



Doc.nr: CATO2-WP1.2F2-D04  
Version: 2013.08.29  
Classification: Public  
Page: 1 of 13

Structure Activity Relationships

---



## CATO-2 Deliverable WP1.2F2-D04

# Report on quantitative structure-activity relationships for nano sized oxide particles and CO<sub>2</sub> capture properties

Prepared by: A.M. Frey  
Reviewed by: P.D. Cobden  
Approved by: J.Brouwer  
(CATO-2 Director)

A handwritten signature in blue ink, likely belonging to J. Brouwer.



## 1 Executive Summary (restricted)

The structure activity relationship of for bulk high surface area CaO and Mg-modified MgO-CaO materials was investigated in order to evaluate the role of Mg in changing the properties of these CO<sub>2</sub> adsorption materials for CO<sub>2</sub> capture under different conditions.

Materials were prepared by sol-gel synthesis, and the influence of synthesis parameters such as water evaporation temperature, metal nitrate to citrate ratio, drying temperature, calcination temperature, heat rate and time were investigated to obtain an optimal high surface area. The materials were examined with SEM, EDX, TEM, BET, Rietveld analysis and CO<sub>2</sub>-TPD.

Magnesium seems to have a promising effect for stability and the possibility for regeneration for sorbent prepared with the sol gel method, but when impregnating it to commercial CaO it has no stabilizing effect. The location of Mg must thus be considered crucial for the impact on the performance of CaO CO<sub>2</sub> capture materials



## Structure Activity Relationships

---

### Distribution List

(this section shows the initial distribution list)

External	copies	Internal	Copies
Harry Bitter	1	Paul Cobden	1
Anne Mette Frey	1	Wim Haije	1
Krijn de Jong	1	Daan Jansen	1
Hans Geerlings	1		

### Document Change Record

(this section shows the historical versions, with a short description of the updates)

Version	Nr of pages	Short description of change	Pages

### Table of Content

<b>1</b>	<b>Executive Summary (restricted)</b> .....	<b>2</b>
<b>2</b>	<b>Applicable/Reference documents and Abbreviations</b> .....	<b>4</b>
2.1	Applicable Documents .....	4
2.2	Reference Documents .....	4
2.3	Abbreviations .....	4
<b>3</b>	<b>Report on quantitative structure-activity relationships for nano-sized oxide particles and CO<sub>2</sub> capture properties:</b> .....	<b>5</b>

## 2 Applicable/Reference documents and Abbreviations

### 2.1 Applicable Documents

(Applicable Documents, including their version, are documents that are the “legal” basis to the work performed)

	Title	Doc nr	Version
AD-01d	Toezegging CATO-2b	FES10036GXDU	2010.08.05
AD-01f	Besluit wijziging project CATO2b	FES1003AQ1FU	2010.09.21
AD-02a	Consortium Agreement	CATO-2-CA	2009.09.07
AD-02b	CATO-2 Consortium Agreement	CATO-2-CA	2010.09.09
AD-03g	Program Plan 2013b	CATO2-WP0.A-D03	2013.04.01

### 2.2 Reference Documents

(Reference Documents are referred to in the document)

	Title	Doc nr	Issue/version	date

### 2.3 Abbreviations

(this refers to abbreviations used in this document)

CCS	Carbon Capture and Sequestration
PC	Pulverised coal power plant
Oxyfuel	Oxyfuel power plant
IGCC	Integrated Gasification combined Cycle
NGCC	Natural Gas Combine Cycle
MFC	Mass Flow Controller
SSA	Specific Surface Area
BET	Brunauer, Emmett and Teller
XRD	X-ray diffraction
TEM	Transmission Electron Microscope
EDX	Energy-Dispersive X-ray Spectroscopy
DFT	Density Functional Theory
TPD	Temperature Programmed Desorption

### 3 Report on quantitative structure-activity relationships for nano-sized oxide particles and CO<sub>2</sub> capture properties:

#### CaO and Mg promoted CaO as post combustion CO<sub>2</sub> capture materials

Anne Mette Frey, Dagmar Tulner, Krijn de Jong and Harry Bitter, Utrecht University

##### Goal

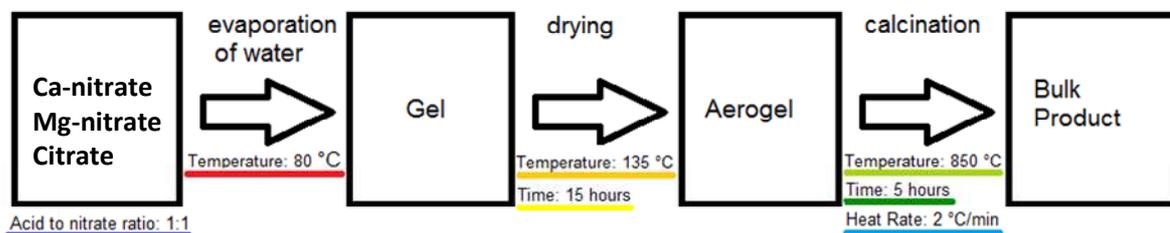
The goal of this study is to evaluate bulk high surface area CaO and MgO-CaO materials for CO<sub>2</sub> capture and to investigate the impact and role of the magnesium.

The materials were prepared by sol-gel synthesis. The influence of synthesis parameters such as water evaporation temperature, metal nitrate to citrate ratio, drying temperature, calcination temperature, heating rate and time were varied in order to obtain an optimal high surface area.

##### Material prepared by sol gel methods:

5.00 g Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (+or 0.42 g or 0.85 g Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) for respectively 5 and 10 wt% Mg containing sample) was dissolved in 25 ml water to which 4.50 g citric acid dissolved in 15 ml water was added (250 ml beaker). The temperature was adjusted to 80 °C while stirring and kept at that temperature until a pale yellow gel was formed. Next the gel was dried in an oven at 135 °C in static air in the beaker for 15 h whereby an intensely colored yellow foam with a volume of around 150 ml was formed. The foam was crushed and heat treated in static air at 850 °C (2 °C/min) for 5 h. The resulting white product, 1.16 g, 20 ml for CaO, 1.24 g, 35 ml for the 10wt% MgO-CaO sample and 1.16 g for the 5 wt% MgO-CaO sample<sup>1</sup>.

The sol-gel method is summarized in the scheme below:



##### Characterization

##### *Specific surface area:*

## Structure Activity Relationships

N<sub>2</sub> physisorption was used to determine the specific surface area, SSA, of the bulk CaO and the Mg containing CaO samples. The standard preparation method described above resulted in a SSA of 10 m<sup>2</sup>/g for CaO and 15 m<sup>2</sup>/g for 5% Mg CaO. This was reproduced finding respectively 11 and 15 m<sup>2</sup>/g for the reproduced sample. Since literature<sup>1</sup> claims that it is possible with this method to obtain SSA of CaO ~40 m<sup>2</sup>/g different parameters i.e. the evaporation temperature of the water to form the gel, the drying temperature, the calcination temperature, rate and time were varied with the expectation that the surface area increased. The SSA's of the CaO and 5% Mg in CaO obtained this way are displayed in Table 1. The standard synthesis described in detail in the experimental is marked with a grey color bar and can thus be compared to the samples where one of the parameters are changed as described in the colored text above the values in the table.

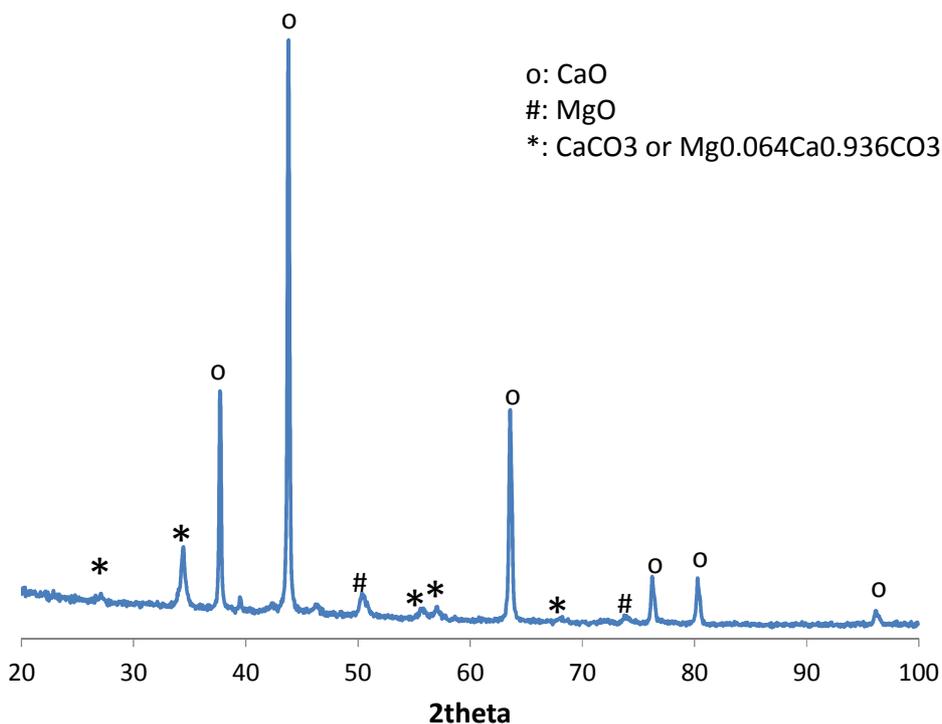
**Table 1:** Specific surface area of CaO and 5% Mg containing CaO prepared in different ways. The gray bar indicates the standard synthesis method. This sample is compared to materials where one synthesis parameter (as indicated with the color bars) has been changed.

BET surface area m <sup>2</sup> /g				BET surface area m <sup>2</sup> /g			
evaporation temperature		CaO	CaO 5 wt% MgO	calcination temperature		CaO	CaO 5 wt% MgO
60 ° C	1a	16	14	800 ° C	3a	19	18
80 ° C	4b	10	15	850 ° C	4b	10	15
100 ° C	1c	13	17	900 ° C	3b	16	15
drying temperature				1000 ° C	3c	11	13
100 ° C	2a	17	21	calcination time			
130 ° C	4b	10	15	1 hour	4a	16	13
150 ° C	2c	16	20	5 hours	4b	10	15
drying time				Reproduced 5 hours	4b REP	11	15
5 hours	7a	15	21	10 hours	4c	6	9
10 hours	7b	15	21	heat rate calcination			
15 hours	4b	10	15	1 ° C / min	5a	18	16
20 hours	7c	13	19	2 ° C / min	4b	10	15
				5 ° C / min	5c	17	18
				acid to nitrate ratio			
				1 to 1	4b	10	15
				2 to 1	6c	16	16

As seen from the screening in the table it is very difficult to draw definite conclusion of the impact of a given parameter. The trends for the CaO and the 5% Mg in CaO are furthermore not the same. However, a few indications about the optimal synthesis route can be deduced: low calcination temperature (800 °C) and short calcination time (most likely between 1 and 5 h) seems to be beneficial for obtaining high SSA products. By keeping the calcination temperature at around 800 °C SSA ~ 20 m<sup>2</sup>/g can be obtained for CaO thus a factor 2 higher than the initial sol-gel synthesis attempt. In order to gain insight in the location of the Mg in the Mg containing CaO samples the samples were characterized by XRD and TEM.

### XRD and Rietveld analysis

Here the XRD of 10% Mg in CaO prepared by sol-gel method is shown in Figure 2 as an example.



**Figure 2.** XRD of 10% Mg in CaO

As can be seen in Figure 2 the most dominant crystalline phase in XRD is originating from CaO. Furthermore peaks originating from MgO are observed. A third phase can either be assigned to CaCO<sub>3</sub> or Mg<sub>0.064</sub>Ca<sub>0.936</sub>(CO<sub>3</sub>). Rietveld analysis was applied and the weight percentages of the three phases are shown below:

Phase	Weight percentage of the Phase
CaO	68.97
MgO	9.27
CaCO <sub>3</sub> / Mg <sub>0.064</sub> Ca <sub>0.936</sub> (CO <sub>3</sub> )	21.77

This analysis clearly shows that most of the magnesium is present as MgO. However it is possible that some Mg is present in a mixed Ca/Mg carbonate. Based on XRD it can thus neither be confirmed nor excluded that some Mg and Ca are interacting closely in a mixed compound.

### TEM analysis

Bright field TEM showed that the sol gel prepared samples consisted of 50-100 nm semi spherical particles clustered together in large particles. In no cases separated particles were observed. In order to gain insight in the location of magnesium line profile EDX experiments were carried out. In Figure 3 an example of a dark field TEM image can be seen (right). The red line indicates where the line profile was intended measured. Due to the long measurement time the sample do, however, move slightly as can be seen by the small holes in the sample (in a curve in the blue box) originating from beam damage by the mapping thus showing the true points measured along a curve deriving slightly from the red line.

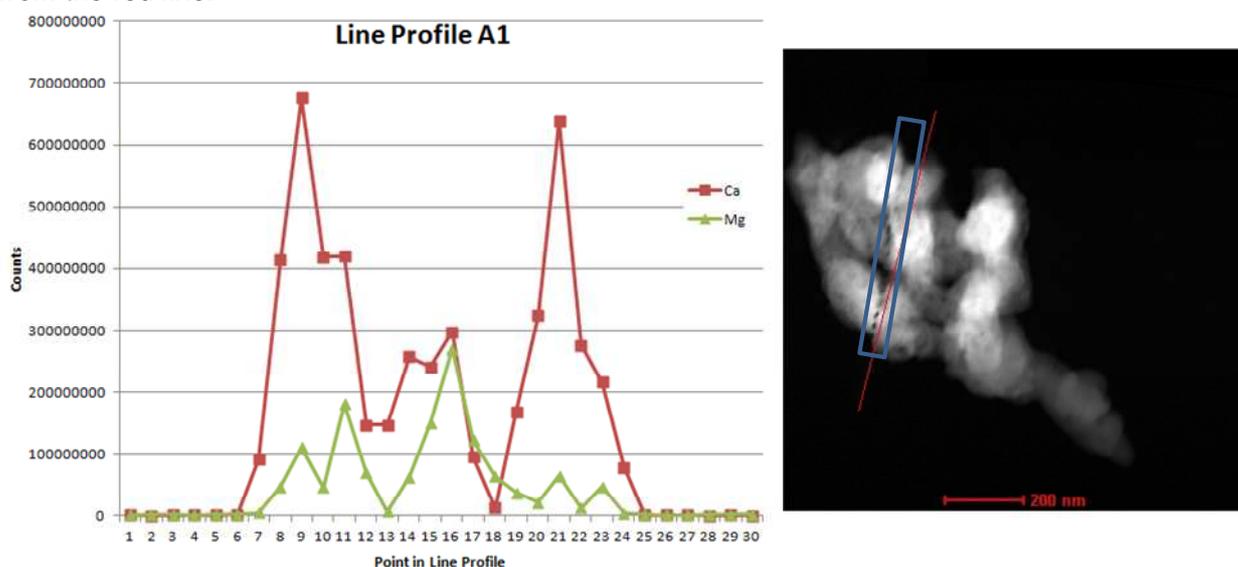


Figure 3. Line profile (left) and dark field (right) TEM images of 10MgO-CaO

In the line profile (Figure 3, left) the intensity for the EDX signal of respectively Ca and Mg are shown. The line profile measured moves along 3 of the semi-spherical particles clustered together and it is clear that all three of these particles contain both calcium and magnesium. The ratio between magnesium and calcium varies however significantly, meaning that the magnesium is not homogeneous distributed in the sample at this nm scale. This is in accordance with the observation in XRD of a separate MgO phase. However, on the other hand the line profile (along with a number of other line profiles of the sample) clearly shows that the MgO and CaO phases must be in proximity of each other since no distant single particles were found.

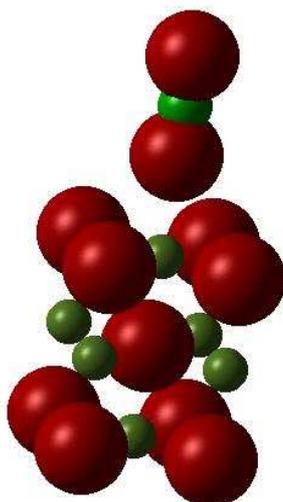
### DFT

A theoretical way to gain insight in the role of Mg as promotor for CO<sub>2</sub> capture in CaO could be using DFT calculations. It might be possible to calculate if there is a stabilization energy effect for small particles (thus avoiding sintering) by having Mg in a CaO structure, or by having small MgO particles in the proximity of CaO particles. Furthermore adsorption energies of CO<sub>2</sub> on respectively CaO, MgO and sites close to

## Structure Activity Relationships

---

both metals could be calculated and compared. Initial calculations of adsorption of CO<sub>2</sub> on MgO and CaO surfaces have been performed. The adsorption of CO<sub>2</sub> on MgO is shown in Figure 4.



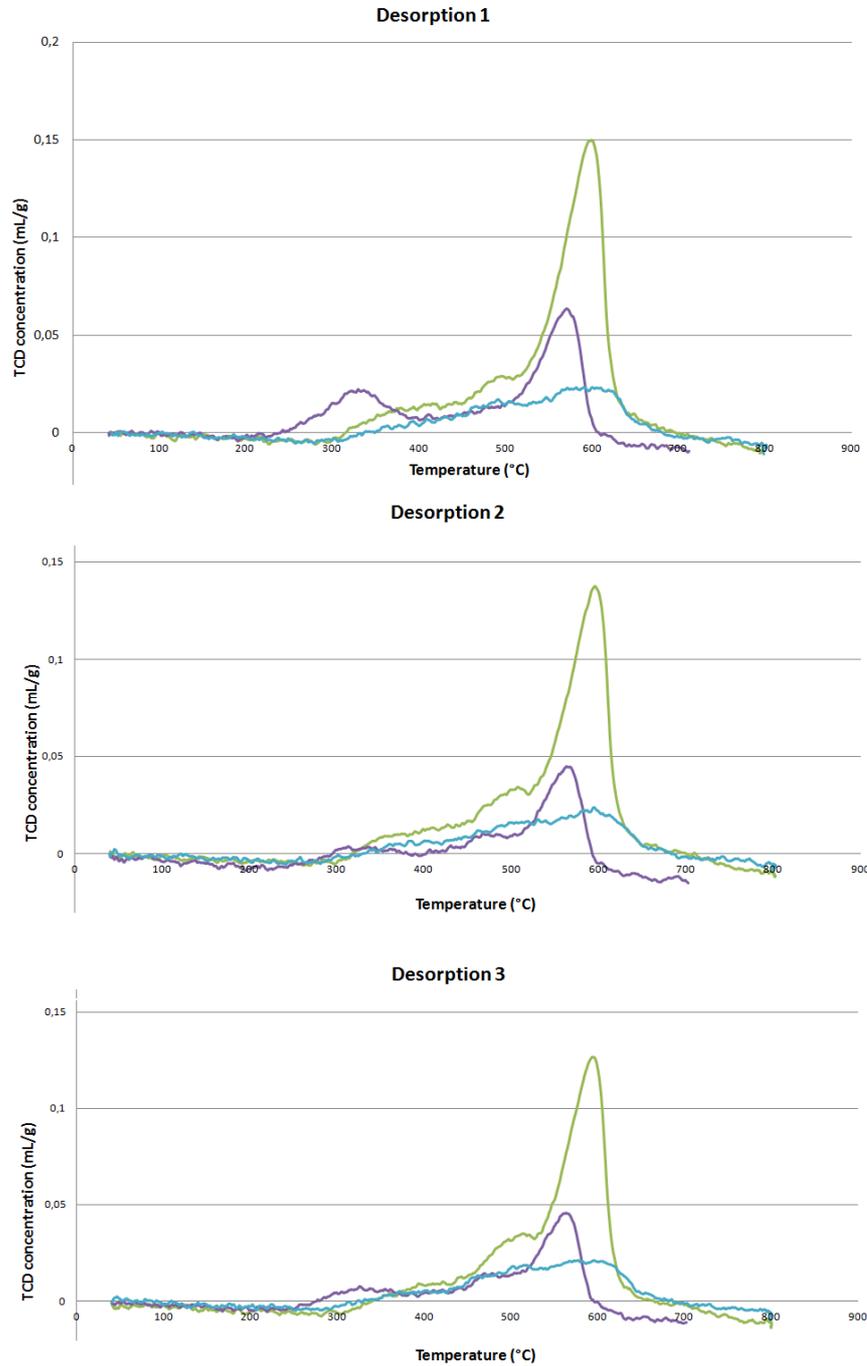
**Figure 4:** CO<sub>2</sub> adsorption on MgO, calculated using CRYSTAL

The conclusion of this preliminary study is however that this will be too complicated to study systematically in the remaining time of the project - unless a collaboration with a research group specialized in these kind of problems and calculations would be possible.

### Performance of the materials for CO<sub>2</sub> capture

The performance for CO<sub>2</sub> capture of the sol gel prepared standard sample CaO and 5% Mg in CaO were investigated and compared to a commercial available high surface area CaO sample (40 m<sup>2</sup>/g). Temperature programmed desorption of CO<sub>2</sub> was used to evaluate CO<sub>2</sub> capture properties. All three samples were activated in the TPD apparatus by heat treatment to 800 °C in He. It should be noted that this pretreatment procedure resulted in a significant decrease in specific surface area of the commercial CaO sample to 9 m<sup>2</sup>/g. After the heat treatment the samples were cooled down to 40 °C where CO<sub>2</sub> was pulsed over the sample until saturation. After the CO<sub>2</sub> pulses the samples were heated in He to 800 °C (10 °C/min) and TPD was performed. Next the sample was cooled to 40 °C and new CO<sub>2</sub> pulse/desorption cycle were performed twice. The results are compiled in Figure 5. A peak in the TPD figure at 600 °C is dominant for all three samples. This signal is representative for the decomposition of CaCO<sub>3</sub>.

**Structure Activity Relationships**



**Figure 5.** Temperature programmed desorption of CO<sub>2</sub> in three recycles of: Green commercial CaO, purple sol gel prepared CaO, blue sol gel prepared 5% Mg-CaO.

## Structure Activity Relationships

It is however noteworthy to mention that there is a distinct peak at 300 °C for the sol gel prepared CaO sample (most clear in the first desorption). Thus a part of the CO<sub>2</sub> must be weaker bounded to CaO.

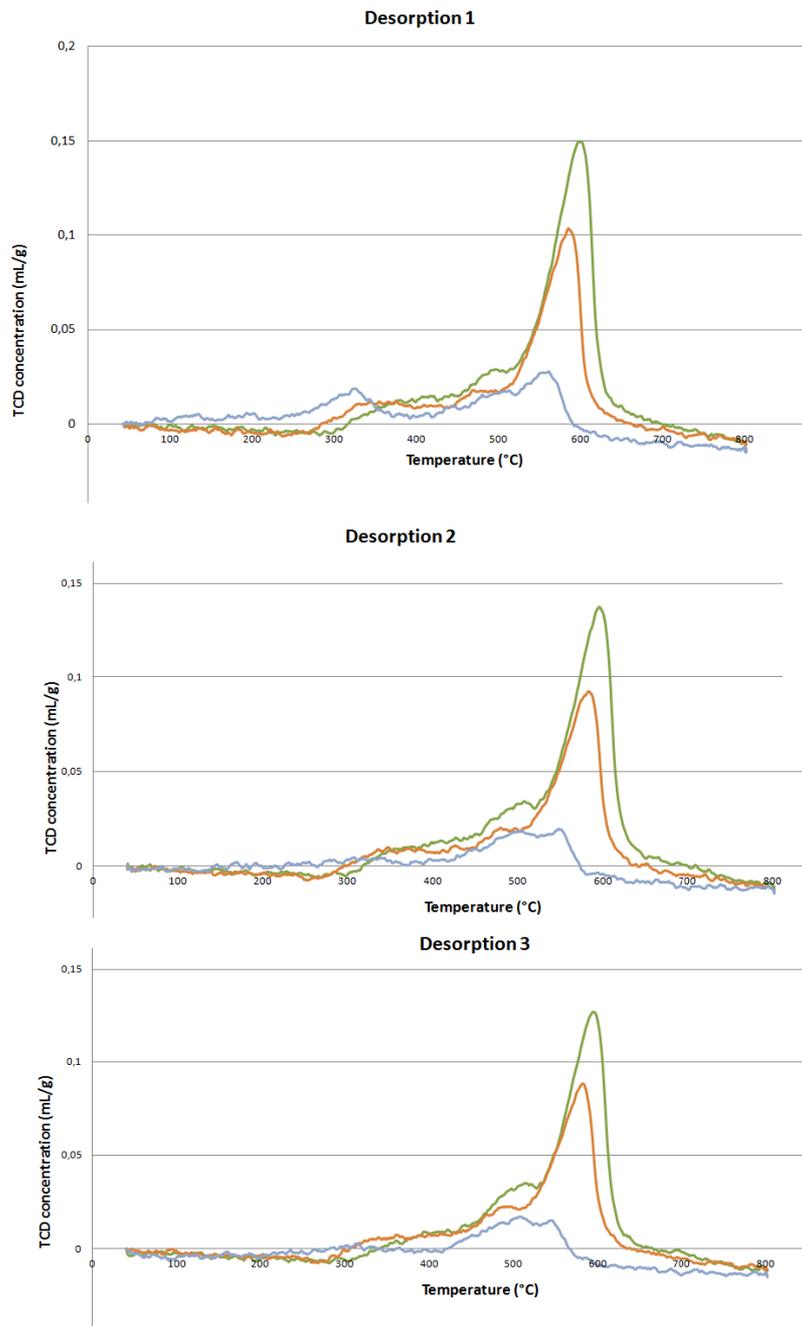
For the Mg containing sample a very broad desorption peak is always observed. The values for the total CO<sub>2</sub> uptake and release in the three cycles can be seen in Table 2 (the three samples in the top of the table). The theoretical max value for the CO<sub>2</sub> uptake is calculated to 399 ml/g CaO.

**Table 2.** Adsorption and desorption of CO<sub>2</sub> in different CaO materials

Sample	adsorption 1 (mL/ g STP)	desorption 1 (mL/ g STP)	adsorption 2 (mL/ g STP)	desorption 2 (mL/ g STP)	adsorption 3 (mL/ g STP)	desorption 3 (mL/ g STP)
Comm CaO	8.0	3.6	4.5	3.6	4.8	3.3
Sol gel CaO	2.7	1.5	2.0	1.2	1.8	1.1
5% Mg solg CaO	2.7	2.2	2.3	2.0	2.5	2.0
Ca(OH) <sub>2</sub>	4.0	3.5	3.8	3.1	3.6	3.1
MgO/CaO	1.2	1.2	0.8	0.9	0.8	0.8

It can be concluded that for all materials less than 1% of the CO<sub>2</sub> capacity is used. In the following we will consider the CO<sub>2</sub> capacity and stability of the materials closer.

For the heat treated commercial CaO sample the desorption (3.6 ml/g) is much less than the CO<sub>2</sub> adsorbed (8.0 ml/g) in the first cycle. This indicates that not all CO<sub>2</sub> is desorbed from the sample. In the following cycle only 4.5 ml/g is taken up which matches well with the fact that the capacity is lowered by some CO<sub>2</sub> being bound irreversibly. The CO<sub>2</sub> uptake decreased 40% from the first to the third cycle for the commercial CaO sample. The two sol gel prepared CaO samples, with and without Mg, showed similar CO<sub>2</sub> uptake in the first cycle. Though this uptake, 2.7 ml/g, was smaller than for the commercial CaO sample, the materials seemed more stable in the recycling. The CO<sub>2</sub> uptake for the sol gel prepared CaO sample decreased 33% from the first to the third cycle while the MgO containing CaO sample decreased only 7%. It should be noted that for all three samples the majority of the change in CO<sub>2</sub> capacity take place between the first to the second cycle, and all samples seems relatively stable between the second and the third cycle. If looking at the difference between adsorption and desorption for the sol gel prepared sample it is clear that the Mg containing sample is performing better. In the first run 80% of the adsorped CO<sub>2</sub> is desorped while only 55% of the CO<sub>2</sub> is desorped from the CaO sample.



**Figure 7.** CO<sub>2</sub> TPD in three recycles of: Green commercial CaO, orange commercial CO<sub>2</sub> treated with water before test, blue 5% Mg impregnated on commercial CaO.

## Structure Activity Relationships

---

Since Mg promotion seems to be the material easier regenerable and increased the stability of the CaO as CO<sub>2</sub> capture material for the sol gel prepared samples, we investigated the impact of magnesium in other CaO materials. Another material was prepared by introducing magnesium to the commercial CaO. This was prepared by incipient wetness impregnation of magnesium nitrate in water, followed by drying and calcination (5 wt% MgO). Since water can interact with CaO (to form Ca(OH)<sub>2</sub>) an additional sample, 'Ca(OH)<sub>2</sub>', was prepared by impregnating CaO with water, drying and heat treating it. This way it could be investigated if the water could damage the CaO material and thereby influenced the CO<sub>2</sub> capture performance.

In Figure 6 the three CO<sub>2</sub> TPD cycles are shown for these two samples (MgO/CaO and 'Ca(OH)<sub>2</sub>') after heat treatment to 800 °C together with the data for the commercial CaO for comparison. The adsorption/desorption values are reported in the lower part of Table 2. It is clear that the CaO and Ca(OH)<sub>2</sub> samples have a comparable TPD profile. The MgO/CaO sample does, however, behave very differently. Again, as it was also seen for the Mg CaO sol gel sample, the TPD peak has become very broad. For the impregnated sample the total amount of adsorbed CO<sub>2</sub> is much less, 1.2 ml/g than for the parent commercial CaO sample, 8.0 ml/g (or for the sol gel samples discussed above 2.7 ml/g). Though the CO<sub>2</sub> capacity is low all CO<sub>2</sub> adsorbed on the MgO/CaO sample is desorbed again in the first cycle. However, the CO<sub>2</sub> capacity decreases tremendously when evaluating the adsorption from 1. to 3. cycle, with 33% for MgO/CaO. Due to the performance of the Ca(OH)<sub>2</sub> sample it could be ruled out that differences between CaO commercial and MgO/CaO was due to the Ca(OH)<sub>2</sub> phase formed by impregnation and the possibly non-reversibility to CaO without e.g. surface area damaged. The changed properties can thus be ascribed to the presence of magnesium in the sample.

Thus magnesium seems to have a promising effect for stability and the possibility for regeneration in the sol gel method, but when impregnating it to commercial CaO it has no stabilizing effect. The location of Mg must thus be considered crucial for the impact on the performance of CaO CO<sub>2</sub> capture materials.

## References

- [1] E.T. Santos et al, Fuel 94 (2012) 624-628