Thermochemical Energy Storage System Development utilising

Limestone

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Abstract

For renewable energy sources to replace fossil fuels, large scale energy storage is required and thermal batteries have been identified as a commercially viable option. In this study, a 3.2 kg prototype (0.82 kWh_{th}) of the limestone-based CaCO₃-Al₂O₃ (16.7 wt%) thermochemical energy storage system was investigated near 900 °C in three different configurations: (i) CaCO₃ was thermally cycled between 850 °C during carbonation and 950 °C during calcination whilst activated carbon was utilised as a CO₂ gas storage material. (*ii*) The CaCO₃ temperature was kept constant at 900 °C while utilising the activated carbon gas storage method to drive the thermochemical reaction. (*iii*) A mechanical gas compressor was used to compress CO_2 into volumetric bottles achieve significant under/overpressure gas to а upon calcination/carbonation, *i.e.* ≤ 0.8 bar and > 5 bar, respectively, compared to the ~1 bar thermodynamic equilibrium pressure at 900 °C. Scenarios (i) and (iii) showed a 64 % energy capacity retention at the end of the 10^{th} cycle. The decrease in capacity was assigned to the formation of mayenite, Ca₁₂Al₁₄O₃₃, rather than the expected Ca₅Al₆O₁₄, which consumed additional CaO. The 316L stainless-steel reactor was investigated in regards to corrosion issues after being under CO₂ atmosphere above 850 °C for approximately 1400 hours, and showed no significant degradation. This study illustrates the potential for industrial scale up of catalysed CaCO₃ as a thermal battery and provides a viable alternative to the calcium-looping process.

Keywords: thermochemical energy storage, limestone, energy storage setups, calcium-looping alternative, scale-up.

1. Introduction

With the decreasing price of renewable energy and the increasing competitiveness with fossil fuels, the remaining hurdle in the green transition towards a renewable energy based society is large scale energy storage [1]. Adoption of renewable energy is a target in the United Nations Sustainable Development Goals (UNSDGs) [2], of which can be significantly enhanced by developing a suitable energy storage option, and/or the development of a low-cost, energy dense, and scalable renewable energy device, capable of both producing and storing energy. Such a device would also address the UNSDG target of reducing CO₂ emissions and curtail climate change. Thermochemical energy storage has recently attracted significant interest due to the vast array of promising candidate materials, *e.g.* metal hydrides, metal hydroxides, and metal carbonates [3–10]. The concept relies on high reaction enthalpies through solid-gas reactions, which implies that energy storage into the system will dissociate the material, *e.g.* the metal carbonate into a metal oxide and CO₂, whilst the reverse reaction liberates an equal amount of thermal energy [8]. An example is limestone, CaCO₃, which has a 1 bar equilibrium pressure at 890 °C [11]:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \Delta H_{890 \circ C} = 165.7 \text{ kJ}; \Delta S_{890 \circ C} = 143.0 \text{ J/K}; \Delta G_{890 \circ C} \approx 0 \text{ kJ}$$
 (1)

Thermochemical energy storage based on naturally occurring minerals, such as metal carbonates, would significantly lower the cost of energy storage materials for commercial application, e.g. for concentrated solar power (CSP) plants as highlighted previously [12–18]. Seasonal energy storage using a thermochemical approach would also benefit compared to state-of-the-art sensible heat storage using molten salts due to chemical energy maintaining its stored capacity upon cooling. A calcium looping (CaL) process has been widely discussed [19-23], primarily as a carbon capture and storage (CCS) technology, but recently also as an energy storage solution, and in some cases in connection with CSP technology [21,24–28]. The CaL process involves two reactors; one for carbonation of CaO and one for calcination of CaCO₃, operating in different temperature intervals and pressure conditions, typically > 800 $^{\circ}$ C at $p(CO_2) > 1$ bar and between 500 – 750 °C at $p(CO_2) < 1$ bar, respectively, to ensure a high electrical efficiency [20]. This design means that solids must be conveyed between high temperature reactors [29]. Hence, the footprint of the plant is increased compared to a scenario with only one reactor while the energy efficiency and energy storage density is also lower [19]. Over the past decade, several projects have designed CaL systems ranging from a few kW_{th} up to 2 MW_{th} for the purpose of either capturing CO₂ or storing energy [19,30]. However, one of the major challenges of the CaL process is the capacity loss during multiple cycles of CO₂ capture and release [24]. Metal carbonates can suffer from slow reaction kinetics and reduced energy storage capacity with increasing cycle number, which is arguably due to sintering of particles at high temperature and subsequent core-shell morphology formation, which may hinder further reactivity [15,31–33]. Several ways of circumventing this inherent property has been investigated, e.g. promoting the CO₂ uptake through a molten salt additive [14,34], prevent sintering of particles by adding an inert material such as MgO [35–37], or by altering the thermodynamics of the metal carbonate formation, hence the reaction pathway, by the addition of a metal orthosilicate [13,38]. One of the most promising systems is the CaCO₃-

Al₂O₃, which has been studied under a variety of operating conditions [30,39–41]. A recent study on the thermochemical properties of limestone with 20 wt% corundum, Al₂O₃, possessing a volumetric energy density of 2257 MJ m⁻³, revealed exceptional energy storage capacity retention (~ 90 %) over 500 calcination/carbonation cycles [12]. The improved cyclic stability was assigned to the irreversible formation of a ternary catalyst, Ca₅Al₆O₁₄ (C5A3) (see reaction scheme 2), which is hypothesised to separate particles and thus prevent sintering, while also allowing Ca²⁺ and O²⁻ to migrate through its layered crystal structure and thus allow CaO to migrate to a reaction site where CO₂ is available to form CaCO₃ [12,42].

$$5CaCO_{3(s)} + 3Al_2O_{3(s)} \rightarrow Ca_5Al_6O_{14(s)} + 5CO_{2(g)}$$
(2)

A range of calcium aluminates have been identified, in particular mayenite, $Ca_{12}AI_{14}O_{33}$ (C12A7), which has been investigated as an electride and an oxide ion conductor [42,43]. However, the Ca-Al-O phase diagram is complex and solid-state synthesis of C12A7 involves the formation of other intermediates, *e.g.* CaAl₂O₄ (CA), Ca₃Al₂O₆ (C3A), and C5A3, depending on the reaction temperature [42,44,45]. The desired product, C5A3, is reported to form below 950 °C, after which the formation of CA and C3A initiates, followed by the formation of C12A7 [42]. However, other research indicates that C5A3 may be a decomposition product of C12A7, depending on the atmospheric conditions applied [46]. Owing to established cyclic stability, the CaCO₃ – 20 wt% Al₂O₃ system forms the basis of this study, where a prototype using 3.2 kg of thermochemical storage material (1.8 kg of active CaCO₃, 0.82 kWh thermal energy) is assessed under different thermophysical operating

conditions using a packed bed reactor coupled with alternative CO₂ storage solutions.

2. Experimental

2.1 Sample Preparation

CaCO₃ (Sigma-Aldrich, > 99.0 %) was hand-mixed with Al₂O₃ (Sigma-Aldrich, Puriss. \geq 98 %) in a 16.7 wt% ratio, before being poured into a 10 L plastic container and shaken thoroughly to mix. The powder was then mixed/milled continuously for 1 hour in batches of ~ 250 g in a custom-made 650 mL 316 stainless-steel canister containing 55 stainless-steel balls, o.d. = 10 mm and *m* ~ 465 g, using a Glen Mills Turbula T2C shaker mixer operating at 160 rpm. Activated carbon (~ 20 kg in gas bottles, granular 12x40 mesh from coconut, All Chemical) was evacuated at 125 °C for 48 h to remove moisture before measurements were undertaken.

2.2. Powder X-ray Diffraction

In-house powder X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer equipped with a CuK $\alpha_{1,2}$ source in flat-plate geometry mode. Data were collected using a Lynxeye PSD detector in the 2Θ -range $10 - 80^{\circ}$ in steps of 0.02° . The crystalline phases were identified using the EVA Bruker software and the International Centre for Diffraction Data (ICDD) PDF4 database. The diffraction peaks were quantitatively analysed by the Rietveld method using Bruker TOPAS v.5 [47,48].

2.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on a Tescan Mira3 FESEM coupled with an Oxford Instruments X-Max SDD X-ray detector and AZtec software. SEM images were collected using a backscattered electron (BSE) detector, an accelerating voltage of 20 kV, an aperture size of 30 μ m, and a working distance of ~ 15 mm. SEM samples were prepared by either dispersing powders onto carbon tape or embedding metallic pieces within an epoxy resin, which was polished using colloidal silica. The dry samples were sputter-coated with a 3 nm thick platinum layer before imaging.

2.4 Thermal conductivity analysis

A TPS 500S (Hot Disk, Thermtest) was used for thermal analysis with a double nickel spiral sensor, laminated by Kapton. A C7577 (2 mm radius) sensor was employed and calibrated using stainless-steel, polystyrene, and NaCl standards. A piece of the solid material from the reactor end was obtained after cycling studies and polished to achieve a smooth surface, and thermal properties were measured 10 times on two different regions. Data for each measurement was collected over 2.5 s at 0.133 W with 15 minutes wait time between each measurement to allow the sample and sensor to cool to a steady-state. The geometric mean of the axial thermal conductivity, diffusivity and volumetric specific heat (in the probed sample volume), and the standard deviations were calculated by the TPS software.

2.5 Pressure-Composition-Isotherm (PCI)

Pressure-composition-isotherm experiments were performed on activated carbon to determine the CO₂ storage properties of the material. 2.0252 g of activated carbon was placed in a stainless-steel high-temperature sample cell, which was attached to a custom-made Sieverts' apparatus [49]. Initially, the sample was heated to 120 °C under dynamic vacuum for 12 hours to remove moisture. Subsequently, an absorption and a desorption curve were obtained under isothermal conditions at T = 20, 60, 100, and 120 °C by increasing/decreasing the pressure in steps of ~1 bar between $p(CO_2) = 0.1 - 20$ bar at each temperature. Each pressure step in the isotherm was maintained for 30 minutes to reach an equilibrium.

2.6 Design of Experimental Setup for CO₂ Cyclic Capacity Measurements

Figure 1 provides an overview of the experimental setup and highlights the experimental differences between the scenarios investigated.

Gas manifold and reactor: A custom-made 316L stainless-steel reactor (tubing: o.d. 5.08 cm, i.d. 4.5 cm, length 138 cm, $V_{internal} = 2195$ cm³, Figure S1) was filled with 3197 g of CaCO₃-Al₂O₃ (16.7 wt%). This resulted in 1792 g of active material, *i.e.* CaCO₃, after the irreversible

reaction with Al_2O_3 was completed to form the C5A3 catalyst according to reaction scheme 2, and allowed for 788 g of CO₂ to be cycled (0.82 kWh_{th}). The stainless-steel reactor was placed in an electrically heated furnace (Furnace Technologies, model P44), and connected to a custom made gas manifold manufactured from Swagelok connections, similar to a previously described apparatus [50]. The manifold consisted of a CO₂ gas inlet, pressure-relief safety valve, and a vacuum outlet to allow evacuation of the system for purging of moisture and loading of CO₂ gas. K-type thermocouples were fitted to the outer steel shell of the reactor at the gas inlet end of the reactor, in the middle, and at the far end of the reactor (opposite the gas inlet) to monitor the temperature of the reactor during carbonation/calcination. The absolute pressure and differential pressure across an orifice (diameter 0.75 mm) between the CO₂ storage gas bottles and the stainless-steel reactor was measured by a Rosemount pressure transmitter (3051SMV). The measured flow rate allowed calculation of the mass flow of CO₂ and thus the CO₂ capacity of the CaCO₃ over multiple cycles, through the equation:

$$q_m = \frac{c}{\sqrt{1-\beta^4}} \cdot \varepsilon \cdot \frac{\pi}{4} d^2 \cdot \sqrt{2\Delta p \cdot \rho} \tag{3}$$

Where *C* is the discharge coefficient, β (0.16) is the ratio between the orifice and pipe diameter, ε the expansibility factor (~1), *d* is the orifice diameter (0.75 mm), Δp the differential pressure in Pa, and ρ is the gas density [51]. When initially connected to the gas system, the CaCO₃ reactor was heated to 150 °C *in vacuo* for 48 hours to eliminate moisture from the system whilst the stainless-steel tubing was thoroughly heated with a heat gun. The experimental setup is visualised in Figure S2.

*CO*₂ *storage*: Three different scenarios were experimentally evaluated where the CO₂ storage method and/or reactor temperature were varied. In *Scenario 1* and 2, ~ 20 kg of activated carbon, kept inside two Aluminium gas bottles (see Figure 1 and S2, V = 15 L each), was used for CO₂ storage (via physisorption to the high surface area material) and to control the system

CO₂ gas pressure (by adjusting the temperature of the activated carbon beds) [52]. This was achieved by varying the temperature of the activated carbon between 20 °C and 110 °C using a Huber CC-505 oil bath that pumped heated oil through copper pipe wrapped around the gas bottles. The oil temperature was set to either 15 or 120 °C over 12 h intervals (3 hours for heating or cooling and 9 hours isothermal), which shifted the equilibrium pressure of CO₂ sorption in the activated carbon based on its thermodynamics of CO₂ sorption. Lower activated carbon temperatures resulted in a lower CO₂ system gas pressure, which in turn initiated calcination of the CaCO₃. Conversely, high activated carbon temperatures increased the CO₂ system gas pressure, resulting in carbonation of CaO. The activated carbon beds enabled a maximum uptake/release of ~ 4.1 wt% CO₂ (*i.e.* ~ 820 g CO₂) when operating between the system gas pressure and temperature conditions (see Figures S3 and S4). Thermocouples were placed on the outside surface of the gas bottles, which were further insulated by 50 mm of Insulfrax S aluminosilicate wool (thermal conductivity = 0.10 W/mK at 400 °C). In *Scenario 3*, the activated carbon CO₂ storage is replaced by compressed gas storage.

Scenario 1: The temperature of the activated carbon was varied between 20 and 110 $^{\circ}$ C (3 hour for heating/cooling and a 9 hour isothermal step) in parallel with the reactor temperature being varied between 850 and 950 $^{\circ}$ C (1 hour for heating/cooling and an 11 hour isothermal step) to create a thermodynamic driving force and thus enhance the reaction kinetics for calcination/carbonation.

Scenario 2: The temperature of the activated carbon was varied between 20 and 110 $^{\circ}$ C (3 hour for heating/cooling and a 9 hour isothermal step), while the temperature of the reactor was kept isothermal at ~ 900 $^{\circ}$ C.



Figure 1. Schematic of the experimental setup based on CO_2 gas storage in (*i*) activated carbon (*Scenario 1 & 2*), or (*ii*) mechanically compressed (*Scenario 3*).

Scenario 3: A CO₂ compressor (HASKEL, model AGT-30/75), a pressure transmitter (Rosemount 3051S), a pressure regulator, and two pneumatic valves were installed between empty CO₂ gas bottles and the gas manifold (see Figure 1), which were configured to keep the system gas pressure below 0.7 bar during calcination and the system gas pressure at above 5 bar during carbonation (see Figure S5). The pressure transmitter allowed for the calculation of the quantity of CO₂ stored in the gas bottles, based on the gas law, pv=nRTZ (p: pressure; v: volume; n: number of moles; R: the gas constant; T: temperature; Z: compressibility factor of CO₂ extracted from the NIST database REFPROP [51]), and also the subsequent quantity of CO₂ involved in the thermochemical reaction with the material in the reactor. Before initiating *Scenario 3*, the CaCO₃-Al₂O₃ material was 'charged' by applying ~ 4 bar of CO₂ pressure for ~ 10 days, at which point no pressure drop was observed over a 24 hour window. By the end of *Scenario 3*, the sample was cooled naturally under 5 bar CO₂.

3. Results & Discussion

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3.1 Thermochemical Energy Storage Performance

A reactor containing 3.2 kg of CaCO₃-Al₂O₃ (16.7 wt%) was cycled through calcination and carbonation stages near 900 °C to assess the system-wide functionality of the energy storage material and different gas storage options. Three different scenarios were investigated as described in the experimental section with the purpose of evaluating the effect of driving forces on calcination/carbonation, *i.e.* a thermodynamic driving force (*Scenario 1*), a steady thermodynamic scenario with minimum pressure differences (*Scenario 2*), and a pressure driving force (*Scenario 3*), *i.e.* over/under pressure compared to the equilibrium pressure at 900 °C. The expectation is that a large driving force, as provided in *Scenario 1* and *3*, will provide faster reaction kinetics and thus, within the timeframe of the experiment, also a larger conversion through calcination/carbonation.

Scenario 1: This scenario represents a large thermodynamic driving force for calcination and carbonation due to the temperature fluctuation of the furnace and thus the CaCO₃-Al₂O₃ material that was driven between 850 °C ($p_{eq} = 0.57$ bar) and 950 °C ($p_{eq} = 2.4$ bar) [11]. Figure 2 illustrates 12 h controlled temperature cycling of the furnace along with controlled temperature cycling of the gas bottles filled with activated carbon used to store/release CO₂ gas from the thermochemical reaction. The resulting system gas pressure either drives CO₂ into the activated carbon gas store from the decomposition of CaCO₃ or drives CO₂ from the activated



Figure 2. Data comparison of the different experimental scenarios investigated, see also Figure 1. Top row shows gas bottle temperature (black curve: gas bottle 1; red curve: gas bottle 2), the middle row shows the furnace and reactor temperatures (thermocouple colour code: black: furnace internal; green: at the reactor inlet; blue: in the reactor middle; red: at the reactor end), while the bottom row shows the CO_2 capacity observed in each scenario (positive number: gas release; negative number: gas absorption; theoretical capacity: 788 g). Some data was lost due to a technical failure in the 8th desorption of *Scenario 2*.

carbon into the CaO, according to the thermodynamics of reaction scheme 1. Despite the large thermodynamic driving force, the CO₂ capacity, *i.e.* the energy capacity, degrades over the 10 cycles from 732 g CO₂ (93 % of the theoretical 788 g CO₂) to a minimum of 484 g CO₂ (61 %) upon calcination. However, the last four cycles stabilise around a capacity of 500 g of CO₂ (63 – 64%). The decrease in capacity may be explained by physical changes in the sample morphology/composition (described below) or by kinetic factors of CO₂ release and uptake.

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There are two different kinetic regimes observed, especially during CO_2 absorption (Figure 2, bottom row, negative curves). The initial carbonation seems fast, however, the absorption curves all indicate that reaction kinetics noticeably slow down once more than 350 g of CO₂ is absorbed (~45% theoretical capacity). The kinetic behaviour is exemplified by the first absorption in Scenario 1 (Figure S6). After a brief induction period, the reaction kinetics accelerate after ~ 25 g of absorbed CO₂, to reach a rapid rate of ~ 128 g CO₂/h. However, after absorbing ~ 350 g CO₂, the reaction kinetics decrease one order of magnitude to ~ 12 g CO₂/h. Indeed, under these reaction conditions the carbonation kinetics are slow and the absorption time (12 hours) may not be sufficient to completely carbonate the large sample mass. Previous research has shown that CO₂ gas release and uptake from the CaCO₃-Al₂O₃ system is rapid (minutes not hours) on the milligram scale [12]. Therefore it is inferred that kinetic limitations may be due to sample evolution, morphology, or thermal gradients on the kg scale. The slow reaction kinetic regime may be overcome by applying a CO₂ overpressure (as highlighted later in Scenario 3), thus the pressure provided by the activated carbon (that is close to the equilibrium pressure of the CaO) may simply be insufficient to provide adequate absorption kinetics, despite the favourable decrease in thermodynamic equilibrium pressure caused by operating at 850 °C. An even larger driving force could have been created by increasing the temperature oscillation window, e.g. operating between 500 °C (carbonation) and 1000 °C (calcination) and thus lower/raise the equilibrium pressure even further. This has previously been shown in many TGA experiments on limestone [27,53,54]. However, from a large-scale operating point-of-view performing the reaction at a lower temperature may lead to decreased reaction kinetics while the heat-to-electricity conversion efficiency would suffer.

Scenario 2: The experimental conditions were kept the same as in *Scenario 1*, except the reactor temperature was fixed at 900 °C, rather than being cycled. CO₂ gas pressure was controlled by driving the temperature (and thus evolved pressure) of the activated carbon gas store. The

influence of maintaining the sample, *i.e.* CaCO₃-Al₂O₃ (16.7 wt%), temperature constant at 900 °C is reflected in the absorption kinetics, which are slower than in *Scenario 1*, *i.e.* 82 g CO₂/h *versus* 128 g CO₂/h (see Figure S6). This is likely a direct function of the higher equilibrium pressure at 900 °C (1.2 bar compared to 0.57 bar at 850 °C, *Scenario 1*) and thus the reduced overpressure provided from the activated carbon gas store, which appears to be required to accelerate the reaction kinetics. The first CO₂ cycle for this scenario entailed a limited carbonation that only reached 384 g CO₂ (47 %) and a subsequent calcination ending at 421 g CO₂ (53 %). This limited capacity is consistent with the final capacity observed in the storage system after *Scenario 1* was completed. Thus, the CaCO₃-Al₂O₃ does not recover its initial storage capacity under these reaction conditions. The CO₂ capacity gradually dropped throughout the cyclic measurements ending with a CO₂ release of 277 g (35 %). In comparison with *Scenario 1*, the second scenario displays slower reaction kinetics, which is assigned to the smaller driving force created when maintaining the sample temperature at 900 °C combined with the smaller fraction of CaCO₃ that is initially available for reaction.

Scenario 3: The kinetics of the thermochemical energy storage system can be driven by controlling reactor temperature (as in *Scenario 1*), but also by controlling CO₂ pressure. Scenario 3 investigated a system operating with a constant 900 °C reactor temperature but a CO₂ gas store that is not based on activated carbon (unlike *Scenarios 1 & 2*). Instead, CO₂ was driven out of the gas manifold and reactor using a mechanical compressor during calcination and to maintain a pressure below 0.7 bar, whilst a gas pressure regulator provided ~ 5 – 6 bar CO₂ during carbonation. The switch between calcination and carbonation was automatically controlled using time regulated pneumatic valves, indicated inside the green box in Figure 1. It should also be noted that the CaCO₃-Al₂O₃ system was regenerated before *Scenario 3* by applying an overpressure of CO₂ for 10 days. The first calcination shows full CO₂ release, *i.e.* 788 g of CO₂ (100 %, Fig. 1, bottom), which indicates that the full theoretical capacity was

restored during the regeneration process before initiating this scenario. Subsequently, 750 g of CO_2 (~95 % capacity) is absorbed during the first carbonation, while the capacity slightly decreased throughout the 10 cycles. The calcination curves seem to plateau before the end of the 12 h cycles, indicating depletion of CO_2 from the material, whereas the carbonation curves do not completely finish within the timeframe (Fig. 1, bottom, positive and negative curve, respectively). Again, this capacity drop is assigned to the presence of a second slower reaction kinetics regime. In the 10th absorption step the initial kinetics of CO_2 uptake rapidly occurs at an average of 426 g CO_2/h , but drops to ~ 5 g CO_2/h in the second kinetic regime (see Figure S6). The final carbonation saw the uptake of 499 g CO_2 (63 %), which is similar to *Scenario 1*.

The three operational scenarios allow for some analysis of the system limitations and its potential optimisation. It is clear from the reactions kinetics observed in *Scenario 3* that it is beneficial to apply a CO₂ over/under pressure compared to the thermodynamic equilibrium pressure of the reaction. Indeed, altering the CO₂ pressure during carbonation and calcination seemed to have a similar effect to controlled variations in the calcination/carbonation sample temperature (*Scenario 3* and *1*, respectively). Essentially, both procedures cause the CO₂ gas pressure to vary from the reaction's thermodynamic equilibrium pressure, thus acting as a driving force. However, the CO₂ over-pressure during carbonation does result in short-lived temperature spikes within the sample during absorption (increased by at least 22 °C, see Figure S7). These temperature spikes were not observed in the *Scenarios 1* and 2 due to the CO₂ pressure being closer to the equilibrium pressure, causing more gentle temperature excursions from slower reaction kinetics. Considering that the temperature spike is measured on the outside of the reactor, it is believed that the temperature inside the powder bed reached a significantly higher temperature. Based on thermodynamic calculations at an equilibrium pressure of 5.2 bar it is possible for the powder bed to reach 1010 °C [11]. Obviously, it is

expected that the thermochemical reactor does produce large quantities of heat when it is releasing energy, but without active heat extraction the large temperature excursions could also modify the powder bed composition and morphology.

3.2 Physical Characteristics of Cycled Material

The CaCO₃-Al₂O₃ (16.7 wt.%) sample composition was evaluated in the carbonated state, after *Scenario 3*, hence after 30 cycles, by XRD at three different regions in the reactor, *i.e.* at the reactor gas inlet, the reactor middle, and the far end of the reactor (see Figure S8). After gas cycling measurements had ceased the CO₂ capacity had degraded to ~ 64 %. Powder samples were prepared by hand grinding the compacted rock-like samples (see Figures S9 and S10). Furthermore, the stainless-steel walls from the reactor were also investigated to observe any degradation from being in a CO₂ atmosphere for a long period of time (~1400 h) at *T* ~ 900 °C, see Table 1.

The XRD results show the presence of two types of Ca–Al–O compounds, Ca₅Al₆O₁₄ (C5A3) and Ca₁₂Al₁₄O₃₃ (C12A7). The expected compound, C5A3 [12], was only identified at the inlet and in the uncompacted powder at the end of the reactor (10.6(3) and 7.2(2) wt%, respectively), whereas it was not observed in the middle of the reactor. The high content of C12A7 indicates that the CO₂ capacity decrease observed in cycling studies was partly due to the formation of large fractions of C12A7 throughout the reactor. C12A7 is calcium-rich compared to C5A3 and results in further consumption of CaO (reaction scheme 4) compared to the expected product (reaction scheme 2).

$$7Ca_5Al_6O_{14(s)} + CaO_{(s)} \rightarrow 3Ca_{12}Al_{14}O_{33(s)}$$
(4)

The formation of Mayenite (C12A7) could be due to excess heating in the reactor bed during CO_2 absorption steps. The sample composition at the middle of the reactor presented the highest content of C12A7 and thus also the lowest content of CaCO₃/CaO. Finally, the positive

effect from C5A3 towards cyclic stability is absent due to the consumption in producing C12A7.

Interestingly, the reactor inlet possessed the largest amount of CaCO₃ and CaO, 46.0(2) and 10.1(9) wt%, respectively, and the lowest amount of the by-product Mayenite, $Ca_{12}Al_{14}O_{33}$ or C12A7 (33.4(2) wt%), although this contributed to almost a third of the sample composition. In the middle of the reactor the content of C12A7 was 49.8(2) wt%, whereas the content of CaCO₃ and CaO was 32.1(2) and 18.1(1) wt%, respectively. At the end of the reactor, 42.0(2) wt% of C12A7 was observed with only 49.3(2) wt% of CaO. Additionally, Ca(OH)₂ was observed, which is assigned to the sample being handled in air after the experiment finished and thus CaO has reacted slightly with moisture. The formed CaCO₃ and residual CaO may be assigned to the formation of core-shell particles (CaO core; CaCO₃ shell) previously reported, which hinders the CaO reaction with CO₂[15,31].

 Table 1. Sample composition (wt%) of cycled CaCO₃-Al₂O₃ (16.7 wt%) and corrosion from 316L vessel walls

 extracted from Rietveld refinement of XRD data (Figure S8).

Compound	Material at	Material at	Material at	Stainless- Steel	Stainless- Steel
	Reactor Inlet	Reactor middle	Reactor End	reactor inside	reactor Outside
CaCO ₃	46.0(2)	32.1(2)	49.3(2)	1.6(3)	-
CaO	10.1(9)	18.1(1)	3.0(8)	-	-
Ca5Al6O14	10.6(3)	-	-	-	-
Ca ₁₂ Al ₁₄ O ₃₃	33.4(2)	49.8(2)	42.0(2)	-	-
Ca(OH) ₂	-	-	5.8(1)	-	-
Fe ₃ O ₄	-	-	-	98.4(3)	-
a-Fe ₂ O ₃	-	-	-	-	58.4(7)
γ-Fe ₂ O ₃	-	-	-	-	41.6(7)

Upon completion of the CO₂ cycling experiments, it was noted that the exterior of the 316L stainless-steel reactor vessel was corroded and flaking. XRD analysis verified that the corrosion on the outside walls that were exposed to air were composed of α -Fe₂O₃ (Hematite – 58.4(7)) and γ -Fe₂O₃ (Maghemite – 41.6(7) wt%, Figure S8). In contrast, the interior of the tube had also undergone a reaction identified by XRD as Fe₃O₄ (Magnetite) and minor fractions of CaCO₃, and an unknown phase (Figure S8).

After a suite of cyclic thermochemical tests near 900 °C, the original powder bed was compacted into rock-like rods (see Figures S9 and S10), which may indicate severe sintering of the material. The rods were unable to be broken by hand and were measured to have an apparent density of ~1.85 g/cm³. This is less dense compared to pristine CaCO₃ and Al₂O₃, 2.71 and 3.95 g/cm³ [55], respectively. From the compositions calculated by XRD and their respective crystalline densities, it was determined that the % of porosity for the inlet, middle, and end of the reactor was 68, 66, and 61%, respectively. This indicates the material is more compact at the furthest part of the reactor. Additionally, the thermal properties of the compact material were measured using the transient plane source method. It was determined that the thermal conductivity was 1.33(5) W.mK, thermal diffusivity = 0.82(8) mm²/S, and specific heat = 1.6(1) MJ/m³·K. This is less than pristine CaCO₃, which has a thermal conductivity of 2.259 W.mK, and is likely attributed to the porosity of the sample as these parameters are highly dependent on sample preparation and properties [56]. Over weeks of storage in air the rock-like sample became more brittle and exfoliated due to hydroxylation.

From scanning electron microscopy and energy dispersive spectroscopy (Figure 3), it is observed that after milling, aluminium and calcium are segregated and present in specific regions of the sample, Figure 3b, which is contrary to the previous observation while the particle size distribution is also larger being around 20 μ m [12]. The large particles and the segregation may be explained by insufficient ball-milling of the sample. Thus, the large contact

surface area between CaCO₃/CaO may have allowed sintering, which would explain the increased particle size of the calcium rich regions observed after the cyclic experiments (< 100 μ m) and the solid chunks that was extracted from the reactor (Figures S9 and S10). The aluminium-rich regions are believed to indicate particles of C12A7 as observed by XRD. The high temperature sample reactor must endure high temperatures for long periods with its exterior surface exposed to air and its internal surface exposed to the sample and CO₂ gas. Large-scale reactor designs may avoid high temperature metallic corrosion through a refractory lining, which may be preferred due to the known corrosivity of steels and other alloys near 900 °C [57]. However, the 316L stainless-steel lab-scale prototype herein was not significantly corroded after operation for 1400 h under the operating conditions described. After the cyclic experiments, the reactor tubing was cut and analysed using SEM (Figure 4). Interestingly, drastically different corrosion mechanisms were experienced by the exterior (region A) and interior (region B) surfaces.





The exterior surface underwent significant exfoliation, with additional flakes being cast off during cooling of the reactor. The exfoliated flakes were chromium- and nickel-rich, indicating preferential elemental oxidation and segregation. In contrast, the interior surface did not display any exfoliation, but instead underwent marked dealloying and/or intergranular attack (see Figure S11).



Figure 4. Scanning Electron Microscope (SEM) micrographs of 2" diameter stainless-steel (316L) tube (2.9 mm walls) after operation near 900 °C for 1400 h and 30 cycles. Corrosion was only observed within ~100 μ m of the exterior (air exposed) and interior (CO₂ exposed) surfaces. Representative corroded regions are shown (A & B) along with an Energy Dispersive Spectroscopy (EDS) map of the elemental composition of the exterior surface in region A where, Ni is aqua, O is blue, Fe is green, Cr is red, and Si is magenta. Samples were embedded in epoxy and polished.

Importantly, the corrosion is only observed less than 100 μ m, into the stainless-steel which is excellent compared to the physical conditions applied. X-ray diffraction of the surface material from the interior and exterior of the tubing (Figure S8) corroborates these observations (Table

1) where the interior surface only presents Bragg reflections for magnetite (Fe₃O₄), whereas the exterior surface only presents reflections for Hematite and Maghemite (α - and γ -Fe₂O₃, respectively).

4. Conclusions

A scale-up 3 kg CaCO₃-Al₂O₃ (16.7 wt%) thermochemical energy storage system has been demonstrated utilising three different configurations. At first, a thermodynamic driving force was created by varying the sample temperature between 850 and 950 °C ($p_{eq} = 0.57$ bar and p_{eq} = 2.4 bar, respectively), while utilising activated carbon as a CO₂ storage material. The energy storage capacity degraded over 10 cycles at real-life conditions (12 h calcination and carbonation) but maintained a steady capacity of ~ 64 % over the last 4 cycles. The second scenario presents an isothermal situation, where the sample temperature is kept at 900 °C. However, the provided CO₂ pressure from the activated carbon proved insufficient in this case, due to the increased equilibrium pressure ($p_{eq} = 1.2$ bar) on carbonation compared to Scenario 1, allowing the energy storage capacity to further drop to ~ 35 %. The final scenario (3) utilised a compressor to increase the carbonation pressure to 5 bar and lower the calcination pressure to < 0.8 bar. After 10 cycles the energy storage capacity retention is ~ 63 %. Thus, the capacity is similar to Scenario 1, which concludes that varying the sample temperature is just as effective as varying the pressure. The latter requires CO_2 compression, which decreases the overall energy efficiency of the system, thus the first scenario may be a better option from an efficiency point of view when scaling up the system further. Although thermal energy needs to be provided to the activated carbon to release the CO_2 , this may be provided by the system itself or be provided by a heat pump on a commercial scale. However, activated carbon has a price of ~3000 USD/tonne [58], which is a severe financial drawback when constructing large-scale facilities. Thus, a techno-economic analysis of the different storage methods is required alongside research into alternative CO₂ storage materials, *e.g.* zeolite materials. Additionally,

the energy capacity retention needs to be improved before initiating further steps of scale-up. However, this study suggests a simplistic and thus cheaper setup compared to the widely discussed calcium-looping process as the engineering requirements in the suggested setup are significantly reduced by: (*i*) avoiding conveying (hot) solids (*ii*) limiting the need for multiple reactors (*iii*) a reduced footprint and thus a higher energy density of the system. Hence, the stationary setup suggested here encourages a more simplistic solution to a complex process. Thus, new avenues for designing an energy storage device based on calcium carbonate are opened.

The observed energy capacity decrease may partly be assigned to the excessive formation of Mayenite, $Ca_{12}Al_{14}O_{33}$, which has previously been observed at temperatures above 950 °C [42,44,59]. This is within the operating temperature in *Scenario 1*, or possibly, from the internal sample temperature exceeding 950 °C upon the exothermic carbonation, highlighted by the temperature spikes observed in *Scenario 3* of up to 22 °C on the outside of the reactor. Hence, the positive effect obtained from $Ca_5Al_6O_{14}$ is absent due to its consumption in the reaction towards C12A7. Additionally, the compact material observed after the experiments also indicates critical sintering, which would restrict the cyclic capacity severely.

Finally, the reactor material, *i.e.* 316L stainless-steel, was evaluated after being exposed to 900 °C and various atmospheres for ~ 1400 hours. The exterior of the steel was determined to be affected by oxidation whereas the interior showed minor corrosion. In both cases, the corrosion was limited to less than 100 μ m from the surface, which is indeed satisfying.

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