	Experiment title: Alkali metal nitrate (MNO_3, M= K, Li) promoted MgO for CO_2 capture: time resolved *in situ* studies on MgO and $MgCO_3$ formation	**Experiment number**: **EV-337**
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Report:

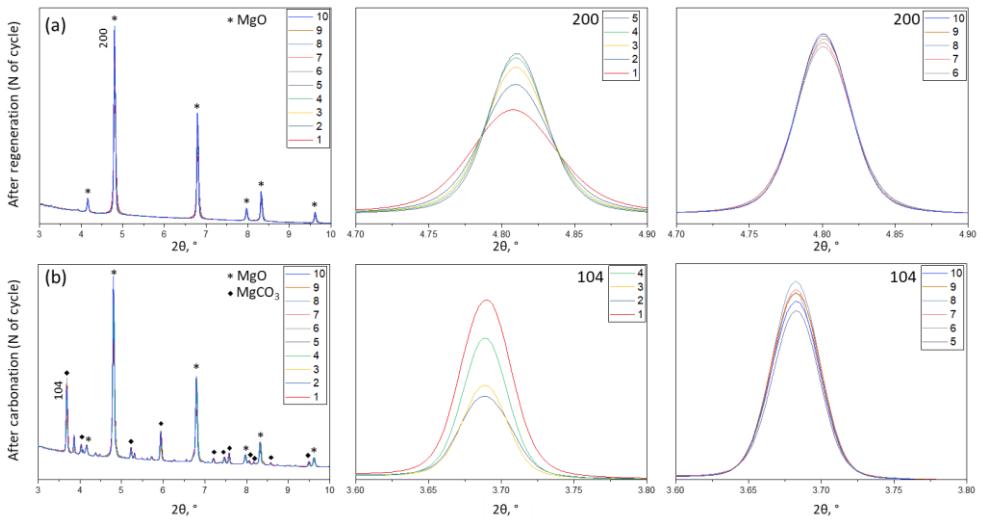

Figure 1. *XRD patterns of MgO-20$NaNO_3$* ***(a)*** *after regeneration, full patterns and insets to the MgO (200) reflection ,* ***(b)*** *after carbonation, full patterns and insets to the $MgCO_3$ (104) reflection.*

The aim of this proposal is to study the structural changes taking place under working conditions in MgO-based CO_2-sorbents. Total scattering experiments have been carried out during carbonation and regeneration processes on a $NaNO_3$-modified MgO sorbent in cyclic operation. For this experiment, the material, MgO-20$NaNO_3$ (molar ratio $NaNO_3$/MgO=0.2), was prepared by mixing MgO and $NaNO_3$ powders. The experiments were carried out in a quartz capillary cell (1.0 mm outer diameter) heated by a gas blower. The sample was first pre-treated at 450 °C under N_2 (7 ml/min); and afterwards subjected to 10 cycles of carbonation-regeneration. The carbonation was performed at 315 °C, under a flow of 7 ml/min of CO_2, followed by a regeneration step at 450 °C under 7 ml/min of N_2. The overall time of the

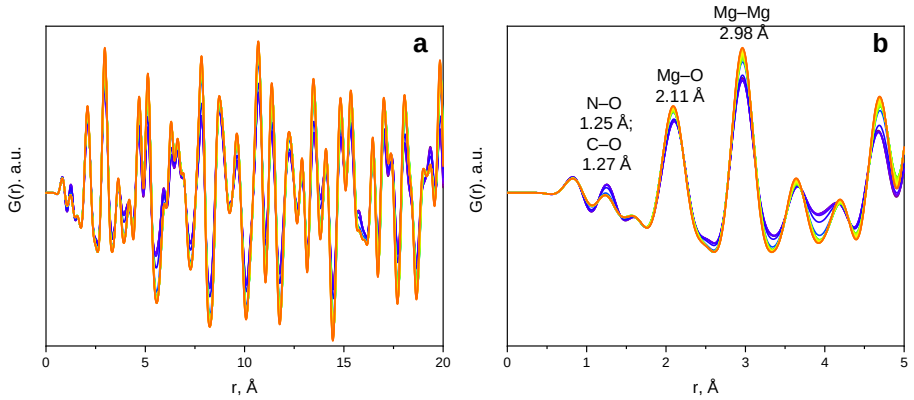

Figure 2. *PDFs obtained during the regeneration treatment of the sorbent in the 9th cycle, PDFs are shown in the ranges* ***(a)*** *0–20 Å* ***(b)*** *0–5 Å with main interatomic distances marked.*

cyclic experiment was ~26 hours. Reference compounds (MgO, $MgCO_3$, $NaNO_3$) were studied under *in situ* conditions (ramp from 50°C to 315°C under 7 ml/min N_2 for MgO and $NaNO_3$ and under 7 ml/min CO_2 for $MgCO_3$). The wavelength was set to 0.1771 Å and the data were collected using a Pilatus3 X CdTe 2M detector positioned at two different sample-to-detector distances (d=83cm and d=23cm for XRD and PDF data analysis, respectively). The data acquisition during each carbonation cycle was the following: i) Time resolved (1s) XRD data were acquired at during the first 50 min of carbonation process to capture the fast changes that may occurring at the beginning of the carbonation stage (as observed in a previous experiment MA-3415). ii) In the following 40 min of carbonation, XRD and PDF data were acquired alternately (time resolution=60s). We should mention that several problems with the data acquisition software occurred during experiment. The ESRF local contact and computing staff have intervened actively to solve the problems.

The overall experiment gave relevant information about the carbonation and regeneration processes. Rietveld refinements of the data in reciprocal space as well as the analysis in real space by PDF have been performed using TOPAS software package. The results of Rietveld refinement combined with kinetic modelling (Avrami-Erofeev model) show the deactivation-activation behavior of the sorbent, which has been attributed to the interplay between increase in average crystallite size of MgO and formation of minor amounts of additional Na_2CO_3/$Na_2Mg(CO_3)_2$ phases (to the best of our knowledge they have never been reported to form during the cycling before). The formation of the phases is associated with the partial decomposition of the molten promoter during regeneration step and further interaction of the decomposition products with CO_2 during the carbonation step. The results of the combined XRD and PDF analyses provide comprehensive understanding of factors affecting the cyclic performance of the sorbent (both for crystalline phases and liquid promoter). A manuscript summarizing the obtained observations is currently under preparation.