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Sorption-enhanced hydrogen production for pre-combustion CO₂ capture: Thermodynamic analysis and experimental results

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ABSTRACT

Hydrotalcite-based materials have been identified as suitable materials for high temperature (400 °C) adsorption of CO₂. In pre-combustion decarbonisation processes for natural gas based power cycles, it should be possible to use this material to improve conversions in the water-gas shift (WGS) and steam-reforming (SMR) reaction. The efficiencies for electricity production from natural gas have been calculated for some different system configurations, in which hydrotalcite-based material could be used. The calculated efficiency penalties ranged from 5.5 to 8.6 percentage points. The assumptions made in the system study have been tested on the laboratory scale. Hydrotalcite-based materials are found to be an excellent choice for use in the sorption-enhanced WGS reactor. The requirements for very low residual concentrations of CO₂ at 400 °C and large amounts of catalyst in the sorption-enhanced SMR reactor make its application less likely. Suggestions are made to how the SE-SMR could be improved.

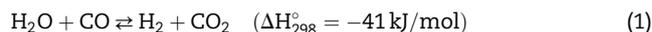
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1. Introduction

In CO₂ capture, transport and storage (CCS) from power production, the capture part of the chain usually accounts for the highest costs. R&D in this field aims at reducing the fuel costs due to the efficiency penalty of CO₂ capture and the capital costs associated with the extra equipment necessary for CO₂ capture. This paper focuses on pre-combustion CO₂ capture, i.e. first converting the fuel into hydrogen and CO₂, subsequently separating CO₂ and using hydrogen as a fuel. The Sorption-Enhanced Reaction Process (SERP) is a special version of pre-combustion CO₂ capture, in which the fuel conversion step and the CO₂ separation step are combined.

Apart from potentially lower equipment costs, SERP also offers interesting opportunities for lower efficiency penalties.

In SERP the equilibrium of a reaction is shifted to the product side by removing one of the products using a sorbent. In the present case two reactions are of interest.



The water-gas shift reaction (1) is an equilibrium reaction in which the energy content of the CO is converted to hydrogen and some heat. In sorption-enhanced water-gas shift (SE-WGS), CO₂ is selectively removed from the reaction zone. The water-gas shift equilibrium shifts to the reactant side at

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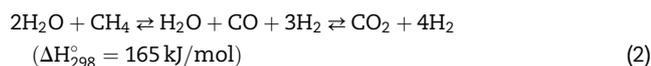
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increasing temperature, which leads to low CO conversions. Industrially, a two-step shift process is applied with a high-temperature shift (HTS) catalyst followed by gas cooling and a low-temperature shift (LTS) catalyst. In the SE-WGS process high CO conversions are made possible at higher temperature by capturing the CO₂, and only one shift reactor can be used. SE-WGS can be applied using syngas from a coal gasifier or a natural gas reformer (Hufton et al., 2004).



The steam methane reforming (SMR) reaction process (2) is strongly endothermic and is industrially operated at high temperatures (850–1000 °C) in order to obtain high methane conversions. In industrial hydrogen plants, SMR is followed by HTS and LTS. In sorption-enhanced steam methane reforming (SE-SMR), a steam reforming catalyst is combined with a CO₂ sorbent and the overall equilibrium is shifted to the product side. SE-SMR can be operated at lower temperatures than ordinary SMR and makes the two shift reactors redundant.

Sorption-enhanced reforming has been developed by Air Products in the 1990s as an alternative technology for the industrial production of pure hydrogen. A potassium carbonate promoted hydrotalcite was used as CO₂ acceptor (Hufton et al., 1999). It was shown that potassium carbonate strongly enhances the CO₂ adsorption capacity of hydrotalcite-based sorbents and that the optimum loading lies around 20 wt%.

With this sorbent, the process was operated successfully at temperatures between 400 and 500 °C. A major obstacle for industrial implementation, however, was the relatively low purity of the hydrogen, caused by incomplete conversion of methane. Another was the high steam demand for regeneration of the hydrotalcite-based sorbent. For application in electricity generation with pre-combustion decarbonisation, the hydrogen purity is much less important. Still, steam is a valuable asset in combined cycle power plants.

Ding and Alpay also studied sorption-enhanced reforming with hydrotalcites as sorbent (Ding and Alpay, 2000). They found that the SE-SMR process benefits from higher pressures and that lower steam to methane ratios can be used than in ordinary reforming. Different hydrotalcite-based sorbents were investigated by the group of Rodrigues (Yong et al., 2001) and in prior work of ECN (Reijers et al., 2006).

The present paper makes a comparison between using hydrotalcite-based materials for sorption-enhanced WGS and SMR. This is addressed through an evaluation of the system efficiencies that could be expected from the application of SE-WGS and SE-SMR in a gas turbine combined cycle. This exercise sets targets for the material and process development. This paper also describes experimental verification of the sorption-enhanced processes on the laboratory scale.

2. Methodology

2.1. System evaluation

The system evaluation was performed using the Aspen Plus simulation tool. The emphasis was to look at the efficiency of

the complete power generation system as opposed to the individual units. The sorption-enhanced reactors are modelled as black boxes and continuous processes. This is not necessarily the expected mode of operation in a final system, where a semi-continuous batch process is more likely. The assumptions made for the SE-unit were based on results from literature (Allam et al., 2005) and of laboratory-scale experiments. However, as shall be shown later, these experiments, performed at low pressure do not necessarily predict the expected behaviour at an industrial scale. Natural gas of IEA specifications (IEA, 2003) was assumed to be the fuel for the system, and the CO₂ was delivered at a final pressure of 110 bar, sufficient for transport and storage. Several simplifications were made: the steam system was assumed to operate at single pressure, isentropic efficiencies were assumed constant and possible pressure drops in the reactors were ignored. The gas turbine inlet temperature and the gas turbine compressor inlet flow were kept the same for all cases, which results in different fuel input and electricity output of the systems analysed. The performance and operating parameters used for the sorption-enhanced reactors were chosen from literature studies and are partially displayed in Table 1. The S/CO₂ value of 1.8 used was taken from the work on SE-WGS by Air Products (Allam et al., 2005) and was assumed to be also valid for SE-SMR.

The main assumptions in simulations are a pressure ratio of the gas turbine of 16.9, and an inlet temperature of 1238.5 °C. The steam pressure is chosen such that the steam turbine outlet liquid content is 10%. Isentropic efficiencies, gas turbine losses, heat recovery steam generator temperature approach, and condenser pressure (0.04 bar) has been chosen such that the power output of the gas turbine itself and the total combined cycle without capture matches that of literature data. Oxygen purity for the ATR is 95%, the 2-stage inter-cooled oxygen compressor taken isentropic efficiency is 85%. Intercooler outlet temperatures were 50 °C for both CO₂ as well as oxygen compression.

Table 1 – Selection of parameters used in ASPEN simulations for sorption-enhanced processes with hydrotalcite based materials

	Air-SE-WGS	O ₂ -SE-WGS	SE-SRM
Adsorption			
Temperature (°C)	400	400	400
Pressure (Bar)	17	17	17
S/C	1.5	1.5	3.0
ΔH _{ads} (kJ/mol)	17	17	17
CH ₄ conv (%)	n/a	n/a	93
CO conv (%)	95	95	96.8
C recovery (%)	90	90	90
Desorption			
Temperature (°C)	400	400	400
Pressure (Bar)	2.8	2.8	2.8
S/CO ₂	1.8	1.8	1.8
ΔH _{des} (kJ/mol)	–17	–17	–17

S/C denotes the steam-to-carbon feed ratio, ΔH_{des} is the heat of adsorption of CO₂, S/CO₂ denotes the purge steam-to-CO₂ ratio: the amount of steam required for regeneration of CO₂.

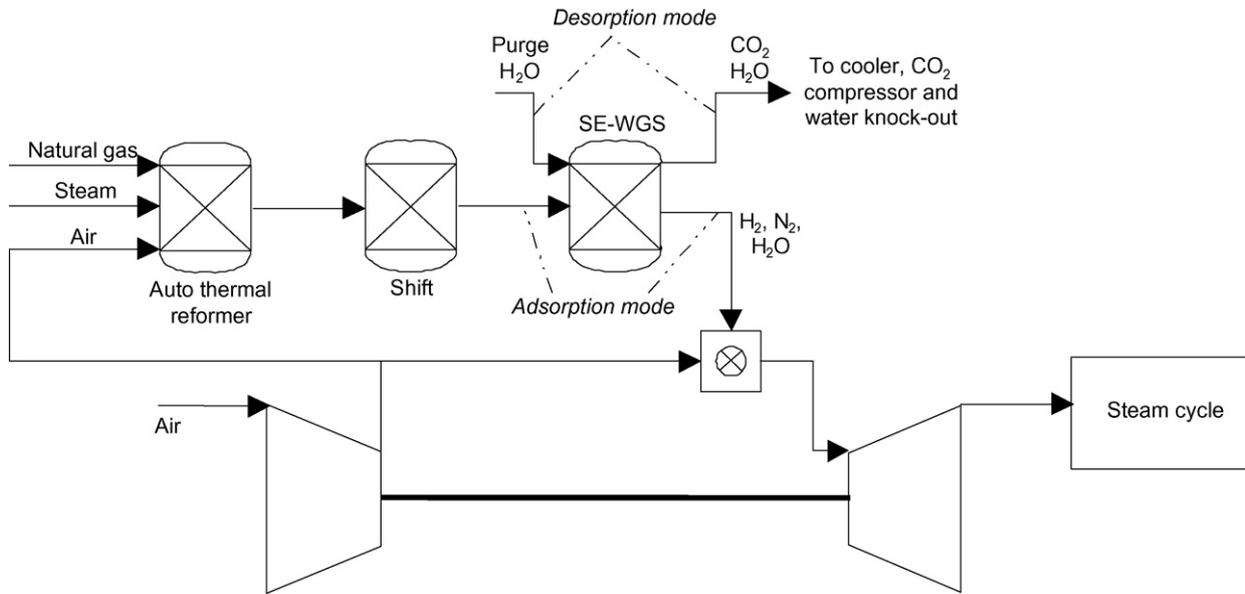


Fig. 1 – Air-driven autothermal reformer with sorption-enhanced water-gas shift (Air-ATR SE-WGS).

In total four systems were evaluated. The base case was a gas turbine combined cycle without CO₂-capture based on a Siemens SGT5-4000F (formerly V94.3A) with a combined cycle power output of 380 MWe, and an efficiency of 57.1%. This represents a state-of-the-art electricity production facility. Four systems are compared with the base case, and are described below:

2.1.1. Air-ATR SE-WGS

This system is a combination of an air-driven autothermal reformer followed by a shift section and then a sorption-enhanced shift reactor as known from the work of Air Products (Allam et al., 2005). Essentially the majority of the feedstock has already been converted into H₂, CO and CO₂ before entering the sorption-enhanced reactor. Air for the ATR was taken from the compressor of the gas turbine. Fig. 1 shows a simplified process scheme for this option.

2.1.2. O₂-ATR SE-WGS

This system is very similar to Air-ATR SE-WGS except that an Air Separation Unit (ASU) is included, which will significantly reduce the size of the ATR reactor. The simplified process scheme is shown in Fig. 2. The previous two types of reactor were already subject to a system evaluation, and were used in this study to validate the results to some extent (Allam et al., 2005).

2.1.3. SE-SMR

This system combines a pre-reformer (for conversion of the heavier fractions of the natural gas) with a sorption-enhanced methane steam reformer. The simplified process scheme is shown in Fig. 3. This reactor requires energy input to drive the steam reforming reaction. Firing of either product (H₂) or fuel (natural gas) can provide this energy. Virtually the whole process takes place in a single reaction vessel. Various

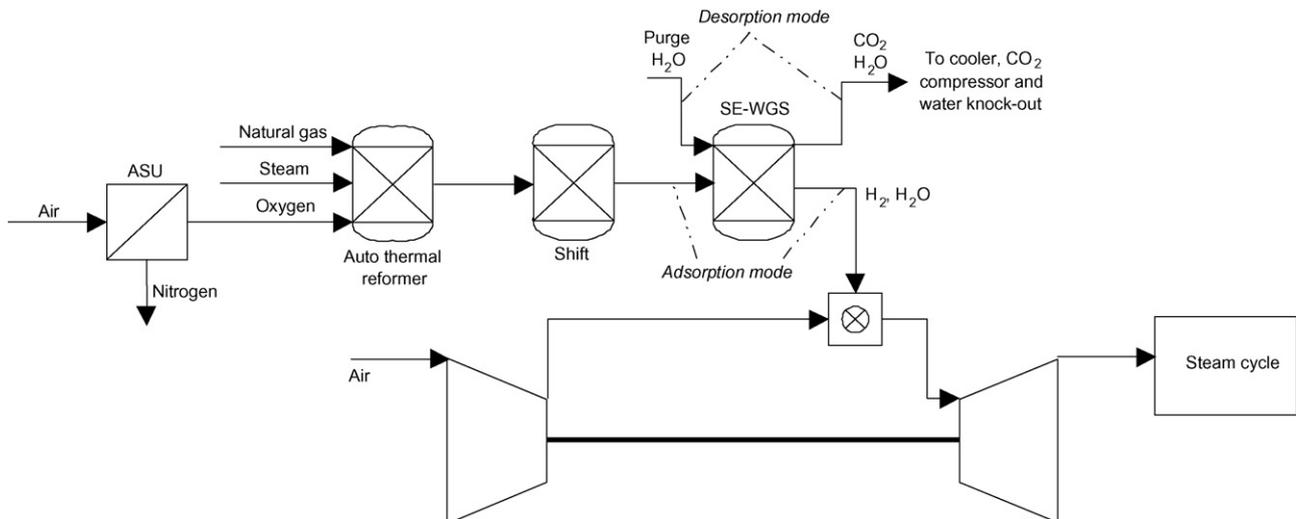


Fig. 2 – Oxygen-driven autothermal reformer with sorption-enhanced water-gas shift (O₂-ATR SE-WGS).

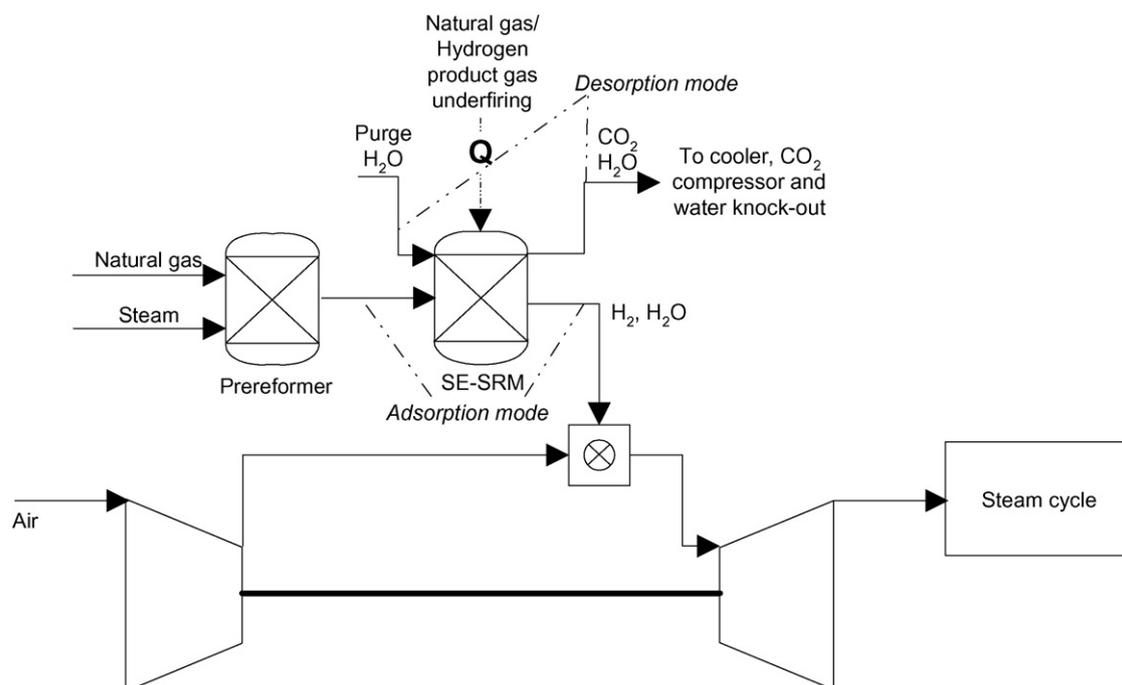


Fig. 3 – Sorption-enhanced steam-methane reformer (SE-SMR).

improvements to all these systems could be made, and are discussed later.

2.1.4. SE-SMR with no capture costs

The efficiency of the SE-SMR system was calculated for the case of the perfect sorbent, i.e. requiring no external energy input or steam for regeneration. This in order to evaluate the efficiency loss due to the steam reforming process itself compared to the base case.

2.2. Laboratory experiments

The laboratory scale experiments, performed with synthetic feed gas were carried out in a computer-controlled flow set-up, which has been described before (Reijers et al., 2006). During sorption-only measurements, a quartz reactor with an internal diameter of 1.0 cm was placed in an oven. Up to 3 g of a sieve fraction (grain size 0.212–0.425 mm) of the sorbent was placed on a quartz grid. The feed consisted of 5–15% CO₂ with 0–30% H₂O in N₂. Regeneration of the sorbents could be performed with a maximum of 30% H₂O in N₂, due to experimental constraints of the equipment. The regeneration could be performed in both co-current and counter-current directions. During sorption-enhanced measurements a stainless steel reactor with internal diameter 1.6 cm was used, which was loaded with up to 6 g of catalyst and sorbent materials. The same sieve fraction (0.212–0.425 mm) was used for both components, which were mixed together in the reactor as homogeneously as possible. The feed could be composed of CH₄, CO, CO₂, H₂O, H₂ and N₂ in various concentrations to mimic conditions present at the entrance of both steam reforming and WGS reactors. The typical flow range in these experiments was 50–150 ml/min (STP), and the pressure could be adjusted to between 1–4 bar.

The sorbent used in all experiments was Pural MG70 (SASOL), impregnated with 22 wt% K₂CO₃ (Merck). Details of the preparation have been published before (Reijers et al., 2006; Nataraj et al., 2000). The WGS catalyst used was a commercially available Fe-Cr HTS catalyst. The SMR catalyst was a pre-commercial sample supplied by a vendor under a non-disclosure agreement.

The reactor could be by-passed for calibration of the gases. H₂O was removed from the exit gases before analysis was performed. Sampling by gas chromatograph for CO₂, CH₄, H₂ and CO occurred every 75 s. The dried exit gases were also passed into a CO₂ analyser for CO₂ breakthrough measurements with a higher temporal resolution. A time interval of 15 s was normally used. The results from the gas chromatograph for CO₂ and the CO₂ analyser after correction were consistent with each other.

3. Results and discussion

3.1. System evaluation

Table 2 shows the efficiencies calculated for the various sorption-enhanced options that are the subject of this paper. Naturally, all CO₂ capture technologies decrease the baseline efficiency of electricity generation. The Siemens V94.3A gas turbine has a listed combined cycle efficiency of 57.1% without CO₂ capture. This does not take into account the effect of running this system at one pressure level. The sorption-enhanced systems have an efficiency penalty of 5.5 percentage points for SE-SMR to 8.6 percentage points for oxygen-blown ATR with SE-WGS. The two SE-WGS systems can be directly compared to the systems analysis of Air Products (Allam et al., 2005). The difference between the air- and O₂-driven ATR

Table 2 – Calculated efficiencies for CH₄ to electricity production for various sorption-enhanced concepts

	Efficiency (%)	Carbon capture ratio (%)
Base case without CO ₂ capture	57.1	0.0
Air-ATR SE-WGS	50.4	90.0
O ₂ -ATR SE-WGS	48.5	90.0
SE-SMR	51.6	90.0
SE-SMR with no capture costs	54.4	90.0

cases is 1.9% points. Air Products found a difference of 1.6% points between these two cases, which induces more confidence in this approach. The overall efficiencies of the Air Products systems were slightly lower, but this might be accounted for in the simplifications made in this systems analysis as outlined in the experimental section.

The SE-SMR case has the lowest efficiency penalty of the explored options. However, several improvements to the system design were required to reach an efficiency of 51.6%. These changes to the system design are shown in Fig. 4. In the first instance a CO₂ desorption turbine was added to the system. This gave an improvement of 0.2% points efficiency. The CO₂ stream during the desorption-regeneration stage contains quite a lot of steam, which needs to be recovered or removed before storage of the CO₂ can take place. It was found to be more efficient to expand this stream, generating extra power, then removing the water and compressing the CO₂ again. Although this only accounts for an efficiency improvement of 0.2%, the effect will become much greater when sorbents that operate at higher temperature are considered. However, this is not the subject of the present publication, where only hydrotalcites are considered.

Secondly, it should be noted that in SE-SMR in order to gain a carbon capture ratio required, it is necessary to use the product gas (H₂) for firing of the steam reformers. The steam reforming reaction is endothermic and requires external heat input. If this is supplied by the combustion of methane, then CO₂ is also produced externally to the pre-combustion separation step. This CO₂ cannot easily be captured because unless the combustion is performed with pure O₂, N₂ will also be present, which will require extra clean-up steps. The firing with product (H₂) does not produce CO₂, although it does compromise overall efficiency. However, there is a choice to be made between pressurised (see Fig. 4) and non-pressurised firing. In the case of pressurised firing, a part of the compressed air from the compressor in the gas turbine is used to combust a part of the product stream from the adsorption reactor. The heat generated is used to drive the steam reforming reaction, and the combustion products are fed back into the expander of the gas turbine. In the case of non-pressurised firing the heat required for driving the steam reforming reaction is produced from the combustion of natural gas and a part of the hydrogen product at atmospheric pressure. If the firing is not pressurised this leads to a loss in efficiency of 2.3% points. It is clear that pressurised firing is essential to reach high efficiencies. Several power levels of the individual stages of the modelled processes are set out in Table 3 to help with the comparison.

It is interesting to note, that if the energy used for regeneration of the sorbent is set to zero in this calculation, then the pre-combustion decarbonisation route has an efficiency of 54.4%, or 2.7% points less than the base case without CO₂ capture. In other words, the minimum loss in energy efficiency by performing pre-combustion decarbonisation is 2.7% points. This loss is caused mainly by the

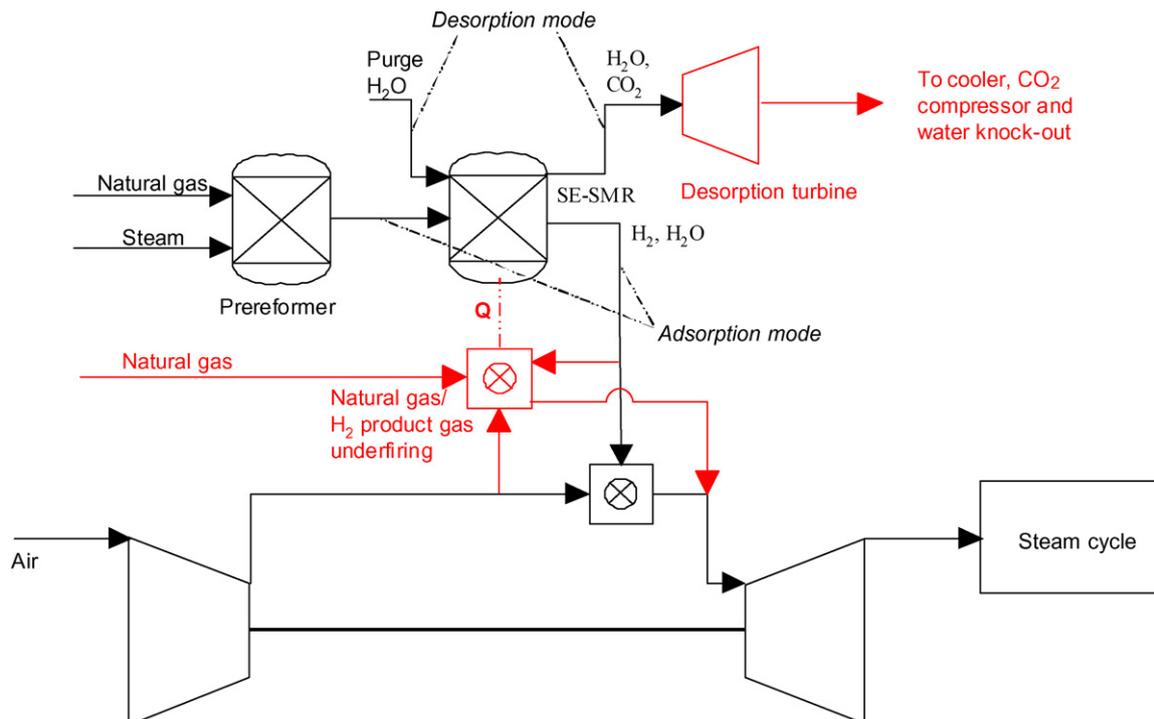
**Fig. 4 – Changes to the SE-SMR system to improve efficiency and achieve the required CO₂ capture ratio.**

Table 3 – Several power levels for the individual stages of the modelled processes

Parameter	Base case	Air-ATR SE-WGS	O ₂ -ATR SE-WGS	SE-SMR
Power input (MW)	665.7	857.8	829.0	733.5
Net gas turbine power (MW)	260.8	281.8	296.3	294.9
Net steam turbine power (MW)	119.5	162.6	144.3	74.9
CO ₂ compression power (MW)	0.0	12.0	11.5	9.7
Power out (MW)	380.3	432.3	402.1	378.5

conversion of natural gas into hydrogen by steam reforming and water-gas shift, and the compression of CO₂. The extra loss in efficiency that occurs when the regeneration of the sorbent is not free has mainly to do with producing the steam to strip the sorbent.

The efficiency of the SE-SMR system as defined here is based to a certain extent on the assumptions made about the operating conditions of the black-box description of the enhanced-sorption reactor. This is based partially on a previous demonstration of this technology at the laboratory scale (Reijers et al., 2006) and reported steam to CO₂ ratios for the SE-WGS system (Hufton et al., 2004). It has also been suggested that SE-SRM could be carried out at lower steam to CH₄ ratios than in conventional reactors (Ding and Alpay, 2000). The effect of these two steam ratios on the system efficiency was the subject of a sensitivity analysis.

Fig. 5 shows that calculated efficiency for natural gas to electricity with production of storage-ready CO₂ as a function of steam/CH₄ ratio in the sorption-enhanced step, and as a function of steam/CO₂ ratio in the desorption-regeneration step. There are obviously two regimes present. At lower S/C ratios the efficiency drops slowly as the steam required is increased. This is until a point that the efficiency rapidly starts to drop. This point is also a function of the S/CO₂ ratio. Above the dividing line shown, there is enough steam in the system to drive both the reforming and the desorption-regeneration cycles. Efficiency decreases because there is less steam available for the steam cycle. Below the line, extra fuel is used in producing this steam and the efficiency drops rapidly. As a simple rule of thumb it is possible to say that the total steam needed for both reforming and desorption-regeneration should not be more than 7 steam mol/mol carbon content. In this case, carbon content refers to the amount of carbon in the fuel and in the regeneration. Using more steam for the

steam reforming will thus impose a restriction on the amount of steam that can be used in regeneration, and vice versa.

The two SE-WGS systems show slightly lower efficiency than the fully integrated SE-SMR option. The range of efficiencies for all the sorption-enhanced systems with hydrotalcites still falls in a rather narrow range. It is timely to note that Air Products chose the less efficient O₂-ATR SE-WGS after the economical evaluation was made (Allam et al., 2005). The system configurations and related efficiencies are insufficient to be able to choose the most suitable system. Ongoing work at ECN is looking at the economical aspects of these system configurations. The following results address the validity of using hydrotalcites as a CO₂ sorbent in the various sorption-enhanced configurations.

3.2. Lab-scale experiments

Experiments have been performed in several modes; adsorption experiments where the capacity of the hydrotalcite-based materials are determined at different temperatures, and sorption-enhanced experiments for both WGS and SMR. The capacity of the hydrotalcite-based material in adsorption experiments decreases as temperature increases beyond 400 °C (Reijers et al., 2006). This is shown in Fig. 6. The layered hydrotalcite structure consisting of positively charged brucite (magnesium hydroxide)-like layers with interlayer space containing charge compensating anions and water molecules is already known to have collapsed before 400 °C (Hutson et al., 2004). The CO₃²⁻ in the interlayer is decomposed and the material is completely dehydrated and partially dehydroxylated, although this material is still capable of adsorbing CO₂ at this temperature. On heating further the material further decomposes with dehydroxylation of the OH⁻ groups. At 600 °C, O₂ is released as the material begins its transition to a

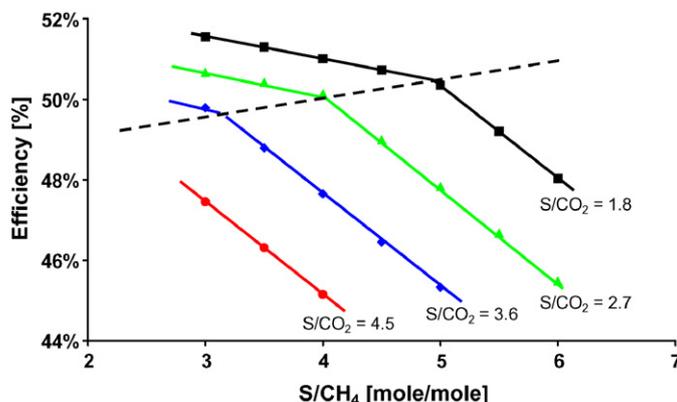


Fig. 5 – Variation in efficiency of the SE-SMR system as function of S/C during sorption-enhanced reforming and S/CO₂ during hydrotalcite-based sorbent regeneration.

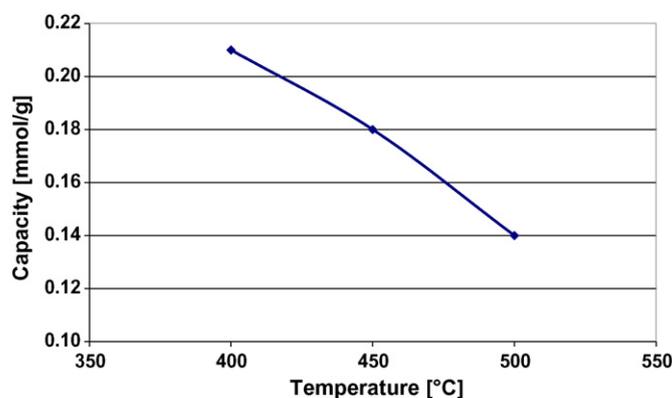


Fig. 6 – Measured capacity of hydrotalcite-based sorbent as function of temperature. Flow = 100 ml/min, pressure = 1 bar, 3 g sorbent, CO₂ 5.0%, H₂O 30%, in N₂.

solid solution of MgO and Al₂O₃, and final transition to a spinel at 900 °C. Above 600 °C, the ability to effectively adsorb CO₂ is lost. This somewhat restricts the use of hydrotalcite-based materials in the range 400–600 °C. Although it may be possible to stabilise the material with promotion or changing of the constituents, as MgAl-hydrotalcite is only one of a whole family of double-layer hydroxides with similar properties.

Fig. 7 shows the adsorption-reaction part of a SE-WGS system. There are several interesting features to note. There is more or less simultaneous breakthrough of CO₂ and CO. Before breakthrough CO conversion is almost complete, with CO concentrations in the 100–250 ppm range. After breakthrough, when the remaining capacity of the hydrotalcite-based sorbent has been utilised, the conversion of CO approached 50% at steady state. This is in-line with expectations and measurement performed for the same amount of catalyst in non sorption-enhanced reactions. Equilibrium conversion would be 82% for these conditions, but there is simply not enough catalyst to reach this equilibrium conversion. This is quite remarkable; even though there is not enough catalyst to reach equilibrium conversion, the sorbent can pull the reaction to completion.

A similar experiment was performed with the steam reforming catalyst. This is shown in Fig. 8. In the experiment

at 400 °C, the breakthrough of CH₄ occurs almost immediately, and well before the breakthrough of CO₂. In an SE-SMR reactor used to produce H₂ for electricity generation, this may however not be as much of a problem as it seems. Unreacted CH₄ will be fed into the gas turbine in any case. Too high carbon slip, however, would strongly compromise the carbon capture ratio. Previous results on the laboratory-scale (Reijers et al., 2006) have shown that a 95% conversion of CH₄ can be achieved if the cycle times for adsorption-reaction and desorption-regeneration are carefully chosen.

There are several experiments that can be performed to address this issue of CH₄ slip. One is also shown in Fig. 8, the experiment was performed at higher temperature, namely 450 °C. The breakthrough of CH₄ is slightly postponed, but the breakthrough of CO₂ also becomes sharper. In order to quantitatively analyse this effect, the total carbon slip can be calculated as a function of the carbon entering the system, as shown in Fig. 9. In a real system, a certain amount of carbon slip, in the form of either CO, CH₄ and CO₂ would be allowed before switching to desorption-regeneration mode. This would probably be of the order of 10–20% depending on the desired carbon capture ratio. It is clear here, that for 10% carbon slip, the reactor at 450 °C far outperforms the reactor at 400 °C, with this amount of slip being reached after 9.5 and

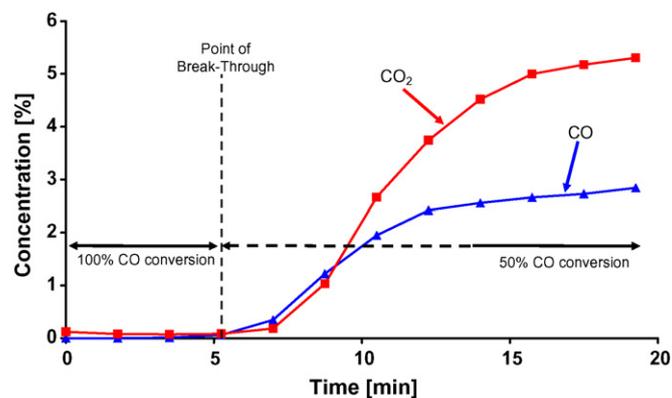


Fig. 7 – Typical adsorption-reaction cycle of sorption-enhanced water-gas shift reaction showing the breakthrough of CO and CO₂. Flow = 100 ml/min, temperature = 400 °C, pressure = 1 bar, catalyst/sorbent ratio 1/6 (w/w), 3 g sorbent, CO 6.0%, H₂O 14.5%, CO₂ 2.5%, H₂ 12.0% in N₂.

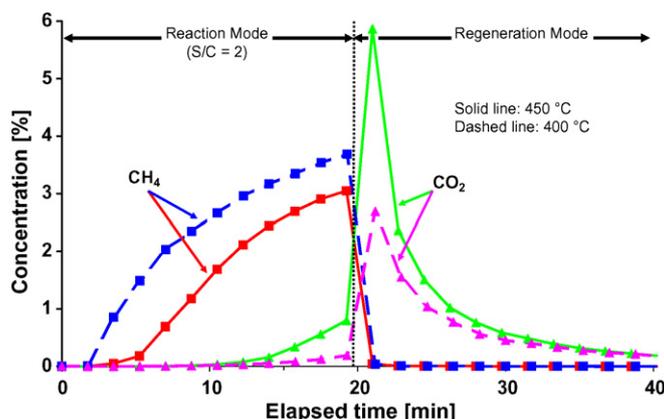


Fig. 8 – Typical adsorption-reaction cycle of sorption-enhanced steam-methane reforming reaction showing the breakthrough of CH_4 and CO_2 . Flow = 100 ml/min, temperature = 400 and 450 °C, pressure = 1 bar, catalyst/sorbent ratio 1/1 (w/w), 3 g sorbent, CH_4 5.5%, H_2O 11%, in N_2 .

4 min respectively. The process can be improved further by increasing the steam/ CH_4 ratio in the reactants. This is also shown in Fig. 9. However, as shown in the systems analysis, this will lead to a drop in efficiency.

Another option is to use even more catalyst. In the SE-WGS experiments, it was possible to use a weight-to-weight catalyst-to-sorbent ratio of 1/6. In these SE-SMR experiments, the amount of catalyst used was 1/1 (w/w). The catalyst used for the SE-WGS experiments is a standard commercially available HTS catalyst, but the catalyst for the SE-SMR reaction is an expensive noble-metal catalyst. Moreover, the kinetics of the steam reforming reaction is rather slow at 400 °C even for these noble metal catalysts. The expense and required volume of catalyst for SE-SMR at 400 °C could actually prove to make the process highly unprofitable. Notably the amount of catalyst used in these laboratory scale experiments was much higher than needed to reach equilibrium under standard non-enhanced conditions. This is in shrill contrast to the SE-WGS case where less catalyst could be used than in the non-enhanced case.

In order to assess the possibility of using SE-SWG and SE-SMR under the process conditions expected in an industrial operation, an exercise in thermodynamics was carried out. Assuming that CO_2 could be removed to any desired level, and

the reaction gases reached equilibrium, the depth of CO_2 cleaning versus the theoretical conversion could be calculated. This is set out in Fig. 10. Firstly, considering the lab-scale SE-WGS experiments at 1 bar, for 90% conversion of the CO entering the reactor, the maximum allowable slip of CO_2 during adsorption-reaction is 3.8% (38,000 ppm). Carbon monoxide conversions of more than 99% are reached at a CO_2 slip of approximately 1000 ppm. This is very easily reached, and obviously why the SE-WGS experiments were successful. It may also offer an explanation for the observation that 99% CO conversion was reached, while the amount of catalyst present was not even enough to reach equilibrium. The overall reaction rate of the WGS reaction is slowed down when nearing equilibrium CO conversion (ultimately becoming zero when equilibrium is reached). Fig. 9 and Eq. (1) indicate that the equilibrium CO conversion is strongly influenced (i.e. shifted) by capturing the CO_2 . As a result, the rate of the reaction is almost not slowed down during the SE-WGS process and it becomes higher than when no CO_2 sorbent is present. In contrast, for reforming, CO_2 removal has a much smaller effect on the equilibrium CH_4 conversion [see also Eq. (2)] so that the overall reaction rate for reforming is enhanced less by the presence of a CO_2 sorbent.

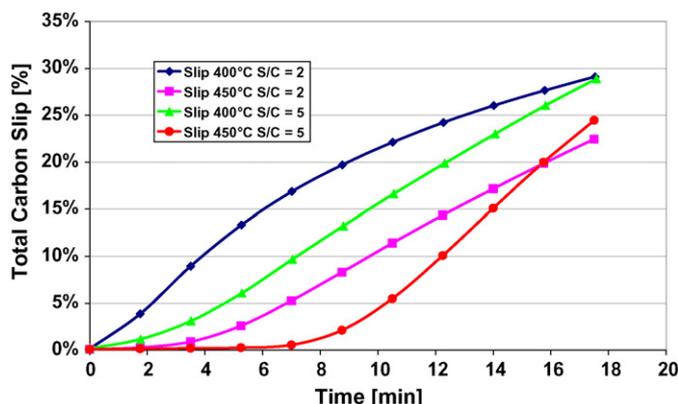


Fig. 9 – Percentage total carbon slip as function of. Flow = 100 ml/min, temperature = 400 and 450 °C, pressure = 1 bar, catalyst/sorbent ratio 1/1 (w/w), 3 g sorbent, CH_4 5.5%, H_2O 11%/27.5%, in N_2 .

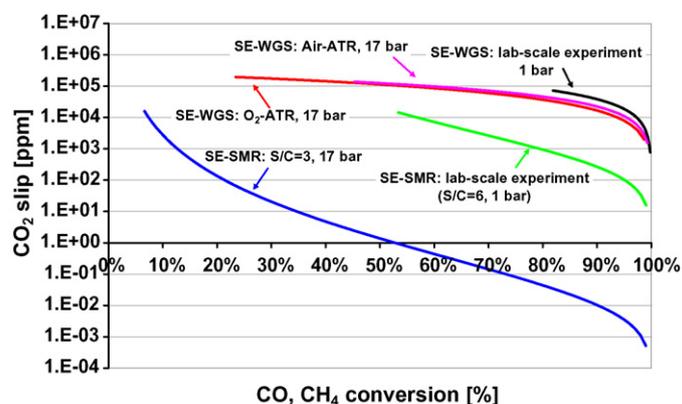


Fig. 10 – Concentration of CO₂ at output of a reactor at 400 °C, assuming equilibrium is reached in the gases above the catalyst and sorbent as a function of the conversion of CO or CH₄ for the SE-WGS and SE-SMR systems on laboratory scale, and on the scale envisaged in the systems study.

Using the two reaction mixtures in the system study for O₂-ATR-SE-WGS and Air-ATR-SE-WGS, which operate at 17 bar, the maximum concentrations of CO₂ allowed for 90% conversion are 1.6 and 2.1% respectively. This is a good indicator that the experiments performed in the laboratory will scale well to industrial scale. The story changes for the SE-SMR reactor. At laboratory scale, for 90% CH₄ conversion, the maximum allowable CO₂ concentration at the outlet of the bed during adsorption-reaction is 270 ppm. This is in good agreement with the levels of CO₂ seen in the relevant experiments. However, if the pressure is pushed up to that more likely to be used on an industrial scale, the depth of CO₂ cleaning increases dramatically to 10 ppb for 90% conversion.

The crucial question is if it is practically possible to get the concentrations of CO₂ low enough to still get sufficient conversion of CH₄. Coupled with the large amounts of catalyst needed, it would seem that SE-SMR at 400 °C with hydro-talcite-based materials might not be the best choice. Increasing the temperature at which the process occurs will help two-fold, in decreasing the amount of catalyst needed (or even allowing a switch to a more traditional catalyst), and leading to better conversion thermodynamically.

4. Conclusions

In a system study using hydro-talcite based materials for SE-WGS and SE-SMR, for CH₄ to electricity generation with the production of storage-ready CO₂, efficiency penalties are calculated of 5.5 percent point sorption-enhanced steam methane reforming to 8.6 percent point for sorption-enhanced water-gas shift downstream an oxygen-blow ATR. In the system evaluation at process pressure of 17 bar was used in the calculations. Coupling these systems to laboratory studies gave promising results at standard pressures. However, when increasing the pressure to that more likely to be used in an industrial environment, a much clearer picture emerges. The SE-WGS system scales well thermodynamically, and is certainly worth further investigation. Further development of the SE-WGS system is continuing at ECN in co-operations with Air Products in the EU-IP 6th framework project CACHET

(www.cachetCO2.eu). It has been shown that the sorption-enhanced reaction is so strong that it is even possible to use less catalyst than would normally be used just to reach equilibrium conversions. However, in the SE-SMR reactor, the required concentrations of CO₂ become prohibitively small as the pressure increases. While the SE-SMR system also deserves more investigation, the direction of research should be pushed towards increasing the temperature at which the process takes place. This will increase the lower limit on allowable CO₂ concentration and decrease the amount of catalyst needed to run the process. To this end, hydro-talcite materials may no longer be the most suitable materials for CO₂ adsorption unless they can be suitably stabilised at higher temperatures. There are of course other materials available for CO₂ capture at higher temperatures.

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