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Kinetics of CO_2 absorption by calcium looping in molten halide salts

Heidi S. Nygård[a], Viktorija Tomkute[b], Espen Olsen[a,*]

[a]Department of Mathematical Sciences and Technology, Norwegian University of Life Sciences, 1430 Ås, Norway
[b]Hydro Aluminium AS, Tangenveien 1, 6885 Årdalstangen, Norway

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Abstract

Carbon Capture in Molten Salts (CCMS) is a high temperature method for extracting CO_2 from a variety of flue gases related to power generation and carbon-intensive industries. The chemical principles are similar to those in calcium looping in the solid state; a carbonation reaction of CaO with CO_2 to form $CaCO_3$ followed by regeneration of CO_2 through the reverse reaction. In CCMS, the active substances ($CaO/CaCO_3$) are dissolved or partly dissolved in molten salts, allowing fast reaction kinetics, high CO_2 sorption capacities, and avoiding solids attrition issues. In our previous studies, the focus has been on the total CO_2 sorption capacity and demonstration of cyclic absorption and desorption. Experiments have been performed with up to 20 wt% CaO in molten $CaCl_2$ and eutectic $CaF_2/CaCl_2$. It has been demonstrated that up to 85% of the CaO reacts during absorption, and ~100% of the $CaCO_3$ is decomposed during desorption. No degradation of the sorbent has been observed after 12 cycles. In the present study, the focus is turned to the reaction kinetics between CO_2 and CaO. The raw data from previous experiments are analyzed to obtain the sorption capacity (g CO_2 / 100 g sorbent) as a function of time, and the linear region of the capacity is further used to evaluate the reaction kinetics. The effect of absorption temperature, molten salt composition, CaO content and cyclic CO_2 capture is studied. The results show that $CaF_2/CaCl_2$ is more favorable for CCMS than pure $CaCl_2$; the kinetically controlled regime lasts longer and the total sorption capacity is higher. For both of the salt mixtures, the sorption capacities are stable during cyclic CO_2 capture, without any deterioration of the reaction kinetics.

Keywords: CO_2 capture; kinetics; calcium looping; molten salts

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* Corresponding author.
E-mail address: espen.olsen@nmbu.no

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1. Introduction

The emissions of greenhouse gases such as CO_2 have increased significantly the last decades. This trend is in pace with growing energy consumption based on fossil fuels, but also with considerably contributions from other carbon-intensive industries such as the manufacture of iron, steel and cement. Because of their established infrastructure for exploitation and distribution, it is likely that CO_2 emitting industries will continue to play dominant roles in the world's economy in the near future. According to the International Energy Agency (IEA), the 2°C scenario cannot be fulfilled without implementation of carbon capture and storage (CCS) [1]. The idea with CCS is to separate CO_2 from waste gases generated by stationary emission sources, followed by compression of the captured gas and transportation to a permanent storage site. The capture step represents the major part of the whole process, both in cost and complexity [2]. Many different capture technologies are pursued. Among these, three approaches are identified with greatest potential for commercial deployment; namely post-combustion CO_2 capture using amine solvents, oxy-fuel combustion, and calcium looping [3]. Calcium looping is an emerging technology that can be used for capturing CO_2 from post-combustion, pre-combustion, or industrial processes [4]. It is based on the reversible reaction between CO_2 and CaO to form $CaCO_3$ [5]:

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

The turning point temperature for this reaction is around 900°C (atmospheric pressure), and cyclic absorption and desorption of CO_2 may be performed by a thermal swing [4]. Alternatively, pressure swing can be utilized, but this is less economically attractive due to more restrictions on reactor materials [6]. The CaO sorbent is usually derived from limestone / dolomite, which is an abundant, cheap and environmentally friendly material. Other advantages of the calcium looping technology are relatively low efficiency penalty on the power / industrial process and possible synergy with cement manufacture [4].

The main challenge for calcium looping in the solid state is that the particles' morphology change over time. This particle degradation is caused by physical / structural stresses and sintering, and leads to less reactive surface and a significant decrease in sorbent reactivity after several absorption – desorption cycles [4, 7]. For CaO derived from natural limestone, the residual sorption capacity falls down to approximately 8g CO_2 / 100g sorbent at long term use [8]. The active surface area could be preserved by modifying solid CaO sorbents and thus reduce the rapid decay in reactivity. Manovic and Anthony [9] have reviewed the research on sorbent modification methods for enhancing the sorbent performance over time. The most promising methods were identified as reactivation by steam/water, thermal pretreatment, and addition of supports or incorporation of CaO into inert solid matrices such as aluminate-based cements. The latter technique is very promising because the inert supports are believed to be able to separate CaO particles and prevent or delay them from sintering at high temperatures [10]. Inert materials that have been used for this purpose are for example Al_2O_3, $Ca_{12}Al_{14}O_{33}$, ZrO_2, and $CaTiO_3$. However, due to high preparation cost of the synthesis methods, the application of these materials at large scale is challenging [11].

Another approach is Carbon Capture in Molten Salts (CCMS) [12-14]. In this concept, molten salts are used as chemical solvents of the active substances in calcium looping, with the main idea of hindering particle degradation. A flue gas containing CO_2 enters an absorption chamber (absorber) where CaO is present in a molten salt matrix. $CaCO_3$ is formed through Eq. 1 and dissolves continuously in the melt, leaving highly reactive surfaces of CaO readily available. The molten salt containing $CaCO_3$ is transferred to a desorption chamber (desorber) operated at higher temperature. The reverse reaction takes place (calcination), and the CO_2 is removed from the desorber. This may for example be performed with superheated steam, which may be separated from the CO_2 by condensation at a later stage. The released CO_2 could further be compressed and transported to a storage site. The cycle is completed by transferring the regenerated CaO-rich molten salt back to the absorber. All the active substances are dissolved or in a supersaturated suspension in the molten salt medium which then acts as a solvent as well as a carrier. Variations of the method has shown to be able to absorb CO_2 down to < 100 ppm in the gas emitted in a small scale batch reactor, indicating a potential to capture CO_2 from very diluted gas mixtures [12]. Recent experimental work has shown CO_2 capture with up to 20 wt% CaO - corresponding to a theoretical sorption capacity of 15.7g CO_2 / 100 g sorbent, in the molten salts $CaCl_2$ and $CaF_2/CaCl_2$ [13-15]. In these systems, it has been demonstrated that up to 85%

of the CaO reacts during absorption, and ~100% of the $CaCO_3$ is decomposed during desorption. No degradation of the sorbent has been observed after 12 cycles.

In previous studies, the main focus was to determine the total CO_2 sorption capacity and to demonstrate cyclic absorption and desorption. In this study, the raw data from the experimental work by Tomkute et al. [13, 14] is used, but now with the focus on the reaction kinetics between CO_2 and CaO. We look further into the effect of absorption temperature, CaO content, and cyclic CO_2 capture on the sorption capacity as a function of time. The linear region of the capacity is further used to evaluate the reaction kinetics.

2. Experimental

The data analysis in the present work is based on earlier experimental work. An overview of the experimental setup and procedure is given here, and more details may be found elsewhere [13, 14].

The experiments were performed at atmospheric pressure in a one-chamber reactor heated by a tubular ceramic furnace (see Figure 1). Anhydrous CaO, $CaCl_2$, and CaF_2 of analytical purity (Sigma-Aldrich) were dried at 200°C for 50h before use. Samples with 5-20 wt% CaO in $CaCl_2$ or eutectic CaF_2-$CaCl_2$ (13.8 wt% CaF_2 in $CaCl_2$) were prepared and placed in a nickel crucible (5.2cm diameter x 35.0cm height). The melt height was kept constant at 10cm, corresponding to a sorbent weight of 470 – 510g, depending on the initial CaO concentration. The nickel crucible was placed in an outer reactor made of stainless steel.

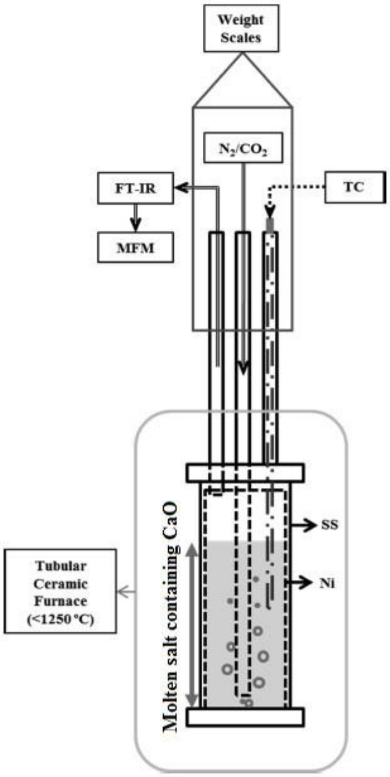

Figure 1. Design of the experimental setup. The reactor with the sorbent (5 – 20 wt% CaO in CaCl2 or eutectic CaF2-CaCl2) was heated by a tubular ceramic furnace. The outer sleeve of the reactor was made of stainless steel, and the inner crucible and the feed tube were made of nickel. Simulated flue gas was bubbled through the sorbent melt, and the absorption and desorption was monitored simultaneously by a FTIR apparatus and an industrial weighing balance. A S-type thermocouple (TC) was used to monitor the sample temperature.

To remove residual water from the compounds, the mixtures were heated slowly (200°C/h) to 850°C under inert atmosphere (Ar) and kept at that temperature for 10h before each experiment. A simulated flue gas consisting of CO_2 (99.99%) and N_2 (99.999%) was bubbled through the melt by a nickel pipe through the top of the sealed reactor, with 14 vol% CO_2 in N_2. The flows were controlled using mass flow controllers, and the total gas flow was set to be 0.6 L/min in all experiments. The melt temperature was monitored by a type S thermocouple (TC). The gas composition from the outlet of the reactor was analyzed by FTIR, and the weight of the whole reactor assembly was continuously monitored by an industrial weighing scale with an accuracy of 0.1g and a logging frequency of 10s. A mass flow meter (MFM) was applied at the outlet of the FTIR gas cell to ensure the system tightness.

The absorption was assumed to be complete when the inlet and outlet CO_2 concentrations were equal. A baseline study of the total reactor weight change was performed at different temperatures under Ar to take into account the weight change because of corrosion of the stainless steel chamber. A comparison of the mass change and FTIR data confirmed that the mass change was solely due to the forward or reverse reaction given by Eq. 1 when the corrosion was taken into account.

3. Kinetic analysis and discussion

In general, the carbonation of CaO in the solid state is characterized by two regimes controlled by kinetics and diffusion, respectively. Initially, the reaction takes place on the free surface of the CaO particles, and the only limitation is the kinetics of the reaction between CaO and CO_2. As the carbonation proceeds, a layer of $CaCO_3$ is formed around the unreacted sorbent, resulting in an increasing stearic hindrance for the CO_2, and the reaction is limited by CO_2 diffusion [16]. The reverse reaction (calcination) typically proceeds rapidly to completion [17].

Several models exist for kinetic analysis of the carbonation of CaO. Most classical are the shrinking core model [18], the grain model [19, 20], and the random pore model [16]. A much simpler, apparent kinetic model called Lee's model has also been proposed [21]. However, all these models are based on gas-solid reactions, and are not applicable when the carbonation is performed in the liquid phase. In the present study, we rely on a model where the $CaCO_3$ formed by carbonation of CaO is constantly dissolved in the molten salt leaving a surface of highly reactive CaO. In this model, the reaction will at any point be governed by reaction control. The raw data from the experimental work by Tomkute et al. [13, 14] are analyzed to obtain the sorption capacity (g CO_2 / 100 g sorbent) as a function of time and further used to calculate kinetic parameters.

As an example, absorption by bubbling a simulated flue gas (14 vol% CO_2 in N_2) through a 10 cm high column with 15 wt% CaO in eutectic $CaF_2/CaCl_2$ at 677°C is shown in Figure 2. The theoretical sorption capacity based on the applied CO_2 flow and conversion of all the available CaO is also included in the figure.

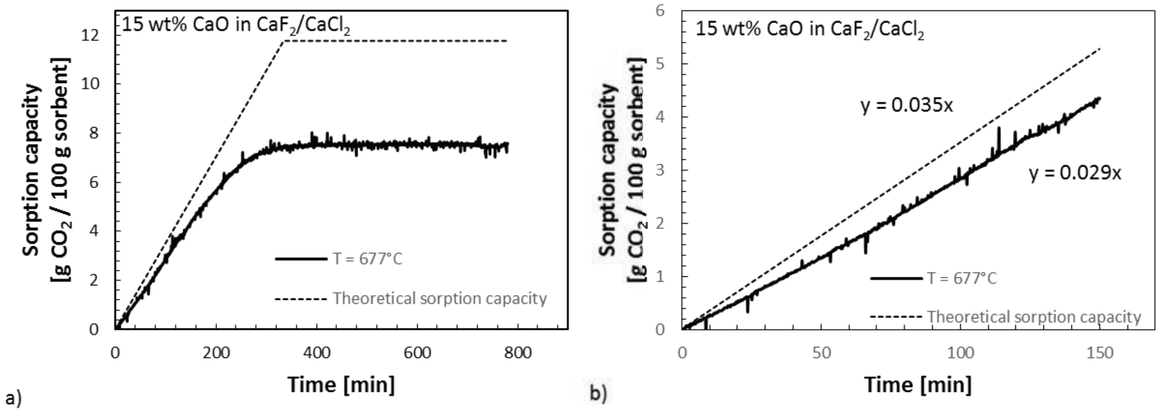

Figure 2. Example of sorption capacity (g CO_2 / 100 g sorbent) as a function of time for CO_2 capture in a mixture of 15 wt% CaO in eutectic $CaF_2/CaCl_2$. (a) Complete absorption process, (b) linear region used for evaluation of reaction kinetics.

In this experiment, the total melt weight was 519.84g. Theoretically, 1 mole of CaO can absorb 1 mole of CO_2 (Eq. 1), giving a maximum absorption of 0.785g CO_2 / g CaO. The initial mass of CaO in the sample was 77.98g, so a maximum of 61.21g CO_2 can be absorbed. This corresponds to a theoretical maximum sorption capacity of 11.8 g CO_2 / 100 g sorbent, where the sorbent refers to the mixture of the CaO and the eutectic $CaF_2/CaCl_2$. As seen in the figure, the total sorption capacity is 7.9g CO_2 / 100g sorbent, which corresponds to a CaO conversion of 66.9%.

The linear region is further used to evaluate the constant rate of CO_2 removal in the kinetically controlled regime (Figure 2b). The theoretical rate in this example is 0.035g CO_2 / 100g sorbent per minute, while the experimental value is 0.029g CO_2 / 100g sorbent per minute. This means that 83% of the applied CO_2 is captured.

3.1. Effect of absorption temperature

The effect of absorption temperature on the sorption capacity for 5.32 wt% CaO (solubility limit [22]) in $CaCl_2$ and 15 wt% CaO in eutectic $CaF_2/CaCl_2$ is shown in Figure 3 and 4, respectively. The theoretical sorption capacity is also included in the figures.

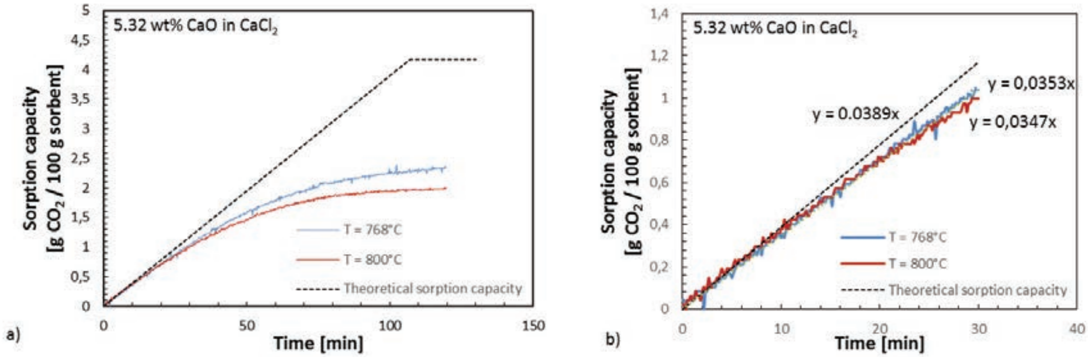

Figure 3. Effect of absorption temperature on the sorption capacity for CO_2 capture in a mixture of 5.32 wt% CaO in $CaCl_2$.
(a) Complete absorption process, (b) linear region used for evaluation of reaction kinetics.

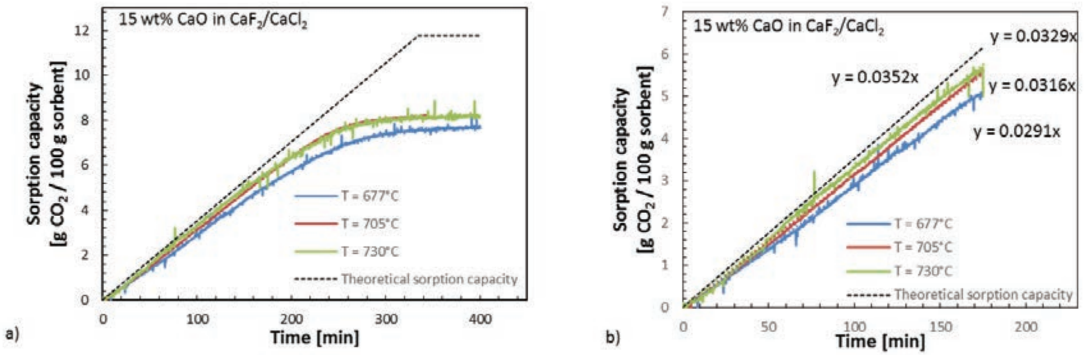

Figure 4. Effect of absorption temperature on the sorption capacity for CO_2 capture in a mixture of 15 wt% CaO in eutectic $CaF_2/CaCl_2$.
(a) Complete absorption process, (b) linear region used for evaluation of reaction kinetics.

The temperature has opposite effect on the sorption capacity for the two different salt mixtures. For CO2 capture in 5.32 wt% CaO in CaCl2, an increase in temperature gives lower capacity and slower kinetics (Figure 3). However, the small difference in the CO2 removal rate could be due to experimental errors. The total sorption capacities are 2.3 and 2.0g CO2 / 100g sorbent for T = 768°C and T = 800°C, respectively. In the linear region, the captured fraction of the applied CO2 decreases from 90.7% to 89.2% for the same temperatures.

For CO2 capture in 15 wt% CaO in eutectic CaF2/CaCl2, an increase in temperature gives higher capacity and faster kinetics (Figure 4). Sorption capacities of 7.9, 8.2, and 8.3g CO2 / 100g sorbent are observed for T = 677°C, T = 705°C, and T = 730°C, respectively, while the kinetics show that 82.7%, 89.8% and 93.5% of the applied CO2 is removed for the same temperatures.

An explanation for this behavior could be that the CaO is completely dissolved in CaCl2, while it is present substantially above the solubility limit in CaF2/CaCl2. This means that when CaO is present in form of a slurry, more of the active substance is accessible for the applied CO2, giving faster reactions, higher capacities and higher capture fractions.

3.2. Effect of CaO content

The effect of CaO content on the sorption capacity for $CaCl_2$ (T = 795 – 800°C) and eutectic $CaF_2/CaCl_2$ (T = 700 – 710°C) is shown in Figure 5.

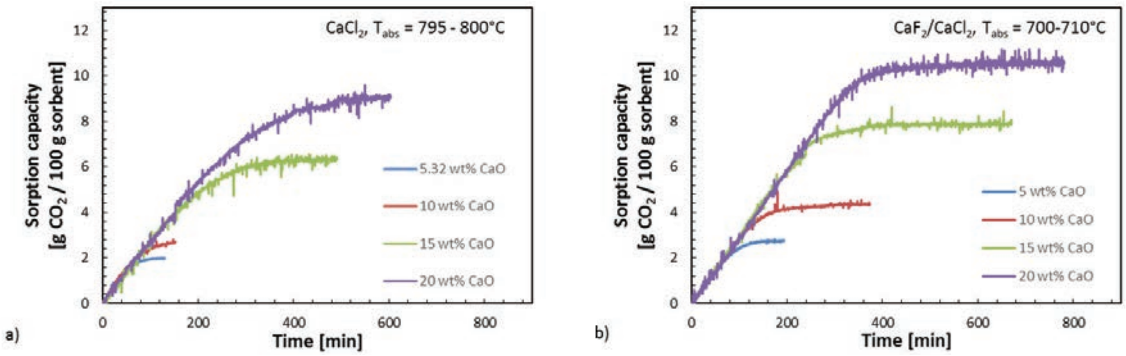

Figure 5. Effect of CaO content on the sorption capacity in (a) $CaCl_2$ with absorption temperature T = 795 - 800°C and (b) eutectic CaF_2-$CaCl_2$ with absorption temperature T = 700-710°C.

Analyses following the same procedure as for the temperature dependence show that the total sorption capacities depend both on the CaO content and the salt mixture, while the reaction kinetics in the linear regions are comparable. Both salts give higher capacities for higher CaO contents. For $CaCl_2$, the total sorption capacities are ranging from 2.0 to 9.1g CO_2 / 100g sorbent, while they are ranging from 2.7 to 10.6g CO_2 / 100g sorbent for eutectic $CaF_2/CaCl_2$. The use of 20wt% CaO in both salts gives higher sustained capacities compared to conventional calcium looping [8]. In the linear region, around 85% and 83% of the applied CO_2 is captured for CaO in $CaCl_2$ and eutectic $CaF_2/CaCl_2$, respectively. The small difference could be due to experimental errors or the difference in absorption temperatures. However, the linear regions last much longer for $CaF_2/CaCl_2$, and this salt mixture is therefore favorable for CO_2 capture in molten salts.

3.3. Cyclic CO_2 capture

The effect of cyclic CO_2 capture on the sorption capacity for 5.32 wt% CaO in $CaCl_2$ (T_{abs} = 787°C) and 15 wt% CaO in eutectic $CaF_2/CaCl_2$ (T_{abs} = 705°C) is shown in Figure 6 and 7, respectively. The theoretical sorption capacity is also included in the figures.

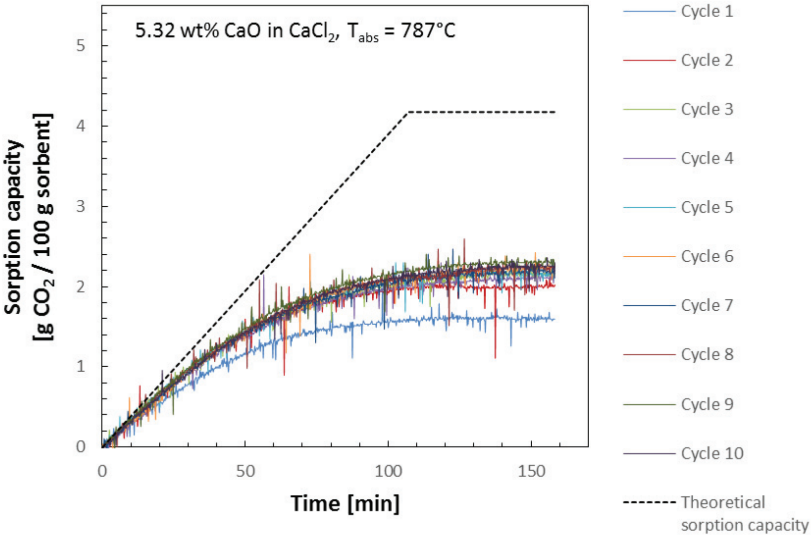

Figure 6. Effect of cyclic CO_2 capture on the sorption capacity in 5.32 wt% CaO in $CaCl_2$ (T_{abs} = 787°C).

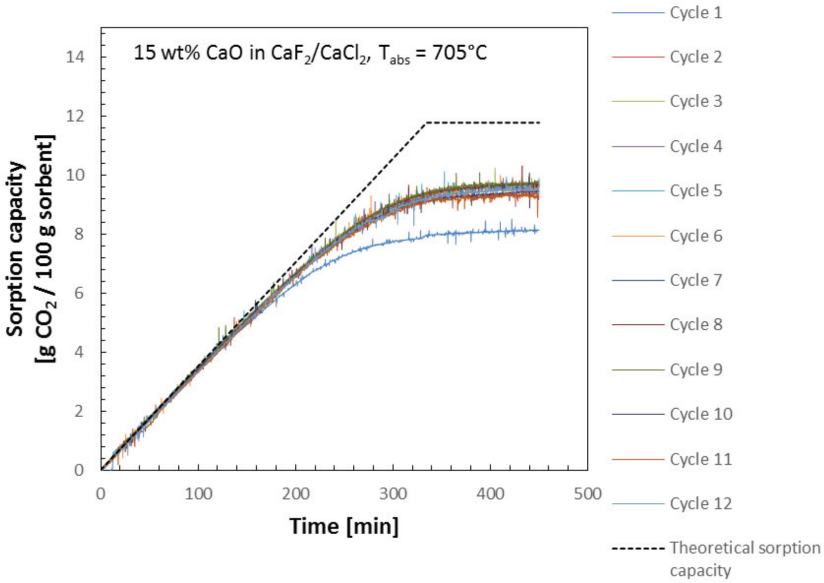

Figure 7. Effect of cyclic CO_2 capture on the sorption capacity in 15 wt% eutectic CaF_2-$CaCl_2$ (T_{abs} = 705°C).

As already established in previous work [13, 14], it can be observed that the total capture capacity increases in the first few cycles. After 10 and 12 cycles the capacity remains close to 2.4 and 9.9 g CO_2 / 100g sorbent for $CaCl_2$ and $CaF_2/CaCl_2$, respectively. Evaluation of the linear region shows that the rate of CO_2 removal is constant in all the cycles for each salt, and around 80% and 92% of the applied CO_2 is captured in $CaCl_2$ and $CaCF_2/CaCl_2$, respectively.

4. Conclusion

The present work investigates the reaction kinetics between CO_2 and CaO in molten $CaCl_2$ and eutectic $CaF_2/CaCl_2$. Mass change data during absorption was used to evaluate the sorption capacity as a function of time, and the linear region of the capacity was further used to evaluate the reaction kinetics.

In general, $CaF_2/CaCl_2$ shows most promise for CO_2 capture. For 5.32 wt% CaO in $CaCl_2$, an increase in temperature gives lower total capacity and slower kinetics, while the opposite is observed for 15 wt% CaO in $CaF_2/CaCl_2$. This is ascribed to the supersaturation of CaO in the latter salt, leading to more accessible active surface for the applied CO_2. Evaluation of the linear region shows the same reaction kinetics regardless of CaO content (5 – 20wt%) and salt, but the kinetically controlled regime is longer and the total sorption capacity is higher for $CaF_2/CaCl_2$. For cyclic CO_2 capture, the capacity increases in the first few cycles for both salts, and then stabilizes without any deterioration of the reaction kinetics. More than 80% of the applied CO_2 was captured in the linear region of all investigated experiments, and the highest capture fraction (93.5%) was obtained for 15 wt% CaO in $CaF_2/CaCl_2$ at 730°C. The highest sorption capacity (10.9 g CO_2 / 100g sorbent) was found for 20 wt% CaO in $CaF_2/CaCl_2$ at 700°C, which is higher than for conventional calcium looping [8]. Higher capacities could be obtained with higher CaO contents, probably with the limitation of increasing sorbent viscosity. This will be pursued in further studies.

Acknowledgements

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References

[1] IEA, Technology Roadmap: Carbon Capture and Storage, in, OECD/IEA, Paris, France, 2013.

[2] J. Pires, F. Martins, M. Alvim-Ferraz, M. Simões, Recent developments on carbon capture and storage: an overview, Chemical Engineering Research and Design, 89 (2011) 1446-1460.

[3] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K. Williams, N. Shah, P. Fennell, An overview of CO_2 capture technologies, Energy & Environmental Science, 3 (2010) 1645-1669.

[4] C.C. Dean, J. Blamey, N.H. Florin, M.J. Al-Jeboori, P.S. Fennell, The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production, Chemical Engineering Research and Design, 89 (2011) 836-855.

[5] J.C. Abanades, E.J. Anthony, D.Y. Lu, C. Salvador, D. Alvarez, Capture of CO_2 from combustion gases in a fluidized bed of CaO, AIChE Journal, 50 (2004) 1614-1622.

[6] M.K. Mondal, H.K. Balsora, P. Varshney, Progress and trends in CO_2 capture/separation technologies: A review, Energy, 46 (2012) 431-441.

[7] J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell, The calcium looping cycle for large-scale CO_2 capture, Progress in Energy and Combustion Science, 36 (2010) 260-279.

[8] G.S. Grasa, J.C. Abanades, CO2 Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles, Industrial & Engineering Chemistry Research, 45 (2006) 8846-8851.

[9] V. Manovic, E.J. Anthony, Lime-based sorbents for high-temperature CO_2 capture—a review of sorbent modification methods, International journal of environmental research and public health, 7 (2010) 3129-3140.

[10] Z. Li, Y. Liu, N. Cai, Understanding the effect of inert support on the reactivity stabilization for synthetic calcium based sorbents, Chemical Engineering Science, 89 (2013) 235-243.

[11] S.S. Kazi, A. Aranda, J. Meyer, J. Mastin, High performance CaO-based sorbents for pre-and post-combustion CO 2 capture at high temperature, Energy Procedia, 63 (2014) 2207-2215.
[12] E. Olsen, V. Tomkute, Carbon capture in molten salts, Energy Science & Engineering, 1 (2013) 144-150.
[13] V. Tomkute, A. Solheim, E. Olsen, Investigation of high-temperature CO_2 capture by CaO in $CaCl_2$ molten salt, Energy & Fuels, 27 (2013) 5373-5379.
[14] V. Tomkute, A. Solheim, E. Olsen, CO_2 Capture by CaO in Molten CaF_2–$CaCl_2$: Optimization of the Process and Cyclability of CO_2 Capture, Energy & Fuels, 28 (2014) 5345-5353.
[15] V. Tomkute, A. Solheim, S. Sakirzanovas, E. Olsen, Reactivity of CaO with CO_2 in molten CaF_2–NaF: formation and decomposition of carbonates, Energy Science & Engineering, 4 (2016) 205-216.
[16] S. Bhatia, D. Perlmutter, Effect of the product layer on the kinetics of the CO2 - lime reaction, AIChE Journal, 29 (1983) 79-86.
[17] A. Silaban, D. Harrison, High temperature capture of carbon dioxide: characteristics of the reversible reaction between CaO (s) and CO_2 (g), Chemical Engineering Communications, 137 (1995) 177-190.
[18] K. Johnsen, J.R. Grace, S.S.E.H. Elnashaie, L. Kolbeinsen, D. Eriksen, Modeling of Sorption-Enhanced Steam Reforming in a Dual Fluidized Bubbling Bed Reactor, Industrial & Engineering Chemistry Research, 45 (2006) 4133-4144.
[19] S. Stendardo, P.U. Foscolo, Carbon dioxide capture with dolomite: A model for gas–solid reaction within the grains of a particulate sorbent, Chemical Engineering Science, 64 (2009) 2343-2352.
[20] B. Khoshandam, R.V. Kumar, L. Allahgholi, Mathematical modeling of CO_2 removal using carbonation with CaO: The grain model, Korean Journal of Chemical Engineering, 27 (2010) 766-776.
[21] D.K. Lee, An apparent kinetic model for the carbonation of calcium oxide by carbon dioxide, Chemical Engineering Journal, 100 (2004) 71-77.
[22] S. Wang, F. Zhang, X. Liu, L. Zhang, CaO solubility and activity coefficient in molten salts $CaCl_2$–x (x = 0, NaCl, KCl, SrCl2, BaCl2 and LiCl), Thermochimica Acta, 470 (2008) 105-107.