

Selected papers from the 10th Trondheim Conference on
CO₂ Capture, Transport and Storage

SINTEF
PROCEEDINGS

4

TCCS-10



Trondheim CCS Conference

CO₂ Capture, Transport and Storage



Organized by: NCCS – Norwegian CCS Research Centre, under the auspices of NTNU and SINTEF - www.TCCS.no

SINTEF Proceedings

Editors:
Nils A. Røkke and Hanna Knuutila

TCCS-10
CO₂ Capture, Transport and Storage
Trondheim 17th–19th June 2019

Selected papers

SINTEF Academic Press

SINTEF Proceedings no 4

Editors: Nils A. Røkke (SINTEF) and Hanna Knuutila (NTNU)

TCCS-10

CO₂ Capture, Transport and Storage. Trondheim 17th-19th June 2019

Selected papers from the 10th International Trondheim CCS Conference

Keywords:

CCS – Carbon Capture, Transport and Storage, CO₂ Capture, CO₂ Transport, CO₂ Storage, CO₂ Utilization, Pre-combustion capture, Post-combustion capture, Oxy-fuel capture, CCS and hydrogen, CO₂ positive solutions, International R&D activities, Whole system issues, Novel CCS technologies, Public Acceptance, Communication, Policy, Business models

Cover illustration: SINTEF Energy

ISSN 2387-4295 (online)

ISBN 978-82-536-1646-9 (pdf)



© The authors. Published by SINTEF Academic Press 2019

This is an open access publication under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

SINTEF Academic Press

Address: Børrestuveien 3
PO Box 124 Blindern
N-0314 OSLO

Tel: +47 40 00 51 00

www.sintef.no/community

www.sintefbok.no

SINTEF Proceedings

SINTEF Proceedings is a serial publication for peer-reviewed conference proceedings on a variety of scientific topics.

The processes of peer-reviewing of papers published in SINTEF Proceedings are administered by the conference organizers and proceedings editors. Detailed procedures will vary according to custom and practice in each scientific community.

CARBON CAPTURE WITH METAL OXIDES IN MOLTEN SALTS: MgO, SrO AND CaO AS SORBENTS

Å. Grøtan*, E. Olsen, H.S. Nygård

Faculty of Science and Technology, Norwegian University of Life Sciences, Ås, Norway

* Corresponding author e-mail: ashild.grotan@gmail.com

Abstract

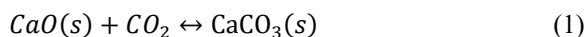
Carbon Capture in Molten Salts (CCMS) is an absorption-based method of separating CO₂ from a flue gas or industrial gas through a thermal swing technique, where the sorbent is dissolved or partially dissolved in molten salts. The method takes advantage of the reversible carbonation reaction of alkaline earth metal oxides and has previously been studied with CaO as sorbent, showing excellent absorption capacity, regeneration and cyclability compared to similar methods. If the molten salt contains certain alkaline metal halides, these may react with the formed metal carbonates in an exchange reaction, shifting the equilibrium towards further carbonation. The CCMS process is however energy intensive and the regeneration of the sorbent has been identified as a main cost driver due to high operating temperatures and high reaction enthalpy. In this study, a screening of alternative chemical systems with MgO, SrO and CaO as sorbents has been performed. The aim is to find chemical systems with lower operating temperatures and reaction enthalpies that work as efficiently as in previous studies, as this could reduce energy demand and thus operational costs. Promisingly high reaction stability and conversion ratio was found with MgO-FLiNaK, but more experiments are needed to see if the absorption efficiency may be sufficiently improved. SrO-NaCl-CaCl₂ showed an even higher conversion ratio, but lower reaction stability which may be improved in a different salt mixture. Furthermore, it was found that the chemical system CaO-LiF-CaF₂, which has been very efficient in previous studies, seemed to have no active exchange reaction when the CaF₂ was replaced by CaCl₂. Another new finding is that even though studies have shown that CCMS may operate well above the solubility limit of the sorbent, the sorbent does need to have a certain solubility in the melt in order to absorb any CO₂.

Keywords: Carbon Capture in Molten Salts (CCMS), Carbonate Looping, Metal Oxides as CO₂ sorbents

1. Introduction

In the 2018 special report on the 1.5DS from IPCC, all four pathways involve net negative CO₂ emissions after year 2050 [1]. It is highly unlikely that the required rate of emission reductions can be covered by a transition to renewable energies alone, which means that carbon capture and storage (CCS) will have to play an important role in reaching the climate goals.

Carbon Capture in Molten Salts (CCMS) is a high-temperature carbon capture technology which could be especially interesting for industrial processes with residual heat at high temperatures, such as ferro-silicon or cement production. The method builds upon the same chemical principle as Calcium Looping (CaL), where CaO reacts reversibly with CO₂, as described in eq. (1).



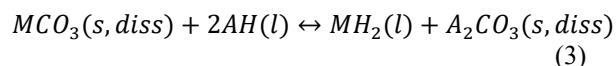
Through a thermal swing technique, the CO₂ may be alternately absorbed and desorbed around an equilibrium temperature $T_{\Delta G=0}$, around 885°C in the case of eq. (1). Alternatively, a pressure swing technique may also be used.

CCMS differs from CaL in that the sorbent is dissolved or partially dissolved in molten salts. The sorbent may also be other alkaline earth metal oxides (MO), as described on its general form in eq. (2).



M: Ca, Mg, Sr, Ba, Be.

Most salts that are used in the melt are inert to the sorbent, but certain alkaline metal halides (AH) lead to an exchange reaction, as in eq. (3).

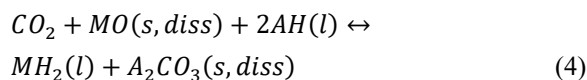


A: Li, Na, K, Rb, Cs

H: F, Cl.

This keeps the activity of the MCO₃ low, shifting the equilibrium in eq. (2) towards further carbonation [2, 3], and thus enabling an even higher absorption efficiency and conversion ratio than in a melt with no alkaline metal halide.

This leads to the total reaction in eq. (4).



Generally, the melt also needs to contain some inert salts in addition to the chemically active AH. The role of the inert salt is mainly to reduce the melting point of the melt, as salt mixtures generally have lower melting points than pure salts, and in this application a melting point well below the equilibrium temperature of eq. (4) is needed. Other important properties of the salt mixtures are explained later in this section.

A simplified flowchart of the CCMS system is illustrated in figure 1. The equilibrium temperature $T_{\Delta G=0}$ and reaction enthalpy ΔH will vary depending on the chosen

MO and AH. One hypothesis from earlier studies is that even though the thermochemical properties of the total reaction in eq. (4) is governing in the system, the properties of the main reaction in eq. (2) and the exchange reaction in eq. (3) also could affect the reaction equilibrium.

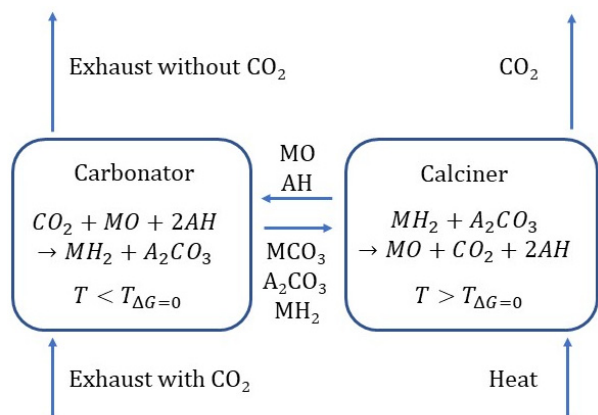


Figure 1: Simplified flowchart of the CCMS process.

CCMS has previously been studied with CaO as sorbent and has shown very promising results with respect to absorption capacity, regeneration and cyclability [2, 4-6]. The hypothesis is that the continuous dissolving of the sorbent and the carbonates in the molten salts liberates sorbent surface area for the CO₂ to react with, leading to faster reaction kinetics than in the solid state. The method also shows excellent cyclability: while similar methods operating in the solid state, such as CaL, experience great challenges with degradation of the sorbent after a few cycles [7, 8], experiments with CCMS have been done with up to 12 cycles without any detectable degradation of the sorbent [9]. Furthermore, chemical systems with exchange reaction have shown close to total absorption of CO₂ from synthetic flue gas with 14vol% CO₂, until saturation of the sorbent. On the other hand, regeneration tends to be less efficient in such chemical systems, as the alkaline carbonates are more stable [2].

The process is energy intensive and the regeneration of the sorbent has been identified as a main cost driver, as this is in an endothermal reaction operating at high temperature. Consequently, the reaction enthalpy ΔH is an important parameter for operational costs, as well as the equilibrium temperature $T_{\Delta G=0}$.

The aim of this study is to investigate alternative chemical systems for CCMS, preferably with low ΔH and $T_{\Delta G=0}$ in order to reduce energy demand and thereby operational costs, as well as generally exploring the properties of alternative chemical systems.

This is first done through a theoretical modelling of thermochemical properties of eq. (2)-(4), with all combinations of alkaline earth metal oxides (MO) as sorbent and alkaline metal halides (AH) as active salt, as listed in eq. (2) and (3). The data is found in the database HSC Chemistry 6.12 [10]. Based on the modelling, some promising chemical systems are then chosen for an experimental screening. The systems are chosen based mainly on the properties of the total reaction in eq. (4), but knowledge to suitable salt mixtures is also a limiting

factor. These need to have properties such as melting point at least 100°C below the equilibrium temperature, low vapor pressure, low viscosity, and they must not hydrolyse in contact with water or form stable carbonates. Melting points of potential salt mixtures are found in the database ACerS-NIST 3.1 [11], and further properties are found through literature search.

2. Modelling

An excerpt of the modelling is given in table 2, below the reference list. The table displays the equilibrium temperature $T_{\Delta G=0}$ and the reaction enthalpy ΔH at this temperature for the main reaction in eq. (2), the exchange reaction in eq. (3) and the total reaction in eq. (4). This is done for each relevant alkaline earth metal oxide (MO) combined with the different alkaline metal halides (AH). Promising combinations should have a low equilibrium temperature, but higher than 400°C (with respect to the possibility of using residual heat for power production), and a reaction enthalpy as low as possible. For reference, the most absorption- and desorption efficient chemical system in previous studies has been CaO-LiF, with $T_{\Delta G=0} = 950^\circ\text{C}$ and $\Delta H = -161 \text{ kJ/mol}$. Alternative chemical systems should have lower values than this.

Systems with BeO and BaO are left out of table 2, as these do not have an equilibrium temperature within the desired range and are therefore not suitable for carbonate looping.

The systems that stand out as interesting in this modelling, are mainly MgO along with fluorides, with equilibrium temperatures from 410°C to 675°C and reaction enthalpies below (absolute value) 136 kJ/mol, as well as SrO along with certain chlorides, with equilibrium temperatures from 396°C to 785°C and reaction enthalpies below (absolute value) 127 kJ/mol.

3. Experimental

3.1 Equipment and preparations

The experimental setup, as shown in figure 2, consists of a tubular electric furnace and a reactor in stainless steel. A ceramic tube separates the reactor and the furnace, for protection of the heating elements in the furnace. The reactor contains a nickel crucible (5.2cm x 16cm inner diameter and height) which in turn contains the molten salt and the sorbent. All equipment which is in contact with the salt during experiments is made from nickel, due to the very corrosive conditions around molten salts. The inlet gas, a synthetic flue gas with 14vol% CO₂ (99.995%) in N₂ (99.999%), controlled by mass flow controllers (Mass-stream, M+W Instruments GmbH) and logged in LabView 8.2, is led through a nickel pipe (7mm inner diameter) to the bottom of the melt. The gas bubbles through the molten salt, where the CO₂ reacts with the sorbent. The outlet gas is led through tubes (PTFE, 4x6mm) to an electrostatic filter where traces of salt are removed, and further to an FTIR (Thermo Scientific, Nicolet 6700 model) for gas analysis. The FTIR interferometer is held at 120°C for at least 24h before experiments. A thermocouple of type S (Pt10%Rh-Pt) or type K (NiCr-NiAl) measures the temperature in the melt. A small, continuous flow of Ar (99.99%) through the furnace ensures inert atmosphere around the reactor to reduce corrosion.

In all experiments, 10wt% sorbent and eutectic salt mixtures are used, as long as the eutectic concentration is known. The sorbents CaO (Sigma-Aldrich reagent, 96-100.5%), MgO (VWR, 99.3%) and SrCO₃ (Sigma-Aldrich, >98%) were calcined before experiments. The calcination was done at 1000°C for 3h and 10h for CaO and MgO respectively, and SrCO₃ was calcined to SrO at 1200°C for 10h. CaCl₂·2H₂O (VWR, 100.3%) was dried under Ar atmosphere through the procedure described by Freidina and Frey (2000) [12] to remove all the crystalline water, due to its hygroscopic nature. The CaCl₂·2H₂O is heated to 300°C at 0.5°C/min, then to 800°C at 2.78°C/min and held at 800°C for 10h. Other salts that are used are CaF₂ (Sigma-Aldrich, 99.9%), LiF (Sigma-Aldrich, 98.5%), NaF (VWR, 100%), KF (VWR, 99%), ZnCl₂ (Sigma-Aldrich, 98-100.5%), KCl (Sigma-Aldrich, 99.5-100.5%) and NaCl (Sigma-Aldrich, >99.8%). These are dried in a heating cabinet at 200°C for at least 24h.

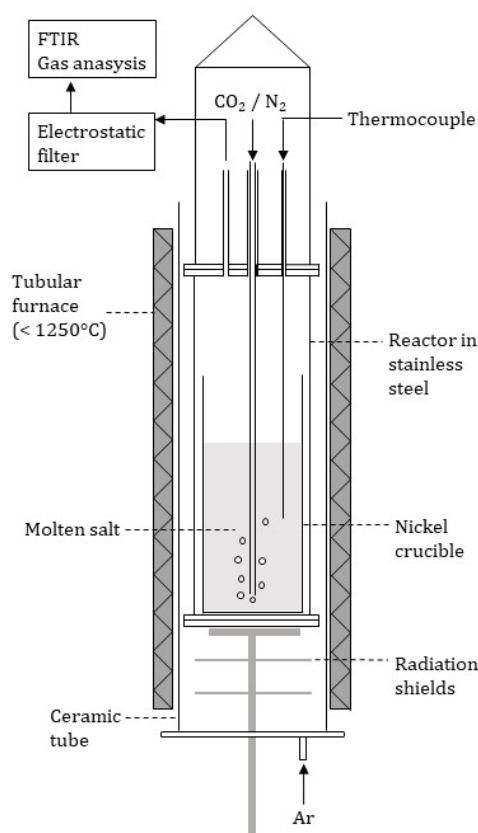


Figure 2: Schematic representation of the experimental setup.

3.2 Experimental procedure

Before experiments, the nickel crucible is filled with as much powder salts and sorbent as there is room for. When melted, the volume of the salt is strongly reduced and the final melt height under the experiments varies from 2-7 cm, depending on the densities of the salts. The crucible is placed in the reactor and in the furnace, and the nickel pipe and the thermocouple are put in place as illustrated in figure 2, but above the powder salt. 0.2 L/min N₂ flows through the nickel pipe for inert atmosphere while the furnace heats up. Once the salt is melted, the nickel pipe and thermocouple are lowered to around 1 cm above the bottom of the crucible. The flow of N₂ through the melt ensures mixing of the salts and sorbent for at least 30

minutes while the temperature stabilizes. Also, the FTIR is purged with 0.6 L/min of N₂ for at least 30 minutes before every experiment.

When the temperature is stable at the chosen absorption temperature, the experiment is started by turning on 14vol% CO₂ in the inlet gas. The CO₂ concentration in the outlet gas is then measured until it is close to the same as in the inlet gas. Absorption calculations are based on these concentration measurements, where the conversion ratio is defined as the amount of absorbed CO₂ as a fraction of the theoretical maximum, given that one mole of sorbent can react with one mole of CO₂. The carrying capacity is defined as the mass of absorbed CO₂ as a fraction of the mass of sorbent in the melt.

Melt heights are found after the experiment by measuring the height from the top of the crucible to the crust of the cooled salt. In some cases, this was not possible due to a very uneven crust, and these are marked with a parenthesis in table 1.

4. Results and discussion

The experiments are summarized in table 1 and discussed in the following, and more experimental details are given in table 3 below the reference list.

Table 1: Overview of the experiments. All salt mixtures are eutectic, except LiF-CaCl₂ for which no phase diagram was found. The exact concentration for this system is also uncertain due to drifting off and corrosion on the crucible during drying of CaCl₂. Melt heights in parenthesis were not possible to measure properly, as they had an especially uneven crust when cooled. A more detailed table (table 3) is given below the reference list.

#	Sorbent	Salt	Melt height (cm)	Conv. Ratio (%)	Carrying capacity (%)
1	MgO	LiF-NaF-KF	2-3	73	80
2	SrO	NaCl-CaCl ₂	6-7	90	38
3	CaO	LiF-CaCl ₂	(4-5)	53	41
4	CaO	LiF-CaF ₂	2-3	98	77
5	MgO	ZnCl ₂ -NaCl-KCl	(2-3)	2	2
6	CaO	LiF-KCl	(2-3)	7	5

4.1 MgO-FLiNaK

One experiment (#1 in table 1) was done with MgO as sorbent, dissolved in the salt mixture FLiNaK, a eutectic mixture of LiF, NaF and KF (46.5-11.5-42 mol%) (figure 3). FLiNaK is being studied for applications in concentrated solar power [13, 14], so its properties are well-known, and it will be suitable to an up-scaling.

In this system, the total reaction with MgO-KF has the highest equilibrium temperature (table 2), and KF will thus be the active component in the salt.

The result is given in figure 3, where it is evident that a great part of the CO₂ is going through the melt already from the first minute, and only around 20% of the CO₂ is absorbed. The absorption is stable at this level for the first 200 minutes, where about 50% conversion ratio is

reached, and after this point the absorption gradually becomes less efficient.

The low absorption efficiency in this experiment is likely due to the low melt height, which was 2-3 cm. A low melt height leads to short residence time in the melt and thus little time for the gas to react with the sorbent. It is likely that the plateau region of the absorption curve would be shifted to more efficient absorption with a higher melt. Also, the plateau shape of the absorption curve indicates stable reaction kinetics for the first 200 minutes (until around 50% saturation of the sorbent). This flat curve shape is typical for systems with an active exchange reaction, so if the plateau region can be shifted toward more efficient absorption by increasing the melt height, this can be a promising result for this chemical system.

Furthermore, the total conversion ratio of the sorbent was high: 73%. This is high compared to what has been reported in recent literature on MgO as sorbent for CO₂, which is typically less than 10% with pure MgO in the solid phase. Yang et al. have summarized the absorption capacities of MgO based absorbents promoted with nitrates and carbonates and found that MgO with an optimal combination of carbonates and nitrates had a stable conversion ratio at 30% [15]. Hwang et al. achieved up to 77% conversion in the first cycle with MgO promoted with alkali nitrates and carbonates, but this capacity was strongly reduced in the second cycle [16]. It could be interesting to see in further work whether the experience with high cyclability of CaO in CCMS compared to similar methods, is transferable to MgO. Hwang et al. also conclude that K₂CO₃ and alkali metal nitrates play an important role for the CO₂ capture capacity of MgO [16]. As the melt in this experiment contains KF which gets carbonated to K₂CO₃, the same effect may be present here.

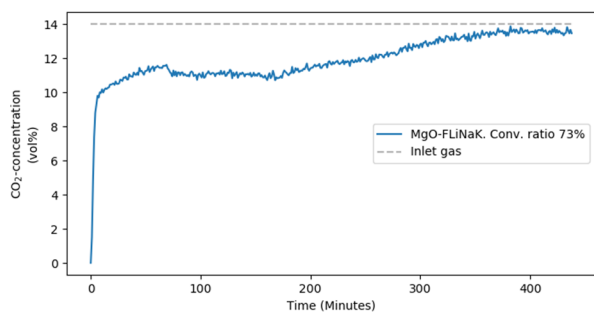


Figure 3: Absorption experiment with 10 wt% MgO as sorbent in the salt mixture FLiNaK (eutectic LiF-NaF-KF). The figure shows CO₂ concentration in the outlet gas (blue) after absorption, and the concentration in the inlet gas (grey). $T_{(abs)} = 600^{\circ}\text{C}$. Melt height: 2-3 cm.

4.2 SrO-NaCl-CaCl₂

Figure 4 shows an experiment (#2) with 10 wt% SrO in eutectic NaCl-CaCl₂ (52-48 mol%). Due to the pre-melting of CaCl₂, the total melt in this experiment was relatively high, around 7 cm.

Roughly 60% of the CO₂ is absorbed for the first hour, but the absorption curve has an increasing slope throughout the experiment as the absorption efficiency gradually decreases. This absorption profile is similar to those from chemical systems without exchange reaction, which could indicate that the NaCl does not react in this

melt. On the other hand, the total conversion ratio of 90% is very high, and typical for a system with an active exchange reaction. A possible explanation for these mixed signals could be that the NaCl is reacting, but that the reaction kinetic is slow and decreasing over time. This is further discussed under section 4.4.

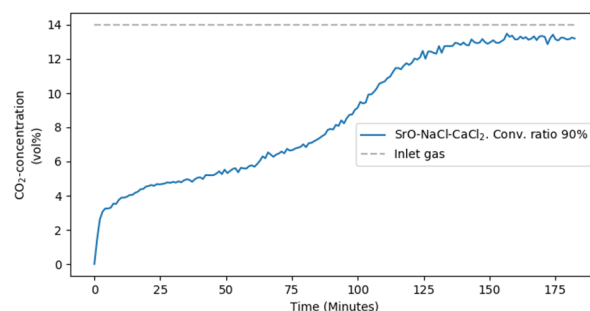


Figure 4: Absorption experiment with 10 wt% SrO as sorbent in eutectic NaCl-CaCl₂. The figure shows CO₂ concentration in the outlet gas (blue) after absorption, and the concentration in the inlet gas (grey). $T_{(abs)} = 663^{\circ}\text{C}$. Melt height: 6-7 cm.

4.3 CaO-LiF

Three experiments were conducted with CaO as sorbent and LiF as the active alkaline metal halide in the melt: one of the experiments was with CaCl₂ (#3 in table 1, LiF-CaCl₂ 25-75 mol%). Eutectic concentration is unknown) and one with CaF₂ (#4, LiF-CaF₂ 80.5-19.5 mol%) as inert salt. These two are discussed in the following, and the third (#6, LiF-KCl) in section 4.5.

Unfortunately, a phase diagram for LiF-CaCl₂ has not been found in literature. The molar fraction of LiF was set to 25% to be above the stoichiometric limit for the total reaction. The exact concentration is uncertain due to salt drifting off and strong corrosion on the crucible during the drying of CaCl₂. The system CaO-LiF-CaF₂ has been investigated in previous studies with very efficient absorption and high capacity, probably due to a very active exchange reaction with LiF [2]. The objective of the experiment with CaCl₂ was to see if the CO₂ absorption abilities of CaO-LiF could also be achieved in CaCl₂, which has some practical benefits compared to CaF₂. For example, water solubility greatly simplifies cleaning out the crucible between experiments. However, for commercial applications, this is of less importance.

The result with CaCl₂ shows a steep absorption profile with gradually decreasing absorption efficiency, and a total conversion ratio of 53%. This was surprising, as it is almost identical, both in absorption profile and conversion ratio, to previous experiments with CaO-CaCl₂, i.e. without any alkaline metal halide for exchange reaction. This strongly indicates that the LiF does not react in the melt with CaCl₂, even though it reacts very actively in the melt with CaF₂. The high efficiency and stable reaction kinetics of the system CaO-LiF-CaF₂, which was known from previous work, was again confirmed in this experiment. Considering that the melt height was very low in the experiment with CaO-LiF-CaF₂, only 2-3 cm, this strongly demonstrates the high efficiency of this chemical system even with a very short residence time. The two experiments are compared in figure 5.

One possible explanation to this surprising difference could be the solubility of Li_2CO_3 in CaCl_2 . The hypothesis from earlier studies, as mentioned in the introduction, is that the dissolving of the sorbent and the carbonates enables continuous contact between the sorbent and the CO_2 , and thereby contributes to fast reaction kinetics. However, if the Li_2CO_3 has low solubility on CaCl_2 , it does not dissolve in the melt and LiF will be unavailable to the CaCO_3 , quickly halting the exchange reaction. Information on the solubility of Li_2CO_3 in CaCl_2 has unfortunately not been found in literature.

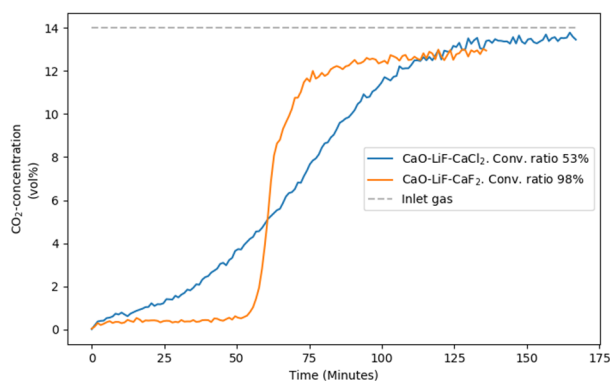


Figure 5: Comparison of two absorption experiments with 10 wt% CaO as sorbent in LiF-CaCl_2 (25 mol% LiF . Eutectic concentration is unknown. Melt height: 4-5 cm) (blue) and in eutectic LiF-CaF_2 (80.5 mol% LiF . Melt height: 2-3 cm) (yellow). The figure shows CO_2 concentration in the outlet gas from the two experiments, and the concentration in the inlet gas (grey). $T_{(abs)} = 787^\circ\text{C}$. The experiments show that the exchange reaction with CaCO_3 and LiF is strongly dependent on which inert salt is present in the melt.

4.4 Comparing the results

If the above-mentioned hypothesis about the solubility of Li_2CO_3 is correct, it could be transferrable to the experiment with SrO-NaCl-CaCl_2 . If the initially formed Na_2CO_3 does not dissolve, or very slowly dissolves, in CaCl_2 , it could in the same way prevent NaCl from further carbonation as the SrCO_3 would have to diffuse through a layer of Na_2CO_3 to react with the NaCl . This could be a fitting explanation to the slow reaction kinetics and high final conversion ratio. Information on the solubility of Na_2CO_3 in CaCl_2 has unfortunately not been found in literature.

One hypothesis from earlier studies is that the Gibbs free energy ΔG of the exchange reaction alone could affect the equilibrium of the total reaction. In the system SrO-NaCl , $\Delta G > 0$ at all temperatures for the exchange reaction (eq. (3)), meaning that the reaction equilibrium always goes towards decarbonation. This, along with the slow reaction kinetics in figure 4, could support the hypothesis mentioned above. For comparison, eq. (3) for the systems MgO-KF and CaO-LiF both have $\Delta G < 0$ for all temperatures and have shown a plateau shaped absorption profile in experiments, also supporting the hypothesis.

4.5 MgO-ZnCl₂-NaCl-KCl and CaO-LiF-KCl

In addition to the already mentioned experiments, two chemical systems were also tested but resulted in close to

no absorption. 10 wt% MgO in eutectic $\text{ZnCl}_2\text{-NaCl-KCl}$ (#5 in table 1, 60-20-20 mol%, figure 6) and 10 wt% CaO in eutectic LiF-KCl (#6, 19-81 mol%, figure 7) had almost identical results with close to no absorption of CO_2 . Also, in both these experiments, lumps were observed in the molten salt after the experiments, which was probably the sorbent which had not dissolved in the melt and likely the reason why no absorption was observed. In the case of MgO , this explanation is supported by the findings of Cherginets (1997) [17], where a low solubility of MgO in NaCl-KCl was shown.

This is also an interesting result, as while earlier studies have shown that CCMS can operate above the solubility limit of the sorbent [2], this result shows that the sorbent must have a certain solubility in the melt.

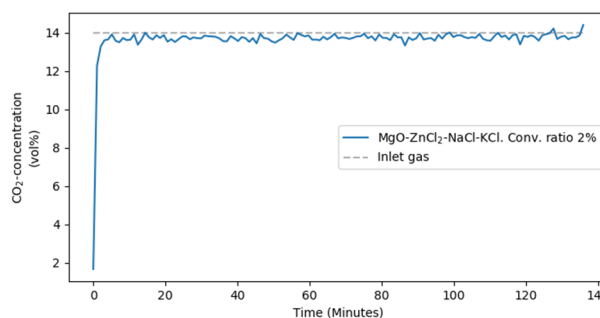


Figure 6: Absorption experiment with 10 wt% MgO as sorbent in eutectic $\text{ZnCl}_2\text{-NaCl-KCl}$. The figure shows CO_2 concentration in the outlet gas (blue) after absorption, and the concentration in the inlet gas (grey). $T_{(abs)} = 260^\circ\text{C}$. Melt height: 2-3 cm.

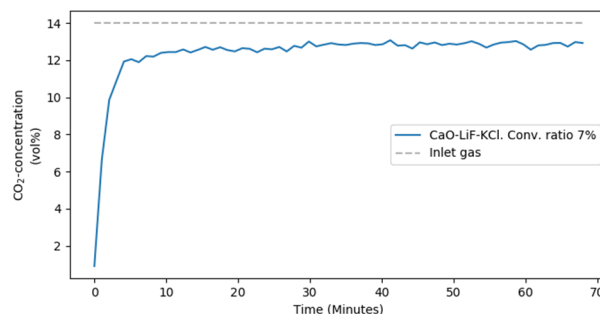


Figure 7: Absorption experiment with 10 wt% CaO as sorbent in eutectic LiF-KCl . The figure shows CO_2 concentration in the outlet gas (blue) after absorption, and the concentration in the inlet gas (grey). $T_{(abs)} = 780^\circ\text{C}$. Melt height: 2-3 cm.

5. Conclusions

An experimental screening of alternative chemical systems with MgO , SrO and CaO as sorbents for CCMS has been conducted. Chemical systems in the screening are chosen based on a broad, theoretical modelling of alternative chemical systems with alkaline earth metal oxides as sorbents and alkaline metal halides as active salts. It was found that MgO , dissolved in the salt FLiNaK , absorbed stably until around 50% saturation, and reached a total conversion ratio of 73%. This is high compared to other studies and shows a potential for MgO as a sorbent for CO_2 . Further research is however needed, especially with regards to the absorption efficiency, which was low in this experiment.

The experiment with SrO-NaCl-CaCl_2 also shows some promising results, particularly with a very high

conversion ratio of 90%, but the reaction efficiency was decreasing. Further research with SrO in different salts could be interesting in the future.

It was also shown that a chemical system with CaO-LiF, which has been very efficient with CaF₂ as inert salt in earlier studies, performed very similarly to a system without LiF when the CaF₂ was replaced by CaCl₂. A suggested explanation to this is the possibility of low solubility of Li₂CO₃ in CaCl₂ compared to in CaF₂, which would limit the exchange reaction. The same explanation could be transferrable to the system with SrO-NaCl-CaCl₂, if Na₂CO₃ dissolved slowly in CaCl₂.

Furthermore, experiments were performed where close to no CO₂ was absorbed, probably due to the low solubility of the sorbent in the salt. These systems were MgO-ZnCl₂-NaCl-KCl and CaO-LiF-KCl. This shows that the sorbent needs a certain solubility in the melt, even though research has shown that CCMS can operate above the solubility limit of the sorbent. A comparison of the experiment with SrO with the systems MgO-FLiNaK and CaO-LiF-CaF₂ support the hypothesis that the Gibbs free energy of the exchange reaction alone may affect the reaction equilibrium of the total reaction.

References

- [1] Masson-Delmotte, V., et al., *Global warming of 1.5C. An IPCC Special Report on the impacts of global warming of 1.5C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change, sustainable development, and efforts to eradicate poverty*. 2018, IPCC.
- [2] Olsen, E. and V. Tomkute, *Carbon capture in molten salts*. Energy Science & Engineering, 2013. **1**(3): p. 144-150.
- [3] Tomkute, V., et al., *Reactivity of CaO with CO₂ in molten CaF₂-NaF: formation and decomposition of carbonates*. Energy Science & Engineering, 2016. **4**(3): p. 205-216.
- [4] Tomkute, V., A. Solheim, and E. Olsen, *CO₂ Capture by CaO in Molten CaF₂-CaCl₂: Optimization of the Process and Cyclability of CO₂ Capture*. Energy & Fuels, 2014. **28**(8): p. 5345-5353.
- [5] Tomkute, V., et al., *Reactivity of CaO with CO₂ in molten CaF₂-NaF: formation and decomposition of carbonates*. Energy Science & Engineering, 2016. **4**(3): p. 205-216.
- [6] Tomkute, V., A. Solheim, and E. Olsen, *Investigation of High-Temperature CO₂ Capture by CaO in CaCl₂ Molten Salt*. Energy & Fuels, 2013. **27**(9): p. 5373-5379.
- [7] Dean, C.C., et al., *The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production*. Chemical Engineering Research and Design, 2011. **89**(6): p. 836-855.
- [8] Blamey, J., et al., *The calcium looping cycle for large-scale CO₂ capture*. Progress in Energy and Combustion Science, 2010. **36**(2): p. 260-279.
- [9] Tomkute, V., A. Solheim, and E. Olsen, *CO₂ Capture by CaO in Molten CaF₂-CaCl₂: Optimization of the Process and Cyclability of CO₂ Capture*. Energy & Fuels, 2014. **28**(8): p. 5345-5353.
- [10] Outotec Research Oy, F., *HSC Chemistry v. 6.12*.
- [11] ACerS-NIST, *Phase equilibria diagrams database, v. 3.1*. 2005.
- [12] Freidina, E.B. and D.J. Fray, *Phase diagram of the system CaCl₂-CaCO₃*. Thermochimica Acta, 2000. **351**(1): p. 107-108.
- [13] Olsin, L.C.e.a., *Materials corrosion in molten LiF-NaF-KF salt*. J. Fluorine Chem Soc Rev, 2009. **130**: p. 67-73.
- [14] Williams, D.F., *Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop*. Oak Ridge National Laboratory: Oak Ridge, TN, 2006.
- [15] Yang, X.F., et al., *Magnesium Oxide-Based Absorbents for CO₂ Capture at Medium Temperature*. Current Pollution Reports, 2018. **4**(1): p. 13-22.
- [16] Hwang, B.W., et al., *CO₂ capture and regeneration properties of MgO-based sorbents promoted with alkali metal nitrates at high pressure for the sorption enhanced water gas shift process*. Process Safety and Environmental Protection, 2018. **116**: p. 219-227.
- [17] Cherginets, V.L., *On studies of oxide solubilities in melts based on alkaline halides*. Electrochimica Acta, 1997. **42**(23): p. 3619-3627.

Table 2: Excerpt from modelling of thermochemical properties of alternative chemical systems for CCMS. The table contains equilibrium temperature $T_{\Delta G=0}$ and the reaction enthalpy ΔH at this temperature for carbonation reactions with combinations of alkaline earth metal oxides (MO) as sorbents and alkaline metal halides (AH) as active salts. $\Delta G < 0$ below the given temperature and $\Delta G > 0$ above the given temperature, except the temperatures marked with *. In cases where $\Delta G < 0$ or $\Delta G > 0$ for all temperatures in the total reaction, the system does not have an equilibrium temperature and is therefore not an alternative system for CCMS. All data is from the database HSC Chemistry v. 6.12.

Sorbent (MO)	Salt (AH)	Total reaction (eq. (4))		Main reaction (eq. (2))		Exchange reaction (eq. (3))	
		$T_{\Delta G=0}$ [°C]	ΔH [kJ/mol]	$T_{\Delta G=0}$ [°C]	ΔH [kJ/mol]	$T_{\Delta G=0}$ [°C]	ΔH [kJ/mol]
MgO	LiCl	0	-48	305	-99	4160	149
	NaCl	$\Delta G > 0$				$\Delta G > 0$	
	KCl	$\Delta G > 0$				$\Delta G > 0$	
	LiF	410	-103			$\Delta G < 0$	
	NaF	475	-93			$\Delta G < 0$	
	KF	675	-125			$\Delta G < 0$	
	RbCl	$\Delta G > 0$					
	RbF	675	-130			$\Delta G < 0$	
	CsCl	$\Delta G > 0$					
CsF	685	-136	$\Delta G < 0$				
CaO	LiCl	690	-194	885	-166	2300	52
	NaCl	235	-73			$\Delta G > 0$	
	KCl	25	-45			$\Delta G > 0$	
	LiF	950	-161			$\Delta G < 0$	
	NaF	1115	-171			$\Delta G < 0$	
	KF	1190	-182			$\Delta G < 0$	
	RbCl	$\Delta G > 0$					
	RbF	$\Delta G < 0$					
	CsCl	$\Delta G > 0$					
CsF	1155	-185	$\Delta G < 0$				
SrO	LiCl	1230	-171	1215	-202	335	-8
	NaCl	785	-127			$\Delta G > 0$	
	KCl	530	-111			$\Delta G > 0$	
	RbCl	425	-100			$\Delta G > 0$	
	CsCl	395	-89			$\Delta G > 0$	
	LiF	1155	-180			1640 *	26
	NaF	1325	-188			800 *	46
	KF	1390	-202			$\Delta G < 0$	
	RbF	1345	-210			$\Delta G < 0$	
CsF	1340	-207	$\Delta G < 0$				

Table 3: Experimental data. All salt mixtures are eutectic, except LiF-CaCl₂ for which no phase diagram was found. The exact concentration of this system is also uncertain due to drifting off and corrosion on the crucible during drying of CaCl₂. Melt heights in parenthesis were not possible to measure properly, as they had an especially uneven crust when cooled.

#	Sorbent	Salt	Salt concentration (mol%)	T_{melt} (°C)	$T_{\Delta G=0}$ (°C)	T_{abs} (°C)	Total mass (g)	Melt height (cm)	Conv. Ratio (%)	Carrying capacity (%)
1	MgO	LiF-NaF-KF	46.5-11.5-42	454	675	600	150	2-3	73	80
2	SrO	NaCl-CaCl ₂	48-52	507	785	663	326	6-7	90	38
3	CaO	LiF-CaCl ₂	25-75 (ca)	-	950	783	228	(4-5)	53	41
4	CaO	LiF-CaF ₂	80.5-19.5	769	950	787	161	2-3	98	77
5	MgO	ZnCl ₂ -NaCl-KCl	60-20-20	203	305	260	150	(2-3)	2	2
6	CaO	LiF-KCl	19-81	710	950	780	250	(2-3)	7	5