ABSTRACT: For the first time, a mayenite based material combining calcium and copper (18.0/37.6/44.4 estimated active wt % CaO/CuO/Ca₂Al₂O₄, CuO/CaO = 2.1 [wt/wt]) has been subjected to three full calcium–copper chemical looping combustion (Ca–Cu Looping) cycles in a fixed bed reactor (70.0 g of combined material and 3.5 g of 18.0 wt % Ni/Al₂O₃ reforming catalyst), demonstrating the feasibility of a combined materials approach to hydrogen production through Ca–Cu Looping. Combined materials were characterized by helium pycnometry, mercury intrusion, nitrogen adsorption, X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and energy dispersive X-ray diffraction before and after reactor testing. A carbon dioxide capture capacity of 14.6–15.0 g CO₂/100 g (640–660 °C, 1.0 MPa, 2.5 kgs⁻¹, kgs⁻¹ h⁻¹), full oxidation, and expected calcination efficiencies (51–64%) were obtained. Combined material performance is comparable to that of segregated materials previously tested in the same experimental rig. Process intensification of Ca–Cu Looping through combined materials development is promising.

1. INTRODUCTION

Development and implementation of carbon capture and storage technologies (CCS) for mitigation of carbon dioxide (CO₂) emissions has gained traction since the mid-1990s, and it is now generally accepted as an important part of the combination of technologies (alongside renewables, increased energy efficiency, etc.) needed for reaching international emission targets. A 2018 report by the IPCC states with high confidence that it is likely that a 0.8–1.2 °C increase in global average temperature relative to preindustrial levels has already occurred, and an increase to 1.5 °C warming is likely to be reached between 2030 and 2052 if the current rate of CO₂ emission continues. In order to avoid a greater increase of the average temperature, development in both renewable energy technology and CCS is needed. The primary role of CCS in a future zero/low-emission scenario is anticipated to be captured from stationary fossil fuel based point-sources in power production and the chemical industry. The International Energy Agency (IEA) has underlined the importance of new CCS technologies and the funding of major CCS pilot projects, as large-scale demonstration of CO₂ capture technology is a current bottleneck for more widespread implementation and acceptance in the industrial sector.

The topic of the presented work is hydrogen production from natural gas with CCS, i.e., CO₂ capture from a stationary point-source within the chemical industry. The annual global production of hydrogen is approximately 65 Mt/year where 95% is produced from fossil fuels (48% from reforming of natural gas) and the majority of hydrogen is “used where it’s produced” in refinery feedstock hydrotreatment or in the production of miscellaneous commodity chemicals (ammonia, methanol, etc.). The associated CO₂ emissions for a large-scale, hydrogen producing natural gas reforming plant are estimated to be in the order of 7.0–8.1 tCO₂/tH₂. As an important side note it should be mentioned that there is political interest and drive toward prioritizing CCS technology in these sectors. In, e.g., Norway, ammonia, methanol, and cement production are important constituents of the industrial sector.
The development of the processing concept can be traced back to ideas of unmixing combustion and chemical looping. An emerging technology for hydrogen production with carbon capture is calcium–copper chemical looping combustion (Ca–Cu Looping), where calcium looping (CaL) and chemical looping combustion (CLC) are combined into a unified approach for hydrogen production with integrated carbon capture using natural gas or other carbonaceous, gaseous fuels (e.g., biogas). The sorbent must be calcined in a high percentage CO₂ (calcination), reducing gas composition, flow conditions, the degree of CaCO₃ loss during oxidation, the degree of carbonation in the SER step, etc. CuO/CaO weight ratios between 2.4 and 3.1 [wt/wt] (CuO/CaO 1.7–2.2 [mol/mol]) have been reported as optimal based on thermodynamic and process modeling for a representative CH₄/CO/H₂ gas. Reducing gas, while using CH₄ only as a reducing gas will require CuO/CaO weight ratios of about 4.5 (3.2 molar).

A 2018 techno-economic assessment of Ca–Cu Looping integrated in a hydrogen plant by Riva et al. shows that Ca–Cu Looping compares favorably to a base-case FT/w/amine capture. Capital cost is a significant contributor to the total economic potential of the Ca–Cu Looping concept, and further process intensification through, e.g., materials development for Ca–Cu Looping, could contribute to driving down capital cost. One method for intensifying the process is demonstrated in this work through a two-particle approach (or “combined materials approach”) to Ca–Cu Looping, in contrast to the commonly implemented three-particle approach (or “segregated materials approach”). In the combined materials approach, CuO and CaO phases are integrated into one particle. Given segregated particles with active weight loadings of 30 wt % CaO and 70 wt % CuO, a 40 wt % CuO loaded combined material would give more active material per gram for the recommended 2.4–3.1 [wt/wt] (1.7–2.2 [mol/mol]) CuO/CaO ratio range. The hypothesized advantages of this approach relative to the segregated approach in addition to process intensification include better heat transfer properties and avoiding hot spots due to the intimate contact between Ca and Cu species during calcination as well as two rather than three materials production lines. However, segregated and combined materials face the same major challenge: stable transient CO₂ and O₂ carrying capacities across a sufficient number of process cycles complicated by CaO sintering and CuO migration.

In a previous study, our research group at IFE evaluated the performance of combined materials based on mayenite precursors in a hydrothermal synthesis. It was shown that materials at 50 wt % CuO loading deactivated regardless of precursor during Ca–Cu Looping relevant cyclic thermogravimetric analysis (TGA, 40 cycles), while 40 wt % CuO loaded materials remained active. The CuO/CaO = 2.0 [wt/wt] ratio was chosen as it (1) represents a maximum expected CaO content for a given CuO loading, (2) if a material is stable at CuO/CaO = 2.0 [wt/wt] at a given CuO loading, it should be stable at higher CuO/CaO ratios at the same CuO loading (increasing the CuO/CaO ratio is equivalent to replacing a
2. MATERIALS AND EXPERIMENTAL METHOD

2.1. Preparation of Material. The combined calcium—copper material was prepared using a hydrothermal synthesis route previously reported by our group where 3.0 g powder batches of combined calcium—copper materials were studied in detail using various CuO loadings and precursors. A theoretical calcined combined material composition of 20/40/20 wt % CaO/CuO/Ca12Al14O33 with an active CuO/CaO = 2.0 [wt/wt] ratio using Cu(OH)2 as CuO precursor was selected for upscaled based on favorable results and precursor cost. Synthesis scale-up to 100.0 g batches, as well as an agglomeration procedure, has been reported. The essential features of materials synthesis and agglomeration of the tested material are summarized here for ease of reference.

For the upscaled synthesis of combined calcium—copper mayenite based material, copper hydroxide (Cu(OH)2) technical grade, Sigma-Aldrich, boehmite (Al(OH)3), 95% Sasol, and calcium hydroxide (Ca(OH)2 >99% Merck) were used as reactants, and isopropyl alcohol and deionized water were used as solvents. Dried reactants (>48 h, 110 °C) corresponding to a theoretical 40 wt % CuO loaded combined material with CuO/CaO = 2.0 [wt/wt] were weighed out and mixed in isopropyl alcohol with a solid-to-liquid ratio of 4.0. The slurry was stirred for 1 h at room temperature, dried overnight in a 110 °C laboratory oven, mixed with deionized water using a solid-to-liquid ratio of 3.0, transferred to a 600 cm³ stainless steel autoclave, and heated to 150 °C (2 °C min⁻¹ heating rate) resulting in an absolute pressure of 0.5 MPa inside the autoclave. The liquid—solid mixture was kept at these conditions for 5 h and subsequently cooled to ambient temperature (2 °C min⁻¹ cooling rate). A laboratory oven was used in order to evaporate the solvent overnight (110 °C, 16 h). The resulting dried solid was crushed to a fine powder and calcined at 1000 °C (1 h, 5 °C min⁻¹ heating rate). A yield of 95—97 wt % can be expected from the described procedure using a theoretical 100.0 g of oxidized and calcined solids production as basis.

Agglomeration through wet granulation is scalable and frequently employed in industry. Calcined powders were agglomerated in a GMX-LAB Micro High Shear Wet Granulator (Vector Corporation). Batches of 95.0 g of material were agglomerated using a 1.0 L agglomeration bowl, 500 rpm impeller, and 500 rpm chopper speed. An aqueous solution of 15 wt % polyethylene glycol (PEG) was used as a binder and added to the solids with a 10 rpm pump speed. 40.0 g of PEG was used per 100.0 g of powder. Sieving after agglomeration resulted in a 35—40 wt % yield in the agglomerate diameter range of 0.5—0.8 mm. This size fraction was selected for reactor testing. Agglomerates were calcined at 900 °C (1 h, 5 °C min⁻¹ heating rate) in order to remove the PEG binder.

The same synthesis and agglomeration procedure was used for the combined material presented in the Supporting Information (Figures S4—S12, Tables S1—S3) using CuO powder (>97 wt % 325 Mesh Powder, Alfa Aesar) as copper(II) oxide precursor.

2.2. Material Characterization. Prepared agglomerates were characterized before and after fixed bed reactor testing. Characterization before testing included cyclic thermogravimetric analysis (TGA) representing process relevant Ca—Cu Looping conditions (section 2.3), X-ray diffraction (XRD), helium (He) pycnometry, mercury (Hg) intrusion, N₂ adsorption, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). After reactor testing the same characterization methods except TGA cycling were used. All characterization before and after testing was performed with materials in a calcined and oxidized state. After reactor testing calibrated gas flows and pressure drops were measured using an entrained flow reactor (EFR) while 227°C was used as the bed temperature.
Table 1. Normal Gas Flow (101.325 kPa, 273.15 K), Set Point Temperature, and Pressure for the Ca–Cu Looping Reactor Tests for 70.0 g of Combined Material (15.0 wt % Active CaO) and 3.5 g Reduced 18.0 wt % Ni/Al2O3 Catalyst

<table>
<thead>
<tr>
<th>pressurization</th>
<th>SER</th>
<th>flash</th>
<th>acc 1</th>
<th>oxidation</th>
<th>acc 2</th>
<th>calcination</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 to 625 °C</td>
<td>625 °C</td>
<td>625 to 700 °C</td>
<td>700 °C</td>
<td>700 °C</td>
<td>700 to 800 °C</td>
<td>800 °C</td>
</tr>
<tr>
<td>0.1 to 1.0 MPa</td>
<td>1.0 MPa</td>
<td>1.0 MPa</td>
<td>1.0 to 0.8 MPa</td>
<td>0.8 MPa</td>
<td>0.8 to 0.1 MPa</td>
<td>0.1 MPa</td>
</tr>
<tr>
<td>15 min</td>
<td>60 min</td>
<td>15 min</td>
<td>30 min</td>
<td>65 min</td>
<td>15 min</td>
<td>20 min</td>
</tr>
<tr>
<td>N2 [NL/h]</td>
<td>46.3</td>
<td>2.7</td>
<td>46.3</td>
<td>36.0</td>
<td>28.8</td>
<td>30.9</td>
</tr>
<tr>
<td>H2 [NL/h]</td>
<td>5.1</td>
<td>5.1</td>
<td></td>
<td>2.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O [NL/h]</td>
<td>38.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CO2 [NL/h]</td>
<td></td>
<td></td>
<td>15.4</td>
<td>19.0</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>CH4 [NL/h]</td>
<td>12.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 [NL/h]</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>total [NL/h]</td>
<td>51.4</td>
<td>53.7</td>
<td>51.4</td>
<td>51.4</td>
<td>51.4</td>
<td>51.4</td>
</tr>
</tbody>
</table>

*Molar S/C = 3.15, sorbent-to-catalyst mass ratio (Z) = 3.0, MHSV_{CH4} = 2.5 h⁻¹. Acc = accommodation step.*
Materials (70.0 g CaO/CuO/Ca12Al14O33 and 3.7 g oxidized 18.0 wt % Ni/Al2O3 catalyst) were top loaded into the vertical reactor bed giving a height of about 13.1 cm. The TC placements were thus at 2.5 cm (TC5), 5.0 cm (TC4), 7.5 cm (TC3), 10.0 cm (TC2), and 12.5 cm (TC1) measured from the bed bottom. The upper part of the solids bed, between 12.5 and 13.1 cm, was not covered by thermocouples. 15.0 wt % active CaO was assumed for the combined material—a reasonable estimate between powder and agglomerate capacities from TGA tests (Table 2).

**Table 2. Characterization Data for Powder and Agglomerates (0.5–0.8 mm) before Reactor Testing**

<table>
<thead>
<tr>
<th>powder</th>
<th>agglomerates</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface area [m² g⁻¹]</td>
<td>2.19 ± 0.01</td>
</tr>
<tr>
<td>true density [g cm⁻³]</td>
<td>3.67 ± 0.01</td>
</tr>
<tr>
<td>average pore diameter [nm]</td>
<td>381.4</td>
</tr>
<tr>
<td>porosity [%]</td>
<td>53.6</td>
</tr>
<tr>
<td>particle density [g cm⁻³]</td>
<td>1.70</td>
</tr>
<tr>
<td>TGA (g CO₂/100 g)max</td>
<td>15.3</td>
</tr>
<tr>
<td>TGA (g O₂/100 g)max</td>
<td>8.2</td>
</tr>
<tr>
<td>TGA wt % CaO</td>
<td>18.0</td>
</tr>
<tr>
<td>TGA wt % CuO</td>
<td>37.6</td>
</tr>
<tr>
<td>TGA CuO/CaO [wt/wt]</td>
<td>2.1</td>
</tr>
</tbody>
</table>

“True density is based on He pycnometry. Porosity, average pore diameter, and particle density are based on Hg intrusion, while surface area is based on N₂ adsorption (BET).”

Prior to initiating the Ca–Cu Looping cycle, a prereduction using the pressurization step gas composition (Table 1) was performed, making sure that the catalyst and combined material were in reduced and calcined states. Materials were heated in N₂ and H₂ to form ambient temperature to 800–850 °C and kept at these conditions until no CO₂ was detected by the gas analyzer and no H₂ was consumed. After this prereduction step, the material was cooled, and the full pressurization conditions (0.1 to 1.0 MPa at 625 °C set point temperature) were imposed and kept for 15 min for conditions to stabilize. When conditions were stable, steps according to Table 1 were performed, representing a full cycle of Ca–Cu Looping. After the calcination step, the materials were cooled at ambient pressure using the pressurization step gas composition (Table 1). Prereduction was performed prior to each reported cycle.

Testing conditions reported in Table 1 were selected based on previous work on segregated materials reactor experimentation and reported optimal operation conditions for Ca–Cu Looping. The SER step was performed using a molar S/C of 3.15, 0.97–1.0 MPa pressure, and set point temperature of 625 °C. These conditions are suitable for high CH₄ conversion at elevated pressure and for avoiding significant CaO hydration. A temperature of 625 °C refers to the reactor set point temperature, and a temperature gradient of 20 °C was observed between the top and bottom TCs during testing. A set point of 625 °C corresponds to initial bed temperatures between 640 and 660 °C. A sorbent-to-catalyst mass ratio (Z) of 3.0 was selected, defined as “mass of active CaO to reduced catalyst particle”, where the catalyst particle is a 15.9–20 wt % Ni Johnson Matthey HiFUEL R110 commercial catalyst described elsewhere and referred to as a 18.0 wt % Ni/Al₂O₃ material in this work. A MHSVₜₐₜ of 2.5 h⁻¹ (≥0.75 h⁻¹) was selected for the SER step based on previous testing of a combined 22/53/25 wt % CaO/CuO/Ca₁₂Al₁₄O₃₃ material.

Oxidation conditions were fixed at 0.8 MPa pressure, a 700 °C temperature set point, and 7.0 vol % O₂ representing dilute air. Several reactors are not operated in parallel in this work. Heat exchange and carbonation after oxidation is thus not possible. Copper oxidation causes an elevation in temperature, and in combination with a CO₂ partial pressure close to zero, calcination will occur. To counter this effect, 37.0 vol % CO₂ was sent in with N₂ and O₂. The slight increment in O₂ volume fraction from 2.5–5.0 vol % to 7.0 vol % was merely a practical consideration in order to keep the flow for each step fairly similar and at the same time allow for oxidation in a reasonable time frame. It will be shown in section 3.2 that this is an appropriate choice.

The calcination step was performed at 0.1 MPa with an 800 °C set point temperature and a reducing gas composition of 27.0 vol % CH₄ and 66 vol % H₂ (balance N₂). With the employed gas composition, 62–81% of the energy required for CaCO₃ calcination is expected from CuO reduction alone, depending on the active weight fraction of CaO. For reference, this value would be 89.2% with a CuO/CaO = 2.8 [wt/wt] and a gas composition of 27.0 vol % CH₄, 54.0 vol % H₂, and 12.0 vol % CO feed composition, i.e., reported optimal conditions for upscaled operation. Although full sorbent regeneration is not expected, the incorporated cooling procedure and precalcination (800–850 °C, 0.1 MPa) provide full calcination/ reduction of the material prior to subsequent Ca–Cu Looping cycling. Future work must be dedicated to fine-tuning of inlet gas composition, flow rate, bed initial temperature, and material composition in order to optimize calcination efficiency, as this is outside the scope of the presented work.

### 3. RESULTS AND DISCUSSION

#### 3.1. Material Characterization before Reactor Testing

The X-ray diffraction pattern of prepared agglomerates prior to reactor testing is presented in Figure 1. All diffraction peaks have been accounted for and identified as Ca₁₂Al₁₄O₃₃ (□), CuO (○), Ca₂CuO₃ (●), and CaCu₂O₃ (■). The presence of mixed calcium–copper phases was expected based on observations.
made previously for combined material powders prepared using Cu(OH)$_2$. 3.0 g of laboratory scale powders was almost exclusively composed of mayenite and mixed phases (e.g., 48.3 wt % CaCu$_2$O$_4$, 15.6 wt % Ca$_2$CuO$_4$, and 0.8 wt % CuO at 20/40/40 wt % CaO/CuO/Ca$_2$Al$_2$O$_3$), while it seems to be a more pronounced contribution from CuO to the agglomerate spectrum. This can be an indication of a less ideal mixing during upscaling, as mixed phases are likely related to intimate contact between Ca and Cu species during hydrothermal synthesis prior to calcination in air (1000 °C). Characterization data for the as-synthesized upscaled powder and 0.5–0.8 mm diameter agglomerates are summarized in Table 2. Transient TGA behavior during 40 Ca–Cu Looping relevant cycles is presented graphically in Figure 2. Particle surface area was determined using N$_2$ adsorption and the theoretical framework of Brunauer–Emmett–Teller (BET). The characterization data in Table 2 show that the agglomerates have high porosity and relatively low surface area. The characterization data reported are all within an expected range of values for combined calcium–copper materials. Satisfactory stability across 40 TGA cycles is observed for both powder and agglomerates. Maximum capacities of 15.3 g CO$_2$/100 g and 8.2 g O$_2$/100 g were registered for the powder, equivalent to a 18.0/37.6/44.4 wt % CaO/CuO/Ca$_2$Al$_2$O$_3$ material with respect to active phases and an active CuO/CaO ratio of 2.1 [wt/wt]. It has been shown in previous work that compositional estimates based on maximum registered TGA capacities and Rietveld refinement are in good agreement for the material in question. The TGA estimate can be taken as an accurate lower estimate of true (active phase + inactive or inaccessible phase) CuO and CaO loading. There is a 26.8 wt % drop in g O$_2$/100 g and 24.2 wt % drop in g CO$_2$/100 g carrying capacity in the agglomerates relative to the powder given the same testing conditions and time duration for carbonation and oxidation in the TGA. Given the similarities in powder and particle phase composition before testing and the similar weight-based reduction in O$_2$ and CO$_2$ capacities both, the difference between powder and agglomerate capacities is attributed to mass transfer limitations. It can be expected that the actual active phase material composition during the reactor test will be between 13.9/28.1/58.0 and 18.0/37.6/44.4 wt % active CaO/CuO/Ca$_2$Al$_2$O$_3$ depending on the extent of mass transfer resistance during the SER and oxidation steps.

In Figure 3(a), the SEM of the agglomerate surface indicates a good dispersion of copper (light gray) and a CaO/Ca$_2$Al$_2$O$_3$ phase (dark gray). An EDX mapping along with a SEM image is provided in Figure 3(b)–(e). A slight tendency toward Cu clustering can be observed in (b), however, the dispersion of elements on the particle level is homogeneous with an abundance of Ca and Al relative to Cu, as expected due to the Ca and Al rich mayenite support structure. A 40 wt % CuO loaded combined material prepared using CuO powder has also been characterized using the same techniques (Supporting Information, Figures S4–S12, Tables S1–S3). The characterization data are comparable. The CuO prepared material has more pronounced CuO clustering and indications of a lower mass transfer resistance in agglomerate TGA performance relative to that of powder. This is consistent with previous observations.

### 3.2. Ca–Cu Looping Tests in a Fixed Bed Reactor

#### 3.2.1. Sorption Enhanced Reforming (SER)

Figure 4 depicts measurements of dry volume percent (vol %) composition in the reactor effluent and thermocouple temperatures as functions of time during the SER step at 0.97–1.0 MPa, S/C = 3.15, MHSV$_{CH_4}$ = 2.5 h$^{-1}$, Z = 3.0, and 640–660 °C initial bed temperatures. A plot of temperature profiles in Celsius can be found in the Supporting Information (Figure S1).

In Figure 4 (left), following the introduction of reactants, the measured vol % of CH$_4$, O$_2$, and H$_2$ go through a 10–15 min transient period (the smooth profile and differences in initial vol % and breakthrough H$_2$ slopes must be seen in relation to a combination of flow dispersion in the condenser, low superficial velocity, and initial transient instabilities in CH$_4$, steam feed) until conditions close to expected SER equilibrium are established in all three cycles (92.7 vol % H$_2$, dry at S/C = 3.15, P = 0.97 MPa at T = 660 °C). The maximum dry vol % H$_2$ registered in the reactor effluent for the three cycles was 91.5, 92.3, and 91.0 vol %, corresponding to 98.7%, 99.6%, and 98.2% of the calculated SER equilibrium values. Thus, ≥98.2% [vol/ vol] of the calculated SER H$_2$ equilibrium value was obtained during testing for all three cycles.

After 10 min at a plateau close to SER equilibrium conditions, the active calcium oxide was carbonated, and a well-defined breakthrough occurred during a 5 min window. The breakthrough is sharp and does not show any significant signs characteristic to that of diffusion regime carbonation. The breakthrough was followed by establishment of SMR equilibrium (63.8 vol % H$_2$ dry at S/C = 3.2, P = 0.985 MPa, and T = 640 °C). A carbon balance over the SER step results in calculated active CaO loadings (CaO/CuO/Ca$_2$Al$_2$O$_3$ basis) of 17.2 wt % (14.6 g CO$_2$/100 g) for the first, 17.7 wt % (15.0 g CO$_2$/100 g) for the second, and 17.5 wt % (causal topic not specified) for the third.
wt % (14.8 g CO₂/100 g) for the third cycle. This corresponds to 95.4%, 98.0%, and 96.7% carbonation of the estimated active CO₂ carrying capacity of the TGA tested powder. Based on these values it seems evident that the mass transfer limitations observed in the TGA (Figure 2) for the agglomerates relative to powder are not present at higher pressure using the stated operating conditions. Previous works have reported lower sorption capacity in packed beds as compared to TGA under atmospheric pressure, ascribable to a convective transport through the bed and toward the reactor exit which makes complete CaO conversion less favorable. In this work, the pressurized condition resulted in 1) high contact time, 2) improved driving force for CO₂ transport through the boundary layer and into the particle—resulting in an increased transfer rate, and 3) as an effect of Le Châtelier’s principle, a shift in the equilibrium toward CO₂ capture—the side of the reaction with lesser gaseous moles—to counterbalance the pressure increase. These factors contribute in making the as-prepared powder CO₂ capture estimate from...
Figure 4. Dry volume percentage measurements (left) and thermocouple (TC) temperature difference $\Delta T$ [°C] (right) as functions of time during the Ca–Cu Looping SER step for the described combined calcium–copper material (0.97–1.0 MPa, 640–660 °C initial temperature, $S/C = 3.15$, $Z = 3.0$, MHSV$_{CH_4} = 2.5$ h$^{-1}$). Solid lines (left) illustrate SER and SMR equilibrium (dry) vol % $H_2$ at the given conditions.
equilibrium composition postbreakthrough, the reduction in peak temperature, the retained CO₂ capture capacity for Cycle 3, and the slightly lowered dry vol % H₂ maximum in Cycle 3 in spite of a higher CO₂ capture capacity than that of Cycle 1.

Overall, the presented material performance is comparable to the performance of segregated materials reported by Diez-Martín et al. for Cu Looping cycling. The active CaO content is around 12.4 g for both combined and segregated materials tests. There is a difference in peak temperature which is lower in this work (690 °C against 720 °C). This is explained by the Z < 3.0 ratio utilized in Diez-Martín et al., the actual Z = 3.5 in this work with close to full powder CO₂ capacity being obtained, as well as differences in total flow rates. A decline in observed CO₂ capture capacity is reported in Diez-Martín et al., an expected loss of capacity due to the established 20.0 g CO₂/100 g residual sorbent capacity. It is of note that the combined material has a stable carrying capacity of 14.6–15.0 g CO₂/100 g from the first to the third cycle, in contrast to the declining capacity of the segregated sorbent. Based on the presented data, it seems the CO₂ sorption capacity of the combined materials performs similar to that of segregated sorbent particles under the specified conditions.

Lastly, it can be noted that, though investigations into governing mechanisms for mass transport (be it convective, intra- or interparticle transport) are out of the scope of this experimental validation work, effectiveness factors ranging from 0.3 to 0.8 (depending on reactant and reaction stage) have been implemented in pseudohomogeneous models able to accurately describe the segregated material process in the same experimental rig. These are indications that intraparticle diffusion might play a role for the process depending on the selection of processing conditions. This must be further explored in future work, and if intraparticle diffusion plays a significant role, the intraparticle mass transport properties can be improved by, e.g., optimizing the agglomeration procedure.

3.2.2. Oxidation. Figure 5 depicts measurements of dry volume percent (vol %) composition in the reactor effluent and thermocouple temperatures as functions of time during the Cu oxidation step. The oxidation was performed at 0.8 MPa with initial bed temperatures between 700–720 °C and a 7.0 vol % O₂ gas stream, representing diluted air, 37.0 vol % CO₂, and balance N₂. A plot of temperature profiles in Celsius can be found in the Supporting Information (Figure S2).

During copper oxidation, O₂ (7.0 vol %), N₂ (56.0 vol %), and CO₂ (37.0 vol %) were fed to the reactor. The expected dry flow with full O₂ conversion is 39.75 vol % CO₂. This value is represented by the dotted line in Figure 5 (left). Initial signs of material calcination are indicated by an overshoot (5–15 min) of the expected CO₂ vol % value followed by a period of what is interpreted as slow carbonation, indicated by an equal area undershoot (15–40 min). However, the scale of the plotted data should be noted as the overseshot is slight with a 0.44 vol % maximum deviation (Cycle 2), and it can for all practical purposes be considered inconsequential.

A breakthrough of O₂ can indirectly be observed by a drop in CO₂ concentration after 62.5 min on stream for all cycles. By assuming a fully converted 3.6 NL/h flow of O₂ over 62.5 min, a theoretical bed mass of 25.8 g of CuO, or 36.9 wt % CuO, is obtained. This is in good agreement with the 37.6 wt % CuO estimate from powder TGA tests (Table 2). This observation is interesting as it indicates that the oxygen transport properties of the combined material is comparable to that of segregates particles despite being oxidized in the presence of CaCO₃ within the same particle.

Based on the thermocouple readings in Figure 5 (right), the material oxidation step is reproducible and indicates full oxidation. Like the SER step, the reaction front can be followed by observing the different temperature maxima in time for TC1–TCS. It is of note that the increase in temperature is rather high (ΔT = 65 °C, 771 °C) even with a low flow rate.

The excellent temperature reproducibility of oxidation is an argument for slight catalyst migration rather than combined material deactivation (section 3.2.1). The catalyst effect on oxidation is negligible (1.1 wt % NiO), and thus oxidation is not strongly affected by the presence of catalyst. Previous experience with combined material powders has shown that Cu functionality is more susceptible to loss of capacity and thus deactivation than the sorbent function. If the copper functionality is retained, it is thus likely that the sorbent function is also retained.

A direct comparison between observed combined material oxygen function versus the segregated material oxygen function
3.2.3. Calcination. Figure 6 depicts measurements of dry volume percent (vol %) composition in the reactor effluent and thermocouple temperatures as functions of time during the calcination step. The calcination was performed at 0.1 MPa with initial bed temperatures between 800 and 825 °C. Prior to sending reducing gases, the reactor set point was changed to 700 °C (effectively stopping reactor heating) in order to minimize effects that could interfere with the calcination temperature profiles. A plot of temperature profiles in Celsius can be found in the Supporting Information (Figure S3).

There is an abrupt change in gas composition once the reducing gas is fed, where close to 100 vol % CO2 evolves for 3 min. CH4 slip is detected after 3 min of reduction, possibly due to differences in CuO reduction kinetics with CH4 and H2. After 7 min, a slow CH4 breakthrough is observed along with sharp, simultaneous breakthrough curves of H2 and CO accompanied by a significant drop in CO2 concentration. The appearance of CO is interesting as only CH4 and H2 are fed through the reactor inlet. CO has been documented in several other works involving calcination.44,45 The CO concentration has been attributed to SMR/WGS activity and/or CH4 decomposition. It should be mentioned that CO is a potential product of CH4 oxidation as well. However, the simplest explanation can be WGS/SMR activity. Initially there are CH4 and H2 in the reactor. As CaCO3 calcines and H2/CH4 oxidize, there will be significant amounts of CO2, H2O, and H2. The only CO source is CH4 oxidation, which is evidently relatively slow, as indicated by the observed CH4 slip. These are conditions for shift toward CO and both elemental Cu and Ni are present in the reactor during calcination (catalytic activity).

The simultaneous breakthrough of H2 and CO is a result of CuO reduction as H2 and CO break through once all CuO is reduced. SMR/WGS is in addition able to explain the drop in CO concentration with time: the CO2 concentration decreases after ended calcination, and there are no sources of H2O or CO2 when there is no more CuO for CH4/H2 oxidation, causing fed CH4/H2 to reach set point values. This effect and the details of CO evolution from the calcination step are fascinating and could be the subjects of a dedicated modeling study.

A carbon balance on the calcination step results in oxidation step duration (60–70 min) and the peak temperature (770 °C) comparable, and the general behavior of the combined material is similar to that of segregated particles.

3.3. Characterization of Materials after Reactor Testing. A diffraction pattern of agglomerates after reactor testing is provided in Figure 7. As expected, the phases identified are CuO, CaO, and Ca12Al14O33. Mixed calcium–copper CaCu2O4 and Ca4Cu3O10 phases observed before cycling segregate into separate CaO and CuO during testing. There is limited information on mixed calcium–copper phases in the literature, but there is evidence suggesting that they are removed by reduction52 and are retained when no reducing steps are implemented.53 In the performed Ca–Cu Looping tests, mixed phases seem to disappear after the prereduction and do not form again during testing in reducing conditions. There are no traces of the Ni/Al2O3 catalyst. Dust and residue
of catalyst material were meticulously removed using a magnet after reactor testing. It is therefore not expected that contamination will obscure the reported characterization results, and it is an indication that potential interaction between the combined material and the catalyst is limited.

Characterization data after reactor testing are summarized in Table 3. Direct comparisons between data presented in Table 2 and Table 3 should be done with caution as the phases are not identical. The particle bulk density is 1.92 after testing and 1.70 prior to reactor testing. The BET area is slightly increased (2.2 to 3.3 m$^2$ g$^{-1}$) after the reactor tests, the average pore diameter has decreased (381.4 to 152.7 nm), and the porosity has decreased (53.6 to 47.5%). While all the changes are all relatively small, they indicate that the agglomerates after testing with the CuO, CaO, and Ca$_{12}$Al$_{14}$O$_{33}$ phases are slightly denser, with a shift toward lower porosity and smaller average pore size resulting in a net increase in BET surface area. Sintering is in general related to a decrease in surface area. An increase in BET area before and after testing shows that there are no clear signs of sintering.

SEM/EDX results after reactor testing are shown in Figure 8(a)−(e). The agglomerate surface SEM image in Figure 8(a) is comparable to that of Figure 3(a), yet there are visible changes at the particle surface. The copper appears more spherical after testing, it does not seem to be equally well dispersed, and there are indications of cluster formation (center left). This is expected from laboratory testing of powders. The elemental dispersion on a particle level is still homogeneous as can be seen from the cross-sectional EDX mappings in Figure 8(b)−(e). No large copper formations are detected, and the characteristic copper migration to the particle surface previously observed for deactivating combined materials is not evident.

Characterization of a 40 wt % CuO loaded combined material after testing is provided in the Supporting Information (Figures S4−S9, Tables S1 and S2). The same trends are observed for this material: no mixed calcium−copper phases are identified (CaO, CuO, and Ca$_{12}$Al$_{14}$O$_{33}$ only), there is a very slight decrease in porosity and increase in surface area, and there are no pronounced changes in phase dispersion before and after testing.

### 4. CONCLUSIONS

A mayenite based combined calcium−copper material prepared using Cu(OH)$_2$ as copper(II) oxide precursor has been validated in three full Ca−Cu Looping cycles in a fixed bed reactor. During SER, the combined material was able to capture 14.6−15.0 g CO$_2$/100 g, reaching peak hydrogen effluent compositions close to those predicted from equilibrium calculations for all cycles (≥98.2% [vol/vol]). The CO$_2$ capture capacity is in good agreement with the active CaO.
content (≥95.4% [wt/wt]) expected from 0.1 MPa TGA tests of combined material powder. The mass transfer resistance observed for the agglomerates in 0.1 TGA tests relative to powder was not observed under the utilized SER conditions—an indication that both the kinetic and diffusion regimes of CaO carbonation were available for reaction. The sorbent carbon capture capacity was stable from the first cycle. This is an advantage with respect to tailoring the combined material CuO/CaO ratio in future work.

949 The Cu oxidation was complete (36.9 wt % CuO) and in close agreement with 0.1 MPa TGA powder estimates (37.6 wt % CuO). The oxidation of Cu does not seem to be affected by the presence of CaCO3 under the relevant conditions.

950 Calcination was predictable with a 51−64% calcination efficiency for Cycles 1−3, consistent with the CO2 capture capacity during SER (62% calcination efficiency expected at full carbonation). CO was observed during calcination. This has primarily been attributed to SMR/WGS activity and shift toward CO. Both the reduction and oxidation steps show high degrees of reproducibility throughout the 3 cycles.

951 Mixed CaCu2O4 and Ca2CuO3 phases are observed for agglomerates before reactor testing. These segregated into CaO, CuO, and Ca2Al14O33 during testing. There are minor structural changes in the material before and after testing where the porosity is lowered (53.6 to 47.5%), the surface area is increased (2.2 to 3.3 m² g⁻¹), and the average pore diameter is reduced (381.4 to 152.7 nm). There are some signs of Cu migration, as expected from previous work on combined material powders. However, there is still good phase dispersion at the particle level after testing, and the number of Ca−Cu Looping cycles employed is not sufficient for establishing nor rejecting long-term stability of CO2 and O2 carrying capacities.

952 Taken together, the validation of the presented combined material has shown good agreement between laboratory characterization (e.g., TGA, XRD) and actual fixed bed reactor behavior under Ca−Cu Looping conditions. The combined material Cu and CaO functions seem to behave like those of segregated particles. These results are promising for the future development of combined materials. The material concept does indeed appear feasible and can be a viable alternative to a segregated materials approach to Ca−Cu Looping in terms of process intensification given the current state of materials development and larger scale demonstrations.

953 Ca−Cu Looping has been experimentally validated in a fixed bed containing about 42 wt % of inert in the combined calcium−copper material. To further enhance the calcination efficiency, the amount of CaO has to be decreased from 20 wt % to 14 wt % (active CuO/CaO = 2.8 [wt/wt]). This will result in an increase of the inert fraction in the combined material to 45.6 wt %—given a maintained CuO loading of 40 wt %. For the sake of comparison, in order to achieve the same amount of inert bed fraction per 100.0 g for the segregated materials concept, assuming an oxygen carrier with 60−70 wt % active CuO content, an active CaO content in the range 42.9−33.4 wt % (33.6−26.2 g CO2/100 g stable carrying capacity) is required from the segregated sorbent. When also considering the plausible incremental improvements in CuO loading that can be made in the [40, 50] wt % interval, and that incremental improvement in CuO and CaO loading will greatly reduce the inert fraction in the combined material, the experimental validation carried out in this work shows that combined materials are competitive and the concept is attractive for further studies.

Establishment of long-term transient stability of CO2/O2 carrying capacities in a fixed bed reactor through multiple Ca−Cu Looping cycles as well as the CuO/CaO ratio and process optimization are challenges that must be addressed for the combined material in future work. Knowledge gained from the presented validation work combined with reactor modeling can be used for achieving these goals.

ASSOCIATED CONTENT

972 Supporting Information

973 The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b02372.

977 Reactor temperature measurements in Celsius for Cu(OH)2 material, characterization results (X-ray diffraction, N2 adsorption, He pycnometry, Hg intrusion, SEM, EDX), and Ca−Cu Looping reactor results for combined material prepared using CuO powder (PDF)

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Notes

989 The authors declare no competing financial interest.

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