**Abstract**

Capture and storage of fossil carbon emitted to the atmosphere from anthropogenic sources has been identified as a key technology for keeping human-induced global warming below 2°C. Available technologies have not achieved widespread impact due to costs related to increased energy consumption and expensive, large process equipment. Here, we show how molten inorganic halide salt-based mixtures containing CaO may be utilized for selective capture and subsequent controlled release of carbon dioxide from diluted flue gases. Highly efficient absorption is demonstrated in a fluoride-based liquid, absorbing close to 100% of the CO$_2$ from a simulated flue gas with an absorbing column height of only 10 cm. Greater than 90% carbonation with >80% regeneration to CaO was recorded. Excellent cyclability has been achieved with a chloride-based liquid with 60% carbonation and 100% regeneration to CaO during four cycles. The high efficiencies may enable extraction of CO$_2$ from highly diluted gas mixtures.

**Introduction**

The capture and storage of CO$_2$ emitted from exploitation of fossil fuels has been identified as an issue, which should be aggressively pursued [1]. High-temperature post-combustion removal (HT-CCS) by carbonate looping has been identified by The European Technology Platform for Zero-Emission Power Generation (ZEP) as one of the most promising methods in the developing stage [2–15]. The concept relies on absorption of CO$_2$ by CaO with formation of CaCO$_3$ in the solid state. CaCO$_3$ is subsequently stripped for CO$_2$ and CaO is regenerated by raising the temperature [4–6]. CaO is frequently chosen as the active substance in the solid-state carbonate looping system, but other alkali-earth metal oxides may be used similarly. These oxides will exhibit thermal decomposition, each at their own, specified temperatures. The cycling may be described by the equilibrium in equation (1), here M denotes an alkali-earth metal element.

$$\text{MO(s)} + \text{CO}_2(g) \rightleftharpoons \text{MCO}_3(s) \quad \Delta G_{\text{M=Ca},\text{bar}}^{\text{ISO}C} = -12.4 kJ/mol$$

(1) M: Mg, Ca, Sr, Ba

At lower temperatures, the equilibrium is shifted toward the right with the compounds on the left becoming increasingly stable at higher temperatures. This enables absorption and desorption of CO$_2$ to be performed, controlled by a simple thermal swing, either in a continuous flow reactor or a batch reactor. Thermodynamic modeling of the cycling has been performed and the Gibbs free energy for the equilibrium in equation (1) for the alkali-earth metals from Mg to Ba is plotted in Figure 1A.

Frequently, CaO is chosen as the active material due to its abundance and relevance with cement manufacture. CO$_2$ reacts with calcium oxide at a defined temperature to
form calcium carbonate in an absorption chamber (carbonation). The carbonate is then transferred to a second reactor chamber and decomposed to regenerate the oxide and pure CO₂ gas at a higher temperature (decarbonation). Transfer of the decarbonated solid (CaO) back to the absorption chamber completes the loop. Fluidized bed (FBR) reactors are normally used with these systems. Repeated absorption–desorption cycles introduce physical and structural stresses as well as sintering, leading to morphological changes in the particles [8,10,16]. For naturally occurring minerals, CaO-based sorbent reactivity is severely reduced after few (~3) cycles representing the main challenge identified with the technology [7–9].

We here report on a process based on the chemical principles involved in carbonate looping, but where the active substances are present as dissolved or partially dissolved in a liquid consisting of molten inorganic halide salts. By dissolving the active substances in a liquid, rapid gas–liquid reactions enable efficient absorption. A slurry state where the active substances are present in amounts exceeding their solubility limits has also been tested. As the active materials are present – at least partly, in dissolved states, they are constantly regenerated and the mechanisms leading to deactivation of solid sorbents will not be present.

**Experimental Procedure**

A sealed, one-chamber reactor was used for batch operation. The reactor chamber was made from stainless steel, with an inner crucible made of nickel (Ni) with inner diameter 5.0 cm containing 10 cm of liquid (400/500 g, NaF-CaF₂-CaO/CaCl₂-CaO). The experimental setup is schematically depicted in Figure 2. Reagent grade chemicals, all provided by Sigma–Aldrich (Steinheim, Germany) were used: CaO 96–100.5%, CaCl₂, anhydrous, ≥97.0, CaF₂,

![Figure 1](image1.png)  
**Figure 1.** Thermodynamic modeling of the Gibbs free energy for the chemical reactions described by equation 1 (A) and equation 3 (B) [17].

![Figure 2](image2.png)  
**Figure 2.** The experimental setup, schematically depicted. (A) The reaction chamber. (B) The full setup. The absorption–desorption processes are monitored by gravimetry and gas analysis (FTIR).
99.0–100.0%, NaF 98.5–100.0%, LiF 99%. To remove traces of water, the powders were dried in Ar at 200°C for 50 h, then slowly heated (200°C/h) to 850°C and kept for 10 h. The reactor chamber and gas lines were first purged by inert gas (N2, 99.999%, AGA, Oslo, Norway) to remove air and to provide a stable environment while the salts and oxide originally added as powders were fused. Absorption was preceded by first bubbling nitrogen through the molten column for 1 h to remove traces of water. Gas analysis was performed continuously by an in-line Fourier transform infrared spectrometer (FTIR) (Thermo Nicolet 6700; Thermo-Fisher Scientific, Waltham, MA) equipped with a 2 m gas analysis cell. The weight of the assembly was monitored by an industrial balance (Mettler Toledo MS 8001S, Mettler-Toledo, Colombus, OH; 0.1 g). The experiments then commenced by submerging the Ni tube into the liquid while keeping the gas flowing. At this stage, CO2 (AGA, instrument grade) was added to the gas flow. The content of CO2 in the gas emitted from the reactor was monitored by FTIR while the weight change was recorded simultaneously. An electrostatic filter was employed in the gas line after the reaction chamber to protect the FTIR analyzer from potentially corrosive substances. Data were logged by using National Instruments Compact FieldPoint. Different molten salt systems were examined; compositions are given in weight% unless otherwise specified. A chloride-based system, which comprised of a 5.3% CaO/94.7% CaCl2 mixture and two fluoride-based systems (48.2% NaF/41.8% CaF2/10% CaO and 52% LiF/38% CaF2/10% CaO) were used. Absorption was performed at 826°C (CaO/NaF/CaF2), 800°C (CaO/CaCl2), and 787°C (CaO/LiF/CaF2). Carbonation was conducted by leading 0.6 Nl/min of a simulated flue gas (14 vol% of CO2 in N2) through the liquid column in the reactor chamber to the FTIR gas cell. The estimated residence time for the gas in the liquid was on the order of 1 sec. The height of the absorbing liquid column was 10 cm. Desorption was performed by stopping the flow of CO2 and raising the thermal set point of the furnace to the temperature required for the CO2 desorption process to commence, while monitoring both the gas composition flowing from the cell and the weight change. To demonstrate the possibility to desorb pure CO2 at ambient atmospheric pressure (pCO2 = 1 atm.), a molten salt containing 20% CaO in CaCl2 was used. Here, the N2 flow was stopped after carbonation had proceeded to its full extent. 100% CO2 was kept flowing through the system while the temperature was raised stepwise to 1070°C. In this case, only the weight change was recorded. The sorption of CO2 was calculated based on the gravimetric data and the efficiencies were estimated based on the measured weight gain/loss compared with the maximally achievable as 1 mol of CaO may absorb 1 mol of CO2. X-ray diffraction (XRD) was performed by a Philips PW1730/10 diffractometer (Philips N.V., Eindhoven, Netherlands) using Cu-Kα (1.5418 Å) radiation and a Philips PW1711/10 proportional detector on melt samples rapidly quenched on an iron plate after removal from the experimental setup and remelting at 1200°C in the nickel inner crucible in a furnace open to the ambience.

Results and Discussion

Absorption with following desorption of CO2 in the fluoride-based melts, as measured by gas analysis as function of time is depicted in Figure 3. Analysis of the gas composition after absorption reveals extremely efficient absorption of CO2 initially. The total conversion rates from CaO into carbonate were in excess of 92% for both fluoride-based systems (CaO/LiF/CaF2 and CaO/NaF/CaF2). The decomposition of carbonate to oxide was recorded to be 47.5% for the NaF-containing, and 83.8% for the LiF-containing system. The content of CO2 in the gas led through the reactor was registered to be below the detection limit of the analyzer (0 ppm recorded) for around 50 min in the initial carbonation stage. Following this, a slowly rising content of CO2 in the emitted gas from the reactor was detected. The exothermic nature of the process was evidenced by a rise in temperature by 4–6°C from the set point when starting the carbonation reaction. The extremely efficient initial absorption was followed by a less efficient absorption stage initiated by an abrupt increase in the content of CO2 being liberated from the reactor. This is seen in Figure 3 at around 200 min of elapsed time.

The high absorption efficiency in the fluoride-based melts is maintained by the simultaneously occurring exchange reaction described by equation (2).

\[
\text{CaCO}_3^{\text{diss}} + 2\text{MF} (l) \rightleftharpoons \text{M}_2\text{CO}_3^{\text{diss}} + \text{CaF}_2(l) \quad (2)
\]

M: Li or Na \quad \Delta G_{800°C}^{M=Na} = -20.3 \text{ kJ/mol}

Equation (2) will be shifted toward the right for the NaF- or LiF-containing salt, keeping the activity of CaO at unity early in the experiments and so lead to a low partial pressure of CO2 to be established in the system. The combined, total reaction occurring with CaO and MF/CaF2 (M = Li or Na) as the active substances is described by equation (3). The Gibbs free energies for the combined reaction for the different alkali-earth metal elements are plotted in Figure 1B.
CaO(diss,s) + CO₂(g) + 2MF(l) \rightleftharpoons M₂CO₃(diss) + CaF₂(l) \quad (3)

M: Li or Na \quad G^{M=Na}_{\text{800°C}} = -27.5 \text{ kJ/mol}

When the readily available (dissolved or dispersed) CaO was consumed, the partial pressure of CO₂ above the melt rapidly increased as the activity of CaO fell toward a low value and the carbonation commenced at a substantially lower rate. This is indicated by the rapid rise in CO₂ being liberated from the cell at around 200 min in Figure 3. Solid CaO \((\rho = 3.3 \text{ g/cm}^3)\) [17] is relatively heavy compared to the molten salt \((\rho = 2.8 \text{ g/cm}^3)\) [18] and may deposit toward the lower edges in the inner crucible during the initial melting of the powdery chemicals. Some of it may as such be less easily available for carbonation as it will need to dissolve in the rather basic melt in order to come into contact with the CO₂ being released in the center. This may explain the slower rate of the carbonation reaction from 200 to 400 min as recorded for the LiF-containing salt. The Gibbs free energy for the combined reaction (Eq. 3) with CaO and NaF as active substances becomes positive above 1120° C [17], shifting the equilibrium toward the left as the temperature increases. Thus, desorption of CO₂ in the CaO/CaCO₃/NaF/CaF₂ system was conducted by raising the furnace temperature to above this level (1150° C). Fast CO₂ desorption appeared as the temperature was raised (Fig. 3). Based on the FTIR gas analyses, 47.5% of the reacted CaO was regenerated in the NaF containing salt. XRD of samples, which remelted at 1200° C and then quenched, showed no signs of other phases than the initial (CaF₂, NaF, CaO), as evident in Figure 4, indicating that the decarbonation had proceeded fully at this temperature. Modeling showed that for a salt based on LiF, the liberation of absorbed CO₂ is supposed to commence at about 160° C lower in temperature as compared with the salt based on NaF [17]. As shown in Figure 3, this was also demonstrated experimentally, as rapid desorption was recorded from a melt containing CaO/Li₂CO₃/LiF/CaF₂ at 1050° C. The conversion rates from CaO into carbonate were in excess of 90% for both systems, while a higher decomposition rate of the formed carbonate back to CaO was observed in the melt containing LiF (83.8% of CO₂ desorbed) than in the NaF system (47.5% of CO₂ desorbed). Cycling was not performed for the fluoride-based melts as the higher desorption temperatures led to corrosion and deterioration of the outer stainless steel vessels by air.

Figure 5 shows absorption/desorption cycles in molten CaCl₂ with 5.3 wt% CaO added. The weight, temperature, and composition of the gas emitted from the reactor as
function of time is shown. In this system, there is no exchange reaction (Eq. 2), and the activity of CaCO₃ is not maintained at a low level. Furthermore, CaCl₂ exhibits a higher solubility of CaO than the fluoride-based melt (6% at 800°C) [19,20]. Absorption followed a predictable manner as the absorption efficiency started at a high level and then dropped, as reactive dissolved CaO in the liquid was consumed. This is evidenced by the recorded content of CO₂ in the gas emitted from the cell during each part of the cycle. During the initial carbonation, 46% CaO is converted into CaCO₃ in the first cycle during the first 70 min. This is followed by a slower reaction until carbonation stops after an additional 70 min. In the following cycles, increased CaO conversion is experienced. Figure 5 shows four completed cycles. The maximum value of CaO conversion into CaCO₃ in the CaCl₂ salt increased from 51.3% to 60.1% during the four performed cycles. When all available CaO had reacted and the gas escaping from the reactor resembled the composition being fed to the system, the feed of CO₂ was stopped and the temperature raised as described for the fluoride-based system. Rapid decomposition of CaCO₃ is evident from the sharp increase in the content of CO₂ in the liberated gas. The conversion efficiencies based on weight for CaO into CaCO₃ and for CaCO₃ back into CaO are plotted in Figure 6. The availability of CaO seemed to increase as higher values for conversion of CaO into CaCO₃ were observed with each cycle. 100% conversion into CaO was recorded in all cycles.
In processes for CCS based on thermal swing, CO₂ is often driven off by addition of superheated steam. Desorption of the pure CO₂ itself (i.e., a partial pressure of CO₂ of 1 atm.) is desirable as costs related to the condensation of water may be avoided. Decomposition at such conditions with a 20% CaO in CaCl₂-based molten salt was performed by stopping the flow of nitrogen while keeping the CO₂ flow. The temperature was then stepwise raised to 1070°C as described above. 74.2% of CaO had reacted with CO₂ when carbonation had proceeded to its full at 800°C. Additional carbonation (4.4% of CaO converted) was observed when the nitrogen was suspended in the gas flow and the temperature increased (Fig. 7). As the temperature increased beyond 900°C a loss of mass was recorded, indicating decarbonation and release of CO₂ from the liquid. A stepwise weight loss in accordance with the stepwise increase in temperature was recorded as depicted in Figure 7. A conversion rate of CaCO₃ into CaO on the order of 90% was found at 1070°C.

Concerns may be raised regarding the energy consumption for the thermal swing with a diluted liquid compared to a solid-based sorbent such as CaO (s). However, our experiments indicate that CaO can be present substantially above its solubility limit – most likely in the form of slurry. In this work, up to 20% CaO in CaCl₂ has been used while the solubility of CaO in CaCl₂ at 800°C is 6% [19]. At 74.2% carbonation, this is equivalent to an uptake capacity of CO₂ of 0.105 g/g liquid if 90% CaCO₃ to Ca conversion as recorded with this composition is assumed. This is similar to numbers recently reported for synthetic, stable sorbents in Ca-looping where CaO is present as nanostructures on a solid, inert carrier [21]. In practice, increasing viscosity will probably be the limiting effect as more CaO is added, however, this was not notable at a content of 20% CaO. Further work will concentrate on optimizing these conditions as they will be closely linked to the overall economics. Some molten salts may be subject to hydrolysis when exposed to water. Hydrolysis is, however, not thermodynamically favored for the salts used in this study [17]. A vapor pressure will be established over a free liquid surface. Potentially evaporated material will condense and deposit in cooler parts of the reactor or the gas line. Such condensate was, however, not found in any significant amounts, implying that the mass loss of due to evaporation was negligible.

To summarize, we have investigated a new method for selectively separating CO₂ from diluted gas mixtures exhibiting efficient gas–liquid reactions. An absorption column height of only 10 cm is shown sufficient to achieve high absorption efficiency. We propose that capture and release of CO₂ from very dilute gas mixtures may be possible with a fluoride-based melt containing NaF or LiF. Due to the robust inorganic chemicals, we propose that the method may be particularly suited for CCS on industrial emissions.

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Conflict of Interest

None declared.

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