



7th European Framework programme:

Caesar: CArbon-free Electricity by SEWGS

Final publishable summary report

Objective

The overall objective of the CAESAR project was: Reduction of energy penalty and costs of the SEWGS CO₂ capture process through optimization of materials, reactor- and process design. It is emphasized that with an optimized SEWGS process CO₂ avoidance costs could be reduced to less than **15 Euro per ton CO₂**. The efficiency penalty is an important contributor to the capture costs and the steam use in the regeneration of the sorbent is a determining factor in the efficiency penalty. So the cost target was translated into a requirement for the overall steam/CO₂ ratio of 2 mole/mole, compared to a ratio of more than 4 mole/mole at the start of the project. The general objective is translated into several operational objectives for the different components of the SEWGS process.

The CAESAR project focussed on the application of the optimized SEWGS process for pre-combustion CO₂ capture from natural gas, but looked also into the possible application of the SEWGS process in IGCC power plants fed by coal or refinery residues, and blast furnace top gas in the steel industry.

WP1 (Materials development)

The objective of this WP is to develop an optimum sorbent/catalyst system for application in SEWGS based on syn gas derived from natural gas, coal, refinery residues, or blast furnace gas feeds. Based on the results of a previous FP6 project on the SDEWGS development a minimal steam use for purge and rinse flows of in total less than 2 mol steam / mol CO₂ and a sorbent lifetime of more than 3 years are the main development targets in the sorbent material development in the CAESAR project.

WP1 Deliverables

- Sorbent: chemically resistant, mechanically stable, minimized steam use on regeneration compared to standard K-HTC (proof at least 2000 cycles stable operation at steam/CO₂ ratio of less than 2).
- Catalyst: Stable catalyst/support under operating conditions, especially under minimal steam (proof at least 2000 cycles stable operation).

In the search for new or improved sorbent material two parallel development routs were followed:

- The first route was focused on improving both chemical as well as the mechanical stability of while minimising the steam use on regeneration of promoted hydrotalcite (K-HTC).
- The second route focussed on screening of new alumina based sorbent by using high by using high throughput techniques.

Improving the performance of promoted hydrotalcite (K-HTC) sorbent.

The CO₂ sorbent used at the start of the project i.e. promoted hydrotalcite (K-HTC) showed unexplainable behaviour in the CO₂ sorption cycle and in the regeneration of the sorbent with steam. This reference hydrotalcite sorbent (denoted as K-MG70) showed poor mechanical stability and increased CO₂ slip during long term testing under realistic conditions. It turned out that this was caused by the MgCO₃ formation which is a slow process. A new HTC sorbent with a lower Mg content (K-Mg30) was selected for long term testing in the single column unit. During bench testing this K-Mg30 (called ALASORB) sorbent showed good capacity so this sorbent was selected for long

term testing in the single column unit (See WP2 results). Although, the ALKASORB sorbent showed good overall performances, the techno-economic assessments showed that sorbent cyclic capacity must be increased with at least 50% (compared to the capacity of ALKASORB) with at least 50% in order to make the SEWGS process substantially cheaper than the more conventional capture technologies. In the final year, sorbent development resulted in a major breakthrough with respect to sorbent capacity. This ALKASORB⁺ sorbent has a 90% higher CO₂ capacity compared to ALKSORB and also uses less steam for the regeneration. Cost calculations performed (see showed that with the new sorbent, SEWGS can capture CO₂ at a price of around 25 Euro per ton CO₂ avoided (see WP4 results).

Catalyst testing

In conventional shift applications, the catalyst operates under reducing conditions. For application in a SEWGS process the catalyst should be able to withstand the oxidising conditions during the cycle, such as during the sorbent regeneration by steam. It should also remain active at the SEWGS operating conditions where only a limited amount of steam in the feed is present. According to the work plan, commercially available catalysts on supports were to be benchmarked at different temperatures and in the presence of actual CO₂ sorbents. However, during breakthrough experiments with promoted hydrotalcite under realistic conditions it was observed that even in the absence of a catalyst the carbon monoxide in the feed gas was completely shifted to carbon dioxide (see **Figure 1**). A stability test showed the stability of the sorbent working capacity as well as shift activity during 2000 cycles, at a minimal steam to carbon ratio (2 mole/mole). Hence, it was demonstrated that the SEWGS process does **not require a shift catalyst**, which brings substantial economic and technical benefits.

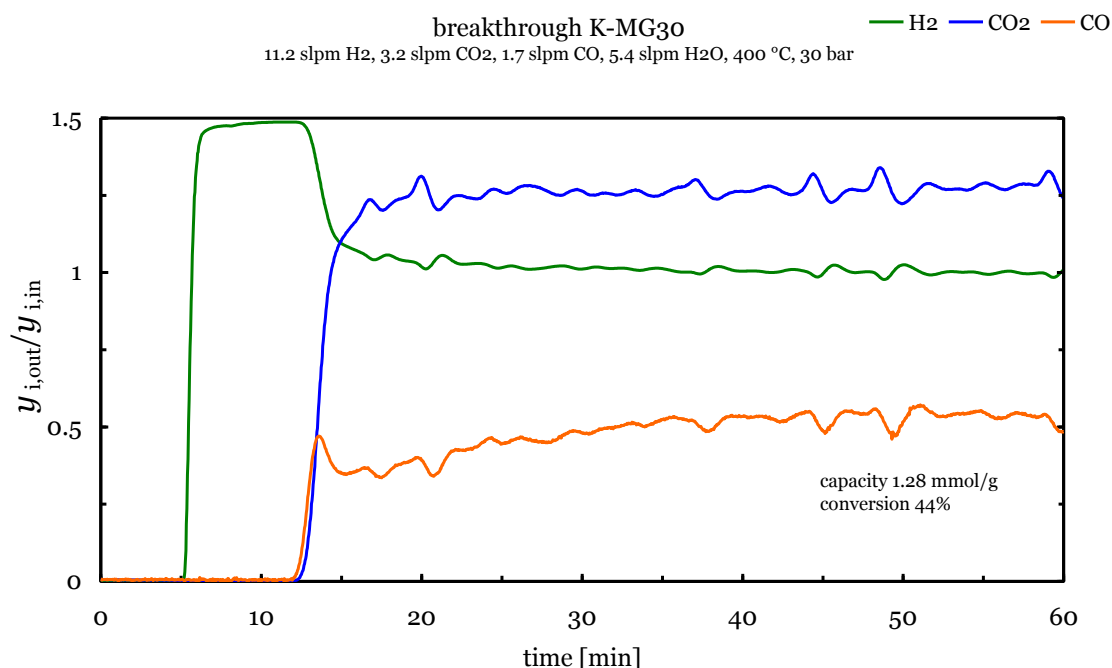


Figure 1: Breakthrough test of a K₂CO₃-promoted hydrotalcite at 400 °C in the SEWGS-1, showing the normalized composition of the top product as a function of time. *CO breaks through almost simultaneously with CO₂. Apparently, the sorbent is active for the shift reaction. After breakthrough conversion is 44%, which is somewhat below thermodynamic equilibrium. Shift activity before breakthrough is relevant for the SEWGS process.*

High throughput testing of new sorbents

In total 432 new sorbent formulations have been prepared, partly characterized and more than 300 sorbents have been evaluated under realistic conditions in a three cycle adsorption-desorption

test. From the evaluation, a comparison with the existing state-of-art sorbents has been made, and four leads have been selected for up-scaling and testing for sorption performance and particle stability under SEWGS conditions. However, none of these four sorbents performed sufficient to scale up the sorbent for testing in the single-column and multi-column test rigs.

WP2 Preliminary reactor design

The objectives of Work Package 2 are:

- The development of a SEWGS reactor model that is validated against experimental results.
- 2,000 cycles of stable operation of the single column unit at a steam/CO₂ ratio of less than 2 mole/mole and more than 95% CO₂ capture.

WP2 aimed at designing reactors for the SEWGS process. The work involved development of a model of the SEWGS process, which incorporated chemical kinetics, mass and heat transfer. Modelling was based on input from experiments on the single-column process development unit (PDU) built in the CACHET project. The model was used to design a SEWGS reactor. For applications in syngas from coal- or oil residue gasification, CO concentrations are relatively high, which means that the temperature increase due to the WGS reaction is also higher. For these applications the use of heat integrated reactors may be necessary. The task of modelling was assigned to Air Products, and the execution of experiments in the PDUs to ECN.

WP2 Deliverables

- Sorbent material, chemically resistant, mechanically stable, minimized steam use on regeneration compared to standard K-HTC developed and test in the single column test rig
- Creation of an experimentally validated single-column sorption-reaction model
- Publication on reactor modelling
- Publication on single-column experimental work
- Evaluation of alternative reactor designs for the SEWGS process

Performance differences single-column vs. multi-column rig

In the CACHET work, it was found that the results obtained for the SEWGS cycle in the multi-column rig was inconsistent with data collected in the single-column rig. The purpose of this task is to run experiments in the single-column to reconcile some of the differences between how these two units were operated and how much this may have contributed to the differences in performance. For example, the multi-column tests in CACHET were run at a higher purge pressure than in the single-column rig. It is difficult to reduce the purge pressure in the multi-column so additional single-column tests were run at higher purge pressure to see what effect this has on performance. The work led to identification of the most important factors that contributed to the differences in observed performance, and as such, the performance differences were resolved. As a consequence, we are able to predict the performance in the multi-column test rig from the observations in the single-column test rig, provided that the same cycles are applied in both test rigs.

Single-column PDU testing

The ALKASORB sorbent was tested under different process conditions to determine heat and mass transfer parameters for the sorption/reaction rates. All tests were performed in the absence of a separate water-gas shift catalyst. From breakthrough experiments at various CO₂ partial pressures, the adsorption isotherms could be approximated. Comparison of the adsorption isotherms showed that ALKASORB has a higher capacity than the sorbent tested previously. Furthermore, adsorption isotherms in the absence and in the presence of steam were measured and compared, indicating that steam may have a detrimental effect on the CO₂ adsorption capacity.

The catalytic activity for the water-gas shift reaction had been measured for both the ALKASORB and the previous sorbent, showing a markedly improved activity for ALKASORB. Small scale tests had indicated that the water-gas shift activity of ALKASORB may even be sufficient to leave out the

separate water-gas shift catalyst in a SEWGS reactor if the syngas contains 200 ppm H_2S . This was confirmed by performing breakthrough tests in the single-column test rig packed with sorbent in the absence of a catalyst, feeding a mixture of CO_2 , CO , H_2 and H_2O , without H_2S . Full CO conversion is obtained until CO_2 and CO started to break through simultaneously.

Cyclic experiments in the SC set-up were also run in order to be able to validate the reactor model. The long-term mechanical as well chemical stability of the sorbent was determined. This information was used to screen ALKASORB before it was tested in the multi-column in Work Package 3. It was demonstrated that the sorbent remained mechanically and chemically stable during operation of at least 1200 adsorption – desorption cycles (**Figure 2**). The cyclic capacity of ALKASORB was 27% higher than the cyclic capacity of the reference sorbent, which was used in CACHET. Moreover, 36% less steam was required for its regeneration. The sorbent pellets also had a 65% higher crush strength than the reference sorbent. Contrary to the reference material, the novel material did not form notable amounts of MgCO_3 under relevant operating conditions (**Figure 3**). Due to the absence of this slow CO_2 uptake process, the sorbent remains mechanically stable (**Figure 4**), the cyclic steady state was reached rapidly, CO_2 slip in the product gas was reduced, and steam requirements were lowered.

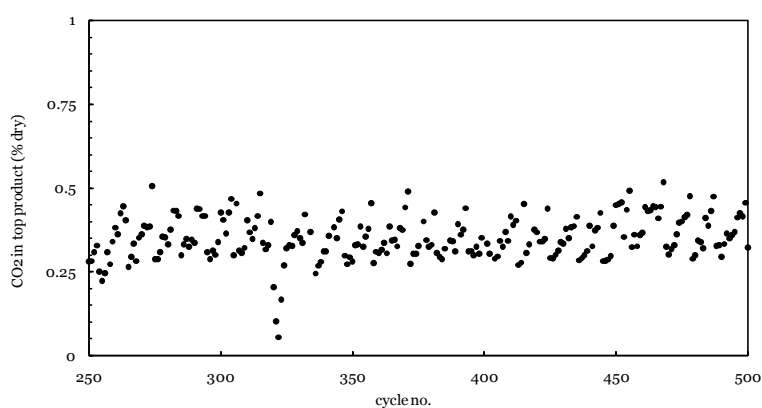


Figure 2 Cyclic stability of the carbon recovery using a steam rinse cycle.

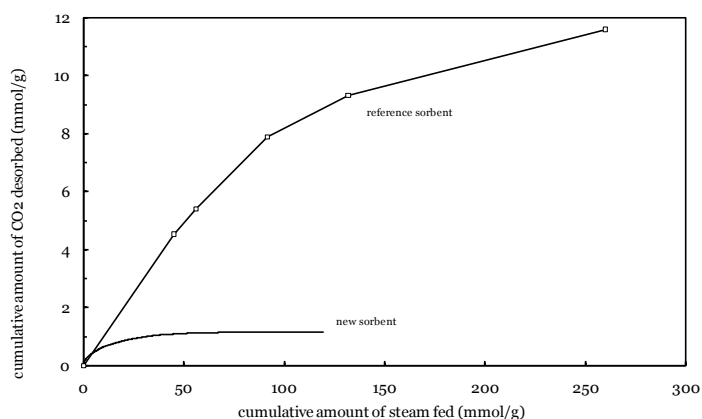


Figure 3 Regeneration of the new (ALKASORB) and reference sorbents, indicating that MgCO_3 formation occurs in the reference sorbent only.

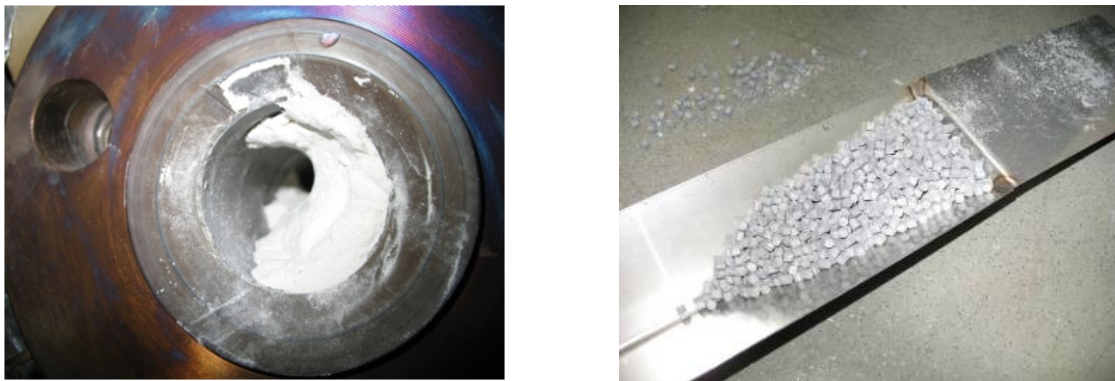


Figure 4 Sorbent unloaded from the reactor after more than 1200 cycles: (left) reference sorbent, fractured (right) new sorbent, mechanically stable.

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.

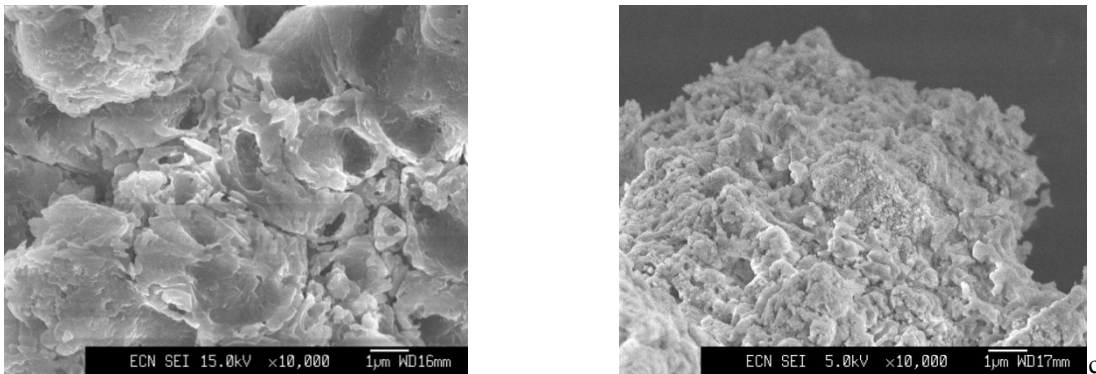


Figure 5 SEM pictures showing at least two different morphologies in the reference sorbent.

In later experiments, it was demonstrated that the sorbent remained mechanically stable during operation of at least 2000 adsorption – desorption cycles, and that the CO conversion and CO₂ slip remained constant as well. With this new, higher density material, carbon capture levels exceeding 95% can be obtained more efficiently and vessels will be smaller.

For testing of the cyclic SEWGS process in syngas from coal, refinery residues or blast furnaces, the test rig was adapted for operation using H₂S containing gases. Breakthrough and cyclic tests were performed in order to investigate the effects of H₂S on the sorbent capacity and stability. Observations confirm the earlier findings of small-scale studies that H₂S did not influence the CO₂ capacity significantly, and the H₂S is cocaptured together with the CO₂. A long-term test comprising 2000 cycles demonstrated that both the CO₂ sorption capacity and the CO conversion were stable for the duration of the test. In total over 7000 cycles have been achieved.

Reactor modelling

In this task a reactor model was developed from first principles that can match the data collected from the single-column test rig at ECN. This model was first used to understand the natural gas based SEWGS system, and then extended to include other adsorbates in coal-based feeds. Experimental results from WP1 were used to provide an understanding on a number of sorbent materials of interest. These results were combined with heat and mass transfer parameters obtained from single-column breakthrough tests to enable a new physical model to be put together for the SEWGS process. The final model was compared against cyclic tests in the single-column test rig to verify and enhance its

predictive capabilities. The model developed provided a basis for a tool created in WP3 in which more complex cycles were analysed.

By combining experimental data collected in WP1 and WP2, **Figure 6** shows pure component isotherms that were generated for both CO₂ and steam at 400 °C. When present together in the gas phase, CO₂ and steam were found to interact on the sorbent and affect the equilibrium capacity of each other. The experimental work carried out under CAEASR has allowed this factor to be evaluated and also be incorporated into the model.

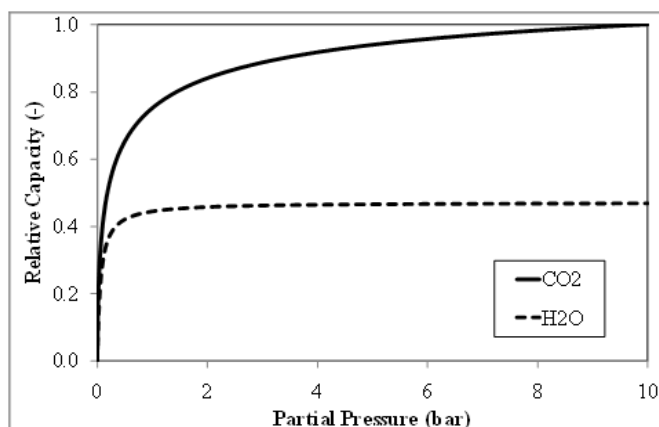


Figure 6 Pure component isotherms for CO₂ and steam at 400 °C

There is a rapid change in the sorbent capacity for both CO₂ and steam for low partial pressures (less than 1 bar), but this flattens out noticeably at higher partial pressures. From a cycle design perspective, the fact that the sorbent capacity for steam is essentially constant over a wide range of partial pressures is beneficial. This limits the amount of steam that is taken up or desorbed from the material over the course of a cycle and the dynamic capacity for steam effectively becomes zero. Unfortunately, in order to achieve a large cyclic capacity for CO₂, the partial pressure in the gas phase must be decreased to a significantly low value to facilitate effective removal. This is achieved in the pressure-swing SEWGS process by reducing the total system pressure for regeneration and supplying purge gas (i.e. low-pressure steam) to further reduce the CO₂ partial pressure and maximize the driving force for desorption.

The plots shown in **Figure 6** are for equilibrium conditions, but SEWGS is dynamic in nature and simulation of the entire process also requires a kinetic model to describe the rate of uptake of steam and CO₂ on the sorbent. For this, a linear driving force model has been employed using empirical rate constants derived from matching breakthrough and cyclic data. Using both the equilibrium and kinetic information for the sorbent material, a full model for the SEWGS process has been developed that solves the coupled mass, momentum and heat balances for every step in the cycle. This can be applied to different feed conditions to help determine the vessel size and steam requirements to meet a given process specification.

Modelling of the ALKASORB Sorbent for the Sorption-Enhanced Water-Gas-Shift (SEWGS) Process

For the ALKASORB sorbent a model is created to simulate its performance. Breakthrough tests and cyclic experiments in both a single column and multi-column apparatus have been used for comparison. The model enables fast evaluation of the technology under different design scenarios and the results have been used to estimate performance on a commercial scale. Optimisation studies have been performed using the model to evaluate the behaviour of the SEWGS process under different designs and operating conditions. With the model matched reasonably well with the experimental data, the tool was used to predict the performance of commercial size units to allow an estimate of sizing and operating cost. Different cycles were investigated of which the counter-current steam-rinse cycle shown in Figure 7 is an example. This cycle varies from that practiced in the multi-column test

rig simply in the introduction of pressure equalisation steps to reduce losses of H₂ and pressure energy. Coupling of the model with full power plant sizing and costing shows that the optimised SEWGS process substantially lowers the cost of electricity when CO₂ emissions must be minimised.

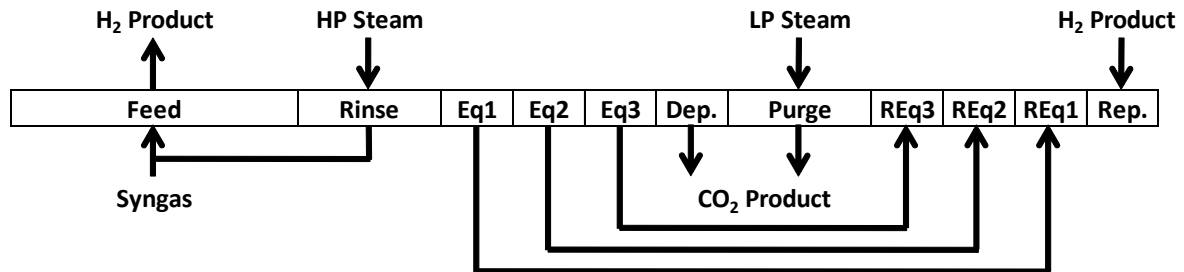


Figure 7 – Example Full-Scale Counter-Current Steam Rinse Cycle

Alternative reactor set-ups

In CACHET, a number of different cycle designs were put together for a fixed bed sorption system. As an extension of this work, alternative sorption/reactor systems and alternative arrangements were evaluated in this task to see if these could bring additional benefits (cost savings) versus the fixed bed approach. Advantages and disadvantages of each were determined.

WP3 Advanced reactor design

The objectives of Work Package 3 are:

- Incorporation of the SEWGS cycles in the SEWGS simulations and experimental validation using the multi-column PDU.
- Using this model to develop a SEWGS process cycle with a total steam/CO₂ ratio of 2 mole/mole.
- Experimental demonstration of the cycle on the multi-column test rig.
- Development and demonstration of the cyclic SEWGS process for application in coal gas and blast-furnace gas.

Figure 8 shows an example of a pressure-swing cycle in which 8 vessels containing packed beds of sorbent are used to continuously process a feed syngas, whilst producing a CO₂-rich product stream. WP3 focused on the design and testing of the cyclic SEWGS process. The multi-column test-rig from CACHET was adapted for novel cycles designed by the model. ECN performed experiments using input gas compositions from the various targeted applications.

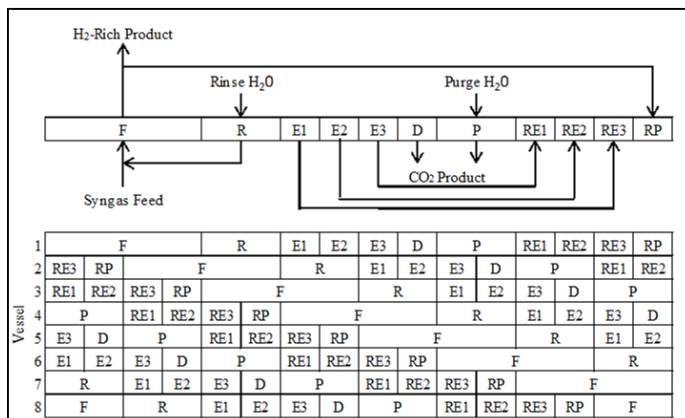


Figure 8 Example of a SEWGS cycle with above the pressure level during the steps.

Key: F = Feed, R = Rinse, E = Equalization (pressure reducing during step), D = Depressurization, P = Purge, RE = Equalization (pressure rising during step), RP = Repressurization

WP3 Deliverables

- Experimental results on SEWGS using the multi-column test rig
- Cyclic SEWGS process model validated with multi-column data
- SEWGS cyclic process model applied to a new sorbent

Adaptation of MC test rig

For testing of the cyclic SEWGS process in syngas from coal, refinery residues or blast furnaces, adaptation was necessary, including adaptations and addition of mass flow controllers in the feed section. Also, based on the CACHET testing, changes were necessary to improve the accuracy and reliability of the multi-column rig.

Multi-column troubleshooting tests

In the CACHET work, it was found that the results obtained for the SEWGS cycle in the multi-column rig seemed to be inconsistent with data collected in the single-column rig. The aim was to determine the differences between the single- and multi-column rigs and evaluate the impact of each on performance. Examples investigated include: bed length, flow rate, pressure, equalisation rate and other cycle steps. The tests led to an understanding as to what factors may have led to differences in performance so that these factors could be accounted for in the modelling. This work also led to a greater confidence in the accuracy of the data collected from the multi-column rig.

Multi-column experiments: new cycles and new applications

After having qualified the ALKASORB materials in the single-column, it was loaded in the multi-column rig. Gas compositions for multiple applications (natural gas, coal gas, blast furnace gas) were tested in the multi-column rig. The aim was to support the modelling work and show that SEWGS cycles can be developed that are economically viable. The tests also showed the effects of the most important operating conditions and the effects of feed composition under realistic conditions. The testing program comprised adsorption (breakthrough) tests, desorption tests, and cyclic tests. Breakthrough tests confirmed that the CO₂ adsorption capacities observed in the multi-column rig were similar to the capacities observed in the single-column test rig. Desorption tests revealed the presence of kinetic limitations during purging. Knowledge of the desorption rates may help to optimise the sorbent regeneration strategy.

Cyclic tests demonstrated that the process reaches quasi-steady state operation in a few cycles, in contrary to the sorbent material tested in the CACHET project, where it could take a few hundred cycles before quasi-steady state operation was obtained. The ALKASORB sorbent is thus suited for performing tests and quality control. The tests showed that the CO₂ stream purity was sensitive to the amount of rinse gas. The effect of the amount of rinse gas became noticeable in the H₂ stream purity when a reactor was overrinsed: carbon would then slip through without improving the CO₂ stream purity. The cyclic tests also showed that with the ALKASORB sorbent a steam-to-carbon ratio below 2 mole/mole is feasible, which is a reduction by 50% compared to the reference material. Tests with various syngas feeds show that the sorbent contained sufficient activity for the water-gas shift reaction that a separate water-gas shift catalyst was not required without substantial slip of CO in the H₂ product gas. Furthermore, very pure H₂ product gas could be obtained, at the expense of decreased cyclic capacity. Purities exceeding 99.99% were demonstrated, which may be relevant for gas purification applications of SEWGS, such as hydrogen production. In **Figure 9** the pressure swing cycles are clearly visible.

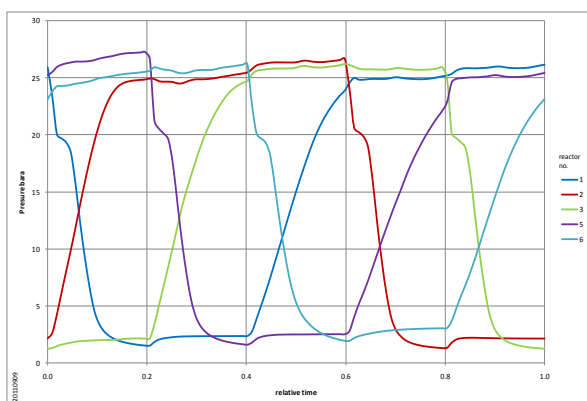


Figure 9 Reactor pressures over time in cyclic operation

Multi-column SEWGS cycle modeling

Using the experience with conventional PSA units along with the fundamentals learnt from the single-column tests at high temperature, Air Products created an updated model for the SEWGS process. Experimental data from the multi-column rig was used to validate the model and enabled corrections to be made for those steps in the cycle that were not present in the single-column tests.

The composition of the syngas derived from a feedstock of natural gas or coal is notably different, and depends on the constituents of the fuel as well as the technology employed to produce the syngas. Within CAESAR, process design work on natural gas is based on an air-fired GHR-ATR combination (gas heated reformer-autothermal reformer). Similarly the performance of a SEWGS unit in an IGCC uses a Shell gasifier with bituminous coal. After reforming/gasification, the syngas is passed through a first water-gas-shift reactor. Whilst the SEWGS unit is capable of carrying out the water-gas-shift reaction, it is preferable to have the bulk of this work done in a separate unit as the resulting temperature increase due to the exothermic reaction negatively impacts the uptake of CO₂ on the sorbent material. The composition of the syngas after the water-gas-shift reactor, which is then fed into the SEWGS unit is given in **Table 1**.

Table 1 Feed syngas compositions to the SEWGS unit depending upon feed type used

		Natural Gas Feed	Bituminous Coal Feed
CO ₂	mol %	11.65	23.71
CO	mol %	5.01	5.64
H ₂	mol %	42.40	35.56
H ₂ O	mol %	8.43	30.88
Others (e.g. N ₂ , Ar, CH ₄ , H ₂ S)	mol %	32.51	4.21

The compositions given are simplified to the major components in the feed used in the subsequent analysis. The most important difference between the two compositions is the substantially higher CO₂ content of the coal derived syngas. This increases the challenge for the SEWGS process as the H₂/CO₂ ratio strongly affects the amount of sorbent material required.

There are a large number of parameters that can go into the design of a SEWGS process including feed conditions, regeneration pressure, steam rinse and purge flow rates, cycle time, vessel size, number of parallel trains. In the following analysis the cycle time, vessel size and number of trains were all kept constant. The cycle design chosen was equivalent to that shown in Figure 8 (although with different numbers of equalization steps) and the feed operating temperature was fixed at 400 °C. The rinse and purge flow rates were then varied for different pressures, feed compositions and equalization steps to obtain a combined CO₂ and CO capture rate of 95% with a CO₂-product purity of 95%.

In general, the modelling work shows that increasing the rinse gas flow rate results in an improved CO₂-product purity as it pushes more of the H₂-rich gas out of the beds after the feed step. However,

this also results in part of the adsorbed CO_2 being removed from the vessel before the regeneration step and added back into the feed. Therefore, adding more rinse gas has the detrimental effect of increasing the sorption challenge for the SEWGS process, thereby decreasing the capture rate. The carbon capture rate can be improved by increasing the amount of purge steam used as this desorbs more CO_2 from the sorbent, allowing more CO_2 to be adsorbed during the feed step for the same cycle time. However, adding too much purge gas ultimately results in an decrease in CO_2 purity given a fixed cycle time and vessel size. This is because increasing the adsorbent capacity decreases the average partial pressure of CO_2 inside the vessel at the end of the feed step. This allows more H_2 -rich gas to be present inside the vessel which must be removed by rinsing or otherwise it will contaminate the CO_2 product. The overall result therefore is that the flows of rinse and purge gas must be balanced against each other to achieve the required carbon capture rate and CO_2 purity.

Natural Gas Case

Figure 10 and **Figure 11** show the effect of varying the feed pressure and number of equalization steps on the amounts of high pressure steam rinse and low pressure steam purge required for a natural gas derived feed stream. These results are based on the ALKASORB compound and are presented in terms of the steam flow required per unit of feed flow.

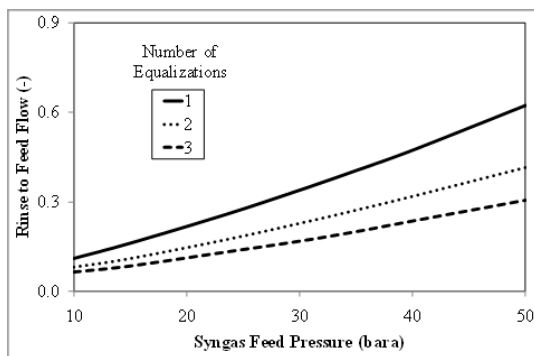


Figure 10 Rinse steam requirements for a natural gas feed at 95 % carbon capture and CO_2 purity

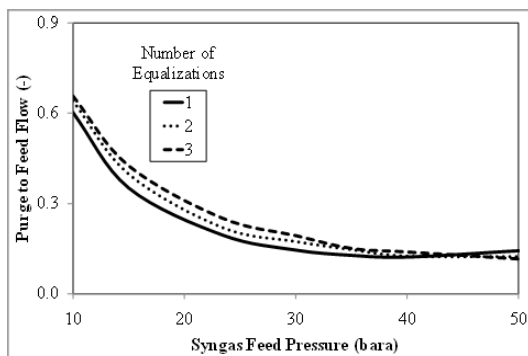


Figure 11 Purge steam requirements for a natural gas feed at 95 % carbon capture and CO_2 purity

The amount of rinse steam required reduces by decreasing the feed pressure and/or increasing the number of equalization steps. A higher feed pressure results in a greater inventory of gas inside the vessel at the end of the feed step. Therefore more rinse gas is required to displace the residual H_2 containing gas to reach the 95% CO_2 purity specification. Adding equalization steps is also beneficial because not all the H_2 -rich gas must be displaced during the rinse step itself. Instead, during each equalization step residual H_2 -rich gas is removed and recaptured in a vessel being pressurized before the feed step. This reduces the amount of H_2 and other contaminants left inside the vessel before regeneration. Using more equalization steps results in a marked reduction in the rinse gas requirement, without significantly increasing the purge gas amount. However, to incorporate an increased number of equalization steps into a cycle, more vessels are required and this therefore increases capital cost. It is found that the purge gas requirement generally increases as the feed pressure falls and/or more equalization steps are used. At the lowest feed pressures there is a large

purge requirement because the maximum achievable capacity falls dramatically due to the reduced feed CO₂ partial pressure (see **Figure 6**). As the maximum achievable CO₂ capacity on feed drops, then the adsorbent must be more thoroughly regenerated during the purge step to maintain a similar dynamic capacity to the higher feed pressure cases. The increase in purge gas requirement with the number of equalization steps is mostly due to the fact that during each equalization step, the most easily removed CO₂ is put into another vessel being pressurized. This not only reduces the amount of CO₂ that can be removed during the subsequent regeneration step (i.e. the driving force for CO₂ removal goes down) but also preloads a regenerated bed with CO₂ so that it has less capacity available for the feed step. Therefore more purge gas is required to counteract these effects and achieve the same dynamic capacity.

The amounts of rinse and purge steam shown in **Figure 10** and **Figure 11** are not absolute requirements and can be changed by modifying the vessel size, cycle time and/or cycle arrangement. The value placed on the high pressure steam used for rinsing is obviously greater than the low pressure steam used for purging, so it is only through a full process optimization that the actual amounts of each to be used can be determined. However, the results indicate that the optimum design for a SEWGS unit is probably towards the middle of this pressure range, 20-30 bara. Operating at higher pressures results in a substantial increase in rinse gas requirement for no improvement in overall performance, whilst at lower pressures the purge gas requirement increases markedly. Fortunately, this pressure range matches well with feeding directly into a gas turbine. For the conditions used in this particular analysis, the 20-30 bara range with 3 equalization steps gives required rinse steam to feed carbon ratios of 0.65-1.00 and similar 1.55-1.15 for purge steam (i.e. a total steam to feed carbon ratio of 2.15-2.20 versus a goal of 2.0).

Coal Case

In the same manner as for natural gas, an analysis on steam purge and rinse flow rates was carried out with a coal-derived syngas feed. The only difference between the two cases in terms of input was that the adsorbent volume was doubled to accommodate the greater CO₂ challenge for the same cycle time. This is because as can be seen from **Figure 6** that the capacity of the sorbent does not increase linearly with the partial pressure of CO₂ in the feed, and is almost flat at high partial pressures. Therefore the amount of adsorbent required to remove the CO₂ in the feed gas must be increased roughly in proportion to that in the syngas.

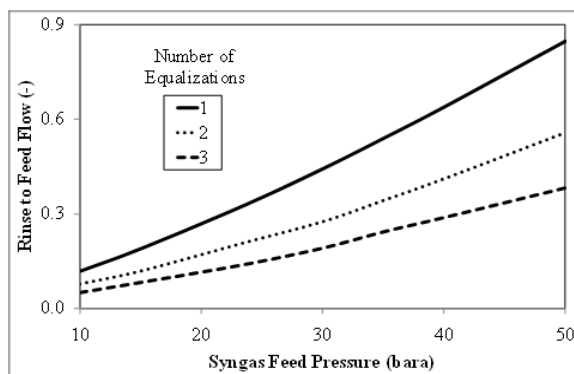


Figure 12 Rinse steam requirements for a coal feed at 95 % carbon capture and CO₂ purity

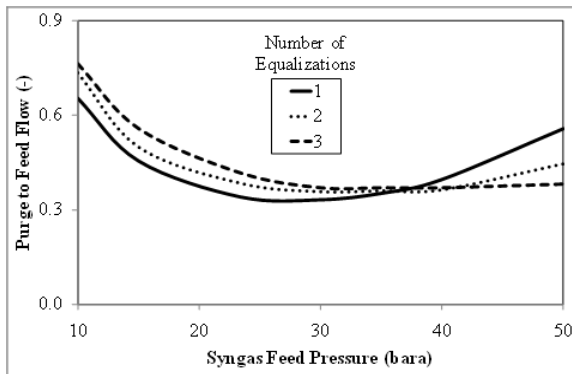


Figure 13 Purge steam requirements for a coal feed at 95 % carbon capture and CO₂ purity

In **Figure 12**, the trend for the amount of rinse gas required in the coal case is the same as for the natural gas case. However, for all conditions more rinse gas per unit of feed gas is required for the coal case because the amount of sorbent was increased, which leads to more H₂-rich gas being present inside the vessel after the feed step. However, the rinse gas required does not double in-line with the increase in adsorbent as the higher CO₂ and steam partial pressures in the feed syngas reduce the residual quantity of H₂ inside the vessel. The purge gas requirement in **Figure 13** follows some of the same trends as for the natural gas case, with the flow rate increasing at the lower end of the feed pressure range. However, for one and even two equalization steps, there is also an increase in purge gas requirement at the upper end of the feed pressure range. The upturn in purge gas flow rate coincides with the rinse gas flow rate increasing above 40% of the feed flow (as shown in **Figure 12**). As with the natural gas case and the optimum feed pressure range appears to be 20-30 bara. This leads to a ratio of steam rinse to carbon in the feed of 0.40-0.65 and similarly a purge steam requirement of 1.50-1.25 (a total steam to carbon ratio of 1.90). Compared with natural gas, this gives a lower steam to carbon ratio, primarily due to a reduction in the requirement of rinse steam to feed carbon. However, the size or number of vessel used for the coal case must be doubled to achieve these results. This is a notable increase in capital cost that must be factored into the economic analysis for using SEWGS with a coal based feed.

The model was used in Work package 4 to develop the most efficient fixed bed cycles for SEWGS in various applications (natural gas, coal, etc.).

WP4 Application and process integration

Development of flow sheet models and costing tools for the new SEWGS set-up for natural gas fired power generation and for coal gas and industrial applications (refinery residues gasification and blast-furnace gas). SEWGS system with an efficiency penalty of less than 5% point and capture costs of 15€/ton CO₂ compared to the CACHET base case i.e. NGCC with ATR-WGS-CO₂ separation & compression or an IGCC with WGS and separation & compression.

WP4 Deliverables

- European bench marking task force (EBTF) and bench mark common frame work definition document to be used in the three EU PF7 RTD projects on capture technology development i.e. CESAR, CAESAR and DECARBit;
- Development (in the framework of the EBTF task force activities) of the reference base case for the SEWGS application in a Natural Gas Combined Cycle (NGCC) power plant, in an Integrated Gasification Combined Cycle (IGCC) power plant and finally in a Blast Furnace gas Combined Cycle power plant
- Techno economic assessments of the SEWGS capture process in NGCC, in IGCC and BFCC including several peer reviewed publications

European Bench mark taskforce (EBTF) and reference base case

The EBTF is a team of participants of three CCS R&D projects, which are DECARBit, CAESAR and CESAR. In their framework document the EBTF defines a set of parameters to be applied to the study of CCS technologies in these three projects and in future European CCS R&D projects. Such parameters are related to ambient conditions, fuels, gas separation, coal gasification, shift reaction, gas turbine, steam cycle, heat exchangers, efficiency calculations, emission limits and economic assessment criteria. Its purpose is to serve as a basis for cycle definition, cycle analysis, comparison of different technologies and comparison of economic evaluations, making such comparisons consistent and reliable, by being based on the same set of fundamental assumptions. It builds on previous work carried out in FP6 projects, in particular ENCAP, DYNAMIS, CASTOR and CACHET. The report begins with the very basic selection of unit system and ambient conditions. It then describes the characteristics of three types of fuel: Bituminous coal, Lignite and Natural Gas. As the objective of the projects of interest is to study the technologies of power generation, the authors think that three standard compositions are sufficient. After these definitions, the report describes the choice of parameters for a number of modules or processes of the power plants objective of study. Such modules and processes are air separation, coal gasification, shift reaction, gas turbine, steam cycle and heat exchangers. Then more general issues are defined: the procedure for efficiency calculation, CO₂ treatment and emission limits from solid fuels. Finally, criteria for economic assessments of new technologies and cycles are established.

Within the framework of the EBTF the reference base cases for the SEWGS technology were defined. For the NGCC the reference base case is the post combustion capture, whereas the reference base case for IGCC is pre combustion with SELEXOL. These two reference cases were defined and approved by the industrial partners in the EBTF (Shell, Alstom, E.ON and Shell). The results of the reference base cases are summarized in **Table 2** and **Table 3**

Techno economic assessments of the SEWGS capture process in NGCC, in IGCC and BFCC

The techno economic assessment for the SEWGS application in NGCC and IGCC are based on the results of the extensive ALKASORB testing in both the single column and multi column test rig and the SEWGS cycle optimisation and cost estimates. The results are summarised in Table 2 and Table 3.

In the final year work to improve the capacity of AKASORB sorbent continued and resulted in a improved sorbent (ALKASORB⁺) with a substantial higher capacity. Therefore, the techno – economic assessments for the SEWGS application both natural gas and coal fuelled power plants have been up-dated in the final month of the project (see Table 2 and Table 3).

SEWGS application in NGCC

Calculated cost of electricity and cost of CO₂ avoided for SEWGS in NGCC and the reference NGCC cases are summarized in **Table 2**. The cost of electricity (COE) for NGCC without CO₂ capture is 54.10 €/MWh. The COE depends on fuel costs (as typical of NG based power plants), while the sum of fixed and variable costs accounts for less than 10%. In the CO₂ capture case, COE increases 15-20 €/MWh as consequence of the higher investment costs and lower efficiency which leads to higher specific fuel consumption. The calculated cost of CO₂ avoided for MEA and MDEA cases are 47.5 €/t_{CO2} and 63.8 €/t_{CO2}.

Table 2: Cost of Electricity and Cost of CO₂ avoided for two SEWGS cases and for two reference NGCC cases.

Plant Component	NGCC No cap	NGCC with MEA	NGCC with MDEA	SEWGS ALKASORB	SEWGS ALKASORB+
SEWGS CCR/CO ₂ purity	-	-	-	95/99	95/99
Net Power Output, [MW]	829.9	709.7	830.0	791.3	797.95
Thermal Power Input _{LHV} , [MW]	1422.6	1422.6	1651.0	1552.1	1547.9
Net Electric Efficiency (LHV base), [%]	58.34	49.90	50.30	50.70	51.55
CO ₂ avoided, [%]	-	88.3	91.5	91.1	91.4
SPECCA [MJ _{LHV} /kg _{CO2}]	-	3.36	3.07	2.90	2.53
Specific costs, €/kW	630.4	969.9	1280.6	1169.6	1069.4
COE, [€/MWh]	54.10	69.10	74.63	72.87	69.85
Cost of CO₂ avoided [€/t_{CO2}]	N/A	47.5	63.8	58.6	49.0

The cost of electricity (COE) for NGCC without CO₂ capture is 54.10 €/MWh. The COE depends on fuel costs (as typical of NG based power plants), while the sum of fixed and variable costs accounts for less than 10%. In the CO₂ capture case, COE increases 15-20 €/MWh as consequence of the higher investment costs and lower efficiency which leads to higher specific fuel consumption. The calculated cost of CO₂ avoided for MEA and MDEA cases are 47.5 €/t_{CO2} and 63.8 €/t_{CO2}. The cost of CO₂ avoided for the MEA case is lower compared to similar studies in the literature, however it can represent advanced solution amine scrubbing.

For the SEWGS cases, the number of SEWGS vessels and the vessel heights were optimised with respect to lowest levelised costs. SEWGS with ALKASORB has a cost of CO₂ avoided lower than reference pre-combustion technology (58.6 €/t_{CO2} vs. 63.8 €/t_{CO2}), but 9 €/t_{CO2} higher compared to post-combustion technology. This is because the higher electric efficiency and CO₂ avoided rate of SEWGS does not compensate the additional costs of pre-combustion lay-out; in addition to the SEWGS unit also a reformer section is necessary negatively affecting specific investment costs.

The use of the improved ALKASORB⁺ sorbent reduces the cost of CO₂ avoided to 49 €/t_{CO2} (see Table 2) which close to the post combustion MEA case. Results showed that for the SEWGS cases, CO₂ purity has a negligible impact from a economic point of view, thus higher CO₂ purity is preferred to reduce transport and storage issues related to the CO₂ quality. Since ALKASORB⁺ requires much less steam, the specific energy consumption (SPECCA) is substantially reduced to 25% below the specific energy consumption for the MEA post combustion technology (2.53 versus 3.36 MJ_{LHV}/kg_{CO2}).

SEWGS application in IGCC

Calculated cost of electricity and cost of CO₂ avoided for SEWGS in IGCC and reference IGCC cases are summarized in Table 3. The COE for the reference case IGCC is about 66 €/MWh. More than 50% of the COE depends on the investment costs, while fuel costs account for about 35%. This result is typical for coal based plants, while natural gas based plants have an opposite trend. COE for the CO₂ capture cases increases 35% because of the higher investment cost as well as higher fuel costs. The resulting cost of CO₂ avoided is 36.5 €/t_{CO2} which is in the range of similar studies proposed in literature supporting the reliability of this analysis.

Table 3: Cost of Electricity and Cost of CO₂ avoided for the two SEWGS case and for the reference IGCC cases

	IGCC	SELEXOL	SEWGS ALKASORB	SEWGS ALKASORB+
SEWGS CCR/CO ₂ purity	-	-	95/99	95/99
Net Power Output, [MW]	425.7	383.5	396.8	404.4
Thermal Power Input _{LHV} , [MW]	896.5	1053.5	1020.6	1018.8
Net Electric Efficiency (LHV base), [%]	47.5	36.4	38.9	38.5
CO ₂ avoided, [%]	--	86.6	92.8	93,7
SPECCA [MJ _{LHV} /kg _{CO2}]	--	3.67	2.49	2.06
Specific costs, €/kW	2077.1	2854.7	2771.1	2586.4
COE, [€/MWh]	65.81	88.74	86.71	81.53
Cost of CO ₂ avoided [€/t _{CO2}]	--	36.5	31.0	23.3

The cost of electricity for reference IGCC is about 66 €/MW_h. More than 50% of the COE depends on the investment costs, while fuel costs account for about 35%. This result is typical for coal based plants, while natural gas based plants have an opposite trend. COE for the CO₂ capture cases increases 35% because of the higher investment cost as well as higher fuel costs. The resulting cost of CO₂ avoided is 36.5 €/t_{CO2} which is in the range of similar studies proposed in literature supporting the reliability of this analysis.

The application of SEWGS ALKASORB in an IGCC allows reducing the cost of electricity to about 86 €/MWh i.e. 2.5% less than in the SELEXOL case. The avoidance rate of SEWGS ALKASORB is however, over 6% points higher. SEWGS reduces investment and also the fuel costs due to the co-capture of sulphur and consequent equipment costs savings, and higher efficiency. Only consumables, which mainly depend on sorbent replacement, are higher. With the new ALKASORB⁺ sorbent the COE is reduced to 81,5 €/MWh. Accordingly, the cost of CO₂ avoided is reduced to approx. 23 €/t_{CO2} which is a reduction of more than 30% compared to the SELEXOL capture case.

Application of SEWGS in blast furnace fuelled combined cycles

Next to the NGCC and IGCC application the application of SEWGS for in a blast furnace combined cycle was assessed. The first step consisted of developing reference cases for this application and it is based on EBTF common framework definition document. Considering that blast furnace gas has a low heating value (both from volumetric and mass flow point of view), a dedicated gas turbine design was taken into account and no significant penalties for this application have been applied. The resulting efficiency is 52.4% with specific emissions of 1.3 kg_{CO2}/kWh, that's about twice coal plant and four times NGCC applications.

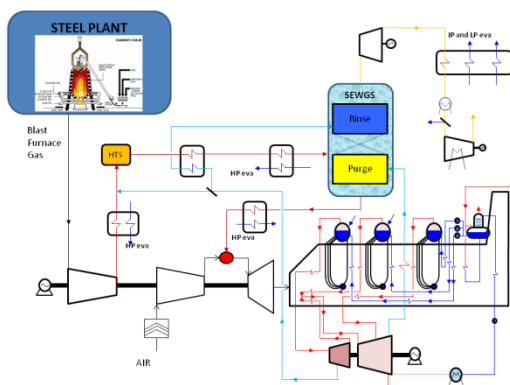


Figure 14: SEWGS integration in blast furnace application

Next, a reference case with CO₂ post combustion capture was performed: CO₂ capture was based on amine technology with ancillaries consumption specifically calculated (the higher CO₂ content in the exhaust gas slightly reduces the specific heat duty for MEA regeneration). Because of the large CO₂ mass flow compared to the heating value, the steam produced in the HRSG is enough only to capture part of the CO₂ even with the adoption of a back pressure turbine plant. Efficiency penalties are in the range of 18 -20% depending on natural gas addition. Performances of cases investigated (see **Table 4**) show that SEWGS reduces Specific Energy Consumptions for CO₂ avoided (SPECCA) with about 70% compared to reference MEA case due to the higher CO₂ avoided rate.

Table 4: Preliminary results SEWGS integration in blast furnace plants

	No capture	MEA	SEWGS
Net Electric Efficiency [%]	52.3	38.7	34.9
CO ₂ specific emissions [g/kWh]	1334.6	870	145
Carbon Capture [%]	--	34.8	89.2
SPECCA [MJ/kg _{CO2}]	--	5.23	2.88

WP5 Process scale-up

The objectives of Work Package 5 are:

- Make a choice, based on the outcome of WP 4, for what application the design will be made.
- Understand the key technical risks of this technology at full scale deploy, and develop the objectives of a pilot plant program that will provide full mitigation.
- Deliver the critical aspects of a Process Design Package for a pilot plant for one of the applications studied, with specific focus on the vessel design and switching valves.

In this WP5 the requirements and objectives of a pilot plant were defined. This information was used as basis to evaluate a number of potential host sites for the pilot unit. Previous work had highlighted that critical design work was needed to include the mechanical design of the vessel and to ensure availability of suitable high temperature, high differential pressure valves which are able to operate reliably with good isolation characteristics over multiple cycles.

Since a suitable site could not be selected in time (originally planned at the last quarter of 2010), site-specific issues could not be taken into the design. Hence, a more general design approach was taken, enabling the work to remain valid should the site selection be re-evaluated at a later date. The generic design issues addressed included the design and costing of the reactor vessels, valve availability, and a general HSE review.

WP5 Deliverables

- Pilot plant scope of requirements and objectives
- Optimised flow sheet with configuration of vessels and switch valves
- Mechanical reactor design for pilot plant
- High temperature valve availability from suppliers
- Learning's from the design, construction and operation of a multi-column unit

SEWGS applications

The SEWGS process has distinct characteristics for separating CO₂ and hydrogen, giving the potential to improve the efficiency and lower the cost of CO₂ capture. The relative merits of these characteristics will affect the value of the integration of the process compared with the state of the art. Analysis of the SEWGS characteristics suggested that the application to combined cycle power production (NGCC, IGCC and BF-CC) remains the most likely application for the SEWGS

technology. Other applications investigated appeared to be less obvious with likely lower economic benefits.

Requirements and objectives

On basis of the conclusion that the highest economic benefits for the SEWGS pre-combustion capture technology in the power generation is either a natural gas fuelled combined cycle combined cycle (NGCC), a coal gas fuelled combined cycle (IGCC) or a blast furnace gas combined cycle (BFCC), the scope of requirements and objectives for a SEWGS pilot plant were established.

The SEWGS technology was evaluated using NASA's technology readiness level methodology. By the end of 2010, the SEWGS process was classified on level 5 – 6, as shown in **Figure 15**. At the end of the CAESAR project (December 2011) SEWGS development was ready to move to the next development level, which is a pilot plant installation of which the capacity is on the order of 100 times larger than the current multi-column Process Development Unit, but still on the order of 100 times smaller than a commercial scale installation. This pilot plant must use real fuel gas to demonstrate long term stability of the ALKASORB sorbent.

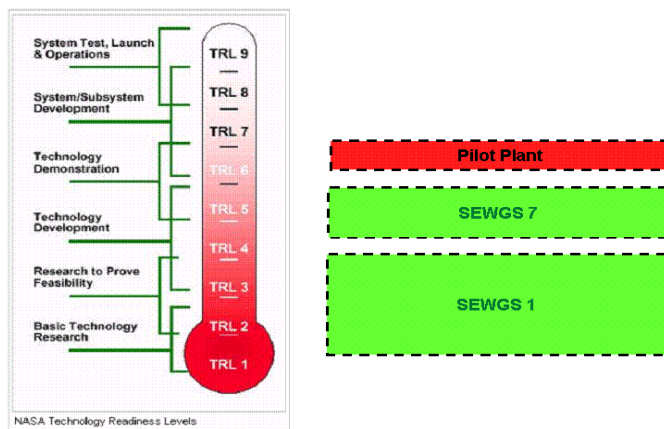


Figure 15 Technology readiness level

The primary objectives of a pilot plant are:

- Prove SEWGS performance on sufficient scale and under field conditions
- Confirm scale-up parameters and assurance of modelling results
- Prove the design is fit for purpose
- Optimise the cycle design

The main requirements of a pilot unit include availability of syngas, power, steam, nitrogen, cooling fluid, instrument air, process water, waste disposal of condensate, CO₂ and H₂.

Furthermore, an inventory of critical items for the SEWGS technology was made. These issues will need to be addressed in the pilot project.

In the course of 2011, a suitable host site was identified, and a SEWGS pilot validation project proposal was made. The pilot project was scheduled for the period 2012 – 2016. The consortium comprised European companies, a research organisation and a university.

Optimised configuration and plant reliability

The optimised cycle and configuration were established, the impact of possible switch valve leakage on the SEWGS process was studied, and ways to minimise the impact through cost effective measures were identified. The impact of the reliability of the switch valves on the overall availability of the SEWGS process was studied and recommendations were made to improve reliability whenever this

would be required from an operability standpoint. Moreover, strategies were proposed and compared in order to allow valve maintenance without shutting down the plant.

Vessel design and availability of high-temperature valves

For the mechanical design of the vessels, the frequent pressure swings are of critical importance for the fatigue analysis. Several design alternatives were proposed and assessed, taking into account the applicable codes and standards, and the best design was selected. Cost estimations for this vessel were obtained.

Specifications for the high-temperature valves were made, using the optimised configuration of vessels and valves established earlier in the project. The availability and prices of the valves were obtained from vendors. Various suitable valves were identified, and valve availability did not appear to be an issue, although delivery times could be substantial. Using the latest cost estimates for vessels and high-temperature valves, it appeared that the updated cost estimate for a SEWGS unit was not in line with prior preliminary cost estimates of a SEWGS unit (cost estimates were corrected for inflation towards the same base year).

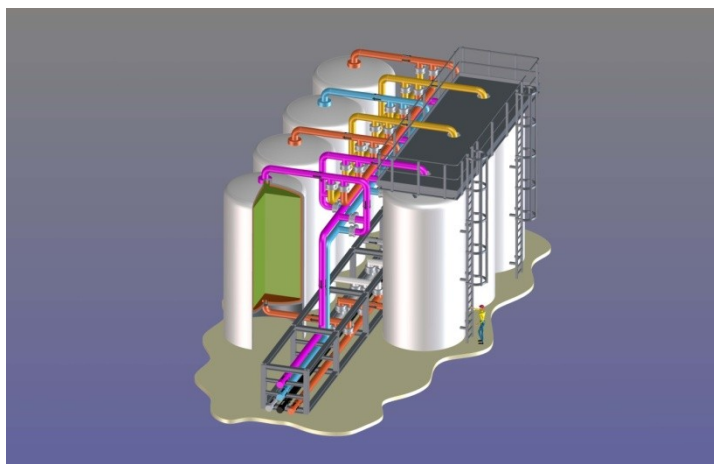


Figure 16 Impression of a 3D design for a commercial size SEWGS unit, capturing 1500 ton CO₂ per day

WP6 Project management and dissemination

The objectives of Work Package 6 are:

- Dissemination of the project results
- Organisation of a yearly EU CCS Conference

Dissemination of project results

In total 11 peer reviewed papers will be published in scientific journals. 8 papers have already been published, another 3 are in the reviewing stage and will be published in 2012. Finally, the consortium has submitted one abstracts for the GHGT11 conference in Kyoto presenting an overview of the headline results of CAESAR and another one on the sorbent (ALKASORB) development in CAESAR. Finally, a publication is in preparation on the SEWGS modelling activities.

The CAESAR consortium performed several dissemination activities including presentations on the CO₂net meetings in 2008, 2009, 2010 and 2011, presentations during the Trondheim CCS in 2009 and 2011 conferences. Furthermore the consortium presented the CAESAR project results during the GHGT-10 conference in Amsterdam and during the Pittsburgh CCS conference in 2009 and 2011. Other dissemination activities concern flyers, posters and a video on the SEWGS technology. This video is available on the CAESAR website : <http://caesar.ecn.nl/home/>

Organisation of a yearly EU CCS Conference

The three FP7 projects on CO₂ capture will organise for the next three years an annual EU CCS conference. A rotating Chairman organisation –and expenses- has been jointly established with

DECARBit and CESAR for three years (2009, 2010 and 2011), inviting new FP7 project to join in during the these years. The CAESAR consortium assisted the coordinators of DECARBit and CESAR in organising of the first two meetings in Oslo (2009) and Rotterdam (2010) and organised the 3rd EU CCS conference in London, (24 – 26 of May) in cooperation with CO2net. Almost all ongoing European projects on CCS (including those in supported by RFCS presented their latest results . As such the conference was a success in establishing a forum for dissemination of project result as well as for sharing information between EU funded projects on CCS. The 160 participant evaluated the this EU CCS conference very positive and suggested that the series will be continued in the coming years. The coordinators of the first three FP7 projects (CESAR, CAESAR and DECARBit) and CO2net therefore invite the commission to discuss how to continue this conference series during remainder of the FP7 programme.