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Research article

Experimental evaluation of chemical systems for CO₂ capture by

CaO in eutectic CaF₂-CaCl₂

Heidi S. Nygård^{1,*}, Maria Hansen¹, Yasen Alhaj-Saleh¹, Piotr Palimąka², Stanisław Pietrzyk² and Espen Olsen¹

- ¹ Faculty of Science and Technology, Norwegian University of Life Sciences (NMBU), N-1432 Ås, Norway
- ² AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Kraków, Poland
- * Correspondence: Email: heidi.nygard@nmbu.no.

Abstract: CO_2 capture by CaO in molten salts is a variant of calcium looping in which the active substances (CaO/CaCO₃) are dissolved or in a slurry with inorganic molten salts. One of the main advantages is the nonexistence of degradation in the reactivity between the active material and CO₂. Previous research has revealed good absorption and desorption characteristics with CaO contents up to 20 wt% in eutectic CaF₂-CaCl₂. The hypothesis is that the formed CaCO₃ continuously dissolves in the melt, leaving highly reactive CaO readily available for the incoming CO₂. In the present study, the CaO content is increased to 40 wt%, and the absorption characteristics is investigated with focus on the sorption capacity and CO₂ removal rate. The chemical system is also evaluated experimentally with regards to viscosity and solubility of the formed CaCO₃ during CO₂ absorption, with the aim of determining chemical upscaling limitations. The results show that the practical CaO content limit is 30 wt%, in which a sorption capacity of 20 g CO₂/100 g sorbent is observed, without any deterioration of the reaction kinetics. For 40 wt% CaO, the sorption capacity is higher, but on the expense of the CO₂ removal rate and CaO conversion. This is attributed to a significant increase in viscosity and the solubility limit of CaCO₃ being exceeded.

Keywords: CO2 capture; calcium looping; molten salts; phase diagram; viscosity

1. Introduction

The emissions of greenhouse gases such as CO_2 have increased significantly the last decades due to growing energy consumption based on fossil fuels. In addition, carbon-intensive industries

such as manufacture of iron, steel and cement are large contributors to the emissions. Carbon capture and storage (CCS) is regarded as an essential technology for achieving sustainability in these industries, as well as in the mid-term future energy supply. In the long term, development of capture technologies for sustainable sources such as biomass could also contribute to carbon negative solutions [1].

The capture step is the major part of the CCS process, both in cost and complexity [2]. Many technologies are under development, and among the most promising are post-combustion CO_2 capture using amine solvents, oxy-fuel combustion, and calcium looping (Ca-looping) [3]. Ca-looping is based on carbonation of CaO with CO_2 (absorption), and calcination of the formed CaCO₃ (desorption), as shown in Eq 1.

$$CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s) \tag{1}$$

Cyclic absorption and desorption can be performed by thermal swing around the turning point temperature, which is around 900 °C at atmospheric pressure. Ca-looping is typically performed in fluidized bed reactors (FBR), and is applicable for post-combustion, pre-combustion, and industrial processes [4].

The CaO sorbent can be generated from cheap and abundantly available limestone/dolomite, and for integration in a power or industrial process, the efficiency penalty is estimated to be relatively low [4]. However, a great challenge for solid state Ca-looping is the decreasing sorbent reactivity after many absorption–desorption cycles. This is ascribed to particle degradation caused by physical and structural stresses and sintering, leading to less reactive surfaces [5]. For long term use, sorption capacities of approximately 8 g $CO_2/100$ g sorbent have been reported for CaO derived from natural limestone [6].

Several lab scale methods for enhancing the sorbent performance over time have been reported; reactivation by steam, thermal pretreatment, and modification of solid sorbent particles by addition of supports or incorporation of CaO into inert solid matrices [7–12]. Inert materials for the latter are for example Al₂O₃, Ca₁₂Al₁₄O₃₃, ZrO₂, and CaTiO₃, and stable sorption capacities of around 21 g CO₂/100 g sorbent have been demonstrated in severe calcination conditions [9]. However, sorbent modifications are usually associated with high preparation costs, making application of these materials challenging at large scale.

Another approach for avoiding sorbent degradation is through a process known as Carbon Capture in Molten Salts (CCMS). In CCMS, the CaO is dissolved or in a supersaturated suspension in a molten salt matrix, and reacts with CO_2 at temperatures around 800 °C according to Eq 1. The cycle is completed by raising the temperature to 950 °C so that the reverse reaction can take place. The hypothesis is that the formed CaCO₃ dissolves continuously in the melt during absorption, leaving highly reactive surfaces of CaO readily available [13]. This is in contrast to carbonation of CaO in the solid state, in which a layer of CaCO₃ is formed around the unreacted sorbent, resulting in diffusion control and slower reactions due to an increasing stearic hindrance for the incoming CO_2 [14].

The CCMS concept has been validated for both absorption and desorption in a one chamber labscale reactor by bubbling simulated flue gases (0.76-15 vol% CO₂ in N₂) through various chloride and fluoride based melts [13,15-17], showing that the method is applicable for capturing CO₂ from a variety of flue gases related to both energy intensive industry and power generation. The most promising salt mixture is eutectic CaF₂-CaCl₂ [16]. In this system, CO₂ capture has been successfully demonstrated in a melt containing up to 20 wt% CaO, The highest observed sorption capacity was 10.9 g $CO_2/100$ g sorbent, where the sorbent refers to the mixture of the CaO and the eutectic CaF₂-CaCl₂. Up to 85% of the initial CaO reacted during absorption, and ~100% of the CaCO₃ was decomposed during desorption. A series of 12 cycles has been performed in the lab scale setup, and the results show an increase in capacity in the first few cycles. This was followed by stable sorption capacities throughout the remaining cycles, without any deterioration of the reaction kinetics [16,18]. Higher sorption capacities could be obtained with higher CaO contents, i.e., more CO₂ could potentially be captured per g sorbent. This would be beneficial for reducing the size-and hence installation cost—of a scaled-up system. In this work, we continue to study CO_2 absorption by CaO in eutectic CaF₂-CaCl₂, but we increase the CaO content up to 40 wt%, and evaluate the sorption capacity and CO₂ removal rates. 40 wt% was found to the upper practical limit in the experimental setup due to difficulties in mixing the CaO and the molten salt. With such high CaO contents, it is expected that the CaO and the CaF₂-CaCl₂ form a slurry due to supersaturation of CaO. This will lead to increased viscosity, which could be a challenge in a scaled-up system where a possible approach is to transfer/pump the melts between the absorber and the desorber. Another potential constraint for high CaO contents is the solubility of the formed CaCO₃. In order to take these possible limitations into account, we have included experimental evaluation of the viscosity of the CaO-CaF₂-CaCl₂/CaO-CaCO₃-CaF₂-CaCl₂ systems and relevant part of the phase diagram for CaCO₃-CaF₂-CaCl₂ in the present work.

2. Materials and methods

2.1. Materials

The salts and gases used for the experimental work in this study are listed in Table 1.

Substance	Grade
CaCl ₂ ·2H ₂ O	VWR/Avantor Performance Materials, normapur, >99%
CaF ₂	Sigma/Acros Organics, puriss, >99.0%
CaO	Sigma, puriss, 96–100.5%
CaCO ₃	Sigma/Avantor Performance Materials, puriss, >99.0%
NaCl	Sigma, puriss, ≥99.5%
N_2	AGA, 5.0, >99.999%
Ar	AGA/Alphagas, 4.0, >99.99%
CO ₂	AGA/Alphagas, >99.99%

Table 1. Chemicals and g	gases used in	the experiments.
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Anhydrous $CaCl_2$ was prepared from $CaCl_2 \cdot 2H_2O$ in a controlled heating procedure following Freidina and Frey [19]. The salt was placed inside a closed, tubular furnace under inert atmosphere (Ar) and heated at the rate of 0.5 °C/min up to 300 °C. The temperature was then raised to 800 °C at the

heating rate of 2.78 °C/min, and kept at that temperature for 10 hours. The weight was recorded before and after the drying process to ensure complete removal of the crystalline water.

CaO was fused at 850 °C for 3 hours in a muffle furnace at ambient atmosphere, while the remaining salts were dried at 300 °C for at least 24 hours. All salts were kept in closed vessels in a drying cabinet at 300 °C until used to prevent moisture adsorption. Before each experiment, the desired salt composition was prepared by direct mixing of the dried salts by means of weighing.

Pure gases provided by AGA were used for all experiments, and the flow rate and compositions were controlled by mass flow controllers (MASS-STREAM, M + W Instruments GmbH). Argon was used as inert gas around the reactors to prevent corrosion. Experiments involving CaCO₃ were carried out in pure CO₂ atmosphere to avoid decomposition of the carbonate.

2.2. Experimental setups and methods

2.2.1. CO_2 capture

 CO_2 capture experiments were performed in an one-chamber atmospheric pressure reactor previously described [16]. Samples were prepared with 10, 20, 30 and 40 wt% CaO (35–140 g) in an eutectic mixture of CaF₂-CaCl₂ (13.8 wt% CaF₂ in CaCl₂) and filled in a nickel crucible (H = 350 mm, ID = 52 mm). The total sorbent weight (CaO-CaF₂-CaCl₂) was kept constant at 350 g for all experiments. The crucible was placed inside a stainless steel reactor that was heated externally by a tubular electric furnace (Figure 1).

The temperature in the molten salt was continuously monitored by a type S (Pt-Pt10Rh, ± 1 °C) thermocouple immersed in the melt. The salt mixture was heated to ~705 °C under inert atmosphere, followed by bubbling pure N₂ for 1 h to ensure stability of the melt temperature before the experiment. The experiment started when the simulated flue gas (15 vol% CO₂ in N₂) was applied. The N₂ and CO₂-N₂ gas mixtures (total flow of 0.6 L/min) were bubbled via a nickel tube immersed to a depth of 1 cm from the bottom of the nickel crucible.



Figure 1. Schematic representation of the experimental setup for CO_2 capture by CaO in eutectic CaF₂-CaCl₂. The inner crucible and the feed tube are made of nickel, and the outer container is made of stainless steel. The melt temperature is measured by a type S thermocouple (Pt-Pt10Rh). The capture process is simultaneously monitored by thermogravimetric analysis (TGA) and gas analysis (FTIR).

The gases from the reactor were led through a purpose built electrostatic filter in order to remove possible particles entrained in the gas stream. High voltage (8.5 kV) was provided from a power supply (Spellman SL300). The gas composition was analyzed using a FTIR gas analyzer (Thermo Scientific, Nicolet 6700) equipped with a 2m path length (200 mL volume) gas cell with KBr windows. The analyzer was operated using the FTIR software package OMNIC 8 (Thermo Scientific) running the commercial Fire Science method (Thermo Fisher).

The weight of the reactor was monitored by an industrial weighing scale (MS8001S, Mettler Toledo, accuracy of 0.1 g), with a sampling interval of 10 seconds. A constant flow of Ar (0.20 L/min) was applied as a purge flow over the outer stainless steel reactor in order to minimize corrosion of the chamber. However, a baseline study of the oxidation of the reactor revealed small amounts of oxidation, and this was taken into account in further calculations. LabView 8.2 (National Instruments) was used for measurements and monitoring of the temperature, gases and weighing scale.

The absorption process was considered to be complete when the outlet gas composition recorded by the FTIR attained the same value as the inlet composition. The mass change was used for further data processing, but it was compared to the FTIR data to confirm that the mass change was solely due to the forward reaction given by Eq 1 when the corrosion was taken into account.

2.2.2. Viscosity measurements

The viscosity measurements were carried out using a high-temperature, rotary rheometer with DV-III Ultra (Brookfield) measuring head. The measuring principle is based on the coaxial cylinders method; one of the cylinders (the penetrator) rotates at a predetermined speed in the sample, which is placed inside the second cylinder (the crucible), see Figure 2. The shear stress created in the liquid layer causes a change of torque, which is indirectly correlated to the viscosity of the liquid. The direct results of the viscosity measurements are the percentage of the maximum torque required for the rotation of the penetrator in the liquid. The value of this torque is indirectly correlated with the viscosity of the salt mixture. Calibration was performed by measuring the required torque for constant rotations of the penetrator in standard oils (supplied by Brookfield) with different viscosities at 25 °C.



Figure 2. Schematic representation of the experimental setup for the viscosity measurements. The experiments were performed by using coaxial cylinders method, which is based on the principle that the torque required to turn the penetrator in the measured liquid is a function of the viscosity of that liquid.

The salt mixtures (120 g) were placed in a molybdenum crucible (H = 70 mm, ID = 34 mm) that was further placed between three special alumina rods (Figure 3). The molybdenum penetrator was suspended on a steel rod and a silver chain. Two types of penetrators with different surface areas were used; a small (6.45 cm²) for liquids with high viscosity (>100 cP) and a large (23.99 cm²) for liquids with low viscosity (<100 cP).

The system was moved down into the furnace and purged with Ar for 12 h. The furnace was further heated to the required temperature and the penetrator was immersed into the molten salt, each time to the same depth. Afterwards, the rotations were set and the torque (as a part of the maximum torque expressed as a percentage) was read.



Figure 3. Penetrator and measuring crucible.

The viscosity measurements in the CaO-CaF₂-CaCl₂ system were performed with 0, 10, 20 and 30 wt% CaO in eutectic CaF₂-CaCl₂ in Ar atmosphere. Experiments for CaO contents above 30 wt% were not possible because the mixtures were too viscous to immerse the penetrator. For the CaO-CaCO₃-CaF₂-CaCl₂ system, the CaO content was fixed to 10 wt%, and experiments were performed with 0, 10, 20 and 30 wt% CaCO₃. These experiments were performed in CO₂ atmosphere.

The experiments started at T = 700 °C, and the temperature was then increased systematically in 50 °C steps. Due to evaporation of the liquid and corrosion of the steel elements of the equipment, the temperature range was limited to 900 °C and 950 °C for CaO-CaF₂-CaCl₂ and CaO-CaCO₃-CaF₂-CaCl₂, respectively.

2.2.3. Phase diagram

The relevant part of the phase diagram for $CaCO_3$ - CaF_2 - $CaCl_2$ was obtained by thermal analysis. Increasing amounts of $CaCO_3$ were added to eutectic CaF_2 - $CaCl_2$ in order to investigate the solubility of the $CaCO_3$ that is formed during carbonation of CaO. All of the experiments were performed under CO_2 atmosphere in order to avoid decomposition of $CaCO_3$.

100-150 g of salt (depending on the composition) was filled in a nickel crucible (H = 60 mm, ID = 60 mm) and positioned in a vertical tube furnace (Figure 4). The furnace was similar to the one used for the CO₂ capture experiments, but with 3 different zones with separate temperature control and water cooling on top and bottom. Nickel radiation shields were applied above and below the crucible in order to minimize heat losses and ensure homogenous temperature throughout the sample.



Figure 4. Schematic representation of the experimental setup for thermal analysis of the system $CaCO_3$ - CaF_2 - $CaCl_2$. The sample is placed in a nickel crucible, and undergoes a controlled cooling (0.5 °C/min) under constant stirring. The experiments were performed under CO_2 atmosphere.

The sample was heated to 800 °C and kept for around 3 h, with constant stirring the last hour (160 rpm). This was followed by controlled cooling (0.5 °C/min) under constant stirring (160 rpm). The heating and cooling rate of the furnace was controlled by LabView 8.2 (National Instruments), and the temperature was measured by a type S (Pt-Pt10Rh, ± 1 °C) thermocouple that was calibrated with pure NaCl (melting point 801 °C). Heating and cooling was repeated several times for each experiment in order to confirm the reproducibility and the accuracy of the process. The cooling curves were further used to determine the melting points of the mixtures.

3. Results and discussion

3.1. CO₂ sorption capacity and viscosity measurements

Figure 5 shows the sorption capacity (g $CO_2/100$ g sorbent) as a function of time for 10, 20, 30 and 40 wt% CaO in eutectic CaF₂-CaCl₂. The sorbent refers to the mixture of CaO and CaF₂-CaCl₂. Absorption is performed by bubbling a simulated flue gas (15 vol% CO₂ in N₂) through the melt at T~705 °C. The theoretical sorption capacity based on the applied CO₂ flow and conversion of all the available CaO is also included in the figure (dashed lines).



Figure 5. Sorption capacity (g $CO_2/100$ g sorbent) as a function of time for CO_2 capture in a mixture of 10–40 wt% CaO in eutectic CaF₂-CaCl₂. The absorption was performed with simulated flue gas (15 vol% CO_2 in N₂) at T_{abs}~705 °C. Dashed lines are the theoretical sorption capacity based on the applied CO_2 flow and conversion of all the available CaO.

The analysis follow the same procedure as in our previous study [18], in which we use the linear region of the sorption capacity to evaluate the reaction between CO_2 and the sorbent. We have previously shown that the CO_2 removal rates are not affected for CaO contents up to 20 wt%. This is confirmed in the present study, as we see similar behavior for 10 and 20 wt% (Figure 5a and b). In the linear region, 92% of the applied CO_2 is absorbed. The total sorption capacity is 5.87 and 12.5 g $CO_2/100$ g sorbent for 10 and 20 wt%, respectively.

The reactions are somewhat slower for 30 wt% CaO (Figure 5c), but still 83% of the applied CO_2 is absorbed. A total sorption capacity of 20.0 g $CO_2/100$ g sorbent is observed, which is in the same range as for the synthetic sorbents reported by Kazi et al. [9]. For 40 wt% CaO, the total sorption capacity increases to 24.8 g $CO_2/100$ g sorbent. However, a significant reduction in the CO_2 removal rate is seen (Figure 5d), in which only 63% of the applied CO_2 is absorbed.

A possible explanation to the slower absorption is the increasing viscosity for higher CaO contents. Higher viscosities will in general give slower reactions, because the dissolved particles diffuse much more slowly and collide less frequently—giving fewer opportunities to react. The experimental results for the viscosity as a function of temperature for 10–30 wt% CaO in eutectic CaF₂-CaCl₂ is shown in Figure 6 (dashed lines). Eutectic CaF₂-CaCl₂ is included as a reference (solid

line). The viscosity increases with increasing amounts of CaO, and for 40 wt% CaO it was not possible to measure with the existing equipment. There is also a decreasing trend with increasing temperature.

All of the CaCO₃ that is formed during carbonation will be decomposed in the desorber, thus giving a mixture of CaO-CaF₂-CaCl₂ that is to be transferred back to the absorber. For 30 wt% CaO in eutectic CaF₂-CaCl₂, the viscosity is 800 cP at T = 700 °C, and decreases to 466 cP at T = 950 °C. For comparison, the viscosity of castor oil at 25 °C is 985 cP [20]. Accordingly, it should be possible to transport/pump a molten salt consisting of 30 wt% CaO in eutectic CaF₂-CaCl₂ in a scale-up system for CO₂ capture.



Figure 6. Results of the viscosity measurement for the CaF_2 - $CaCl_2$ -CaO- $CaCO_3$ systems. The experiments containing $CaCO_3$ were performed under CO_2 atmosphere in order to suppress $CaCO_3$ decomposition, and the remaining experiments were performed under Ar atmosphere.

Viscosity measurements were also performed for the system $CaF_2-CaCl_2-CaO-CaCO_3$ (Figure 6, dotted lines). The aim of these measurements was to look into the pumpability from the absorber to the desorber, after carbonation is performed. The measured mixtures also contain CaO, because previous experiments have shown that it is not possible to convert all of the initial CaO, thus leaving unreacted CaO in the melt that is to be transferred. The results show that CaCO₃ has much less effect on the viscosity compared to CaO, and all measured values are below 30 cP. From this, it is clear that the transportation of the melt from the absorber to the desorber is not an obstacle in a scale-up system.

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3.2. CaO conversion and solubility of CaCO₃

As already discussed, the total sorption capacity increases with increasing CaO content of the melt (Figure 5). However, it is also of interest to look into the CaO conversion, i.e., how much of the initial added amount of CaO that reacts with CO_2 .

The CaO conversion for 10–40 wt% CaO in eutectic CaF_2 -CaCl₂ is shown in Figure 7. We have also included numbers from Tomkute et al. [16], who studied CaO contents up to 20 wt%.



Figure 7. CaO conversion as a function of CaO content in eutectic CaF₂-CaCl₂. The absorption is performed at T~705 °C. The black squares are numbers from Tomkute et al. [16], while the red triangles are the results from this work.

The numbers for 10 and 20 wt% are in good agreement with the previous work by Tomkute et al. [16], with CaO conversions of 75 and 80%, respectively. For 30 wt% CaO, the conversion increases to 85%, while it decreases to 80% for 40 wt% CaO. This decrease is a new observation, as all previous studies have shown increasing conversions for increasing amounts of CaO, both in CaCl₂ [15] and CaF₂-CaCl₂ [16].

A possible explanation to this is the solubility of the formed $CaCO_3$. As stated in the introduction, the hypothesis is that the formed $CaCO_3$ dissolves continuously in the melt during absorption, leaving highly reactive surfaces of CaO readily available. If the solubility limit is being exceeded, it means the incoming CO_2 will have to diffuse through a solid $CaCO_3$ layer around the CaO-particles, thus giving slower reactions. Figure 8 shows the experimentally determined liquidus and solidus temperatures obtained by adding $CaCO_3$ to eutectic CaF_2 -CaCl₂. The liquidus line is the one of main interest for the CCMS technology, as this determines how much of the formed $CaCO_3$ that will be dissolved during the absorption process. A ternary eutectic was detected at 22 wt%

CaCO₃, and the solubility of CaCO₃ at the typical absorption temperature T_{abs} ~705 °C is found to be ~35 wt%.



Figure 8. Effect of CaCO₃ in eutectic CaCl₂-CaF₂. The data was derived experimentally by adding CaCO₃ to eutectic CaF₂-CaCl₂: \bullet liquidus line; \blacksquare and \blacktriangle solidus lines.

Theoretically, 1 mole of CaO can absorb 1 mole of CO_2 (Eq 1). Mass wise, conversion of 1 gram CaO corresponds to the formation of 1.78 grams CaCO₃. Calculated values for the CaCO₃ concentration as a function of CaO conversion are shown in Figure 9, with separate curves for initial CaO concentrations of 10, 20, 30 and 40 wt%.



Figure 9. Concentration of the formed CaCO₃ as a function of CaO conversion for initial CaO concentrations of 10, 20, 30 and 40 wt%.

Calculations show that for an initial concentration of 40 wt% CaO, a conversion of 80% will give a CaCO₃ concentration of 45.6 wt%. If we do not take the effect of the remaining CaO into account, this is above the solubility limit at this temperature, and could be an explanation to the reduced capacity. For 30 wt% CaO, the solubility limit is exceeded at 78% conversion, while it is never reached for 10 and 20 wt%.

These results strengthen the hypothesis that the rapid carbonation is due to continuously dissolution of the formed $CaCO_3$, and that the solubility could limit the CaO conversion. This is no problem for initial CaO concentrations up to 30 wt%, as the formed $CaCO_3$ is just above the solubility limit.

4. Conclusions

The purpose of the present study is to evaluate and determine limitations of chemical systems for CO_2 capture by calcium looping in molten salts when the initial amount of CaO is increased. Absorption experiments have been performed with CaO contents from 10 to 40 wt% in eutectic CaF₂-CaCl₂, and an evaluation of the sorption capacity and CO₂ removal rates have been performed. Possible constraints such as increasing viscosity with high CaO contents and solubility limits of the formed CaCO₃ during carbonation have been studied experimentally.

In general, the observed results for 10 and 20 wt% show good agreement with previous work, both for CaO conversion (75–80%) and CO₂ removal rates (>90% of applied CO₂ is absorbed). The increased viscosity for 30 wt% CaO will give somewhat slower reactions, but the slurry is still pumpable and transportation between the absorber and desorber is not regarded as a hinder for a scaled-up system. More than 80% of the applied CO₂ is absorbed, and the formed CaCO₃ will dissolve in the melt until 80% of the initial CaO is converted, which is within an acceptable range for

commercial purposes. The sorption capacity for 30 wt% CaO was found to be 20 g $CO_2/100$ g sorbent, which is in the same range as for synthetic sorbents, but preparation of the sorbent for CCMS is expected to be much less costly.

40 wt% CaO gave higher sorption capacity (24.8 g $CO_2/100$ g sorbent), but on the expense of the CO_2 removal rate and CaO conversion. This is attributed to higher viscosity and the solubility limit of the formed CaCO₃ being exceeded.

Based on the results from the present study, 30 wt% CaO is regarded as the upper limit for a continuous process in a scaled-up system for absorption of CO_2 by CaO in CaF₂-CaCl₂.

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Conflict of interest

The authors declare no conflict of interest.

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