

Available online at www.sciencedirect.com**Energy
Procedia**

Energy Procedia 4 (2011) 1090–1095

www.elsevier.com/locate/procedia

GHGT-10

Improved sorbent for the sorption-enhanced water-gas shift process

E.R. van Selow^{a,*}, P.D. Cobden^a, A.D. Wright^b, R.W. van den Brink^a, D. Jansen^a^aEnergy Research Centre of the Netherlands, P.O. Box 1, 1755 ZG Petten, The Netherlands^bAir Products PLC, Molesey Road, Walton on Thames, Surrey KT12 4RZ, UK

Abstract

For the sorption-enhanced water-gas shift (SEWGS) process, a new sorbent material has been developed. The sorbent is a potassium-carbonate promoted hydrotalcite-based material. The material has been tested under realistic process conditions in an experimental rig of 2 m length. The cyclic capacity of the material is 27% higher than the cyclic capacity of the reference sorbent, which was used in CACHET, a previous R&D project. Moreover, 36% less steam is required for its regeneration. The sorbent pellets also have a 65% higher crush strength than the reference sorbent. Contrary to the reference material, the novel material does not form notable amounts of MgCO₃ under relevant operating conditions. Due to the absence of this slow CO₂ uptake process, the sorbent remains mechanically stable, the cyclic steady state is reached rapidly, CO₂ slip in the product gas is reduced, and steam requirements are lowered. It is demonstrated that the sorbent remains mechanically stable during operation of at least 1200 adsorption – desorption cycles. With this new, higher density material, carbon capture levels exceeding 95% can be obtained more efficiently and vessels will be smaller.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND](https://creativecommons.org/licenses/by-nc-nd/4.0/) license.*Keywords:* sorption enhanced reaction; carbon capture; high temperature sorbent; pressure swing; hydrotalcite

1. Introduction

Pre-combustion carbon capture technologies are potentially well suited for decarbonising gas turbine fuels. The sorption-enhanced water-gas shift (SEWGS) process is an advanced pre-combustion carbon capture technology that can yield high capture ratios at lower efficiency penalties and at lower costs than mature technologies using solvents. The SEWGS process operates at much higher temperatures than these processes.

SEWGS is a pressure swing adsorption (PSA) process based on reversible CO₂ adsorption on solid materials at elevated temperatures between 350 and 550 °C. Accordingly, cooling and partially condensing the fuel gas and

* Corresponding author. Tel.: +31-224-564116; E-mail address: vanselow@ecn.nl.

subsequent reheating upstream of the gas turbine are avoided. The reactor vessels are loaded with sorbent pellets. As CO_2 is removed from the synthesis gas by adsorption, CO is simultaneously converted to CO_2 by the water-gas shift reaction, which ultimately ensures low CO_2 emissions and high carbon capture ratios. The sorbent is periodically regenerated by purging with steam at low pressure.

At GHGT-9, the technical feasibility and economic competitiveness of the SEWGS process was substantiated [1, 2]. However, in order to reduce the costs of CO_2 mitigation with respect to the current reference technology by 50%, some breakthroughs are required in addition to incremental improvements. A critical issue observed in the CACHET project was that the sorbent pellets were fractured and powdered throughout the reactor when cycled for typically a several hundred cycles [3]. Since friable materials may lead to valve sealing failures, blocked filters, and increased particulates to the gas turbine, their mechanical stability is critical for the SEWGS process. A second issue that came up with this material is that under realistic process conditions, that is, elevated partial pressures of CO_2 and H_2O , a slip of CO_2 in the H_2 product appeared, which gradually increased with increasing cycle number. Both problems were found to be related to the formation of considerable amounts of MgCO_3 [4]. The sorbent used in the CACHET project was a magnesium and aluminium containing hydrotalcite-based material, which was promoted with potassium carbonate. It was shown that formation of MgCO_3 in this material was reversible, but much slower than CO_2 adsorption and desorption. As a result, the carbon capture rate decreased over time. Compensation by increasing steam consumption was possible, although at a substantial efficiency penalty [5, 6].

In the CAESAR project, a European FP7 project, R&D is focused on addressing these issues with the hydrotalcite-based sorbent [7, 8]. The goals are to increase the cyclic capacity, reduce the amount of steam needed for regeneration, and increase the mechanical strength of the sorbent pellets. The key has been to develop a sorbent that does not form notable amounts of MgCO_3 under the relevant process conditions. The new sorbent is K-MG30, a potassium-carbonate promoted hydrotalcite-based material with 30 weight per cent Mg, much lower than in the reference material [9 – 12]. The reference material is the sorbent from the CACHET project.

2. Experimental setup

The new sorbent material was tested under realistic operating conditions in a single-column experimental rig comprised of a 2 m tall reactor vessel. Figure 1 shows a flow scheme of the single vessel test rig. The vessel was packed with calcined pellets of the new sorbent material. Pure gases and superheated steam were mixed in desired quantities in order to obtain the desired feed gas composition and flow rate. Feed gases were heated to 400 °C in electric heaters and the reactor walls were kept at 400 °C by electric heating and insulation. Product gases were cooled down to 5 °C and condensate removed in knock-out drums. Gas quantities of dry product gases were recorded by volumetric dry gas meters. Additionally, flow rates of product gases were measured by thermal mass flow sensors. The stability of the sorbent was investigated in the rig under cyclic conditions. A cycle consisted of several steps in a fixed order and with a fixed duration. Various industrial cycles have been suggested for CO_2 recovery and a cycle with a steam rinse was used [12]. The consecutive steps were: (1) feed, during which adsorption and shift reaction occurred; (2) countercurrent rinse with high-pressure steam, for removing the gas 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.

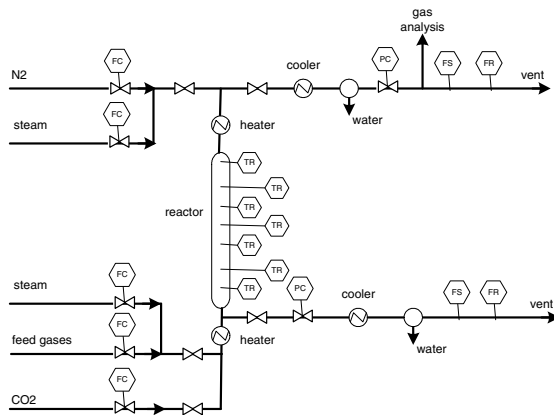


Figure 1 Flow scheme of the test rig.

3. Experimental results

During the cyclic testing, the feed pressure was 28 bar, and the feed gas consisted of 20% CO₂, 16% H₂O, balance N₂. These conditions were equal to the conditions during a cyclic test with the reference sorbent [5]. Rinse and purge flow rates were set such that the steam-to-CO₂ ratio was 1.6 mole/mole for both flow rates. This implies a 16% lower steam consumption for rinsing and 36% lower steam consumption for purging compared to the test with the reference sorbent. Figure 2 shows the cycle-averaged CO₂ fraction in the product gas as a function of cycle number for cycles 250 to 500. The carbon slip is so low that CO₂ recoveries of 99% are obtained, similar to CO₂ recoveries with the reference sorbent [4]. The tests showed that the sorbent material is mechanically stable over at least 1200 adsorption – desorption cycles without loss of activity. Due to its higher density, the working capacity of the sorbent on volume basis is 27% higher compared to the reference sorbent. Performance of the new sorbent during cyclic testing at lower steam consumption was thus better than the performance of the reference sorbent.

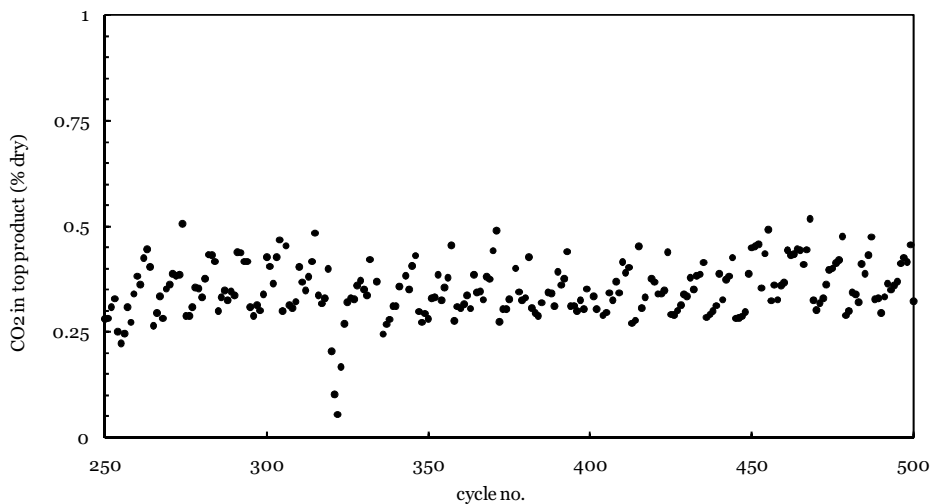


Figure 2 Cyclic stability of the carbon recovery using a steam rinse cycle.

Although bulk formation of MgCO_3 is a reversible process, it is too slow to be exploited in a pressure swing cycle [5]. Formation of MgCO_3 is even detrimental to SEWGS performance and mechanical stability of the sorbent. In order to investigate the formation of MgCO_3 , the sorbent was fully regenerated with steam at atmospheric pressure after the cyclic testing. The regeneration temperature was $400\text{ }^\circ\text{C}$. Figure 3 shows the amount of CO_2 recovered as a function of the amount of steam supplied, both normalized with respect to the sorbent mass. For comparison, this is also shown for the reference sorbent. The figure shows that regeneration of the new sorbent yielded 1.2 mmol/g . This is similar to its breakthrough capacity. By comparison, almost 12 mmol/g is recovered when regenerating the reference sorbent, which is ten times higher than the initial breakthrough capacity. The explanation is that under the relevant process conditions essentially no MgCO_3 was formed in the new sorbent, whilst large amounts of MgCO_3 were formed in the reference sorbent, continuing after initial breakthrough.

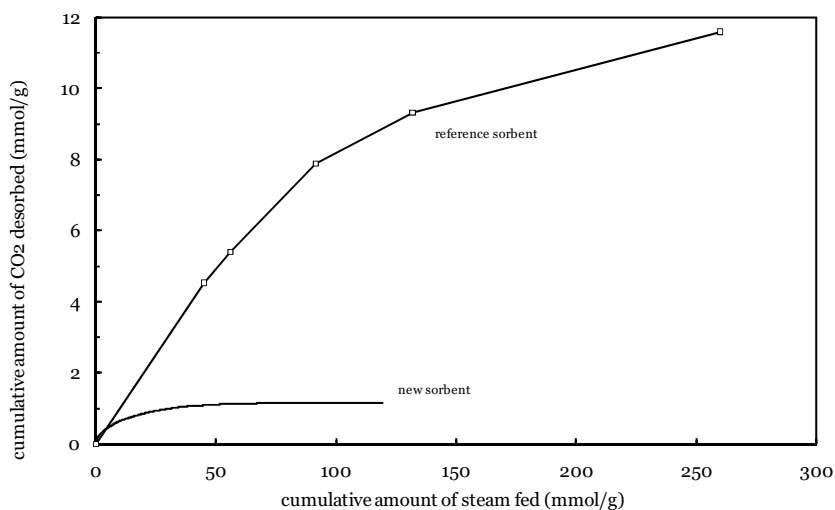


Figure 3 Regeneration of the new and reference sorbents, indicating that MgCO_3 formation only occurs in the reference sorbent.

Bulk formation of MgCO_3 in the reference sorbent led to mechanical degradation of the sorbent tablets. This was not observed for the new sorbent material. The new material also requires less steam to regenerate, as the cyclic formation and decomposition of MgCO_3 are relatively slow processes. Furthermore, due to the absence of this slow CO_2 uptake process, cyclic steady state is reached rapidly. For the new sorbent, cyclic steady state is reached within a few cycles, whereas for the reference sorbent, it takes several hundred of cycles to reach cyclic steady state.

The new sorbent tablets also have a 65% higher crush strength than the reference sorbent pellets (as received). After the cyclic tests, crush tests revealed that the pellets had lost 25 to 50% of their initial crush strength but had remained intact, in comparison to the reference sorbent pellets, which were fractured and powdered throughout the entire reactor upon repeated cycling. Hence, it is concluded that the new sorbent pellets remain mechanically stable during operation of more than 1200 cycles, as Figure 4 shows. The mechanical stability is attributed predominantly to the absence of MgCO_3 formation.

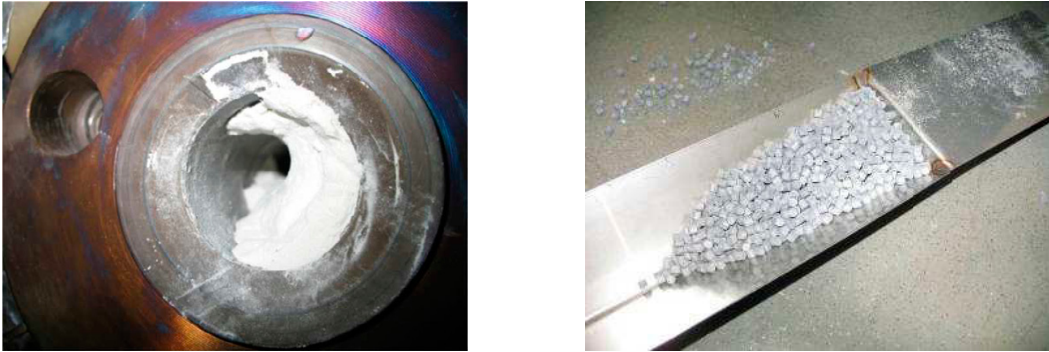


Figure 4 Sorbent unloaded from the reactor after more than 1200 cycles: (left) reference sorbent, fractured (right) new sorbent, mechanically stable.

Figure 5 shows at least two different morphologies present in the fractured reference sorbent, after several hundred cycles. Such morphologies have not been observed in the spent new sorbent.

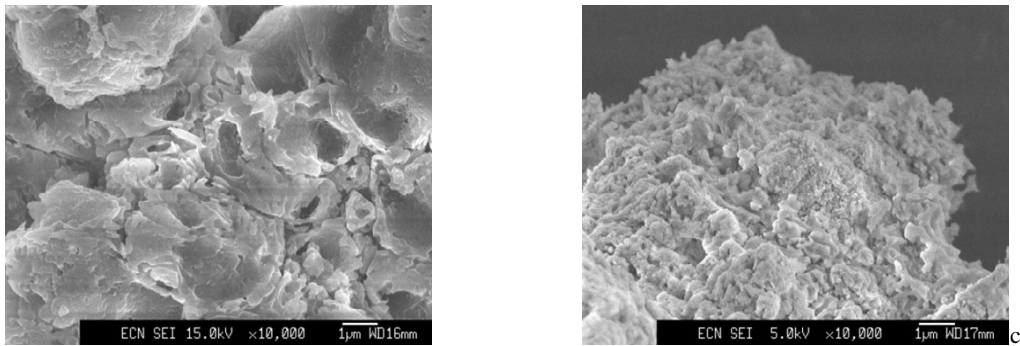


Figure 5 SEM pictures showing at least two different morphologies in the reference sorbent.

4. Conclusions

A new sorbent for the SEWGS process has been developed. Key was to develop a sorbent that does not form notable amounts of MgCO_3 under the relevant operating conditions. The new sorbent is a potassium-carbonate promoted hydrotalcite-based material with a much lower amount of Mg than the material used in previous work. Pellets of the new sorbent were tested under representative cyclic operating conditions. Compared to the reference sorbent, cyclic capacity was 27% higher and steam requirement for regeneration 36% lower under equal conditions. Formation of undesirable MgCO_3 was essentially absent, which is important since formation of MgCO_3 can lead to mechanical failure of the sorbent pellets and can decrease the carbon capture ratio. Mechanical stability has been confirmed for over 1200 adsorption – desorption cycles without loss of activity. With this new material, carbon capture levels exceeding 95% can be obtained more efficiently and in smaller vessels.

5. Acknowledgement

The research leading to these results has received funding from the European Community's Sixth Framework Programme under grant agreement no. 019972 and Seventh Framework Programme grant agreement no. 213206.

6. References

- [1] Van Selow ER, Cobden PD, Van den Brink RW, Hufton JR, Wright A. Performance of sorption-enhanced water-gas shift as a pre-combustion CO₂ capture technology. Proc. GHGT-9, Washington 2008.
- [2] Hufton JR, Hinderink P, Van Selow ER, White V, Wright A. Reduction in the cost of pre-combustion CO₂ capture through advancements in sorption-enhanced water-gas-shift. Proc. GHGT-9, Washington 2008.
- [3] Van Selow ER, Cobden PD, Van den Brink RW, Wright A, White V, Hinderink P, Hufton JR. Pilot-scale development of the sorption enhanced water gas shift process. In: Eide LI, editor. Carbon dioxide capture for storage in deep geologic formations, Berks, CPL Press; 2009, p. 157 - 80.
- [4] Walspurger S, Cobden PD, Haije WG, Westerwaal R, Elzinga GD, Safonova OV. In situ XRD detection of reversible dawsonite formation on alkali promoted alumina: a cheap sorbent for CO₂ capture. Eur J Inorganic Chem 2010; 17: 2461 – 64.
- [5] Van Selow ER, Cobden PD, Verbraeken PA, Hufton JR, Van den Brink RW. Carbon capture by sorption-enhanced water-gas shift reaction process using hydrotalcite-based material. Ind Eng Chem Res 2009; 48, 9: 4184 – 93.
- [6] Van Dijk HAJ, Walspurger S, Cobden PD, Van den Brink RW. Testing of hydrotalcite based sorbents for CO₂ and H₂S capture for use in sorption enhanced water gas shift. Proc. GHGT-10, Amsterdam 2010.
- [7] Bakken E, Pakdel Henriksen P, Fosse Håkonsen S, Spjelkavik AI, Stange M, Stensrød RE et al. Development of CO₂ sorbents for the SEWGS process using high throughput techniques. Proc. GHGT-10, Amsterdam 2010.
- [8] Wright A, White V, Hufton J, Quinn R, Cobden P, Van Selow E. CAESAR: Development of a SEWGS model for IGCC. Proc. GHGT-10, Amsterdam 2010.
- [9] Walspurger S, Boels L, Cobden PD, Elzinga GD, Haije WG, Van den Brink RW. The crucial role of the K⁺-aluminium oxide interaction in K⁺-promoted alumina- and hydrotalcite-based materials for CO₂ sorption at high temperatures. ChemSusChem 2008; 1: 643 – 50.
- [10] Cobden PD, van Eijk S, Pirgon-Galin Ö, Walspurger S, Van Selow ER, Van den Brink RW, Jansen D. Optimisation of alkali promotion of Mg-Al hydrotalcites: improving high temperature CO₂ sorption capacity and mechanical strength. Proc. GHGT-10, Amsterdam 2010.
- [11] Cobden PD, Walspurger S, Van den Brink RW, Van Dijk HAJ. Patent No. WO2010/059055 A1; 2010.
- [12] Walspurger S, Cobden PD et al. Chem Eur J 2010 (accepted).
- [13] Reijers HThJ, Van Selow E, Cobden PD, Boon J, Van den Brink RW. Development of a Model for SEWGS: Validation and Process Cycle Optimization. Proc. GHGT-10, Amsterdam 2010.