

Preliminary Assessment of Sorption Capacity on Solid CO₂-Sorbents at Conditions for Sorption-Enhanced Processes

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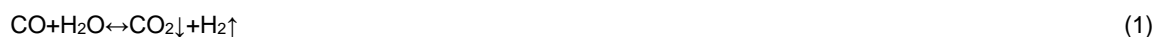
This work aims to assess solid sorbent capacity to operate CO₂ capture under industrial conditions relevant to biogas/bio-syngas upgrading systems to green H₂ and food-grade CO₂ through Sorption-Enhanced Water Gas Shift (SEWGS) technologies. The pursued degree of innovation is the process intensification to remove CO₂ in a more sustainable industrial practice reducing the CO₂ footprint of a potential H₂ production process.

A lab-scale apparatus is appropriately designed and built to operate at relevant industrial scale conditions. The core of the system is a fixed-bed reactor equipped with mass flow meters/controllers and online gas analyzers. CO₂ capture experiments were carried out to investigate the effect of pressure (1.0-1.4 MPa) on different commercial and synthesized solid sorbent materials (hydrotalcite-like compounds). The best sorbent is a commercial hydrotalcite impregnated with 20 wt% of K₂CO₃, with an average sorption capacity of 0.85 mmolCO₂/g_{ad} at 1.4 MPa and 623 K. The explored conditions are compatible with an industrial operation where syngas is available at low-to-moderate pressure.

1. Introduction

The global H₂ market will increase from 70 million tons in 2019 to 120 million tons in 2024 (Atilhan et al., 2021) as an indispensable chemical feedstock and a promising energy carrier (Masoudi Soltani et al., 2021)

Currently, the dominant technology to produce H₂ is steam reforming of fossil natural gas (Masoudi Soltani et al., 2021), a highly energy-intensive industrial process. Sorption-Enhanced processes, such as Sorption-Enhanced Reforming (SER) (Fernández et al., 2016) and Sorption-Enhanced Water-Gas Shift (SEWGS) (Boon et al., 2017) exploit in-situ CO₂ capture to produce high-purity hydrogen by intensified processes. SEWGS is a carbon capture technology combining water-gas shift reaction (WGS) with simultaneous adsorption of CO₂ on a solid sorbent, typically carried out by a pressure swing adsorption (PSA) system at an intermediate temperature of 473-673 K and pressure of 1-4 MPa (Boon et al., 2017). Syngas produced by methane reforming or gasification can be fed to the SEWGS units, passing through a packed bed of unique sorbent materials that selectively removes CO₂. The CO₂ removal shifts the thermodynamic equilibrium of the WGS reaction towards the H₂ production, according to Le Châtelier principle (1):



Wright et al. (2009) showed that SEWGS is a suitable technology for pre-combustion applications when natural gas is the feedstock and investigated the possibility of applying this technology to fuels such as coal integrated gasification combined cycles (IGCC). The industrial realization of SEWGS at intermediate temperature (> 573 K) would allow eliminating one or more of the most expensive steps for syngas purification (gas cooling, 2-steps WGS, use of physical - Selexol®, Rectisol®, Purisol® - or chemical - MEA, DMEA, Benfield, Sulfinol - sorbents for CO₂ capture, syngas reheating, etc.), simplifying the configuration and reducing operating costs of the plant (Intergovernmental Panel on Climate Change, 2011).

Hydrotalcites (HTs) are suitable CO₂ sorbents to bring in sorption-enhancing effects at SEWGS conditions. HTs belong to the anionic and basic clays, also known as mixed-metal double hydroxides or layered double hydroxides. HTs are generally used after thermal treatment, which induces dehydration, dehydroxylation, and loss of the charge-compensating anions resulting in mixed oxides with interesting CO₂-sorbent/catalytic properties, such as high surface area, basic properties, capability to form homogeneous mixtures of oxides with small crystal size (Miyata et al., 1977), and a peculiar memory effect (Miyata, 1980), which makes HT suitable for several repetitive adsorption/desorption cycles.

(Hoffman et al., 2001) reported that HTs behaviour in terms of adsorption improves by impregnation with potassium carbonate (K₂CO₃).

HTs can be synthesized by the Low Supersaturation (LS) co-precipitation method, which brings the formation of precipitates with higher crystallinity (Cavani et al., 1991).

This research group previously developed HTs and verified the success of the applied synthesis method via XRD, BET-BJH, FTIR, and SEM-EDS analyses; their sorption capacity and cyclic stability were evaluated by a purposely designed micro-reactor at the maximum allowed pressure of 0.6 MPa (Gallucci et al., 2015; Zhenissova et al., 2014). Their behaviour in the SEWGS process was validated by the ENEA Trisaia research center (Gallucci et al., 2015).

In this work, three different HT-based CO₂-sorbents were tested in preliminary experiments of CO₂ capture at 623 K and 1.0-1.4 MPa, conditions informed by industrial gasification plants testing SEWGS for the first time ("Swindon Plant | Advanced Biofuel Solutions Ltd," 2023). Experiments were carried out in a newly packed bed plant at a laboratory scale, which allows pressures higher than those previously investigated by this research group. The tested sorbents include: (i) calcined commercial HT as reference material; (ii) commercial HT impregnated with potassium carbonate; (iii) HT based on magnesium and aluminum synthesized via the LS method and impregnated with potassium carbonate. Their sorption capacities were experimentally quantified at SEWGS relevant conditions and so made available for the future design of the industrial scaled-up process and validation of the related models. The compared investigation of sorbents derived from commercial H.T.s and those synthesized by LS aims to evaluate whether an intensive time-spending preparation of sorbents, such as LS, is justified for an industrially scaled-up SEWGS system.

2. Materials and methods

2.1 Materials

Three different types of hydrotalcites were experimentally tested.

1. A commercial hydrotalcite (CAS n. 11097-59-9; Mg/Al=3:1 molar ratio) calcined at 723 K, hydrated with distilled water, and recalcined at 723 K, hereinafter called *HT*
2. A commercial hydrotalcite (CAS n. 11097-59-9 Mg/Al=3:1 molar ratio) calcined at 723 K, impregnated with 20 wt% of K₂CO₃ and recalcined at 723 K, hereinafter called *20KHHT*
3. A hydrotalcite synthesized at laboratory scale by the LS method detailed by (Narayanan et al., 1998), with the molar ratio Mg/Al=2:1, then calcined at 723 K, impregnated with 20 wt% of K₂CO₃ and eventually recalcined at 723 K; the obtained material is hereinafter called *20KHHTLS*.

Please note that K₂CO₃ impregnation was performed on particles resulting from the respective first calcination. The average granulometry of impregnated particles of commercial H.T. was about one order of magnitude lower than that of H.T. synthesized by LS method (10⁻¹ mm vs. 10⁰ mm).

2.2 Methods

The laboratory plant (Figure 1) was designed for Pressure Swing Adsorption (PSA) tests to measure the instantaneous CO₂ concentration in the outlet gas stream as a function of time and quantify the CO₂ uptake on the solid sorbent material. For each test, two main steps (CO₂ adsorption and sorbent regeneration by pressure swing) were carried out and alternatively repeated for five cycles.

A blank test was performed at the same operating condition as the capturing test, where inert solid material (zirconia) of the same volume of the sorbent samples was loaded in the reactor.

A simplified approach derived from the first order with dead time model for gas mixing was applied to evaluate the sorption capacities through the comparison with the blank test (di Felice et al., 2011). This dynamic test identified CO₂ in the whole system hold-up (blank test) and actual CO₂ captured on the hydrotalcites material (capturing test). Sorption capacities were estimated according to Eq(2):

$$q_i = F_{CO_2,in} \frac{\int_0^\infty \frac{c_{CO_2,b}(t)}{c_{CO_2,b}(\infty)} dt - \int_0^\infty \frac{c_{CO_2}(t)}{c_{CO_2}(\infty)} dt}{m} \quad (2)$$

Please refer to the Nomenclature section for the meaning of symbols in Eq(2).

A flowsheet of the PSA lab-scale plant is in Figure 1. The sorbent ($425 < d_p < 1180 \mu\text{m}$) was packed between two layers of inert zirconia in the reactor (ID $\sim 1 \text{ cm}$), heated at $T = 623 \text{ K}$. Gaseous N_2 and CO_2 were fed to the system by mass flow controllers (Bronkhorst, El-Flow series). A pressure regulator (Bronkhorst pressure controller) was installed downstream of the packed bed to control the operating pressure. The whole system was kept at 1.0 or 1.4 MPa, both relevant feed conditions in the real case of the syngas produced by ABSL plant (U.K.) ("Swindon Plant | Advanced Biofuel Solutions Ltd," 2023). The main operating conditions are summarized in Table 1. For each material, two pressure levels were explored, and five cycles of sorption/regeneration steps were repeated. The measured sorption capacity at the i^{th} cycle is named q_i (quantified by Eq(2)) and the average sorption capacity of the five cycles is named q^{av} .

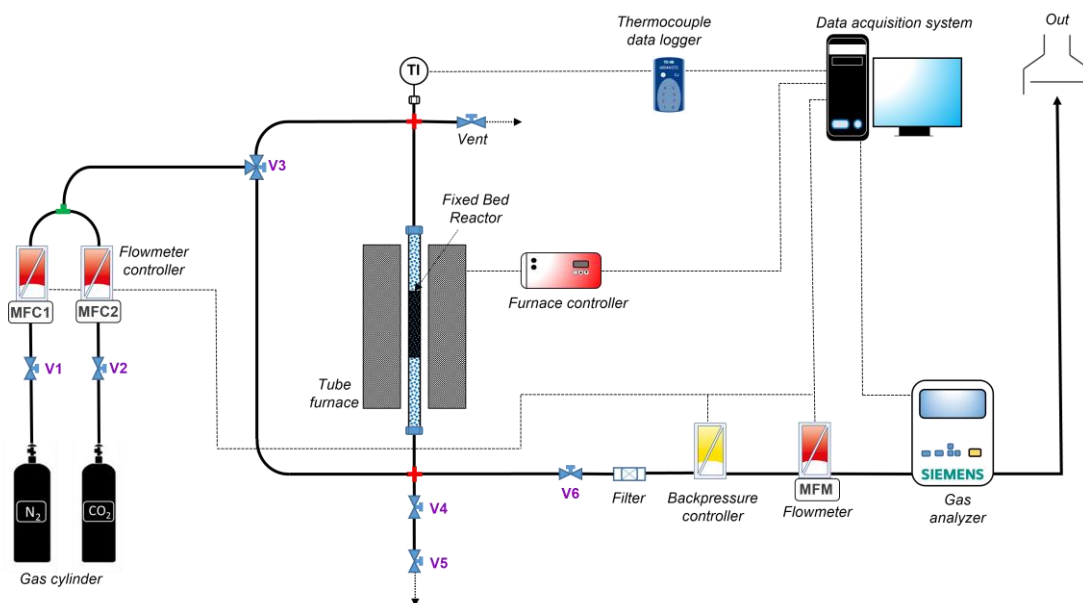


Figure 1: Sketch of lab-scale experimental apparatus.

Table 1: Operating conditions of experimental tests

Reaction temperature [K]	623
Reactor pressure [MPa]	1.0-1.4
CO_2 flowrate [Nml/min]	156.5
N_2 flowrate [Nml/min]	250

3. Results and Discussion

The pressure of 1.0 MPa was exerted consecutively on the same bed sample after the test at 1.4 MPa in order to save sorbent material and the time demand of the experimental campaign. This approach does not affect the evaluations concerning the sorption capacity as verified in the case of *20KHTLS*: a fresh sample directly tested at 1.0 MPa exhibited a q^{av} of $0.22 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$; a sample previously tested at 1.4 MPa and then tested at 1.0 MPa, had q^{av} of $0.26 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$. This result enables us to be confident that the procedure is valid.

The results obtained at 1.4 MPa and 1.0 MPa are reported in Table 2 and Figure 2c: they show the positive influence of the pressure increase.

The first important result was related to the pressure effect. The increase from 1.0 MPa to 1.4 MPa made sorption capacities significantly increase for all investigated samples (Figure 2c, Table 2): having the performance at 1.0 MPa as a reference, q^{av} at 1.4 MPa was higher by $\sim 110\%$, 230% and 170% for *H.T.*, *20KHT* and *20KHTLS*, respectively. These results are a good indication as 1.4 MPa, and 623 K are within typical operating conditions for the SEWGS process (at about 573-773 K and 1.0-4.0 MPa (Boon et al., 2015)).

20KHT was the best sorbent at 1.4 MPa, with $q_1 = 0.86 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$, increasing up to $q_2 = 0.96 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$ in the second cycle, finally stabilized at about $0.8 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$ for the following cycles. These results agree with literature values for hydrotalcites, such as $0.88 \text{ mmol}_{\text{CO}_2}/\text{g}_{\text{ad}}$ (Rodrigues et al., 2017).

The comparison between *20KHT* and *HT* enables to evaluate the influence of K_2CO_3 impregnation on commercial hydrotalcite: q^{av} was increased by about 34% at 1.4 MPa (Figure 2c, Table 2), while the effect of the K_2CO_3 was negligible at 1.0 MPa (Figure 2c, Table 2).

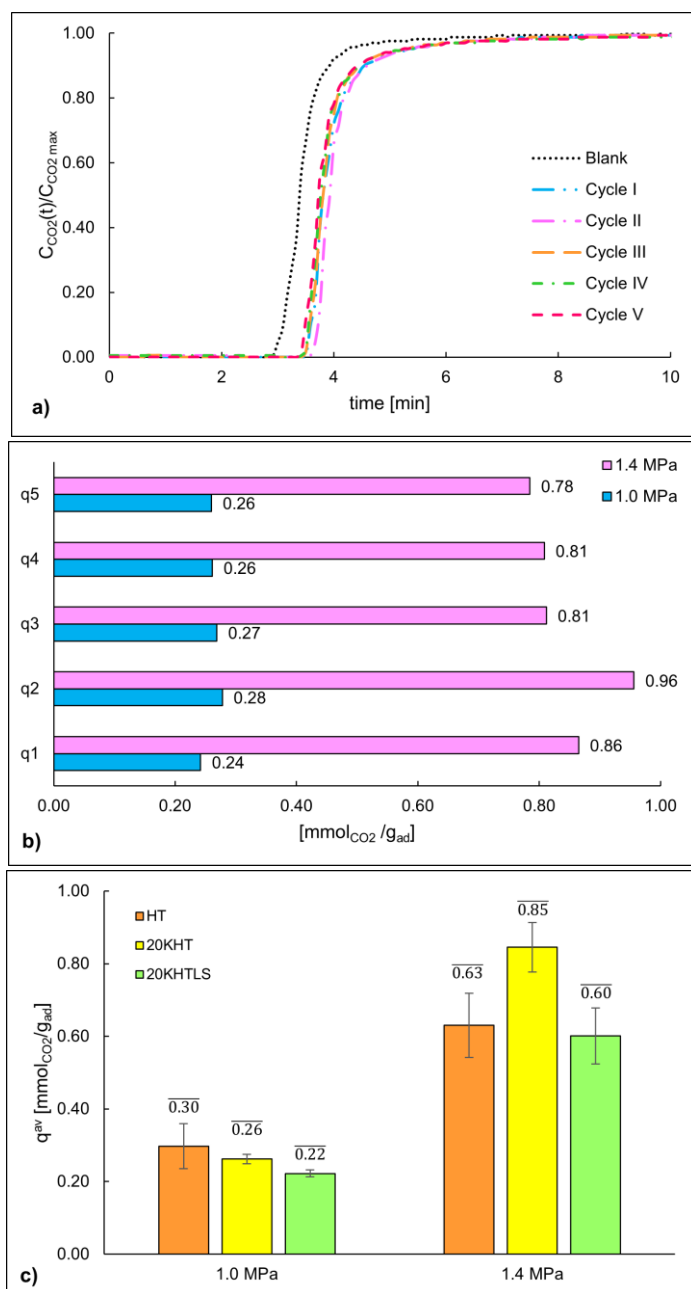


Figure 2: Experimental results of CO_2 capture tests: a) Breakthrough curves with 20KHT at 623 K, 1.4 MPa, 156.5 Nml/min CO_2 ; b) Cyclic capture capacity (q_i) for 20KHT at 1.0 MPa and 1.4 MPa, 623 K; c) Cycles average sorption capacity (q^{av}) for H.T., 20KHT, 20KHTLS at 1.0 MPa and 1.4 MPa, 623 K.

The comparison between 20KHTLS and 20KHT evidenced that the former material had poorer performances at both 1.4 and 1.0 MPa, even though with acceptable values of q_i (Table 2) and q^{av} (Figure 2c); this could be related to the lower Mg/Al molar ratio of 20KHTLS compared to that of 20KHT; the different particle size of hydrotalcites impregnated to obtain 20KHT and 20KHTLS (see Section 2.1) could be an additional factor that contributed to lower the sorption capacity of 20KHTLS. The decreasing q_i trend along with cycles at 1.4 MPa for 20KHTLS (Table 2) was probably due to incomplete regeneration throughout pressure swing cycles or different material textures. At 1.0 MPa, 20KHTLS showed a stable but lower sorbent capacity (Table 2).

In a previous paper of this research group (Zhenissova et al., 2014), *20KHT* was tested under different operating conditions (623 K, total pressure of 0.5 MPa, 20 mol% of CO₂), showing performances comparable to data presented in this work (723 K, total pressure of 1.4 MPa, 38.5 mol% of CO₂), taking into account the different partial pressures of CO₂.

A former sample of *20KHTLS* showed a promising value of $q_1 = 0.32$ mmol_{CO₂}/g_{ad} at a very low partial pressure of CO₂ (723 K, total pressure of 0.1 MPa, 6.3 mol% of CO₂ (K. Gallucci et al., 2015)) when tested in a fluidized bed. In the reactor of the present work, the potential negative effects from the fixed-bed configuration and the consequential higher dimension of sorbent particles were both compensated by the higher CO₂ partial pressure. Even though the nature of the performed tests is preliminary (e.g., tests were carried out with a mixture of CO₂ in N₂, instead of feeding real syngas for SEWGS), some relevant indications emerged for the convenience of hypothetical scale-up of the SEWGS process. The effort related to the applied L.S. synthesis seems not compensated by the CO₂-capture performance of *20KHTLS* (Figure 2c, Table 2): at both 1.0 MPa and 1.4 MPa, q^{av} resulted in the lowest. According to these results, considering a hypothetical amount of hundreds of kilos for commercial SEWGS, the scale-up of LS synthesis method (as performed in this work) may be less convenient and more time-demanding than the provision of commercial hydrotalcites by current commercial networks. On the other hand, the scale-up of the impregnation step with K₂CO₃ appeared worthy of further investigations, because of the important increase of q^{av} that emerged by the comparison of *20KHT* and *H.T.* (Table 2).

Table 2: Sorption capacities of the five cycles (q_i) and average sorption capacity (q^{av}) with related standard deviations (σ).

	Pressure [MPa]	q_1	q_2	q_3	q_4	q_5	q^{av}	σ
<i>HT</i>	10	0.20	0.37	0.33	0.30	0.28	0.30	0.06
	14	0.48	0.69	0.65	0.63	0.69	0.63	0.09
<i>20KHT</i>	10	0.24	0.28	0.33	0.30	0.28	0.26	0.01
	14	0.86	0.96	0.81	0.81	0.78	0.85	0.07
<i>20KHTLS</i>	10	0.23	0.21	0.23	0.21	0.22	0.22	0.01
	14	0.73	0.61	0.58	0.55	0.53	0.60	0.08

4. Conclusion

The hydrotalcite-like compounds *H.T.*, *20KHT*, and *20KHTLS* were tested for CO₂ capture in a fixed-bed reactor, at 723 K, 38.5 mol% CO₂ in N₂, at 1.0 or 1.4 MPa, for five PSA cycles. Captured CO₂ increased along with increasing pressure for all tested materials. K₂CO₃ impregnation improved the sorption capacity of commercial hydrotalcite: *20KHT* proved to be the best sorbent at 1.4 MPa with an average sorption capacity value of 0.85 mmol_{CO₂}/g_{ad} and good stability during the five cycles. For all tested materials, the measured sorption capacities had values that can be considered suitable for the industrial use of the SEWGS process applied to biogas/bio-syngas and in agreement with other literature values for similar CO₂ sorbents. Despite the preliminary nature of proposed laboratory scale experiments, important suggestions for future scale-up of SEWGS were obtained: the operation at 1.4 MPa allows the better exploiting of investigated hydrotalcite-based sorbents (with the related increase of the operating costs to be taken into account); Commercial hydrotalcites ensure acceptable performances so possibly avoiding the need of scaling-up hydrotalcites lab-scale L.S. synthesis; impregnation with K₂CO₃ is a step that allows an important upgrade of commercial hydrotalcite.

Nomenclature

$c_{CO_2}(t)$ – outlet CO₂ concentration in capture test, vol%
 $c_{CO_2,b}(t)$ – outlet CO₂ concentration in blank test, vol%
 $c_{CO_2}(\infty)$ – final outlet CO₂ concentration in capture test, vol%
 $c_{CO_2,b}(\infty)$ – final outlet CO₂ concentration in blank test, vol%
 d_p – particle diameter, μ m
 $F_{CO_2,in}$ – inlet CO₂ molar flowrate, mmol_{CO₂}/min

m – adsorbent packed bed mass, g
 q_i – sorption capacity of i^{th} cycle, mmol_{CO₂}/g_{ad}
 q^{av} – average sorption capacity, mmol_{CO₂}/g_{ad}
 t – time, min
 I.D. – internal diameter of a reactor, cm
 PSA – pressure swing adsorption
 WGS – water-gas shift
 SEWGS – sorption-enhanced water-gas shift

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