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Performance of sorption-enhanced water-gas shift as a pre-combustion CO_2 capture technology

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Abstract

The sorption-enhanced water-gas shift (SEWGS) process is a promising technology for pre-combustion decarbonisation. It is well suited for decarbonising syngas produced from natural-gas and coal based fuels in combined-cycle power production schemes. Higher capture rates could be obtained by SEWGS at lower efficiency penalties and at lower costs than by absorption. In the SEWGS process, multiple reactor vessels are packed with mixtures of CO_2 sorption pellets and water-gas shift catalyst pellets. The technology is developed using potassium promoted hydrotalcite-based materials as the CO_2 sorbent.

In a first series of experiments, the performance of this material is investigated under typical SEWGS process conditions. The sorbent was loaded in 2 m and 6 m tall fixed-bed reactor vessels. Breakthrough capacities of 1.3 – 1.4 mmol/g are reported. After breakthrough the sorbent continues to take up CO_2, albeit at a much lower rate. Total sorption capacities exceeding 8 mmol/g are observed. This capacity is attributed to the formation of $MgCO_3$ in the bulk of the sorbent material and requires moderate to high partial pressures of CO_2 and steam. The stability of the sorbent material during cyclic operation was demonstrated for more than 4,000 adsorption and desorption cycles. A stable and low slip of CO_2 was established, corresponding to a carbon capture ratio of well above 90%.

After investigation of the relevant sorbent characteristics, the reactor was loaded with sorbent and catalyst material in order to provide a proof-of-principle of the SEWGS technology and establish the performance and stability of sorbent and catalyst material. When the reactor was fed with a gas mixture that simulated a syngas typically produced by auto-thermal reforming of natural gas, it was demonstrated that carbon monoxide conversion can be enhanced from 55% in absence of a sorbent to 100% in the presence of a sorbent. Neither the change of gas composition nor the mixing of sorbent with catalyst did significantly impact CO_2 breakthrough capacity. In a cyclic duration test, the carbon capture rate and carbon monoxide conversion were confirmed to be above 98% without excessive steam demand, and reasonably stable for at least 500 cycles. The experimental data will be used for modelling, cycle optimization, and scale-up to a pilot unit.

Keywords: sorption-enhanced, hydrotalcites, water-gas shift reaction, pressure swing adsorption, pre-combustion capture, decarbonization, power plants, hydrogen production

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1. Introduction

The sorption-enhanced water-gas shift (SEWGS) process is a promising technology for pre-combustion decarbonisation. It is well suited for decarbonising gas turbine fuels, for instance in natural-gas based and coal based power production [1 – 4]. High capture rates can be obtained by SEWGS at lower efficiency penalties and at lower costs than by absorption [5]. The technology can also be adapted for application in industrial hydrogen plants.

The heart of the process is a reactor vessel packed with a mixture of CO_2 sorbent and water-gas shift catalyst pellets. CO_2 is removed from a synthesis gas by adsorption and CO is simultaneously converted to CO_2 by the water-gas shift reaction. Conversion of CO and forward shift reaction rate are enhanced by sorption of CO_2 according to Le Chatelier's principle. The sorbent is periodically regenerated by purging with steam at low pressure. As such, the separation process is operated in a cyclic mode and bears similarities to a Pressure Swing Adsorption (PSA) process, although here the operation temperature remains high (c. 400 °C) throughout the cycle. Two product streams are obtained: a hot, pressurised H_2-rich fuel gas, and a mixture of relatively pure CO_2 with steam. The SEWGS process has the advantage of capturing CO_2 at elevated temperature and pressure, without the need for large cooling and reheating equipment. Moreover, essentially all CO is removed from the syngas as well, increasing carbon capture.

Potassium promoted hydrotalcite-based materials are known to have excellent properties for capturing CO_2 at 400 °C in the presence of steam [1 – 4, 6 – 15]. These sorbents appear to be particularly well suited for application in the SEWGS process. The main interaction of CO_2 with such materials at 400 °C is due to an aluminium-potassium-carbonate species, subject to modification by the presence of magnesium [13]. In the European FP6 project CACHET the SEWGS technology is developed and demonstrated using potassium-promoted, hydrotalcite-based materials under realistic conditions.

2. Experimental setup

For the development of the SEWGS process two dedicated test rigs were designed and constructed. The first comprised a 2 m tall reactor vessel, and the second six reactor vessels, each 6 m tall. Experiments were performed in both test rigs at typical feed rates of 10 – 30 standard litres per minute (slpm). The reactor walls were kept at 400 °C by electric heating and insulation. Figure 1 shows a flow scheme of the single vessel test rig. The test rig with six vessels was built to demonstrate the full cyclic process yielding continuous carbon capture and was commissioned in December 2007 [16]. The flow scheme is similar to the single vessel rig, but it contains six parallel vessels instead of one, as Figure 2 shows.

For initial breakthrough experiments, the single vessel was packed with calcined pellets of K_2CO_3 promoted hydrotalcite-based material. After these experiments, this vessel was packed with a mixture of these sorbent pellets and high-temperature shift catalyst pellets. The reactor vessels in the multi vessel rig were packed in a similar way.

The stability of the sorbent was investigated in the single vessel rig under cyclic conditions. A cycle consists of several steps in a fixed order and with a fixed duration. Various industrial cycles have been suggested for CO_2 recovery [2]. A cycle with a countercurrent steam rinse was used. The consecutive steps are: (1) feed, during which adsorption and shift reaction occur; (2) countercurrent rinse with high-pressure steam, for pushing out the gas that is present in the voids; (3) countercurrent depressurization; (4) countercurrent purge with low-pressure steam, for regeneration of the sorbent; and (5) repressurisation with N_2 and steam.

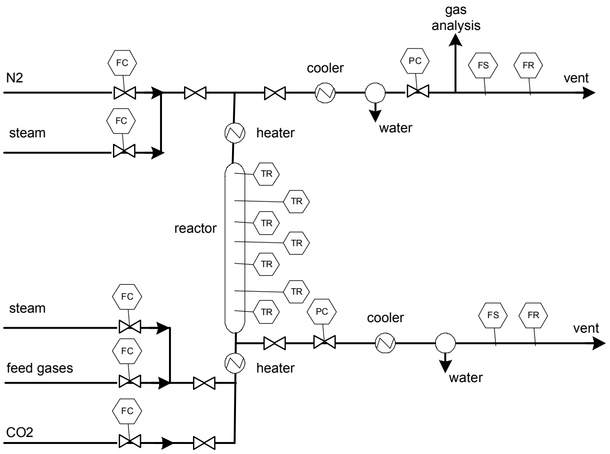

Figure 1 Flow scheme of the single vessel test rig. Pure gases and superheated steam are mixed in desired quantities in order to obtain the desired feed gas composition and flow rate. Feed gases are heated to 400 °C in electric heaters. Product gases are cooled down to 5 °C and condensate is removed in knock-out drums. Gas quantities of dry product gases are recorded by volumetric dry gas meters. Additionally, flow rates of product gases are measured by thermal mass flow sensors.

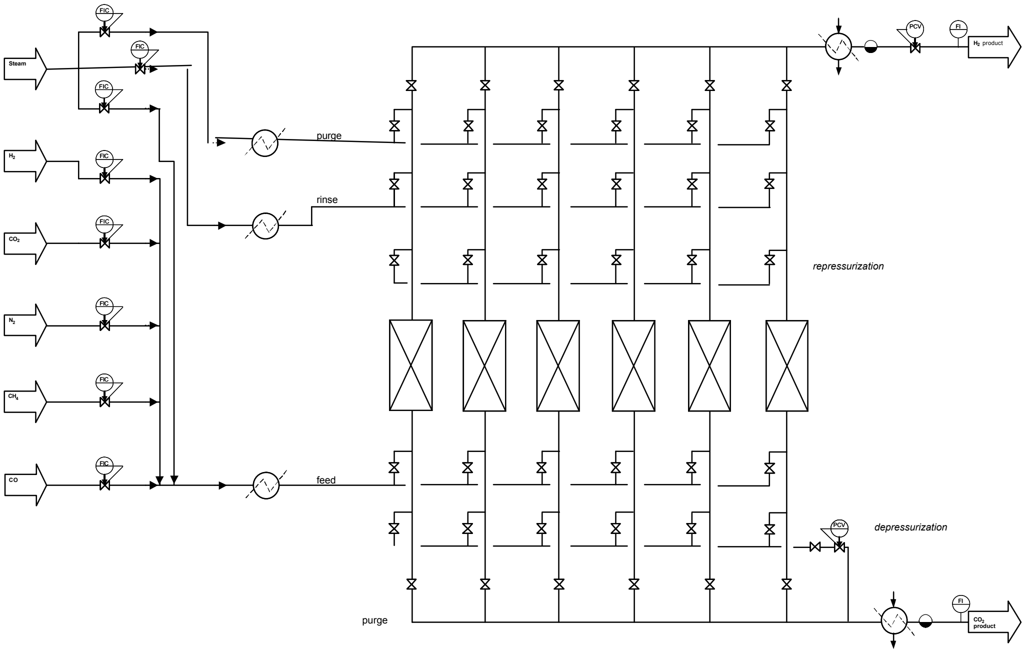

Figure 2 Flow scheme for the multi vessel test rig with six reactor vessels of 6 m tall. In this rig, the cyclic process can be demonstrated at realistic temperatures, pressures, space velocities, and gas compositions.

3. Results and discussion

3.1. Breakthrough test

Breakthrough experiments were conducted under realistic conditions to determine the breakthrough capacity and sharpness of the adsorption front. CO_2 breakthrough tests were completed with the 2 m vessel packed with sorbent pellets only. CO_2 and CO breakthrough tests, under sorption-enhanced reaction conditions, were completed with 6 m vessels packed with a mixture of sorbent pellets and high-temperature shift catalyst pellets.

Figure 3 shows the CO_2 level of the effluent $y_{CO2,out}$ relative to the CO_2 level of the feed $y_{CO2,in}$ as a function of time *t* when feeding a mixture of CO_2 and N_2 to the reactor at 400 °C and a total pressure of 28 bar. Breakthrough of CO_2 starts 16 minutes after starting the feed. The breakthrough curve is very sharp, which demonstrates the adequate kinetics of this material for CO_2 adsorption. The material is calculated to have a breakthrough capacity of 1.4 mmol/g. After breakthrough, the material still takes up CO_2, although at a lower rate than before breakthrough. Breakthrough curves with similar shapes have previously been reported for potassium promoted hydrotalcites [2, 8, 11, 12].

3.2. Extended breakthrough tests

In order to investigate the uptake of CO_2 after breakthrough, extended breakthrough tests were performed. At the same time, the effect of steam on the CO_2 uptake was investigated, as several authors report that steam improves CO_2 adsorption capacity under most circumstances [3, 4, 6, 15]. Nonetheless, only rarely have experiments been reported in which these materials have been exposed to high-pressure steam. Allam et al. [2] reported a total capacity of 8.3 mmol/g CO_2 after exposure of promoted hydrotalcite to industrial-like conditions for a week. Anand et al. [17] investigated the stability of promoted hydrotalcite after thirty days of exposure to 10 bar steam and 0.3 bar CO_2 conditions. The adsorption capacity of the exposed material under 1 bar CO_2 remained essentially unchanged. In order to investigate the effect of steam on the uptake of CO_2, two extended breakthrough experiments were conducted, one with a feed composed of 40% steam, 20% CO_2 and balance N_2 , and the other with 60% steam, 20% CO_2 and balance N_2.

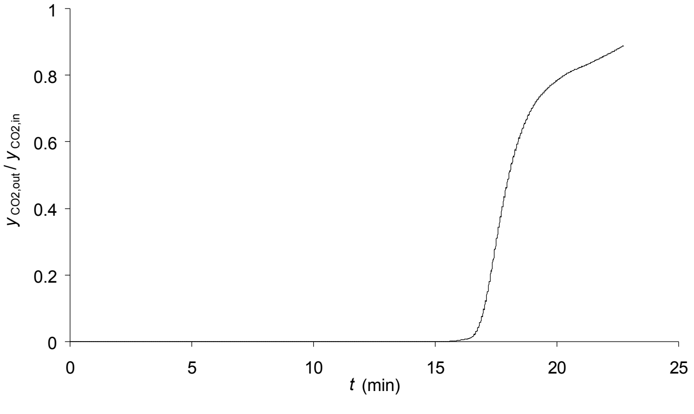

Figure 3 Breakthrough curve for an experiment conducted at a temperature of 400 °C and a pressure of 28 bar. Feed was 2 slpm CO_2 and 7 slpm N_2. The reactor contained previously unused material. The beginning of the breakthrough profile, starting after 16 minutes, is sharp, but then levels slowly.

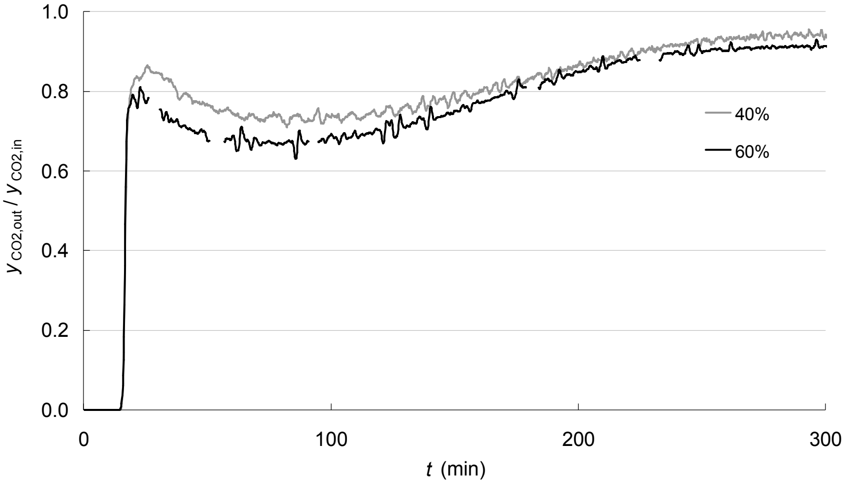

Figure 4 Slow uptake of CO_2 continues for hours after breakthrough. Inlet composition 20% CO_2, 40/60% H_2O, balance N_2, total flow 11 slpm, total pressure 28 bar, temperature 400 °C.

In Figure 4 the normalised CO_2 fraction of the effluent versus time is shown, reflecting the uptake of CO_2 before and for several hours after breakthrough under conditions of high-pressure steam. Before CO_2 breakthrough, the sorbent material adsorbs all CO_2 fed, except for the CO_2 in the void gas, until the adsorption front has reached the end of the bed. Breakthrough times are essentially equal for both steam levels. After breakthrough, the CO_2 level increases sharply as expected, then drops slightly, before starting to increase again. The sorbent continues to take up part of the CO_2 fed for several hours. After five hours the CO_2 capacity reaches 8 mmol/g and is still increasing. Apparently, in addition to the fast adsorption there is a much slower process of CO_2 uptake with a considerably higher capacity. This slower process is somewhat faster for the higher steam partial pressure case. This process is presumably associated with uptake of CO_2 in the bulk of the active phase of the sorbent, and could be the transformation of Mg into $MgCO_3$. Interestingly, if all Mg in this sorbent is transformed into $MgCO_3$, and only Mg were to take part in the sorption process, a capacity of 9.5 mmol/g would be expected. Other authors may not have observed these very high capacities due to differences in material composition and preparation method, shorter exposure times, or much lower operating pressures.

3.3. Sorption-enhanced breakthrough tests

The vessels of the multi-vessel rig were consecutively fed with a gas mixture that simulated a syngas typically produced by auto-thermal reforming of natural gas, followed by a high-temperature shift reactor. The measured effluent composition as a function of time for one of the reactor vessels is shown in Figure 6. In the first two minutes all N_2 is purged from the reactor voids and attached piping. Then a nearly pure H_2 stream breaks through. All CO is converted to CO_2 and all CO_2 is taken up by the sorbent. This is evidence that sorption can enhance the shift reaction under realistic SEWGS conditions. Six minutes after starting the feed CO and CO_2 start to break through simultaneously. A breakthrough capacity of 1.3 mmol/g was calculated, matching previously established values. After breakthrough of CO_2 the gas composition is calculated to be close to thermodynamic equilibrium at the reactor temperature of 400 °C, indicating sufficient catalyst activity in the bed. The observed CO conversion of 55% approximates the calculated conversion in absence of sorption.

3.4. Stability tests

The stability of the sorbent under extended cycling conditions was demonstrated using the single vessel rig. Before the first cyclic experiment, the reactor was loaded with sorbent material only. During the adsorption step, the reactor was fed with 20% CO_2, 16% H_2O, balance N_2. The average CO_2 level in the H_2 product stream during the feed step is plotted against cycle number in Figure 6. Over the first 450 cycles, the CO_2 slip slowly rises until a cyclic steady state is obtained. This gradual increase of CO_2 slip may be attributed to the slow formation of $MgCO_3$ and its impact on the fast adsorption process. After 450 cycles, a stable and low slip of CO_2 was demonstrated, corresponding to a carbon capture above 98%. In this experiment, the stability of the sorbent material during cyclic operation was demonstrated for more than 1,400 adsorption and desorption cycles. In additional experiments, the stability was demonstrated for more than 4,000 cycles.

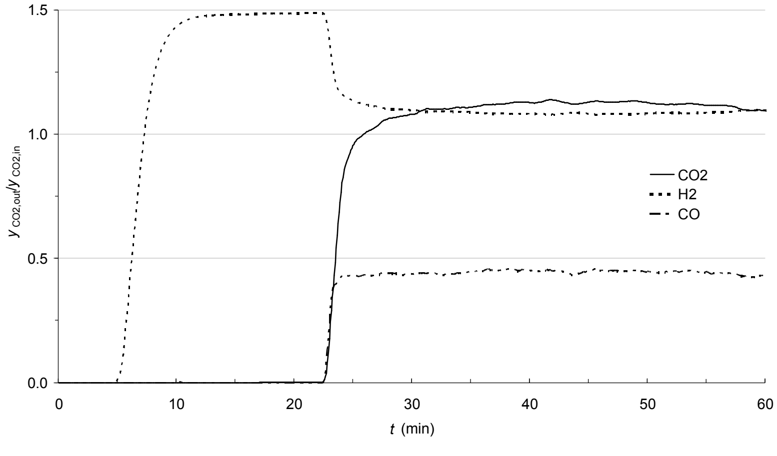

Figure 5 Breakthrough curves for H_2, CO_2, and CO. Before breakthrough, CO conversion is enhanced to 100%. After breakthrough, observed conversion is 55%, which corresponds to thermodynamic equilibrium. Breakthrough capacity is 1.3 mmol/g. Molar fractions y_i are dry basis. Inlet composition 15% CO_2, 9% CO, 52% H_2, 24% H_2O, total flow 21 slpm, total pressure 28 bar, temperature 400 °C.

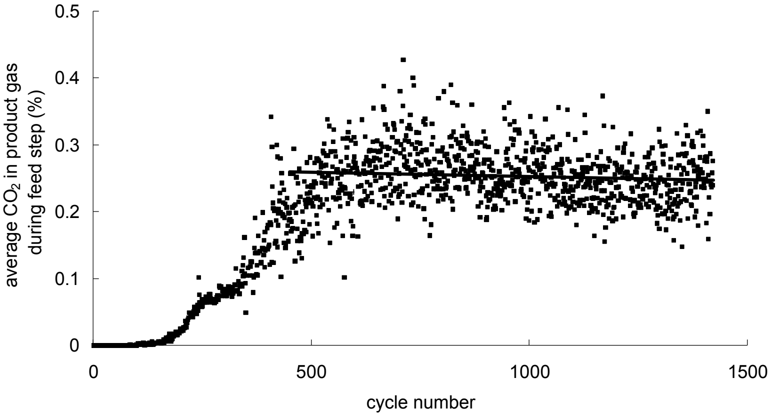

Figure 6 Cycle-averaged CO_2 level of the top product during the feed step over 1,400 cycles, showing cyclic stability after 450 cycles. The line shows the linear trend over cycle nos. 450 through 1,422. Reactor at 400 °C, 28 bar. Feed composition 20% CO_2, 16% H_2O, balance N_2.

The stability of the sorbent and catalyst was demonstrated in the same rig under extended cycling conditions. The 2 m vessel was now packed with a mixture of sorbent pellets and high-temperature shift catalyst pellets. During the adsorption step, the reactor was fed with 30% H_2, 12% CO_2, 1.6% CO, 21% H_2O, balance N_2. The time-averaged CO and CO_2 levels of the H_2 product during the feed step are plotted against cycle number in Figure 7. The level of impurities in the H_2 product stream rises slowly but is still very low for at least 550 cycles. The associated carbon capture level is again above 98%. CO conversion is above 98% as well.

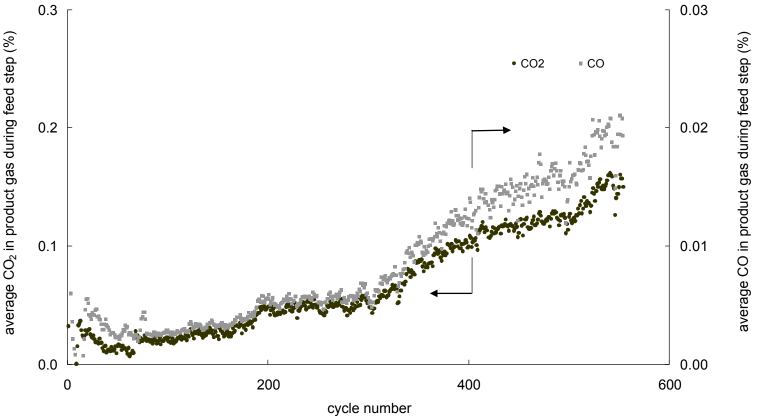

Figure 7 Cycle-averaged CO_2 and CO levels of the H_2 product during the feed step over 550 cycles. Feed at 400 °C, 28 bar, 12% CO_2, 1.6% CO, 30% H_2, 21% H_2O, balance N_2.

4. Conclusions

A potassium-promoted hydrotalcite-based material was shown to reversibly take up CO_2 at temperatures near 400 °C with associated promising breakthrough capacities of 1.3 – 1.4 mmol/g under realistic conditions. Total capacities for this material can exceed 8 mmol/g if feed partial pressures of CO_2 and H_2O are sufficiently high.

However, this high capacity is presumably associated with formation of $MgCO_3$ and the kinetics of this chemisorption is too slow to exploit in a pressure-swing adsorption process such as SEWGS. The stability of the sorbent material was shown for more than 4,000 cycles of adsorption and desorption at the envisaged industrial operating conditions. A proof-of-principle of the SEWGS process was given on the scale of 6 m tall reactors. Stability of the combination of sorbent and catalyst pellets was shown for more than 500 cycles. Experiments are on-going that will generate process data for modelling, cycle optimisation and scale-up to a pilot unit. Sorbent development, reactor development and process improvement are imperative to meet cost targets for commercialization of the SEWGS technology in power plants and hydrogen production plants.

Acknowledgments

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