	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:

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 in a mortar. 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 (Figure 1). The overall time of the

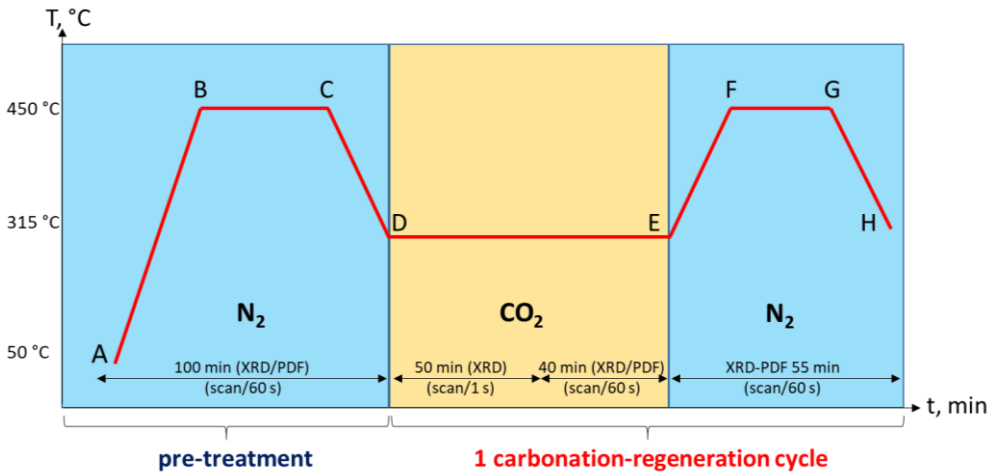

Figure 1. *Scheme of the temperature profile and gases applied during cyclic experiment: pre-treatment and 1 carbonation-regeneration cycle. The carbonation-regeneration cycle was repeated 10 times.*

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 0.177Å 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. However, we lost track of the data at several stages in the experiment. In spite of this, the overall experiment gave relevant information about the carbonation and regeneration processes. Figure 2 shows the XRD patterns collected at the begging (point D in Figure 1) and at the end (point E in Figure 1) of each carbonation cycle. Rietveld refinements of the data in reciprocal space as well as the analysis in real space by PDF is under progress. The preliminary observations are briefly described as follows: i) Upon cyclic operation, the material shows a complex evolution of the carbonation rate. After the first carbonation cycle a sudden drop of the extent of carbonation is observed (deactivation). From cycle 2 to cycle 8, carbonation extend steadily increases (re-activation). For cycle 9 and 10, the carbonation extend slightly decreases. ii) Crystal growth of MgO phase is observed upon cycles, however, the carbonation performance of sorbent does not continuously decrease, suggesting that other aspects than crystal growth affect the performance of the sorbent upon cyclic operation. The reason of the deactivation is being investigated based on Rietveld and PDF analyses (currently under progress). The results of the XRD and PDF analyses are expected to give comprehensive understanding of factors affecting the cyclic performance of the sorbent. A manuscript is expected to be published based on these results within the following months.

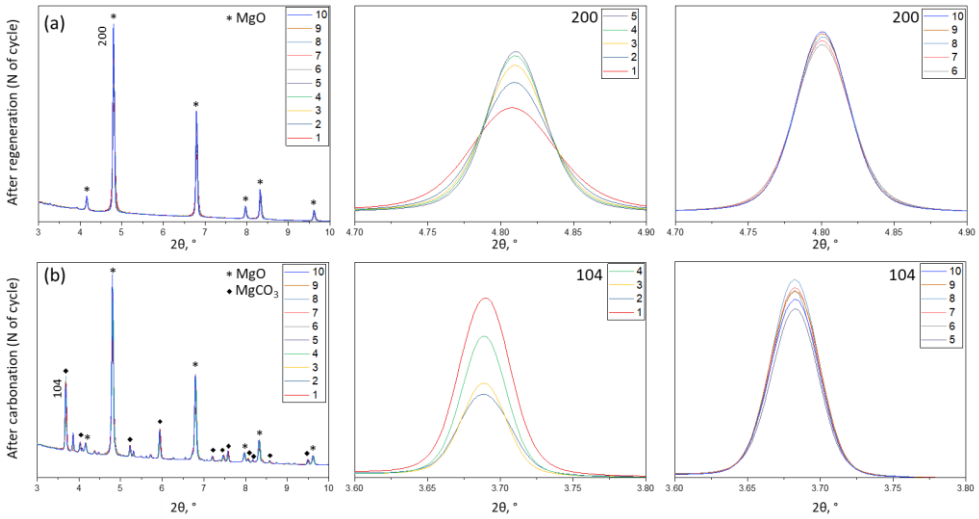

Figure 2. *XRD patterns of MgO-20$NaNO_3$* ***(a)*** *after regeneration(point D, Figure 1), full patterns and insets to the MgO (200) reflection ,* ***(b)*** *after carbonation (point E, Figure 1) full patterns and insets to the $MgCO_3$ (104) reflection.*