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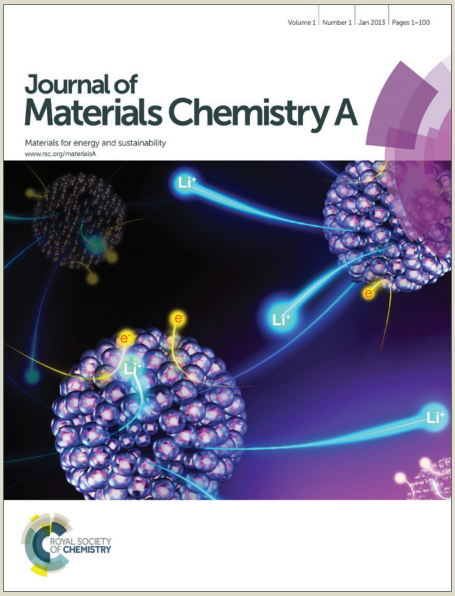

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Multiple sorption cycles evaluation of cadmium oxide/alkali metal halide mixtures for pre-combustion CO_2 capture

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Abstract:

Cadmium oxide/alkali metal halide mixtures for pre-combustion CO_2 capture were made using a wet mixing approach. Some of the samples were pelletised, also using SBA-15 mesoporous silica as an additive. In a multiple CO_2 sorption cycle test via thermogravimetric analysis, the best performing powder material by capacity and kinetics (a cadmium oxide made from carbonate doped with 17.5 wt% sodium iodide) exhibited a sorption capacity loss from 17 to 2 wt% after 25 cycles of partial pressure swing sorption at atmospheric pressure and temperatures of 285 and 305 °C. When the initial decomposition of the carbonate took place in inert gas (Ar or N_2 instead of air), the cyclic stability was improved. Water addition (1 vol-%) to the sorption gas further improved the cyclic CO_2 sorption stability and capacity. Elemental analysis of the samples after cyclic exposure to CO_2 revealed that the capacity loss is associated with loss of iodine, whereas the sodium remains. Water addition, however, had no significant effect on this iodine loss. Pellets made from carbonate performed with a working capacity of 10 wt%, but lost their mechanical integrity during multicyclic sorption. If made in the oxide state, pellets remained sturdy, but showed almost no working capacity. The addition of 13.7 wt% SBA-15 improved the working capacity of the oxide pellet to a stable value of 5.2 wt% over 25 cycles. In-situ powder X-ray diffraction showed the reversible isothermal phase transformation of CdO to $CdCO_3$ during three cycles of sorption and also revealed the presence of a crystalline sodium iodide phase, which appeared to be lost with increasing number of sorption cycles.

1 Introduction

The Integrated Gasification Combined Cycle (IGCC) process with water-gas shift reaction (WGS) and carbon dioxide capture has been proposed as a promising new power generation technology which could help reduce anthropogenic greenhouse gas emissions and thereby halt global warming and climate change [1, 2]. The process consists of the gasification of coal to synthesis gas (syngas) mostly consisting of water, hydrogen, carbon monoxide and carbon dioxide. A WGS reactor is employed downstream of the gasifier to enrich the gas by converting the carbon monoxide to carbon dioxide and hydrogen by reaction with water. Subsequent carbon dioxide capture from the shifted syngas would then result in a hydrogen-rich fuel gas, the combustion of which can power a gas and steam turbine combined power plant process, leaving water vapour as the only major exhaust gas [2, 3].

Separating the carbon dioxide in-situ at the temperature of the WGS reactor would be beneficial, as it would reduce the energy penalty arising from cooling or heating the syngas to the required carbon dioxide capture/separation temperatures. Syngas typically exits the final stage of the WGS reactor at a temperature between 250 and 400 °C [3]. A range of metal oxide based sorbents have been proposed to operate in this temperature window, including layered double hydroxides [4-6], lithium zirconates [7], magnesium/potassium double salts [6, 8] and a magnesium-cesium mixed metal oxide [9]. These materials accommodate the CO_2 by reacting with it to form carbonated products. However, most working capacities are reported to be lower than 10 weight-% in the temperature range studied here, whereas the lithium zirconates require higher temperatures to perform with acceptable reaction kinetics and capacity. A high working capacity is always desirable as it would help to keep carbon capture costs to a minimum.

Calcium oxide based materials, which have been considered for carbon dioxide capture at higher temperatures (typically 600 to 900 °C) by a number of research groups, show a decay in capacity during several carbonation-decarbonation cycles. In the case of calcium carbonate, this decay is considered to be due to sintering at high temperature and the filling of inter-micrograin void spaces, which happens upon carbonation [10]. A successful attempt to solve the decay in capacity was performed by calcium carbonate sorbent synthesis via CO_2 introduction into a calcium hydroxide aqueous slurry [11].

The carbonation of cadmium oxide was first studied by Doiwa et al. [12, 13], who showed that the presence of a sodium halide was essential. We have more recently reported that cadmium oxide/sodium iodide mixtures can sorb up to 24 wt% CO_2 in the temperature range of 250 to 310 °C [14]. This study showed that mixtures of various sodium and lithium halides with cadmium carbonate were able to sorb and then desorb carbon dioxide after decomposition to cadmium oxide by heating. This reversible sorption is due to the formation and decomposition of cadmium carbonate as confirmed by Fourier-transform infrared spectroscopy and powder X-ray diffraction (XRD). The best-performing material, made from 17.5 wt% sodium iodide (based on cadmium carbonate), showed a maximum weight increase of 26 wt% as CO_2 was sorbed at 265 °C. The sorption was reversible and the carbon dioxide was recovered at the same temperature by reducing the partial pressure of CO_2. Due to its high sorption capacity, this material appears prospective for carbon dioxide capture from syngas and worthy of more detailed study. It is important to determine whether any capacity loss occurs under cyclic conditions as has been reported for calcium oxide. In comparison to calcium oxide-based sorbents, the carbonation of cadmium oxide provides a more suitable temperature range for carbon dioxide sorption at pre-combustion conditions, as WGS reactor outlet syngas temperatures [3] are more in the range of cadmium oxide carbonation (250 to 310 °C) rather than calcium oxide carbonation temperatures (600 to 900 °C).

In the present study, cadmium oxide/alkali halide mixtures were examined under cyclic sorption conditions via thermogravimetric analysis (TGA) to investigate the stability of their working capacities. Samples were examined both as powders and pellets since the latter are more likely to be used in industrial applications. SBA-15 silica was added to the sample prior to the pelletisation process in an attempt to improve gas diffusion into the pellet. An assessment of the mechanical stability of the pellets was also performed before and after cyclic CO_2 sorption in TGA.

CdO-NaI powder samples were separately investigated by inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) to determine their cadmium, iodine and sodium content before and after cyclic exposure to CO_2. In-situ powder XRD experiments at 325 °C were performed to more directly observe the reversible transformation of cadmium oxide to carbonate.

2 Experimental section

2.1 Preparation of cadmium oxide/alkali halide composite samples

Cadmium oxide/alkali metal halide composites were prepared via a wet mixing method as previously described [14] and as summarised in Table 1. Cadmium carbonate was mixed with either sodium iodide (17.5 wt%), sodium bromide (12.9 wt%), lithium iodide (15 wt%) or lithium bromide (10 wt%). Water was removed from suspensions of cadmium carbonate dispersed in the respective alkali metal halide aqueous solution by heating and evaporation during continuous stirring . The precipitated samples were then dried overnight in a nitrogen-purged oven at 120 °C, resulting in completely dry powder samples.

Some of the dried powder samples were subsequently calcined in a muffle furnace (CM Inc., model Rapid Temperature 840940) in atmospheric air at either 370 °C or 500 °C. Other samples were also separately calcined under nitrogen (Carbolite ORF-810 furnace with internal gas-purged steel tube assembly). Samples were either calcined for 3 or 24 hours. After synthesis or calcination, samples were stored in sealed vials for further use.

The sample designations indicate the mass % of the alkali metal halide as a fraction of the cadmium carbonate as calculated from the mass of reagents used. Samples with no percentage indicator comprise samples made with 17.5 wt% NaI.

2.2 Preparation of SBA-15 silica

SBA-15 type mesoporous silica was prepared by a method similar to that reported by Zhao [15] and adapted by Knowles et al. [16] using poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Sigma Aldrich), tetraethylorthosilicate (Sigma Aldrich), ethanol absolute (Merck) and hydrochloric acid (Merck). The synthesis mixture was initially stirred overnight, then aged three days at 105 °C in a polypropylene jar contained within a Hawkins 'Big Boy' 22 L pressure cooker. The product was subsequently filtered, air dried and then calcined at 575 °C for two days. A pore size distribution and nitrogen physisorption isotherm of the SBA-15 used in this study is given in the supplementary material.

2.3 Pelletised samples

For pelletisation, the as-synthesised and oven-dried (i. e., carbonate form) powder samples as well as a sample calcined in nitrogen in a muffle furnace (500 °C, 3 hours) were used. Mixtures of the calcined sample with SBA-15 silica were also prepared and fed to the pellet press. Mass percentages of SBA-15 are reported with respect to the mass of calcined CdO/NaI mixed sample.

Pellets of a nominally 17.5 % NaI sample were made using a Specac brand hydraulic press and 13 mm diameter circular pellet die. 0.5 g of sample was placed into the pellet die, evacuated for ten minutes and then compressed by up to 10 tons equivalent force for another ten minutes. The force was continuously brought back to 10 tons as it decreased over time. Afterwards, the pellet was removed from the die and segments cut off using a sharp blade. Up to three such segments of approx. 1 mm width were used in a TGA experiment, so as to have sample masses of approx. 20 mg (oxide state) and 30 mg (carbonated state). The physical integrity of the pellets was documented photographically and the pellets were examined manually by trying to break them using a spatula or rubbing between two gloved fingers.

2.4 Thermogravimetric analysis of carbon dioxide sorption

A Setaram TAG 24-16 thermoanalyser, equipped with Bronkhorst model F-201DV-RAD-11-K programmable mass flow controllers for the supply of argon and CO_2, was used in this study. TGA of multiple isothermal CO_2 sorption and desorption cycles (up to 25 cycles) was achieved by varying the CO_2 partial pressure over samples within the instrument (0 vs. 50 vol%, close to the value of 38 % CO_2 as reported for a water gas shift reactor outlet gas stream [17]). A gas flow of 70 mL/min was always maintained, which was split into reference and sample gas flow (35 mL/min each) as per the instrument design. A sample mass of approx. 20 mg of an oxide material or 30 mg of a carbonate material was used for the experiments.

Samples were pre-treated in-situ at 380 or 510 °C in argon purge for one hour as noted in Figure 1 and Table 1. Tests were performed in both long (one hour each for sorption and desorption) and short cycles (12 minutes adsorption, 24 minutes desorption) at temperatures of 285 and 305 °C. A final step at 380 °C in argon flow ensured that samples were brought back to fully decarbonised state, i. e., cadmium oxide. This was necessary to provide a standardised basis for subsequent sample analysis by dissolution and elemental analysis (ICP-MS, AAS) of some of these samples.

Wet gas experiments were performed with argon and carbon dioxide bubbled through separate wash bottles filled with distilled water, which were maintained at 10 °C in a cooling bath. The wetted gas was mixed with a stream of dry argon originating from the balance device purge, resulting in 1 vol-% water concentration at the sorbent sample. Wet CO_2 and wet argon were used as sorption/desorption gases, whereas pre-treatment and after-treatment were performed in dry argon.

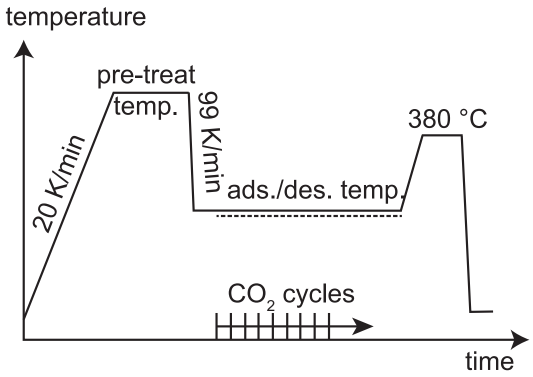

Figure 1: Adsorption/desorption TGA program. The dashed line on the temperature graph indicates mass readings used in subsequent data processing.

Table 1: Samples used in multicyclic adsorption/desorption tests.

sample name	composition $CdCO_3$ + … (wt%)	pre-treatment in muffle furnace	pre-treatment in TG analyser, in Ar	ad-/desorption cycle mode
285-a510-s [*]	17.5 % NaI	500 °C in air 3 h	510 °C	short, 285 °C
285-Ar380-s [*]	17.5 % NaI	- none -	380 °C	short, 285 °C
305-a510-s [*]	17.5 % NaI	500 °C in air 3 h	510 °C	short, 305 °C
305-Ar380-s [*]	17.5 % NaI	- none -	380 °C	short, 305 °C
285-Ar380-l	17.5 % NaI	- none -	380 °C	long, 285 °C
305-a380-s	17.5 % NaI	370 °C in air 3h	380 °C	short, 305 °C
305-N500-s	17.5 % NaI	500 °C in N_2 24 h	510 °C	short, 305 °C
LiBr-305-Ar380-l	10 % LiBr	- none -	380 °C	long, 305 °C
LiI-305-Ar380-s	15 % LiI	- none -	380 °C	short, 305 °C
NaBr-305-Ar380-s	12.9 % NaBr	- none -	380 °C	short, 305 °C
LiI-285-Ar380-s	15 % LiI	- none -	380 °C	short, 285 °C
NaBr-285-Ar380-s	12.9 % NaBr	- none -	380 °C	short, 285 °C
carbonate pellet Ar380 305-s	17.5 % NaI	- none -	380 °C	short, 305 °C
carbonate pellet Ar380 305-l	17.5 % NaI	- none -	380 °C	long, 305 °C
oxide pellet Ar380 305-l	17.5 % NaI	500 °C in N_2, 3h	380 °C	long, 305 °C
oxide pellet Ar380 305-s-d	17.5 % NaI	500 °C in N_2, 3h	380 °C	short, 305 °C
oxide pellet SBA15 4.22 % Ar380 305-s	17.5 % NaI, 4.22 % SBA-15 [#]	500 °C in N_2, 3h	380 °C	short, 305 °C
oxide pellet SBA15 13.7 % Ar380 305-s	17.5 % NaI, 13.7 % SBA-15 [#]	500 °C in N_2, 3h	380 °C	short, 305 °C

‘short’ = 12 min sorption, 24 min desorption, ‘long’ = 1 h sorption, 1 h desorption

[*] wet and dry gas experiments

[#] 17.5 wt% NaI based on $CdCO_3$, SBA-15 amount (wt%) based on mixed CdO/NaI sample after calcination

2.5 Elemental analysis

All mass determinations for the elemental analysis of a 17.5 % NaI sample were performed using a Mettler H54 balance with an accuracy of 0.00001 g. Samples of 20 mg were dissolved in 40 g of 1 wt % hydrochloric acid. For cadmium and iodine analysis, the samples were further diluted down to expected values of 20 to 30 µg/kg of cadmium and iodine using 1 % hydrochloric acid. For the determination of sodium, dilutions were performed using deionised water, giving an expected value of 1.5 mg per kg solution of sodium.

Cadmium carbonate and sodium iodide standard solutions for instrument calibration were prepared in a similar manner. 20 mg of sodium iodide or cadmium carbonate (same batch of pure chemicals as used for synthesis, refer section 2.1 and [14]) were used. Cadmium and iodine standards were produced with concentrations of 10, 20, 40 and 60 µg cadmium or iodine per kg solution. For a sodium standard, dilutions of 0.5, 1, 1.7 and 2.5 mg sodium per kg solution were made. Hydrochloric acid (I and Cd determination) and deionised water (Na determination) was used as a blank (zero concentration) standard.

Elemental analysis for cadmium and iodine was performed by inductively coupled plasma time of flight mass spectrometry (ICP-MS) on a GBC Optimass 9500 model instrument. For sodium determination, atomic absorption spectrometry (AAS) was employed and a GBC XplorAA model instrument was used.

The results of ICP-MS and AAS were calculated into weight percentage amounts of cadmium, iodine and sodium in the powder subsamples used for dilution. Theoretical amounts were calculated assuming 17.5 % NaI in cadmium carbonate, the decomposition of carbonate to oxide during calcination, and that Na and I are inert and non-volatile.

2.6 Powder X-ray diffraction

In-situ powder X-ray diffraction studies were undertaken at the Australian Synchrotron. A fresh 17.5 % NaI sample (calcined at 500 °C, 3 h) was used for the experiment. A quartz capillary was used as sample holder, which was purged with either nitrogen or pure carbon dioxide and heated by a hot air blower to 325 °C during data acquisition. Experiments were performed by interchanging the purge gas between pure nitrogen and carbon dioxide for three cycles, starting with the calcined sample. After each gas change, XRD patterns were observed until no more change was apparent (between 40 and 90 minutes).

Powder XRD patterns of pure materials (CdO and $CdCO_3$) for comparison were acquired on a Bruker D8 focus diffractometer using Cu-Kα radiation (1.5418 Å wavelength). Intensities were multiplied with a factor (as indicated) to make them comparable to the higher-intensity synchrotron patterns on the same intensity scale.

The wavelength, zero offset and unit cell parameters of cadmium oxide and cadmium carbonate were refined via the software package GSAS-EXPGUI [18, 19] using the Le Bail method. Powder Diffraction File 4+ 2011 entries 04-001-3770 (cadmium oxide) and 04-014-4823 (cadmium carbonate) were used as starting values for the unit cell parameters. For comparing the lab data with the synchrotron data, XRD patterns were converted from 2θ with the respective wavelength λ to the wavelength-independent values of Q using the software CMPR [20], according to Eq. 2-1.

$$Q = \frac{4\pi \sin\frac{2\theta}{2}}{\lambda} \qquad \text{Eq. 2-1}$$

3 A lanthanum hexaboride standard (NIST 660b) was used to refine the wavelength and zero offset of the synchrotron diffractometer at ambient temperature. The wavelength was found to be 0.8267593 Å and the zero offset -0.0206908 degrees *2θ*, as determined by a Le Bail refinement (refer supplementary materials for detailed results).Results and discussion

3.1 Thermogravimetric analysis of the sample stability

Figure 2 shows two examples of thermograms of 25 cycle sorption/desorption experiments, given as excerpts with the mass at the start of the cycles set to 100 %. Full thermograms can be found in the supplementary material. The derivation of the working capacities is indicated for the last cycle as the difference in relative mass for each cycle, as shown in Figure 2a. The full multicyclic plots for all materials reported can be found in the supplementary material (sample designators are listed in Table 1). In general, the results show that the working capacity decays for samples calcined in air (Figure 2). Apart from the working capacity, there is a mass loss/baseline shift before and after cyclic exposure evident in most of the full thermogravimetric plots (refer dashed arrows in the first thermogram in the supplementary material). This can be observed in the baseline of the mass signal in the full thermograms showing higher values before than after the cyclic exposure. This suggests that some part of the sample mass must be lost by reaction and/or evaporation during the experiment and this motivated a detailed analysis of the samples for their elemental composition (section 3.2).

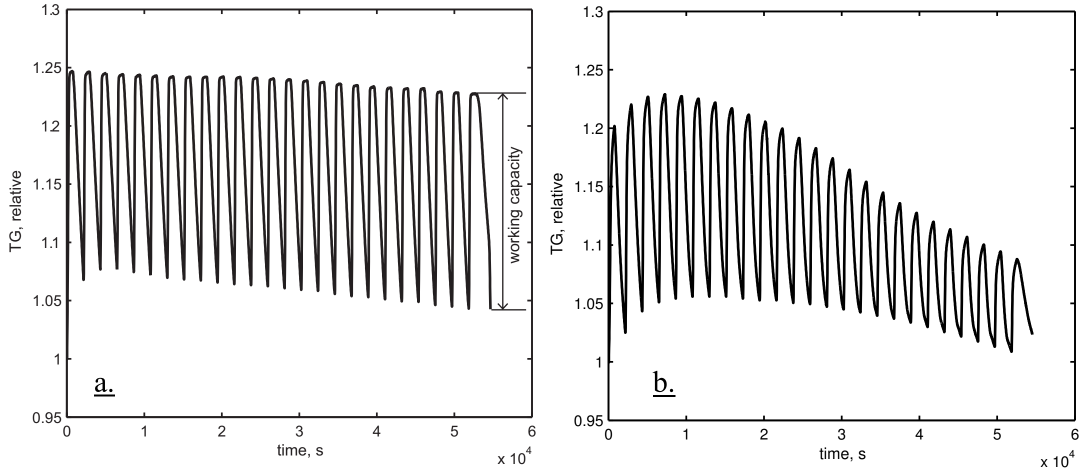

Figure 2: Thermograms of 17.5 % NaI samples, cycles at 285 °C, 25 cycles (12 min sorption, 24 min desorption), 100 % mass set at the beginning of the sorption cycles after in-situ pre-treatment, wet sorption gas. a. Pre-treatment of carbonate sample in Ar (285-Ar380-s-w), working capacity derivation shown at final cycle. b. analogue a, sample calcined in air (285-a510-s-w)

Plots of the working capacities versus cycle number for all materials studied here are given in Figure 3. These results show that the sorption capacities of some materials were reduced over several adsorption-desorption cycles. Generally, it can be observed that the samples pre-treated in air at any temperature showed a fast decay during multicycle sorption and the effect was more pronounced at a temperature of 305 °C than at 285 °C (Figure 3a). Sodium iodide containing samples that had not been in contact with air, i. e., the samples calcined in an inert (nitrogen or argon) atmosphere, maintained their capacity to a much more significant extent. 1 % water addition increased both the stability and the capacity (Figure 3b), whereas higher temperatures resulted in a capacity reduction. The time of pre-treatment did not seem to play a significant role in the long-term performance of the materials (Figure 3c); rather it seems to be a matter of exposure to air at high temperatures (380 or 510 °C) that determines the capacity stability. Non-calcined samples containing lithium iodide, however, exhibit capacity decay similar to the sodium iodide samples calcined in air (Figure 3d). The rates of CO_2 uptake (evident in the full thermograms, refer to supplementary material) of the lithium bromide sample were relatively slow, so that this experiment was only performed using long (1 hour) cycles. Alternative dopants to NaI, in general, show an overall lower capacity than NaI (Figure 3d).

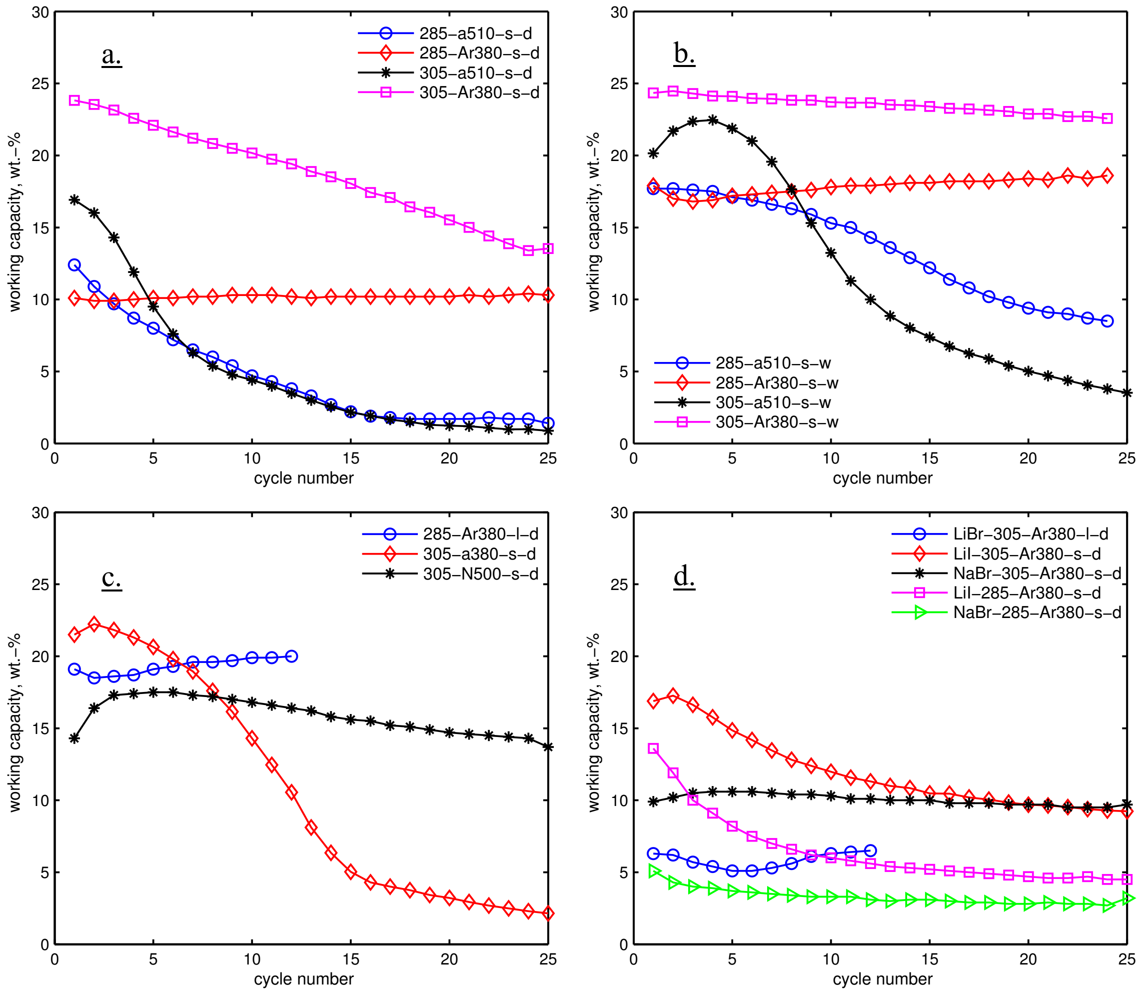

Figure 3: Multicyclic adsorption-desorption of various alkali halide/CdO samples at different temperatures. Refer to Table 1 for sample designators. a. 17.5 % NaI samples pre-treated in Ar and in air, no water added during TGA; b. as for a but with 1 % water addition in TGA; c. 17.5 % NaI samples and different pre-treatments; d. other alkali halides. Last letter d = dry gas, w = wet gas.

3.2 Elemental analysis

Figure 4 shows the composition of as-synthesised and calcined samples as well as theoretically expected values. The expected values were based on the mass ratios of cadmium carbonate and sodium iodide used during synthesis. It was assumed that cadmium carbonate decomposed to oxide upon calcination, and that sodium iodide was inert. The absolute cadmium content of the sample was assumed to be unchanged throughout synthesis, calcination and testing runs, since it is not volatile at the temperatures used in this study (its sublimation point is reported at 1559 °C [21]). The results for the calcined and non-calcined 17.5 % NaI samples investigated in dry and wet gas TGA cycles at 285 and 305 °C (refer to Figure 3a and b) are shown in Figure 5. The results given in Figure 4 and Figure 5 are both showing wt% and also the mass ratios relative to Cd content.

It can be noted in Figure 4 that the elemental composition of cadmium, iodine and sodium of the as-synthesised sample in the carbonated state was found to be lower than the expected theoretical values. This may be due to inaccuracies in weighing the amount of powder sample used for the dissolution. A dry sample was assumed, but the sample might have adsorbed water during handling before the dissolution. Furthermore, it is evident that the iodine to cadmium ratio (Figure 4b) is lower than the value that was expected. It is speculated that a certain amount of iodine may have been lost during wet synthesis.

Figure 4b shows that the unused/as-synthesised sample after calcination had a lower iodine content than expected if it is assumed that only cadmium carbonate decomposes to oxide and that sodium iodide remained inert during calcination. Calcination in air led to an even lower iodine content compared to calcination in nitrogen. Slightly increased Na/Cd levels that accompany lowered I/Cd ratios were attributed to a heavy element (iodine) leaving the sample. Consequently, the sodium ratio, on a mass basis, had to rise, if is assumed that the iodine is replaced by a lighter element.

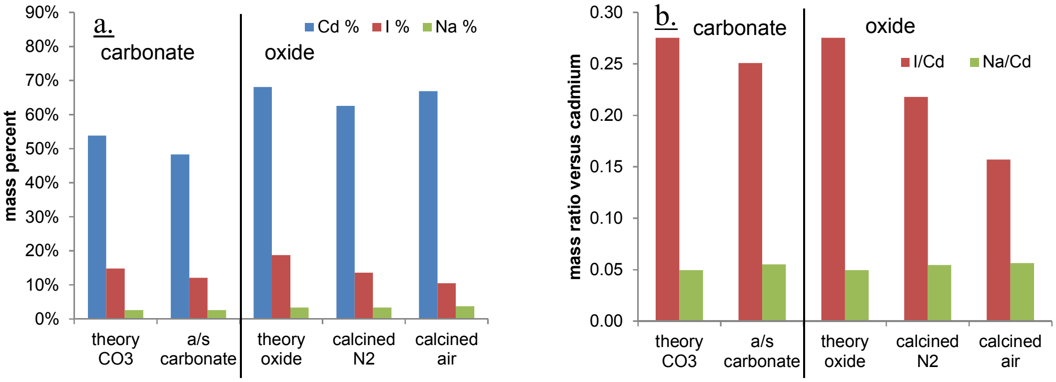

Figure 4: Elemental analysis of as synthesised (a/s) 17.5 % NaI samples calcined in air, N_2 and uncalcined (carbonate state), a. mass-%, b. Na and I relative to amount of Cd. Max. error 5.29 % (absolute) for Cd of a duplicate measurement of N_2 calcined sample.

The elemental compositions of the samples after multicyclic exposure are presented in Figure 5. It can be observed that the iodine content was lowered significantly during the TGA experiment, while the amounts of the other elements remained at similar magnitudes. Figure 5c and d also shows that the concentrations of iodine decreased relative to cadmium. It can be concluded from this observation, together with the loss of capacity after multiple carbonation-decarbonation cycles (Figure 3), that halide is an important promoter of the carbonation reaction. The maintenance of higher CO_2 sorption capacities appears to be associated with the maintenance of higher iodide content within the sample. Interestingly, sodium appeared to remain incorporated within the sample during the carbonation-decarbonation experiments, while the halide was removed from the sample. Water addition during cycling has no significant influence on the elemental composition of the samples.

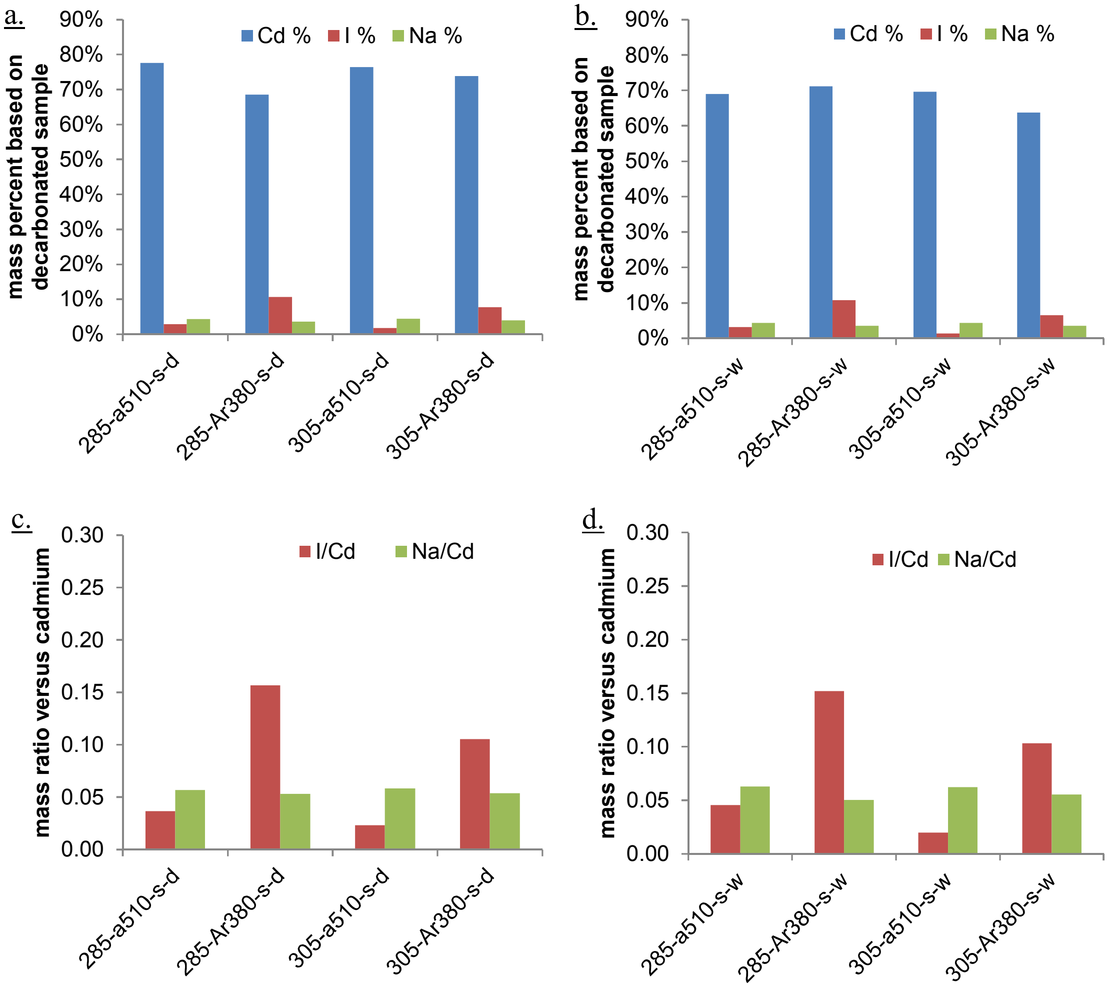

Figure 5: Elemental analysis of 17.5 % NaI/CdO samples after cyclic CO_2 sorption experiments, a. dry gas, b. wet gas, c. & d. like a, b with I and Na content relative to Cd. Samples correspond to Figure 3 a and b.

Given the loss of iodine occurring in some samples, the question must be asked how the composition of the sample changes with respect to stoichiometry. As sodium iodide was added to the sample initially and sodium levels do not change significantly, sodium iodide must be somehow changing into a different form upon the removal of iodine from the sample. Furthermore, calcination in air leads to a more substantial loss of iodine than calcination in an inert environment (N_2), both after initial calcination and multicyclic CO_2 sorption. It is hypothesised that oxidation of iodide to iodine in air is involved in this mechanism. However, as iodine loss over sorption cycles (compared to initial samples) is also observed for samples calcined in inert conditions, CO_2 seems to play a role in the decay mechanism as well. The investigation of the iodine loss mechanism is the subject of ongoing studies.

3.3 Powder X-ray diffraction

The results of the in-situ powder XRD studies performed at the Australian Synchrotron are given in Figure 6. A 17.5 % NaI sample (calcined in air at 500 °C) was used in this experiment. Upon heating to 325 °C in nitrogen purge, the first scan (labelled 'start') was obtained (Figure 6a). Afterwards, the gas flow was switched to CO_2 and the pattern changed (Figure 6b). Three cycles of nitrogen and CO_2 purge resulted in carbonation and decarbonation of the material as indicated by the diffraction patterns changing from cadmium oxide to carbonate and vice versa. Cadmium carbonate and oxide patterns are given for comparison.

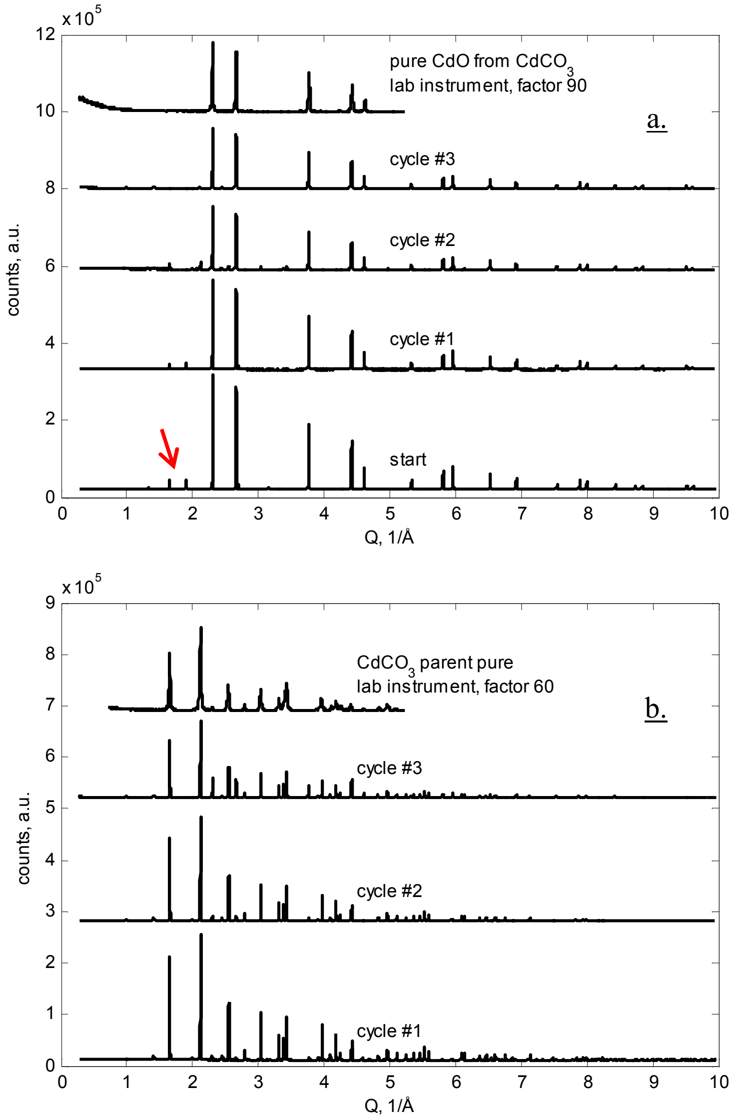

Figure 6: Powder XRD patterns of a 17.5 % NaI sample obtained from in-situ synchrotron experiments at the end of each cycle at 325 °C: a. decarbonated state, b. carbonated state. Arrow indicates two peaks assigned to NaI. Sample calcined in air at 500 °C before experiment.

Initially, a cadmium oxide phase was observed when purged with nitrogen. After exposure to pure carbon dioxide, a cadmium carbonate phase evolved. Noteworthy is the temperature of 325 °C, at which this experiment was performed. This conflicts with the results of TGA experiments reported in the previous study in this series [14], which showed that a temperature beyond 318 °C is too high for CO_2 sorption. This discrepancy is probably because the temperature measurement for the in-situ XRD system was not located within the sample cavity but, rather, adjacent to the hot air outlet that blows on the sample capillary. The XRD capillary was also purged with cool gas, which may have contributed to the actual sample temperature being below the setpoint. The true sample temperature was almost certainly lower than the measured one, though by how much is unknown. By contrast, the temperature sensor of the thermoanalyser was located immediately underneath the sample crucible and was thus probably a more realistic representation of the true sample temperature.

Le Bail refinements of the unit cell parameters of the cadmium carbonate and oxide phase observed in the in-situ XRD experiments have also been performed on the raw synchrotron data (i. e., at a wavelength of 0.8267593 Å). The results are given in the supplementary material. It can be noted that the unit cell lengths are marginally larger (4.71 Å) than the ones given in the Powder Diffraction File database (4.69 Å) and the ones reported in [14]. This can be explained by thermal expansion at the elevated temperatures used in these experiments. There is no new structure or unit cell modification due to the carbonation reactions and/or the doping with sodium iodide apparent here.

However, another noteworthy observation was the decrease of a sodium iodide phase at 325 °C in the in-situ synchrotron experiment. An XRD scan of the fresh/calcined 17.5 % NaI sample at the synchrotron at 325 °C showed a sodium iodide phase at very low intensity (see arrow in Figure 6a, two peaks between 1.5 to 2 $Å^{-1}$). During multicyclic sorption at 325 °C, the intensity of the sodium iodide peak decreased significantly with the progressing number of cycles. This suggests a loss of iodine, which is consistent with the elemental analysis results in section 3.2. However, despite the use of high-resolution diffraction analysis employing synchrotron radiation, a new sodium-containing phase was not identified.

3.4 Pelletised material

The working capacities for the pelletised sorbents are presented in Figure 7. Multiple short (12 min sorption, 24 min desorption) and long cycles (one hour each) for the material pressed in the carbonated state, as well as long cycles for the pellet made in the oxide state (with and without SBA-15 addition) were performed and the working capacities determined.

It is evident that the pelletised materials provided lower working capacities than their powder counterparts in equal short cycles (compare Figure 3). This is presumed to be due to the formation of a significant diffusion barrier within the fused pellet, which limited the access of the carbon dioxide. It can be observed that the carbonate pellets showed a capacity decrease for the long cycles. This also occurred, but was much less significant for the short cycles.

The reversible CO_2 capacity of the oxide pellets was observed to improve with cycle number. This might be due to expansion of the oxide as soon as it transformed into carbonate, thus creating fine voids within the pellet. These, in turn, could lead to better permeation of the gas through the pellet, resulting in higher working capacities in the subsequent cycles. In short cycles, the oxide pellet did not give any significant working capacity (< 0.5 %).

Pellets pressed using a mixture of the calcined CdO/NaI sample and SBA-15 silica initially exhibited a higher working capacity than the oxide pellet. The incorporation of 13.7 wt% SBA-15 led to a working capacity of 5.2 wt%. However, the adsorption rate is slow and CO_2 saturation was not achieved for this material, as can be seen in the full thermogram (refer to supplementary materials). The mass showed an overall increasing trend over the 25 cycles for this material, which might be attributed to the sorption rate being slightly less diffusion-limited than the desorption rate, or an expansion of the structure over multiple sorption/desorption cycles. Decreasing the amount of SBA-15 to 4.22 % led to more stable cycling (i.e., the baseline is more horizontal); perhaps there was a better balance between sorption and desorption rates in this case. However, the working capacity reduced further to 2.8 wt%.

The fact that adding SBA-15 improved the CO_2 uptake of the pellet during short cycles supports the view that CO_2 is less able to diffuse into the inner reaches of the pellet, relative to the powder samples. If a porous material is interspersed into the sorbent pellet, it can be imagined that the gas can penetrate into the core of the pellet more easily by diffusing through the void volume provided by the porous material particles. This is indeed evident in Table 2, showing that the fraction of the potential (stoichiometric) mass uptake achieved was higher for the pellets containing SBA-15. Adding a lower amount (4.22 instead of 13.7 wt%) of SBA-15 led to a lower working capacity, as accessibility was reduced by the reduced amount of empty volume. It appears that the higher amount of SBA-15 benefitted the reversible CO_2 sorption working capacity, but came with limitations in the mechanical strength of the pellets, as discussed next.

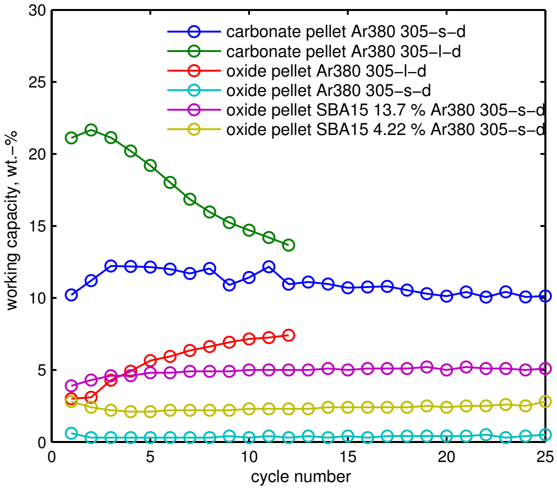

Figure 7: Working capacities of pelletised 17.5 % NaI material. Pelletisation performed in oxide (N_2 calcination) and carbonate state. Dry gas.

Table 2: Theoretically achievable mass gains by full carbonation compared with the working capacities achieved in Figure 7 in the short cycle experiments. 17.5 % NaI based on $CdCO_3$ is assumed here to be inert during initial decarbonation, SBA-15 throughout the experiment.

sample	CdO (wt%) in activated state	max. weight gain (wt%) by full carbonation of CdO to $CdCO_3$	average working capacity (wt%) achieved	fraction of max. working capacity achieved
pure CdO, theory	100	34.3	n/a	n/a
carbonate pellet	77.84	26.7	12.2	45.7 %
oxide pellet	77.84	26.7	0.6	2.2 %
4.22 % SBA-15	74.63	25.6	2.8	10.9 %
13.7 % SBA-15	67.17	23.0	5.2	22.6 %

Figure 8 shows photographs of the pellets. The pressing of the carbonate sample gave a sturdy pellet (Figure 8a). The segments used in the TGA experiments are shown in Figure 8b. After the multicyclic exposure, the pellet fragments maintained their shape (Figure 8c), but only slight manipulations with a spatula caused them to fall apart (Figure 8d). For comparison, two whole carbonate pellets were calcined in nitrogen at 500 °C (Figure 8e). These also were very brittle and easily crushed between the fingers (Figure 8f). It might be concluded that the weakening of a carbonate pellet already occurred during the initial activation of the pellet rather than during the cyclic sorption tests. By contrast, the pellet made in the oxide state (Figure 8g) maintained its integrity well throughout a multiple cycle TGA experiment. After the TGA experiment, the pellet fragments maintained their original shape (similar to Figure 8c) and did not easily crumble when crushed or rubbed between the fingers (though some minimal amount of material did rub onto the gloves in a similar manner to a hard pencil writing on paper). The two pellets with SBA-15 added behaved in an intermediate way. After 25 CO_2 sorption cycles, the inner portion of the pellet remained sturdy, but was covered by a powdered layer, which was easily removed by rubbing the pellet between two fingers. The remainder of the pellet core and the removed powder after cyclic CO_2 exposure is shown in Figure 8h.

The results show that the material can be pelletised and that pelletisation is best performed in the oxide state so as to maintain the mechanical integrity of the pellet during sorption cycles. However, the working capacity of the pellets is relatively low, and the addition of a porous filler material causes the pellets to partially crumble to powder during CO_2 sorption cycles. In order to overcome this problem, future studies might also consider the use of suitable binding agents.

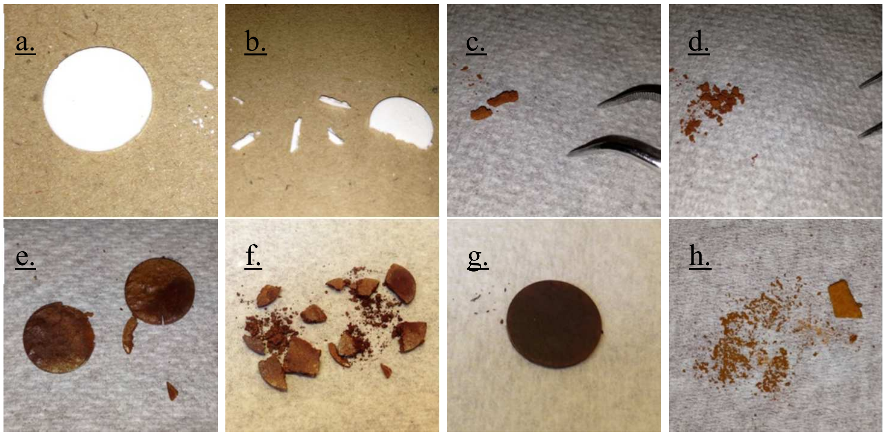

Figure 8: Images of 17.5 % NaI pellets. a. fresh carbonate pellet, b. segments cut off for TGA, c. & d. brittle segments after sorption cycles, e. & f. brittle carbonate pellet calcined at 500 °C in N_2, g. sturdy pellet pressed as oxide, h. 4.22 % SBA-15 pellet after 25 CO_2 sorption cycles. Diameter of pellet after pressing 13 mm, width of tweezers (shown for comparison) 10 mm.

4 Summary and Conclusions

In this study, cadmium oxide/alkali halide mixtures made from both lithium and sodium bromide and iodide were characterised in multiple sorption-desorption cycles. All materials exhibited reversible mass gains and losses under CO_2 partial pressure swing processing via TGA. The best-performing material, a sample made from 17.5 wt% NaI and $CdCO_3$, was analysed in detail, as samples with alkali halides other than NaI exhibited lower working capacities, slower carbon dioxide sorption and/or weak multicyclic CO_2 sorption stability. It was shown by TGA that a cyclic exposure to carbon dioxide in argon and pure argon induces cyclic sorption and desorption of carbon dioxide at constant temperature. It was confirmed by powder XRD that this was due to the reversible formation of cadmium carbonate and oxide. From the TGA results, it became evident that the working capacity of the material is severely reduced over 25 cycles if the initial material activation (decomposition of the carbonate) is performed in air. Avoiding exposure of samples to air at elevated temperatures prior to use significantly improves their multicycle sorption stability. 1 % water addition to the feed gas stream also has a beneficial effect on the overall capacity and cyclability. In a TGA experiment in wet gas with 12 minutes sorption and 24 minutes desorption, at 285 °C, a comparably stable working capacity of approx. 18 weight-% per cycle was achieved.

Exposure to air at elevated temperatures prior to use results in a severe CO_2 capacity loss of the samples and is associated with a loss of iodine. The sodium content, however, was unaltered during the capacity loss and appears to be completely retained within the sample. This has been confirmed by elemental analysis using AAS and ICP-MS. This must mean that sodium takes on a new form, but its exact nature so far remains unidentified. It can be speculated that the loss of iodine is related to the oxidation of iodide to iodine, which then evaporates. This is consistent with the result that samples calcined in air exhibit a greater iodine loss than if they are calcined in inert conditions (i. e., where no oxygen is available as oxidiser). Mass losses during the multicycle experiments, determined by the baseline shift, also confirm alteration and loss of sample constituents over multiple sorption cycles. Water addition during cyclic experiments apparently had no noticeable effect on the loss of iodine.

Pelletisation of the samples and subsequent multiple cycle sorption of the pelletised material resulted in lower working capacities than their powder counterparts. Pellets pressed after pre-treatment (as oxides) had better mechanical stability, but only achieved a relatively low CO_2 sorption working capacity. The reduction of the working capacity caused by pelletisation is assumed due to fusion of powder particles, resulting in diffusion limitations due to greater material thickness. For a pellet prepared from the oxide form of the sorbent with the addition of SBA-15, an improved cyclic sorption capability is presumed to be due to the porous material enabling better gas diffusion into the core of the pellet. In comparison to an oxide pellet without additive, the pellets containing silica were found to be less robust and partially crumbled into powder after 25 CO_2 sorption cycles.

The cadmium oxide/alkali halide sorbent was found to exhibit promising potential as a sorbent to reversibly capture from CO_2 from syngas associated with power generation via IGCC. The cyclic capacity of a sorbent in powder form was successfully maintained over 25 cycles without deterioration under appropriate operating conditions. Future research must now be directed at maintaining the physical integrity of pelletised samples and improving chemical stability over multiple sorption cycles.

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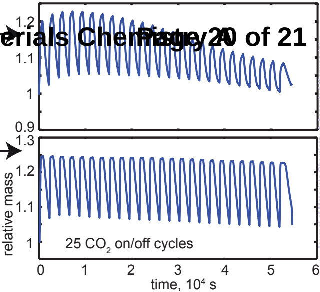
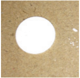
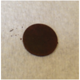
CdCO$_3$/NaI calcined in air exhibits CO$_2$ sorption capacity reduction

less capacity reduction if calcined in inert gas



sorbent powders
& pellets

Both powdered and pelletised CdO/NaI composite CO_2 sorbents were tested in reversible CO_2 sorption experiments. Sorption capacity stability improved in moist environments and if pre-treated in inert gas.