of (crystalline) MgCO3 (data collected at 308 °C) was used as

a reference for the fitting of both samples. The PDF of either  $HM_{(MgO-308)}$  or  $HM-20NaNO_{3(MgO-308)}$  were used as a second reference in the fitting. The LCF was performed in the range of distances from r = 1 to 6 Å (Figure S14) for each PDF data collected (Figure S13).

The results of the LCF for HM-20NaNO<sub>3(MgO-308)</sub> show a gradual conversion of MgO to MgCO<sub>3</sub> during the 30 min of CO<sub>2</sub> treatment. The carbonation curve is of sigmoidal shape, typical of nucleation and growth processes<sup>10</sup> and similar to our previous TGA observation.<sup>11</sup>At the end of the carbonation reaction, the sorbent contained 80 wt.% of MgCO<sub>3</sub> and 20 wt.% HM-20NaNO<sub>3(MgO-308)</sub>.

In the case of  $HM_{(MgO-308)}$ , during the first 7 min the LCF showed that only ~4 wt. % MgCO<sub>3</sub> was formed and no further significant changes were observed. The behaviour was also similar to the one observed for the carbonation of pristine MgO in our previous TGA experiments.<sup>11</sup>

7. Morphological characterization of MgO obtained by thermal treatment of HM and HM-20NaNO<sub>3</sub>



Figure S24. TEM images of (a) HM precursor, (b) HM after thermal treatment at 450°C, (c) HM-20NaNO<sub>3</sub> precursor, and (d) HM-20NaNO<sub>3</sub> after thermal treatment at 450°C.

Precursor	$A_{BET}, m^2/g$	Pore volume, cc/g	Pore diameter, nm
HM	306	0.63	3.6
HM-20NaNO <sub>3</sub>	33	0.25	1.0

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