AIMS Energy, 5(6): 873-886.
DOI: 10.3934/energy.2017.6.873
Received: 19 July 2017
Accepted: 19 October 2017
Published: 30 October 2017

http://www.aimspress.com/journal/energy

Research article

Hydrolysis of molten $CaCl_2$-CaF_2 with additions of CaO

Espen Olsen *, Maria Hansen, and Heidi S. Nygård

Faculty of Science and Technology, Norwegian University of Life Sciences (NMBU), Drøbakveien 31, N-1432 Ås, Norway

* **Correspondence:** espen.olsen@nmbu.no; Tel: +476-723-1566; Fax: +476-723-1501.

Abstract: Calcium halide based molten salts have recently attracted interest for a number of applications such as direct reduction of oxides for metal production and as liquefying agent in cyclic sorption processes for CO_2 by CaO from dilute flue gases (Ca-looping). A fundamental aspect of these melts is the possible hydrolysis reaction upon exposure to gaseous H_2O forming corrosive and poisonous hydrogen halides. In this work experiments have been performed investigating the formation of HCl and HF from a molten salt consisting of a 13.8 wt% CaF_2 in $CaCl_2$ eutectic exposed to a flowing gas consisting of 10 vol% H_2O in N_2. Hydrolysis has been investigated as function of content of CaO and temperature. HCl and HF are shown to be formed at elevated temperatures; HCl forms to a substantially larger extent than HF. Addition of CaO has a marked, limiting effect on the hydrolysis. Thermodynamic modeling of the reaction indicates activity coefficients for CaO above unity in the system. For cyclic CO_2-capture based on thermal swing, it is advisable to keep the temperature in the carbonation (absorption) reactor well below 850 °C while maintaining a high CaO content if molten $CaCl_2$ is employed. Similar conclusions can be drawn with regards to CaF_2.

Keywords: carbon capture; molten salts; hydrolysis; flue gases; Ca-looping

---

1. Introduction

Carbon capture and storage (CCS) has been identified to be a key technology for achieving sustainability in the mid-term future energy supply which should be aggressively pursued [1]. Combustion of fossil fuels will be performed in the foreseeable future to supply electricity to feed a rapidly growing demand in emerging economies as well as in existing power facilities. In the long term, carbon negative solutions rely on the development of efficient and low-cost processes for carbon capture from combustion of carbon from sustainable sources such as biomass.

Calcium looping (Ca-looping) is one of the new approaches to carbon capture which have attracted most interest [2,3,4]. The process relies on using solid CaO generated from cheap and abundantly available $CaCO_3$ in a closed loop process based on thermal swing. The process may be performed continuously in fluidized bed reactors (FBR) and is at an advanced state of development. The chemical principle can be described by Eq. 1. and is performed at elevated temperatures around 900 ℃.

$$CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s) \qquad \Delta H_{1173K} = -170 \text{ kJ/mol} \qquad (1)$$

CO_2 is absorbed from a flue gas in a carbonator reactor vessel at temperatures around 800 ℃ while desorption takes place in a calciner at around 950 ℃. The main cost relating to this technology has been identified to be related to the process enthalpy [2]. While the Gibbs free energy is negative in the carbonator vessel at 800 ℃, the reaction between CaO and CO_2 is strongly exothermic as seen from Eq. 1. At temperatures above 900 ℃ in the calciner, the Gibbs free energy of Eq. 1. is positive, enabling the reaction to be reversed liberating CO_2 in an endothermic process. At this stage, energy corresponding to the process enthalpy has to be supplied to the system. Economic analysis show this to be the main cost driving factor for the process [4]. There are several possible ways of achieving this, however, the most common way is to introduce hot gas from firing of oxygen and coal [2]. The main obstacles for this technology to achieve widespread impact are associated with the solid sorbing particles which are found to exhibit deactivation due to sintering in the high temperature desorbing step, as well as the formation of fine dust particles disturbing FBR operation [5,6].

Several strategies for avoiding the challenges mentioned above have been reported. The application of modified solid sorbent particles has been the topic of a number of studies [7,8,9]. Another approach is to apply molten halide salts as an inert, liquid, carrying agent [10]. The introduction of such a salt has been shown in laboratory studies to give rapid reaction rates and high selectivity as well as good utilization of the $CaO/CaCO_3$ carrying capacity and cyclability, avoiding sintering and fine sorbent dust formation with simulated flue gases containing N_2 and CO_2 [11,12]. The application of a molten salt, however, introduces other possible challenges for real-world applications as the halide salts may be sensitive to other substances present in the flue gas such as water (H_2O), SO_2 and NO_x. In this paper we address the reactivity of the molten salt sorbent carrying agent with H_2O.

In general, rather sparse studies have been found in the searchable literature on hydrolysis of $CaCl_2$. Molten $CaCl_2$ has been the subject of rather large interest in recent years due to the so called de-ox or FFC-process for direct reduction of metal oxides from powders of a wide range of elements [13,14,15]. This calls for such studies to be performed and published.

1.1. Hygroscopicity of metal halides

Hydrolysis of metal halides in general follow the reaction described by Eq. 2. here shown for a alkali earth metal halide for simplicity:

$$MX_2(l) + H_2O\ (g) \rightleftharpoons MO(s\ or\ diss) + 2HX(g) \qquad (2)$$

The tendency to be subjected to hydrolysis is very different for the actual compounds but is in general a function of the stability of the halide, as lesser tightly bound compounds tend to be more susceptible to the reaction. Following the periodic system, fluorides exhibit the tightest bonding evident in higher melting points. Chlorides exhibit lower melting points, lower binding energies and tend to more easily undergo hydrolysis. Bromide-situated below Cl forms salts with even lower melting points which tend to be even more reactive. This is also evident in their hygroscopicity in the solid state. Chlorides are frequently associated with several crystal water molecules in their natural stable state, i.e. $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot xH_2O$, $AlCl_3 \cdot 6H_2O$. In some of them, the water molecules are quite tightly bound making it necessary to use elaborate drying procedures for preparation of the pure substances [16]. Fluorides, on the other hand do not tend to form crystal water in their naturally occurring states. CaF_2 and NaF are notable examples. When a salt is used as liquidizing carrying agent in carbon capture from industrial flue gases, only a very limited reactivity towards water present in the gas can be tolerated. Strict emission control regimes exist so, unless a separate cleaner/scrubber is employed - adding costs, the salts used should not hydrolyze to any significant degree. The Gibbs free energy and the corresponding equilibrium constant for the reaction described by Eq. 2. have been calculated using the simulation tool HSC Chemistry 6.1 for $CaCl_2$ and CaF_2, summarized in Table 1 [17].

Table 1. Gibbs free energy and corresponding equilibrium constant for the substances studied.

	ΔG_{1173K} [kJ/mol]	**K**
$CaCl_2$	90.951	$8.91 \cdot 10^{-5}$
CaF_2	141.753	$4.87 \cdot 10^{-7}$

From Table 1 it is evident that hydrolysis of $CaCl_2$ and CaF_2 is not thermodynamically favoured at relevant process temperatures (1173 K) as the Gibbs free energy of their reaction with water is substantially positive. However, all reactions are in equilibrium and the hydrolyzing halides form gaseous compounds which will be constantly removed from a system where a flue gas is cleaned and so the vapour pressures of the formed compounds above the molten salts will be low. This will tend to drive reaction (2) towards the right. The oxide formed in the reaction (CaO for $CaCl_2/CaF_2$) is present at the right of the equation so to maintain the equilibrium constant K at the given value, the presence of the appropriate oxide is expected to suppress the reaction and stabilize the molten salt.

1.2. Thermodynamic modeling

The reaction described by Eq. 2. exhibits an equilibrium constant described by Eq. 3.

$$K = \frac{a_{CaO} \cdot a_{HX}^2}{a_{CaX_2} \cdot a_{H_2O}} \tag{3}$$

In (3) a denotes the activities of the substances in their chemical environment. The activity of a substance Z in a chemical system can be expressed via its molar fraction (concentration), [Z] or partial pressure, p_Z by Eq. 4.

$$a_Z = \gamma_Z [Z] \; or \; \gamma_Z p_Z \tag{4}$$

In (4) γ_Z will be the activity coefficient for Z. At infinite dilution, $\gamma_Z = 1$. For solids and substances at or above its solubility limit, the activity is said to be unity. The equilibrium constant K is related to the Gibbs free energy of the reaction through Eq. 5.

$$\Delta G^0 = RT \cdot lnK \tag{5}$$

Combining (3), (4) and (5) and rearranging, we get Eq. 6.

$$\frac{\gamma_{CaX_2}[CaX_2]\cdot\gamma_{H_2O}[H_2O]}{\gamma_{CaO}[CaO]\cdot(\gamma_{HX}[HX])^2} = e^{\frac{\Delta G^0}{RT}} \tag{6}$$

In this work, several assumptions can be made. If CaO is present close to saturation, the activity can be assumed to be unity. As $CaCl_2$ constitutes 81.5 mol% of the halides it does not seem inappropriate in the context of this work to put its activity also to unity. CaF_2 constitutes 18.5 mol% of the halides. A first approximation can be that the activity coefficient of this is unity making the activity equal to the concentration. However, this is of more speculative nature and whether this assumption is valid will likely be expressed in the results. The gaseous hydrolysis product HX is not thermodynamically favoured (Eq. 2) and if only formed in minor degree its activity can be approximated with the partial pressure. As this compound is constantly removed from the system this assumption is expected to be valid. These considerations makes it possible to evaluate the recorded experimental data and compare them with theoretical calculations using data from a thermodynamic modeling tool such as HSC Chemistry [17].

1.3. Previous work

Previous studies of carbonation-decarbonation of CaO dissolved or partly dissolved in $CaCl_2$ + 13.8 wt% CaF_2 have shown that HCl and HF form when the molten salt is subjected to a nominally dry N_2/CO_2 gas mixture [12]. Carbonation and decarbonation were performed at 705 ℃ and 945 ℃, respectively, in 12 cycles. In the initial cycle, 200 ppm HCl was measured during carbonation at 705 ℃ while 1200 ppm HCl was recorded during decarbonation at 945 ℃. The corresponding values for HF were 25 ppm and 90 ppm. The values decreased with time. Upon further cycling, the values decreased, however, stable values of 40 ppm HCl and 14 ppm HF were noted during decarbonation at 945 ℃ after 5 cycles. The initial, high, values were attributed to incomplete drying of $CaCl_2\cdot 2H_2O$, while water contamination of the source gases were suggested as the source for the long term, stable behaviour even though instrument grade gases (grade 5.0, <3 ppm H_2O) were used.

Hydrolysis of $CaCl_2$ has been investigated in conjunction with preparation of Ni [18]. Hydrolysis was recorded as function of supply of wet N_2-gas with H_2O content in the range 12–24% and at temperatures between 840 ℃ and 950 ℃. Increased water content and temperature led to increased formation of CaO and, thereby, also HCl at temperatures above 840 ℃. At water contents above 24%, formation of $Ca(OH)_2$ was found to occur alongside formation of CaO. Other studies have concluded that hydrolysis of $CaCl_2$ is a rather complex process with formation of both CaO and $Ca(OH)_2$ at high water contents even if the calcium hydroxide is not favoured above 570 ℃ [19]. A study regarding solubility and activity coefficients of CaO in equimolar salt melts of the form $CaCl_2$-X (X = 0, LiCl, NaCl, KCl, $SrCl_2$, $BaCl_2$) showed that the solubility was smaller in the mixtures than in pure $CaCl_2$ and that the activity coefficient was larger than 1 [20]. The solubility increased with temperature, while the activity coefficient decreased.

1.4. Approach

The hypotheses to be tested in this study can be expressed as: $CaCl_2$ and CaF_2 will-to a certain extent, be subject to hydrolysis when exposed to an inert gas containing H_2O. The presence of CaO will suppress the reaction.

2. Materials and Method

2.1. Experimental set up

The experiments were performed at ambient pressure in a set up previously described [10,12]. The set up consisted of a tubular, sealed reaction vessel (stainless steel) with an inner crucible of Ni containing the salt. A flow of N_2 (5.0, AGA, 99.999%) was set by a computer controlled mass-flow controller (MFC) (Mass-Stream, M + W Instruments). Unless otherwise noted, LabView 8.2 (National Instruments) was used for all measurements and monitoring. For the experiments with water in the gas, H_2O was then added by bubbling the gas through a closed, water filled vessel on a hot plate (VWR Advanced VMS-C7) with temperature control. A constant value was achieved by keeping the vessel at 46 ℃ ensuring a water partial pressure of 10 kPa (10 vol%) [21]. The temperature was monitored by a type K thermocouple fastened directly to the vessel by aluminium tape. After humidification, heated gas lines were employed in the whole system. PTFE (Teflon) tubes were equipped with heating elements (H 900°, Tyco Thermal Controls) and kept at a constant temperature of 170 ℃ to avoid condensation of water in the lines. Gas (0.7 Nl/min) was supplied to the bottom of the molten salt column by a Ni tube inserted in a sleeve being an integral part of the stainless steel reaction vessel. In this set up, the gas will flow to the top of the molten salt bath in the form of bubbles and then release to the volume above the molten salt. A type S (Pt/Pt + 10% Rh) thermocouple was immersed in the molten salt for continuously monitoring of the reaction temperature.

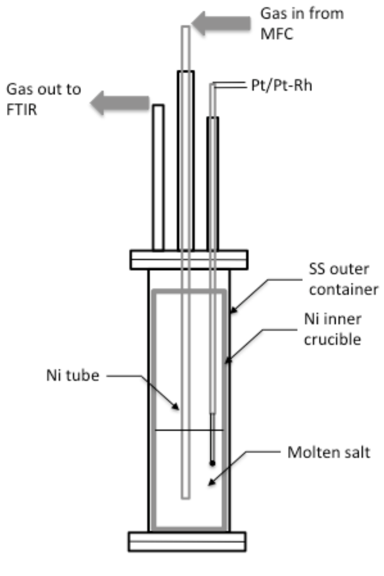

Figure 1. The chemical reactor used in the experiments. An inner crucible of Ni is contained in an outer compartment of stainless steel. A Ni tube supplies gas to the bottom of the pool of molten salts. The temperature in the salt is monitored by a Pt/Pt + 10% Rh type Sthermocouple.

After reaction, the gas was led out from the reaction vessel first through a stainless steel tube. Subsequently, heated teflon tubes were used. The gas was analyzed by a FTIR unit (Thermo Nicolet 6700) equipped with a 2 m gas cell running the commercial Fire Science method (Thermo Fisher). Before the analyzer, a purpose-built electrostatic filter where particles are removed by electrostatic forces was employed in order to remove possible particles entrained in the gas stream. High voltage was supplied from a power supply (Spellman SL300). The voltage was kept at as high value as possible without arcing (8.5 kV). The reactor is depicted in Figure 1.

2.2. Materials

The chemicals used in the experiments are listed in Table 2.

Table 2. Chemicals and gases used in the experiments.

Substance	**Grade**
N_2	AGA, 5.0, >99.999%
$CaCl_2 \cdot 2H_2O$	VWR, Normapur, >99%
CaF_2	Sigma, Puriss, >99.9%
CaO	Sigma, puriss
H_2O	De-ionized, >15 MΩcm

CaF_2 is not hygroscopic, however, water may be adsorbed on the surfaces of fine powders. CaO may absorb H_2O from air at low temperatures forming $Ca(OH)_2$. CaO and CaF_2 were dried in a muffle furnace in ambient atmosphere at 1000 ℃ for 24 hours. Subsequently they were kept in closed vessels at 300 ℃ for as short time as possible before the experiments.

$CaCl_2$ was prepared from $CaCl_2 \cdot 2H_2O$ in a controlled drying process as first reported by Freidina and Frey [22]. The dihydrate was dried in a closed, tubular furnace under inert (Ar, AGA 4.0, 99.99%) atmosphere. A controlled heating procedure was used where the powder was first slowly heated to 300 ℃ (0.5 ℃/h). The temperature was then raised to 800 ℃ more quickly (1.25 ℃/h). The powder was kept at 800 ℃ for 10 hours. The weight was recorded before and after drying. For all runs, a mass loss of 24.5% were recorded, corresponding to full removal of H_2O. This procedure has been used in a number of studies where the absolute purity with regards to trace amounts of CaO is not considered critical. This issue will be further addressed below.

After drying, all agents were kept in closed vessels at 300 ℃ before use. Below, all concentrations are given in wt% unless otherwise noted.

2.3. Method

Eutectic mixtures of 13.8 wt%/18.5 mol% CaF_2, rest $CaCl_2$ were prepared in the experimental vessel and furnace from the dried powders. The powders were added to the crucible in ambient atmosphere, however, care was taken for the powders not to cool unnecessary from 300 ℃ in order to prevent uptake of water. A Ni crucible was used and CaO (0 wt%, 5 wt% and 10 wt%) was added at this stage. The mixtures were then fused by heating to 900 ℃. A constant melt height of 6 cm in the Ni crucible, corresponding to 160–175 g was used. To ensure homogenous melts and to ensure that all water was removed, N_2 was then bubbled through the melt kept at 900 ℃ at a rate of

0.2 Nl/min for at least 20 hours while monitoring the gas composition escaping from the system. Experiments were not started before no HCl and HF were detected. All compositions were exposed first to dry, and subsequently with humidified gas (10 vol% H_2O).

At the start of the experiments, the tube supplying gas to the system was positioned 1 cm above the crucible bottom. Gas was then applied at a rate of 0.7 Nl/min when dry gas was used, as monitored by the MFC described above. In the experiments with humidified gas, the N_2 flow was 0.64 Nl/min in order to secure a similar gas flow with a water content of 10 vol% as described above. All experiments were performed first without and, subsequently, with water. Between the experiments with dry and humid gas, the melt was kept above its melting point (660–790 ℃, depending on composition), while HCl and HF were monitored in the escaping gas to ensure zero levels of the formed products. The gas escaping from the system was continuously monitored by FTIR. The temperature was varied from close to the melting point (660 ℃) to 1000 ℃. The melt was kept at each temperature interval for 30 minutes.

Three series of experiments were conducted with varying amounts of water and CaO. During each experiment, the temperature was varied in order to study the effect of temperature on the hydrolysis reaction. The content of CaO was 0, 5 and 10 wt% for each series, respectively. For 5 and 10% CaO, three parallels were conducted, whereas for 0% CaO there were two parallels due to severe problems with corrosion of the reactor vessel, most likely due to the formation of corrosive HCl. Before commencing the experiment, the reactor was held at 900 ℃ and fed with pure N_2 until no HCl or HF could be detected. The temperature was then lowered to the lowest operable temperature with the system still in its molten state. The lowest temperature used was selected based on available phase diagrams (Acer-NIST) to ensure that all CaO was present in dissolved state (0%, 660 ℃; 5%, 700 ℃; 10%, 790 ℃) [23,24]. The temperature was then increased systematically in 50 ℃ steps up to 1000 ℃.

3. Results and Discussion

3.1. HCl formation

The measured contents of HCl in the dry gas (0% H_2O) after exposure to the molten salt are shown in Figure 2a–c. With no added CaO (Figure 2a) some formation of HCl is noted at 800 ℃ (10–20 ppm). Increasing levels of HCl are detected for temperatures up to 1000 ℃ (~100 ppm). As the feed gas contained no water, this is unexpected, in particular since the melt was pre-conditioned with N_2 at 900 ℃ until no detectable HCl was found in the gas exiting the vessel. For the higher temperatures (950 ℃ and 1000 ℃), a decreasing trend with time is observed. The most likely cause to hydrolysis occurring at these conditions is incomplete drying of the chloride. The fact that the melt was pre-conditioned contradicts this. There are, however, few other possible explanations since humidity from the ambient is not supposed to enter either the feed gas or the vessel as there is always overpressure being present in the gas pathway. In a prior study, Tomkute et al. makes similar observations [12]. They attribute the hydrolysis to be due to H_2O being present in the feed gas. As instrument grade N_2 was used (<3 ppm H_2O), this is difficult to support. Addition of CaO to the molten salt increases the formation of HCl notably at temperatures above 800–850 ℃ as seen in Figure 2b and c. CaO was dried at 1000 ℃ before the experiments and kept in closed vessels at 300 ℃ before loading to the Ni crucible. CaO is associated with hygroscopicity as

$Ca(OH)_2$ may form as previously noted. Care was taken for this not to happen and if minor amounts of hydroxide were formed during loading of the reaction vessel, one would expect the HCl formation to diminish with time as H_2O was driven off. This, however, does not seem to be the case as very stable values of HCl formation with time is detected. Again, this behaviour is hard to explain and should be subject to further studies.

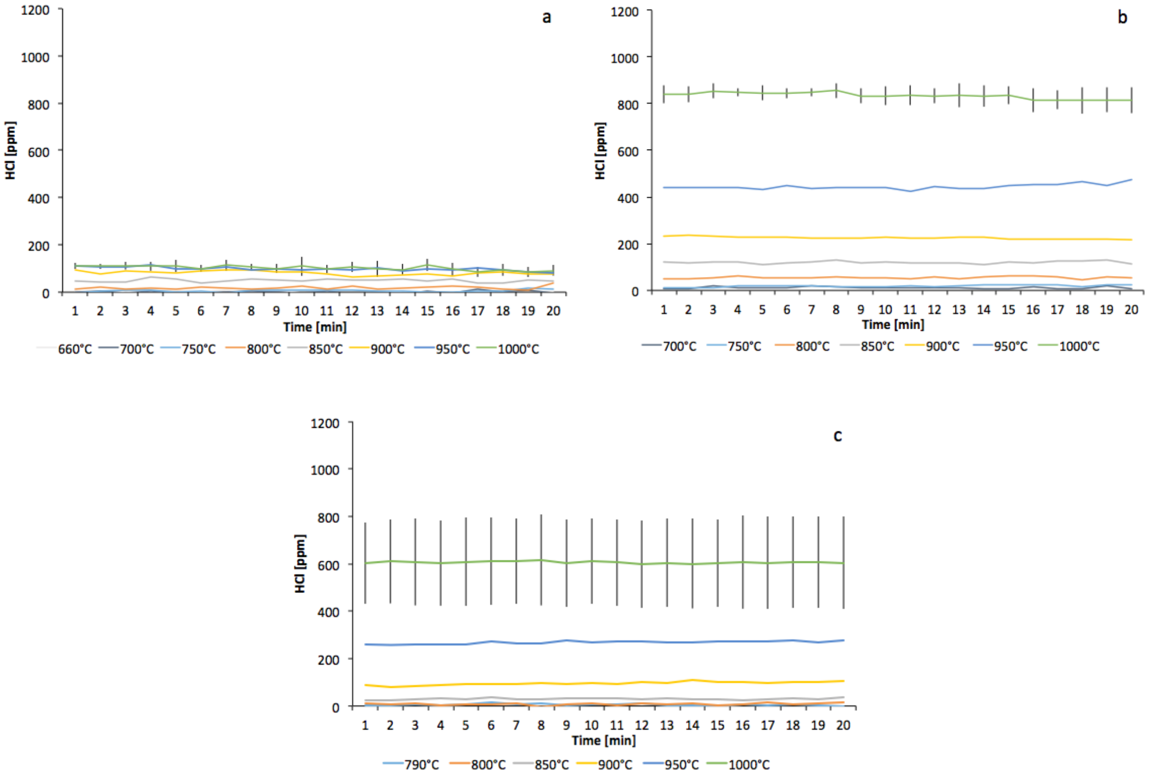

Figure 2. The content of HCl in the exit gas. 0% H_2O. a: 0% CaO, b: 5% CaO, c: 10% CaO. Error bars are based on three parallel experiments.

With humidified gas, the behaviour is different as shown in Figure 3. HCl forms readily at and above 700 °C with no added CaO (0% CaO). HCl formation shows a strong, systematic and linear increase with temperature from 3500 ppm at 700 °C to 15,000 ppm at 1000 °C as shown in Figure 3d. Minor amounts are detected at the lowest temperature (660 °C). Addition of CaO seems to raise the temperature for onset of hydrolysis. HCl forms at and above 800 °C for 5% CaO and at and above 900 °C for 10% CaO added. Again, the formation of HCl seems to increase linearly with temperature. This partly follows the behaviour for HF (Figure 4). HCl, on the other hand, forms at systematically larger degree with increased temperature unlike HF which is released at a stable value of 30–40 ppm at all tested temperatures above a certain threshold value. Addition of CaO lowers the tendency for hydrolysis as the levels formed at 1000 °C systematically decreases from 15,000 ppm (0% CaO) via 9,000 ppm (5% CaO) to 5,500 ppm (10% CaO).

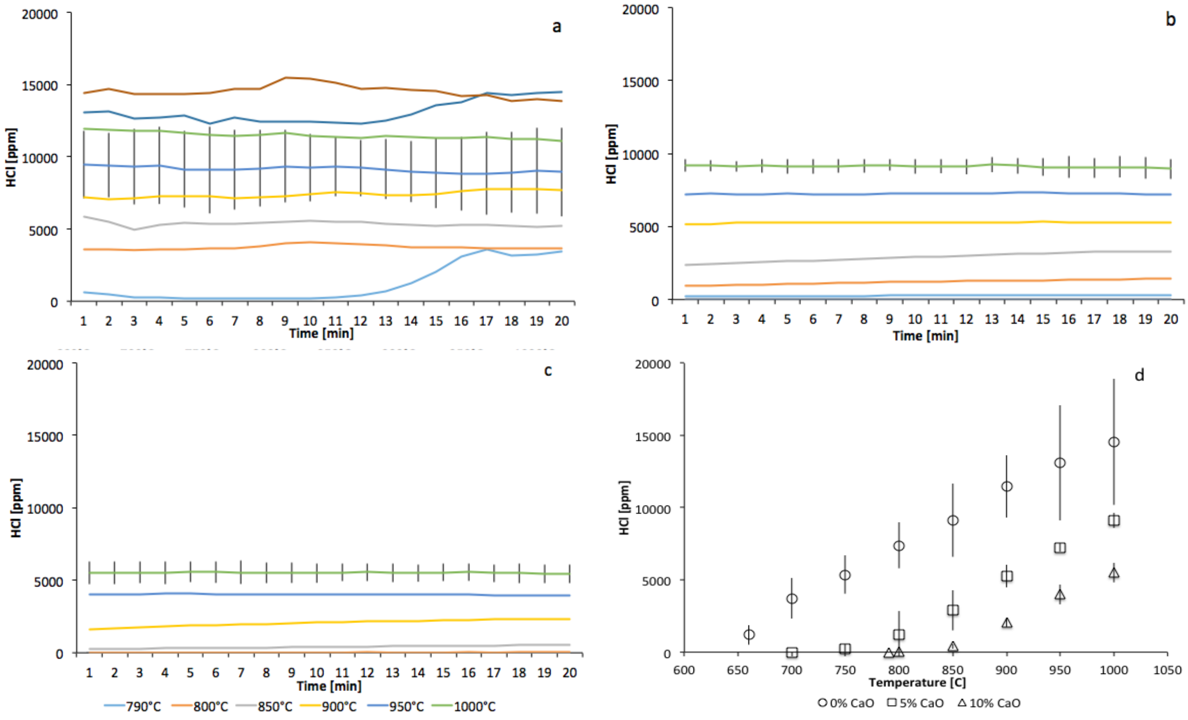

Figure 3. The content of HCl in the exit gas. 10% H_2O. a: 0% CaO, b: 5% CaO, c: 10% CaO, d: Average HCl evolution in a, b and c as function of temperature.

3.2. HF formation

The measured contents of HF in the gas after exposure to the molten salt for the case where no water was present in the feed gas are shown in Figure 4a–c. The measurements of HF all showed a very fluctuating, noisy manner likely reflecting the sensitivity of the FTIR system for this gas. The actual values should therefore only be used as a general guideline for the extent of formation of HF. No error bars are therefore included. It is apparent that HF does not readily form from hydrolysis of CaF_2 without H_2O in the feed gas. This is as expected based on Eq. 2. The measured contents of HF in the gas after exposure to the melt for the tested cases with humidified feed gas are shown in Figure 5a–d. For these cases where the feed gas contained 10 vol% H_2O, a stable level of 30–40 ppm HF is formed by hydrolysis of CaF_2 at elevated temperatures. For 0% CaO, this level is formed at temperatures at or above 700 °C. No significant amounts of HF are detected at the lowest temperature (660 °C). With 5% CaO added, the steady level of HF at 30–40 ppm is noted at temperatures at or above 800 °C. No significant HF is detected at 700 °C and 750 °C. For 10% CaO added, a steady level of HF at 30–40 ppm is noted at temperatures above 900 °C. At 850 °C, an intermediate level of 10–20 ppm is formed. No significant HF is detected below 800 °C. An interpretation of these results can be that hydrolysis of the CaF_2-related part of the molten salt occurs to a certain extent at a stable rate above a temperature threshold. It is dependent on water being present in the feed gas and it can be noted that the content of CaO shows a marked impact on the temperature dependence. Increased amounts of CaO seems to increase the temperature for the onset of hydrolysis. It is notable that increasing the temperature above the threshold value does not lead to increased formation which remains stable at 30–40 ppm HF.

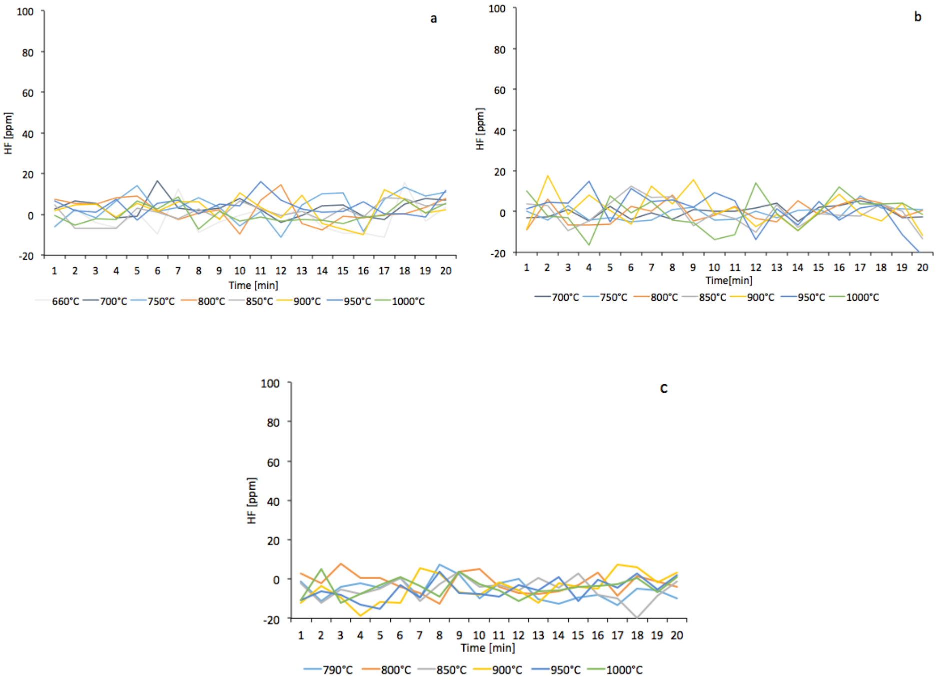

Figure 4. The content of HF in the exit gas. 0% H_2O. a: 0% CaO, b: 5% CaO, c: 10% CaO.

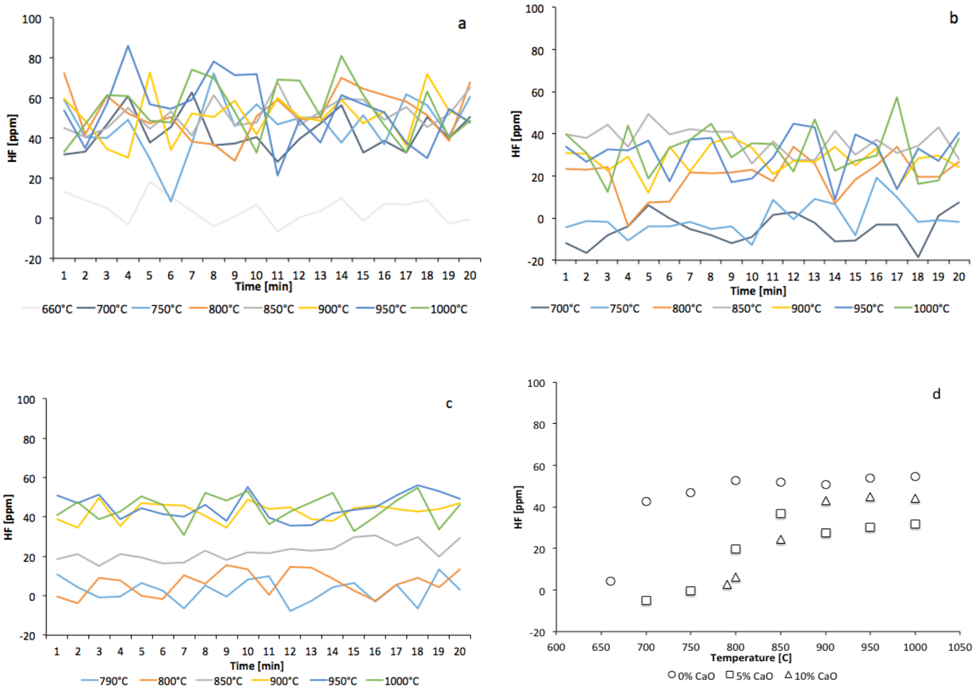

Figure 5. The content of HF in the exit gas. 10% H_2O. a: 0% CaO, b: 5% CaO, c: 10% CaO, d: Average HF evolution in a, b and c as function of temperature.

3.3. Comparison with calculated data

In order to do thermodynamical calculations and compare theoretical vs. recorded data a number of assumptions must be made. The theoretical background has been presented in section 1.2. For the formation of HCl we can assume the activity of $CaCl_2$ to be unity-it constitutes 81.5 mol% of the halides. Further, we can as a first approximation assume the activity of CaO to be unity in the experiments with 10 wt% (5.39 mol%) CaO as it is close to the solubility limit-at least at the lower temperatures. For the experiments with 0% added CaO, the activity of this substance is unknown as only trace amounts will be present. This case will therefore not be evaluated. Water is present at a partial pressure of 0.1 atm. (10 kPa) and as a starting point we can assume the activity coefficient to be unity. For the hydrolysis of CaF_2 to HF similar assumptions can be made, however CaF_2 is present at 18.5 mol% and a unity activity coefficient may not be applicable. If we apply the assumptions to Eq. 3 and/or Eq. 6 we can calculate an estimated value for the content of HCl and HF in the gas after exposure. Results from the calculations for HCl are found in Table 3. A first estimate was calculated based on the average measured content of HCl for all the temperatures with an activity coefficient for CaO of 1. Upon examination, the results for the three highest temperatures showed a quite similar ratio of measured/calculated values for both 5% and 10% CaO. More realistic activity coefficients for CaO (5% CaO: 3.83, 10% CaO: 5.15) was then calculated based on this ratio and the calculations were then performed again using these values. Comparing the results for HCl with Figure 5c we note that, at least for the higher temperatures, the results seem to match relatively well with the measured values. Attempts were made to similarly model the formation of HF, but these were not successful as HF does not seem to follow a similar pattern with rising content with temperature. In addition, the measured values showed a large degree of variation or noise, as described above. On the contrary, HF does not seem to form at temperatures below a certain threshold. At temperatures above this value HF does seem to form at the same rate, seemingly unaffected by temperature. The results found in this study confirm unexpected formation of HCl as previously recorded without H_2O in the

Table 3. Estimated and measured values for the content of HCl above a $CaCl_2/CaF_2$ molten salt based mixture as function of content of CaO. The activity coefficients for CaO used in the calculations was 14.7 and 26.5, based on an average for the three highest temperatures.

Temperature [°C]	**Content HCl [ppm, molar] K**				
	5% CaO		**10% CaO**		
	Estimated	**Measured**	**Estimated**	**Measured**	
660	-	-	-	-	4.788×10^{-7}
700	612	0	-	-	1.483×10^{-6}
750	1165	267	-	-	5.368×10^{-6}
790	-	-	953	4	1.298×10^{-5}
800	1995	1211	1050	11	1.574×10^{-5}
850	3143	2900	1654	405	3.907×10^{-5}
900	4748	5265	2499	2054	8.914×10^{-5}
950	6913	7239	3638	4010	1.890×10^{-4}
1000	9745	9115	5128	5518	3.755×10^{-4}

feed gas. However, no HF is found to form with no added H_2O in this dedicated study, while Tomkute et al. reports a stable formation of 13–14 ppmw of HF [12]. The recent results agrees better with theory which predicts hydrolysis to occur to larger extent as temperatures rise (Eq. 6).

4. Conclusions

Hydrolysis of molten $CaCl_2$ and CaF_2 by 10 vol% H_2O in N_2 has been studied experimentally. The results show that when exposed to humidified N_2, both $CaCl_2$ and CaF_2 in a eutectic melt consisting of 13.8 wt% CaF_2 in $CaCl_{2,}$ will react and form HCl and HF. Adding CaO to the halides suppresses the reaction according to theory. Thermodynamic modeling indicates activity coefficients for CaO above unity, supporting previous studies. Only minor amounts of HF form from CaF_2, while the $CaCl_2$ part of the investigated melt will form HCl more readily. The reactions are quite temperature dependent—in particular the formation of HCl. HF does not seem to form below a certain threshold temperature depending on the content of CaO. Adding CaO to the melt increases the temperature for onset of the reaction. In the application of such melts for CCS-purposes, it is therefore advised to keep the temperature in the carbonation reaction, where the melt is in contact with gas containing water, as low as possible. The behaviour of the system when subject to dry N_2 is difficult to explain, the most likely reason for hydrolysis in these conditions is not completely water free chemicals. The relationship beteween activity and concentration should be further explored by performing substantially more experiments with varying concentrations of CaO. These issues remains the subject for further studies.

Acknowledgments

This work has been funded by the Norwegian Research Council (NFR) through the CLIMIT programme (grant number: 233804/E20). The support is greatly appreciated.

Conflict of Interest

Espen Olsen and Heidi S. Nygård holds shares in SALCAPE AS with license to the patented technology for CO_2 capture using molten halide salts aiming to develop the technology for commercialization. The patent is owned by Norwegian University of Life Sciences (NMBU).

References

1. Chu S (2009) Carbon capture and sequestration. *Science* 325: 1599.
2. Macdowell N, Florin N, Buchard A, et al. (2010) An overview of CO_2 capture technologies. *Energ Environ Sci* 3: 1645–1669.
3. Dean CC, Blamey J, Florin NH, et al. (2011) The calcium looping cycle for CO_2 capture from power generation, cement manufacture and hydrogen production. *Chem Eng Res Des* 89: 836–855.
4. Junk M, Reitz M, Strohle J, et al. (2016) Technical and economical assessment of the indirectly heated carbonate looping process. *J Energ Resour Technol* 138.

5. Abanades JC, Alvarez D (2003) Conversion limits in the reaction of CO_2 with lime. *Energ Fuel* 17: 308–315.
6. Donat F, Florin NH, Anthony EJ, et al. (2012) Influence of high-temperature steam on the reactivity of CaO sorbent for CO_2 capture. *Environ Sci Technol* 46: 1262–1269.
7. Aljeboori MJ, Nguyen M, Dean C, et al. (2013) Improvement of limestone-based CO_2 sorbents for Ca looping by HBr and other mineral acids. *Ind Eng Chem Res* 52: 1426–1433.
8. Liu W, Yin J, Qin C, et al. (2012) Synthesis of CaO-based sorbents for CO_2 capture by a spray-drying technique. *Environ Sci Technol* 46: 11267–11272.
9. Stendardo S, Andersen LK, Herce C (2013) Self-activation and effect of regeneration conditions in CO_2-carbonate looping with CaO-$Ca1_2Al_{14}O_{33}$ sorbent. *Chem Eng J* 220: 383–394.
10. Olsen E, Tomkute V (2013) Carbon capture in molten salts. *Energy Sci Eng* 1: 144–150.
11. Tomkute V, Solheim A, Olsen E (2013) Investigation of high-temperature CO_2 capture by CaO in $CaCl_2$ molten salt. *Energ Fuel* 27: 5373–5379.
12. Tomkute V, Solheim A, Olsen E (2014) CO_2 capture by CaO in molten CaF_2-$CaCl_2$: optimization of the process and cyclability of CO_2 capture. *Energ Fuel* 28: 5345–5353.
13. Chen GZ, Fray DJ, Farthing TW (2000) Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. *Nature* 407: 361–364.
14. Chen GZ, Fray DJ (2006) A morphological study of the FFC chromium and titanium powders. *Miner Process Extr Metall Imm Trans* 115: 49–54.
15. Vishnu DSM, Sanil N, Mohandas KS, et al. (2017) Factors influencing the direct electrochemical reduction of Nb_2O_5 pellets to Nb metal in molten chloride salts. *Acta Metall Sin* 30: 218–227.
16. Kipouros GJ, Sadoway DR (2001) A thermochemical analysis of the production of anhydrous $MgCl_2$. *J Light Metals* 2: 111–117.
17. Roine A (2008) HSC Chemistry 6. 6.1 ed. Pori Finland. Outokumpu Research.
18. Kondo H, Asaki Z, Kondo Y (1978) Hydrolysis of fused calcium chloride at high temperature. *Metall Trans B* 9: 477–483.
19. Hanf NW. Nickel Segregation Research at Anglo American Research Laboratories. Part 2. Hydrogen Chloride Evolution in the Nickel Segregation system. In: Dor AA, editor. Proceedings of the Panel Discussion on Nickel Segregation, 1972 Feb.23, San Francisco CA. American Institute of Mining, Metallurgical, and Petroleum Engineers, 62–71.
20. Wang S, Zhang F, Liu X, et al. (2008) CaO solubility and activity coefficient in molten salts $CaCl_2$–x (x = 0, NaCl, KCl, $SrCl_2$, $BaCl_2$ and LiCl). *Thermochim Acta* 470: 105–107.
21. Sonntag RE, Borgnakke C (2007) Introduction to Engineering Thermodynamics. Hoboken NJ : John Wiley & Sons, 489 pl.
22. Freidina EB, Fray DJ (2000) Phase diagram of the system $CaCl_2$–$CaCO_3$. *Thermochim Acta* 351: 107–108.
23. Shen VK, Siderius DW, Krekelberg WP, et al. (2010) ACerS-NIST Phase Equilibria Diagrams NIST Standard Reference Database, 3.1 ed., Westerville OH : The American Ceramic Society, 04908.

24. Wenz DA, Johnson I, Wolson RD (1969) $CaCl_2$-rich region of $CaCl_2$-CaF_2-CaO system. *J Chem Eng Data* 14: 250–251.