

ZEG Power



The ZEG-technology

Status, June 2008

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1 Zero Emission Gas power – concept

The ZEG-technology (Zero Emission Gas power) is a novel innovative zero emission power production concept, developed as a joint venture project between Institute for Energy Technology (IFE) and the Christian Michelsen Research group (CMR Instrumentation and CMR Prototech). In this hybrid power plant concept, co-production of hydrogen and electricity with integrated high temperature CO₂-capture is facilitated by using the waste heat from a solid oxide fuel cell (SOFC) for sorption-enhanced steam reforming of natural gas (SE-SMR). CO₂ is captured at high temperature (500-600°C) during the reforming step and released, also at high temperature (880°C), in a regeneration step. Moreover, CO₂ is delivered from the plant as a pure concentrated CO₂ stream and can be pressurized for further industrial use or storage, as appropriate. The pressurized hydrogen product can be utilized depending on the market demands.

The main idea with the technology is, based on natural gas, gasified coal or biogas, to be able to produce electricity and hydrogen at the same time without any CO₂ emissions, with high overall efficiency and at favourable production costs.

The basic technologies in the concept are electricity production by SOFC and hydrogen production by SE-SMR.

2 Basic Technologies

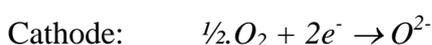
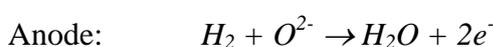
2.1 Electricity production by solid oxide fuel cells (SOFC)

The traditional way of converting the chemical energy stored in a fuel to electricity is by combustion. The chemical energy is then converted to heat that is used in a heat engine. The mechanical energy from the heat engine is led to a generator which converts it to electric energy.

An alternative way of converting chemical energy to electricity is by the use of a fuel cell. Using a fuel cell, the chemical energy is not first converted to heat, but directly to electric energy. This potentially makes a fuel cell more efficient than a heat engine.

A general fuel cell is made up of an electrolyte placed between two electrodes. For a SOFC, air is led to the porous cathode where oxygen collects two electrons and gets absorbed into the electrolyte. The oxygen ion then travels through the electrolyte to the anode where it reacts with hydrogen to form water. In this reaction the electrons are released again. They travel through an external circuit, driving some electrical load, and back to the cathode where the whole process starts again. The basic structure and process of a fuel cell running on hydrogen and oxygen is shown in Figure 2.1.

The chemical reactions at the anode and the cathode are the following:



Single fuel cells can be added together in stacks to increase the electric potential and total power output. Interconnects are then added to each electrode. The interconnects separate the anode and cathode gas streams, while at the same time collecting the current and distributing the gases uniformly. Each fuel cell stack can then be connected in series or parallel to make larger power producing units. An illustration of such a SOFC-stack is given in Figure 2.2.

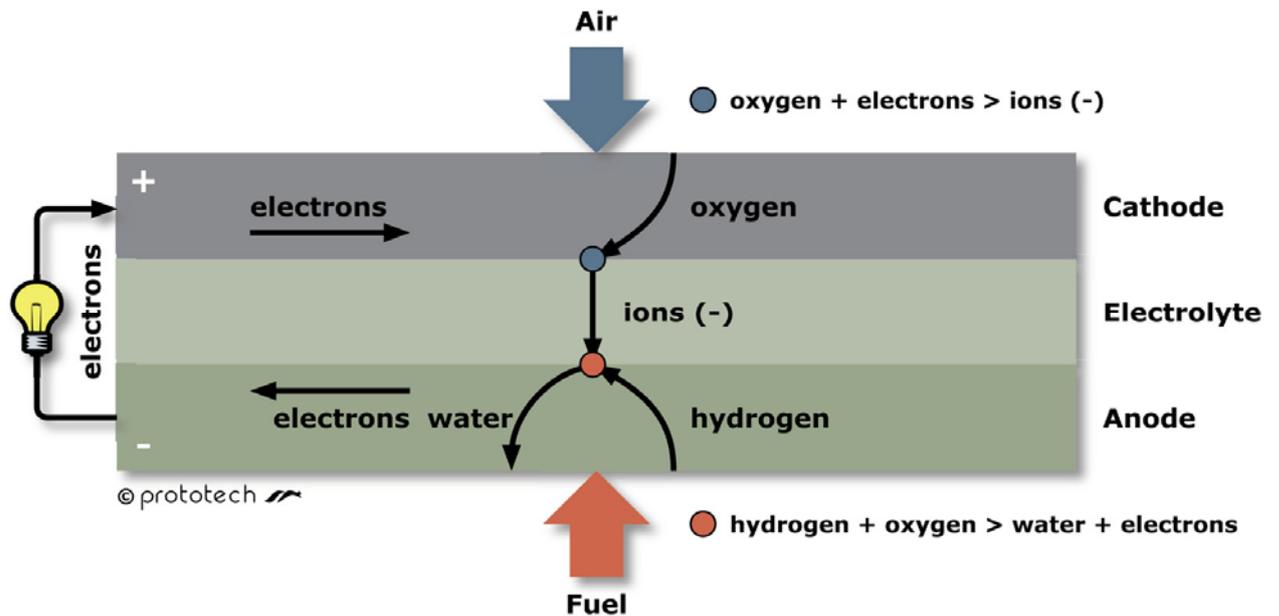


Figure 2.1 A schematic drawing of a single fuel cell running on oxygen and hydrogen

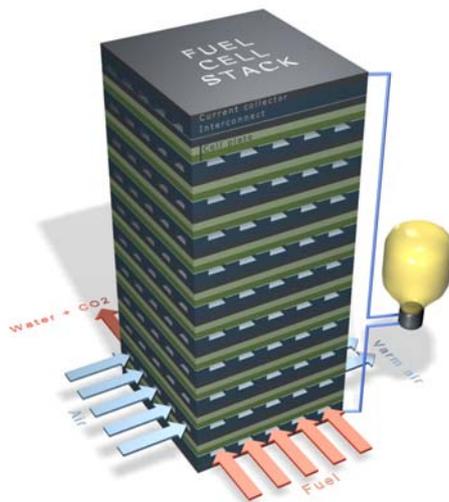


Figure 2.2 Single SOFC- cells added together in a stack

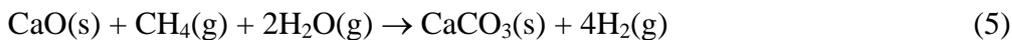
2.2 Hydrogen production by sorption enhanced –steam methane reforming (SE-SMR)

Sorption-enhanced steam methane reforming (SE-SMR) is a novel concept for hydrogen production from natural gas with integrated CO₂-capture. In this process both the reforming and CO₂ capture is integrated within two vessels. Moreover, the water gas shift (WGS) section is eliminated.

When a CO₂-sorbent (in this work mainly calcined dolomite; CaO-MgO) is mixed with a reforming catalyst, the CO₂ in the synthesis gas mixture is removed as it is formed, causing the reforming and water gas shift reactions to proceed simultaneously beyond the thermodynamic limits. Moreover, when CO₂ is captured *in situ*, high purity CO₂ can be obtained from regeneration of the sorbent, eliminating costly separation steps downstream. The reactions with CaO as sorbent are:



Reaction (3) is the summation of (1) and (2). The overall reaction is:



Advantages with SE-SMR compared to conventional methane reforming is a process simplification; reforming, water gas shift and CO₂-separation occur simultaneously in the same reactor in a reaction showing larger process flexibility. In addition it is obtained an increased hydrogen yield in the single step reaction; > 95% H₂ yield in the temperature range 500 - 650°C, reducing the needs for downstream H₂- purification and with a potential for increased efficiency, energy savings and reduced production costs

Figure 2.3 shows a simplified drawing of SE-SMR process, utilising CaO as a sorbent.

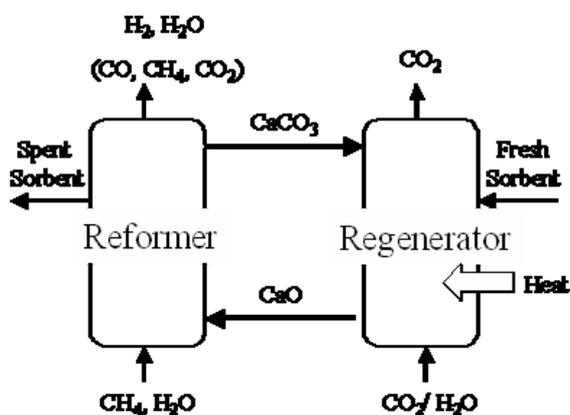


Figure 2.3 Schematic drawing of SE-SMR

3 Technology development

3.1 SE-SMR

The main challenges related to sorption-enhanced steam methane reforming is with respect to reactor technology and design, high temperature heat exchange, thermal integration and the choice of a high temperature CO₂-sorbent.

3.1.1 Reactor design and technology

Two major types of processes, batch and continuous are considered:

- A system with several batch reactors where the gas atmospheres are shifted alternatively, OR
- A dual circulating fluidised bed system where the solid particles are moved from one reactor to the other continuously.

Both systems are tested; a fixed bed reactor batch process and a fluidised bed reactor system for a continuous process. Preliminary laboratory experiments (Figure 3.1 and 3.2) has shown that both systems permit hydrogen production in one single step with high hydrogen yields (> 95%) in the temperature range between 500 – 650°C in an overall flexible process with almost 100% CO₂ –capture.

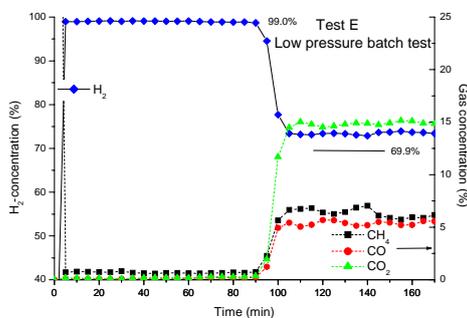


Figure 3.1 Hydrogen production in a fixed batch SE-SMR process at 525°C and 1 bar with calcined dolomite

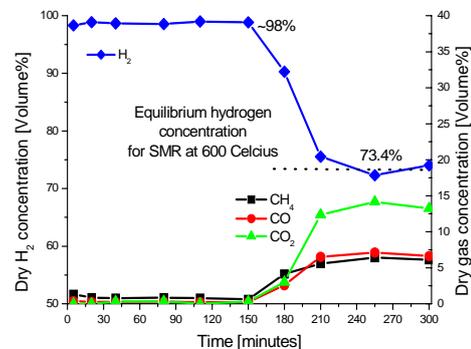


Figure 3.2 Hydrogen production in a fluidised bed SE-SMR process at 600°C and 1 bar with calcined dolomite

A continuous process in a fluidised bed system represents a series of technological advantages, especially for large scale operations such as more compact reactor design and easier reaction optimization; rapid mixing of solids and uniform temperature distribution and solids can be purged and filled continuously.

Fluidised bed reactor technology is commonly used in processes where catalysts must be continuously regenerated (like Fluid Catalytic Cracking, FCC), while also facilitating heat transfer and temperature uniformity. A dual bubbling bed system where reformer and regenerator operate in a bubbling mode is chosen for the SE-SMR process. The preliminary design of a dual bubbling fluidised bed reactor unit producing 10 Nm³/h hydrogen is carried

out using a two-phase steady state bubbling bed MATLAB-model. The realisation of this test unit includes three phases:

1. Design, building and testing of a bubbling reformer/regenerator batch reactor to confirm reaction kinetics and optimise the reactor design for both reformer and regenerator.
2. Design and building of the circulating system.
3. Testing of the reactor unit and optimising of process parameters.

Sketches of the reformer/regenerator batch reactor and of the dual fluidised bed reactor system are shown in Figure 3.3.

The natural gas is mixed with steam, pre-heated to 150°C and fed to the reformer at atmospheric pressure. The reformer is operating at 600°C, and additional heat is supplied by the solids returned from the regenerator, which is operated at 880°C. The product gas from the reformer then mainly consists of hydrogen and steam, with only minor quantities of CO, CO₂ and unconverted methane. The solids from the reformer are transported to the regenerator by using a transport riser, using a part of the product reformat gas as transport medium. Solids and reformat gas are separated in a cyclone-unit and the reformat gas is further cleaned in a hot filtration unit before further processing. Solids are then returned to the regenerator. To be able to produce pure CO₂, heat to the regenerator has to be supplied indirectly either by burning a part of the reformat gas or by using an external heat source, like a SOFC. Indirect heating allows producing essentially pure CO₂ for further sequestration, e.g. industrial use or geological storage, eliminating the need for downstream CO₂-separation. To avoid separation processes downstream, steam is used as fluidising gas in the regenerator. Non-mechanical valves, called loop-seals, are placed to ensure that there is no mixing of gases between the reactors. Cyclones at the exits of both reformer and regenerator insure the collection of entrained fines which are returned to the respective vessels.

3.1.2 High temperature CO₂-sorbents

The most conventionally used sorbents are natural Ca-based materials such as limestone and dolomites. They have a high initial absorption capacity, good absorption and regeneration kinetics and are largely available at low price. However, natural sorbents show a rapid decrease of their absorption capacity with carbonation/calcination cycles (Figure 3.4). This loss of CO₂ capacity is due to a grain sintering mechanism and a loss of porosity at elevated temperature. Several other synthetic sorbents such as lithium or sodium based zirconates are tested, but are not favorable choices for SE-SMR processes. The addition of an inert material as support for fine CaO sorbent is recently proposed by several authors in the literature and received increased attention. However, CO₂-sorbents with good long-term multi-cycle properties in realistic conditions combined with high CO₂ absorption capacity must be investigated.

The long-term stability of new synthetic Ca-based sorbents is studied by thermo-gravimetric analysis (TGA) in severe conditions (carbonation at 780°C and regeneration at 870°C in 50% CO₂/50% H₂O). Some results are illustrated in Figure 3.3 and compared with those obtained for natural dolomite. The results are promising with respect to a possible future use in SE-SMR processes.

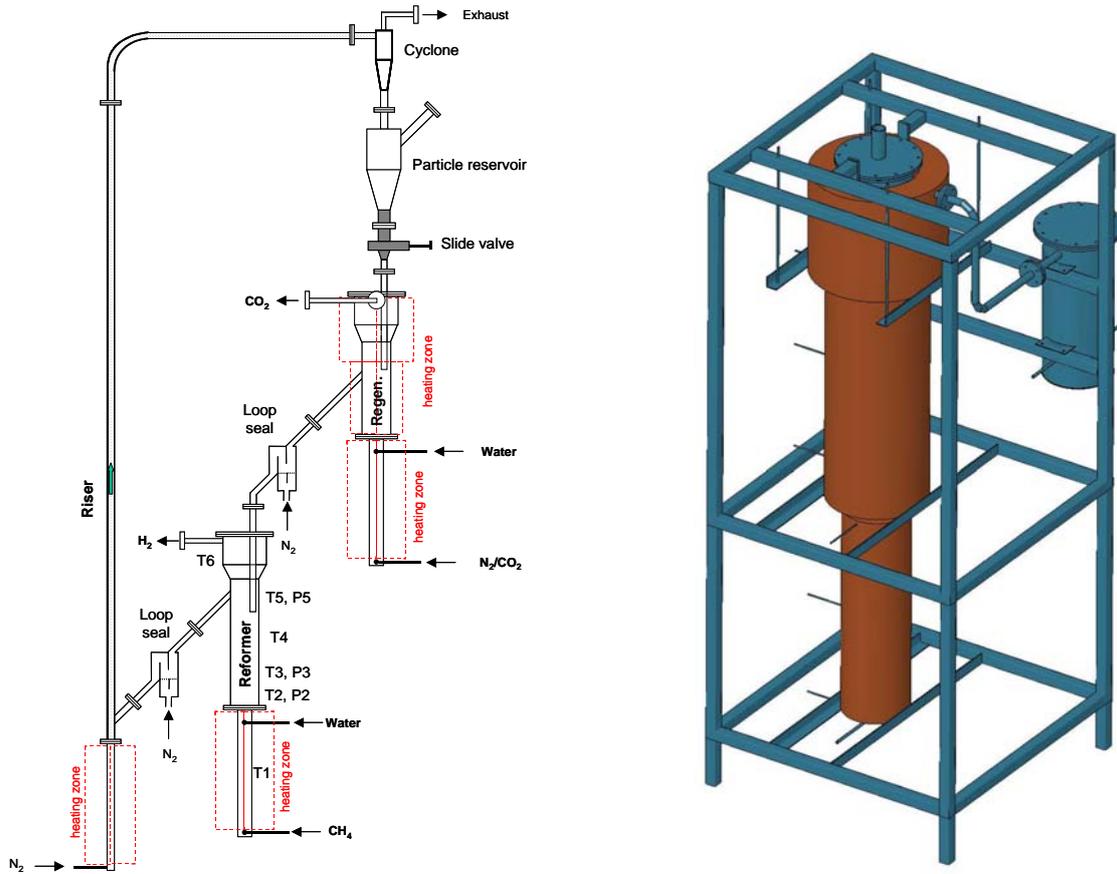


Figure 3.3 Sketches of the reformer/regenerator batch reactor and of the dual fluidised bed reactor system

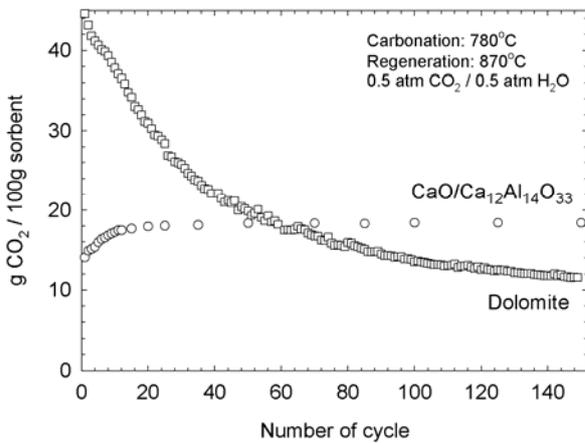


Figure 3.4 Evolution of the absorption capacity of Ca-based sorbents during multicycling in severe conditions

3.2 SOFC technology

The materials used in the SOFC stacks as well as the stack design have to be developed and tested for the specific application and operating conditions. The focus for the fuel cell technology development has been to identify and evaluate the use of SOFC technology in a large scale ZEG-technology power plant. Typical requirements are:

- High operation temperature (900°C – 1000°C)
- High power density
- Low degradation rates
- Long time performance on stable load

A numerous of SOFC stacks are built and tested. Cells from three different suppliers and stacks with both ceramic and metallic interconnects are tested in various conditions. The focus has been to characterize the performance of each cell type at different temperatures and loads. Long term test are carried out, both on short stacks and single cells.

3.2.1 Cell performance

The best performance of three different SOFC cells from three different suppliers is shown in Figure 3.5. The cells from Indec and Jülich are anode supported cells with approximately 8µm electrolyte, while Nextcell is an electrolyte supported cell with thickness of approximately 0.1 mm. The electrodes are Ni-based and (La,Sr)MnO₃-based for all cells. The active area of each cell is 81 cm² and the fuel is a 2:1 mixture of hydrogen and CO₂. The conditions for each experiment are shown in Table 3.1. The area specific resistances (ASR) are calculated from the performance at 20 A. These numbers can not be compared directly because of different fuel flows, however, calculating the potential drop from the water production at the anode, ASR values corresponding to an infinite fuel flow is calculated. These values are presented in Table 3.1 as ASR adjusted.

The presented data shows some variations between the different cells, with Indec cells as the best. The electrolyte supported Nextcell cells show the lowest power density, but as the cells are thinner the volumetric power density is comparable with the Indec cells. All cells may reach at least 0.3 W/cm² at 0.7 V, which is a satisfactory performance for applications in power plants, and are candidates for future applications.

3.2.2 Interconnects

The ZEG-technology demands high operation temperature for heat to be utilized in regeneration of the CO₂-sorbent. Although a significant effort has been dedicated to the development of high temperature alloys for SOFC stacks, only stacks made with ceramic interconnects can currently achieve sufficient life time at these temperatures. The ceramic interconnects are today manufactured with high quality, and cost analyses show that the cost targets may be reached by introducing industrial manufacturing processes.

3.2.3 Long term tests

Extended long term test are carried out on a Jülich button cell, shown in Figure 3.6. The “hiccups” in the cell voltage is a result of changes in the gas flows due to water droplets in

the exhaust outlet. However, the trend is that from approximately 2000 hours the cell resistance is increasing steadily at constant rate. After 8000 hours of operation, the ASR is approximately 40% higher than after 2000 hours of operation. However, no degradation is observed after for the last 3000 hours, so it seems likely that the target of 50 thousand hours can be reached.

Long term tests on stack level are performed for durations up to 2500 hrs, and show that the performance of the single cells can be reproduced in stacks and systems.

3.2.4 Conclusions

Solid oxide fuel cells have shown satisfactory performance in small scale experiments for use in ZEG-technology applications. Both anode supported cells and electrolyte supported cells are available. Hence, the technology development is focused on stack upscaling, heat integration and cost reductions.

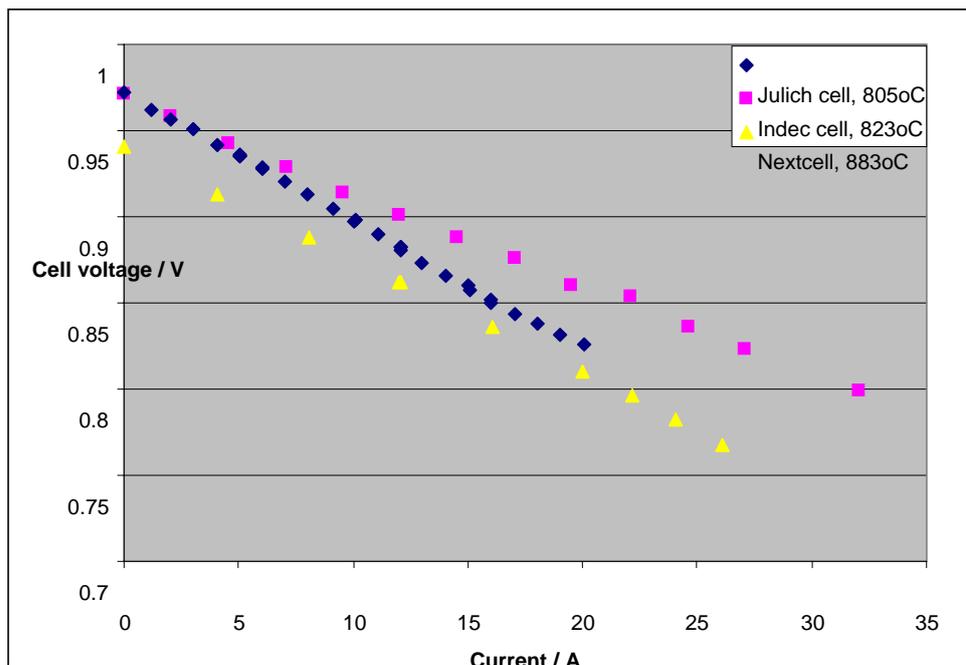


Figure 3.5 I-V curves for three different cells

Table 3.1 Conditions and resistances for the actual tested cells

	T	Flow pr cell	H ₂ : CO ₂	ASR	ASR adjusted
Julich	805°C	450 Nml/min	2:1	0.59 Ω·cm ²	0.35 Ω·cm ²
Indec	823 °C	625 Nml/min	2:1	0.44 Ω·cm ²	0.27 Ω·cm ²
Nextcell	883 °C	800 Nml/min	2:1	0.53 Ω·cm ²	0.39 Ω·cm ²

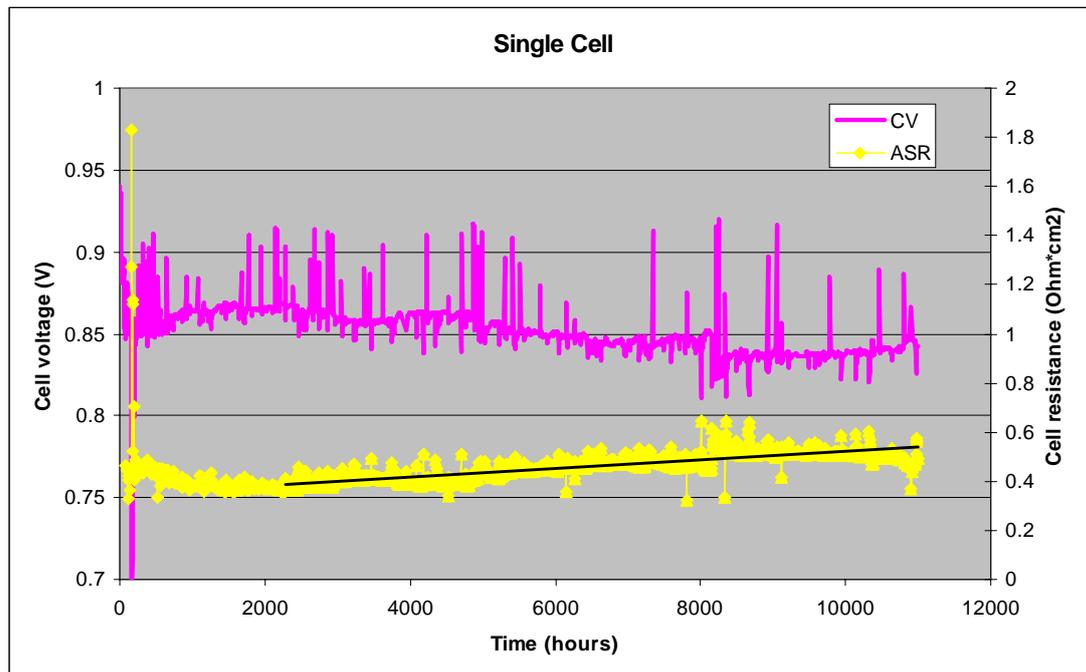


Figure 3.6 Long term single cell experiment

3.3 Supporting technologies

In high temperature processes like the ZEG-technology, it is an advantage to be able to measure the gas composition of flowing gas at process temperatures, e.g. 600°C. The development of a NIR-based measurement system for this purpose has been addressed. In order to realize this objective, first NIR gas characterization at low temperatures (below 70 °C) is carried out. Thereafter, the high temperature application is addressed.

Both in the low temperature and the high temperature application, focus has been on continuous measurement of the gas composition in a system. The gas to be measured flows continuously through a measurement cell where NIR light is transmitted in order to measure the absorption over the NIR frequency range. A chemometric model is developed for the estimation of the gas composition from the measured spectrum. This model is based on calibration measurements at known gas compositions.

A low temperature and a high temperature measurement cell are developed. Two low temperature cells (below 70°C) and one high temperature cell (600°C or more) are built.

Three different applications are addressed in particular:

- Low temperature 1: H₂ + small amounts of other gases
- Low temperature 2: CO₂ + small amounts of other gases
- High temperature: H₂ + water vapour + small amounts of other gases

The absorption spectrum depends on the temperature. This means that measurement of both pressure and temperature is important in order to determine the gas composition precisely.

In addition to development and manufacturing of the measurement cells, calibration set-ups are addressed. For low temperatures, this is established and used. The high temperature calibration set-up is designed, but not yet completed and used.

Chemometric models for CO, CO₂ and CH₄ are established, based on calibration measurements. The models are so far based on measurements for temperatures from 20 °C to 60 °C, for low temperature measurement cell applications. A temperature effect on the spectrum is observed in the sense that the absorption minima are weaker and broader as the temperature increases. This is in agreement with theory. In addition, calibrations are taken both on flowing and static gas. It is not observed any significant effect by the flow on the measured spectra. Several validation measurements are carried out under varying calibration conditions in order to verify that the models are optimal for the present set-up and gas compositions.



Figure 3.7 High temperature NIR gas characterization measurement cell

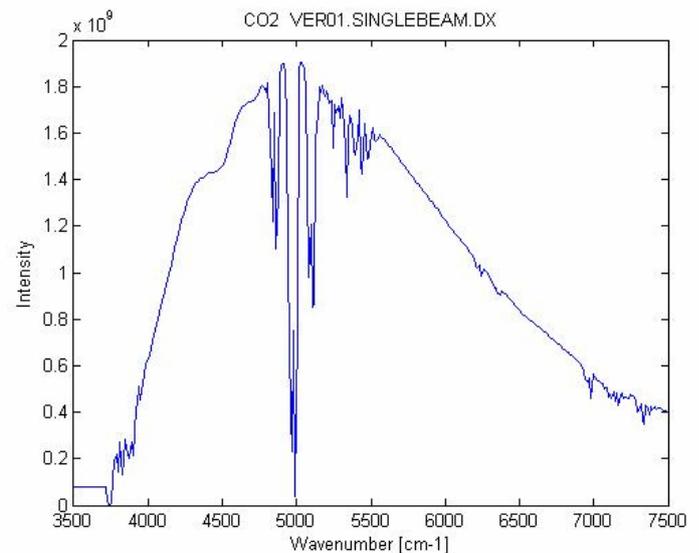


Figure 3.8 Measured spectrum for CO₂ in nitrogen for calibration of low temperature NIR gas characterization measurement cell

3.4 2 kW verification unit

SE-SMR and SOFC have been individually tested with success in laboratory scale. In June 2008 the installation of an integrated unit at Risavika Gas Centre (Figure 3.9) was completed. This laboratory scale verification unit plant has a capacity of 1 kW electricity and 1 kW hydrogen, with integrated CO₂ capture. The first test program has been successfully completed, and verified the integration of the SE-SMR and SOFC as well as the CO₂ capture process.

In this test program the two processes were run simultaneously in different modes of the process sequence:

- H₂-production from reformer reactor with integrated CO₂ capture, feeding the SOFC with H₂-rich fuel.
- Heating and calcinations using heat from the SOFC output stream, producing a close to pure CO₂ stream.
- Cooling using a separate airline.

The tests have gathered significant knowledge on system integration, heat integration, operational conditions, process control and safety aspects.

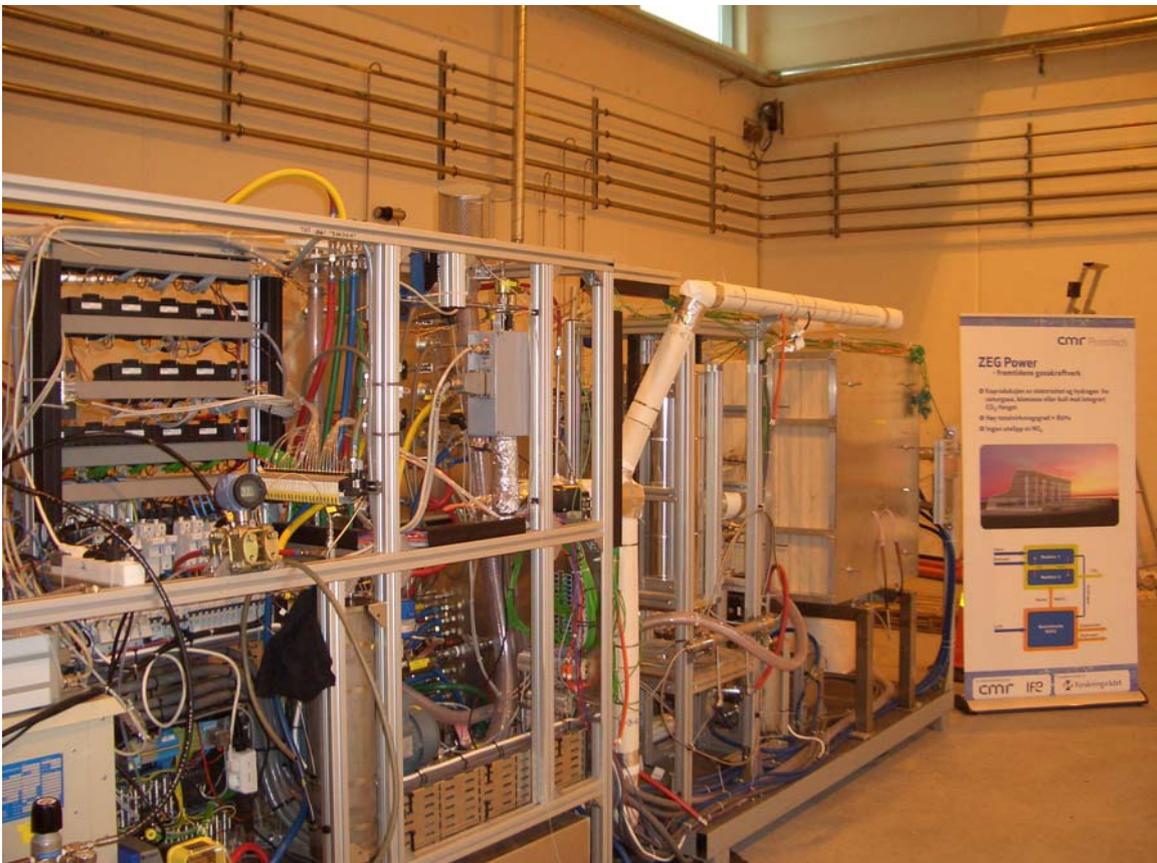


Figure 3.9 ZEG 2 kW verification unit at Risavika Gas Centre

4 Technical and economical feasibility study

Upscaling is an important part of the technology development and a technical economical feasibility study with cost estimates including CAPEX and OPEX calculations and net present value analysis (NPV) has been performed as a part of the study. Two cases are defined, which both are based on reforming of natural gas. The chosen technologies are the following:

- Hydrogen production by sorption-enhanced steam methane reforming (SE-SMR) with calcined dolomite as high temperature CO₂-sorbent, run continuously in a dual fluidised bed reactor system
- Hydrogen purification by pressure swing adsorption (PSA)
- Power generation with a high temperature solid oxide fuel cell (SOFC) using planar technology

The hydrogen and electricity production in the two cases are summarized in Table 4.1, while Figure 4.1 shows a schematic process layout for the two cases.

Table 4.1 Case studies

Case #	Alias	Hydrogen production (MW _{th} LHV based)	Electricity production (MW)
ZEG-Case 1	H ₂ +EL – 700+400	~700	~400
ZEG-Case 2	H ₂ +EL – 50+400	~50	~400

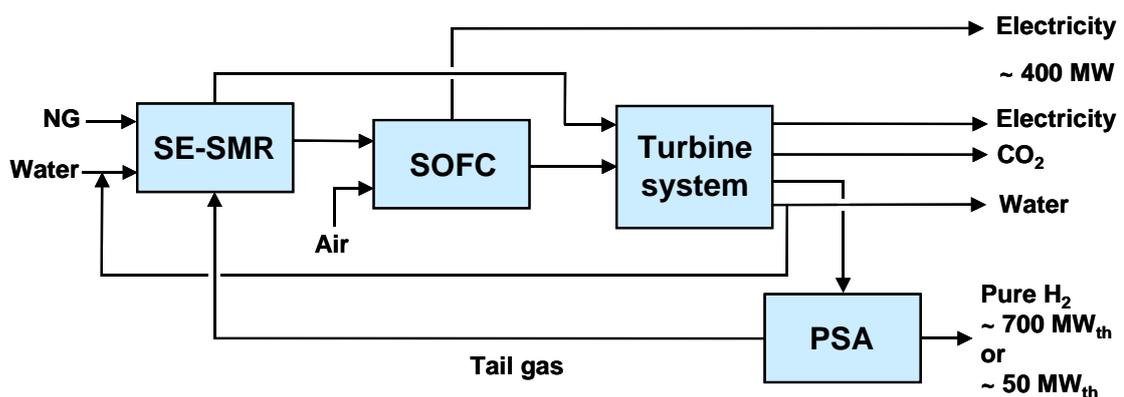


Figure 4.1 Schematic process layout of co-production of hydrogen and electricity, ZEG-Case 1 & 2

The main processes include:

- Sorption-enhanced steam methane reforming (SE-SMR)
- Heat integration

- Power generation section – SOFC + turbine system
- Hydrogen purification – Pressure Swing Adsorption
- Hydrogen compression
- CO₂ compression

A turbine system is included in order to utilize all waste heat in the system in order to obtain high total efficiencies.

The process simulation software HYSYS is used to simulate industrial size ZEG-technology power plants running on natural gas. The reformer-regenerator system for hydrogen production, with in-situ CO₂ capture, is modelled separately in MATLAB, and its output values are manually specified in the HYSYS models. Pressure losses and heat losses are calculated separately, and included in the overall efficiency calculations.

4.1 System design

The major components of the process are the reformer/regenerator reactor system, the SOFC, the PSA unit and compressor trains. Figure 4.2 shows an illustration of the total process and arrangement of the sub-units. Performance and operating conditions are defined for all major components, as well as auxiliaries down to a reasonable detailed level, as a basis for sizing and material selection.

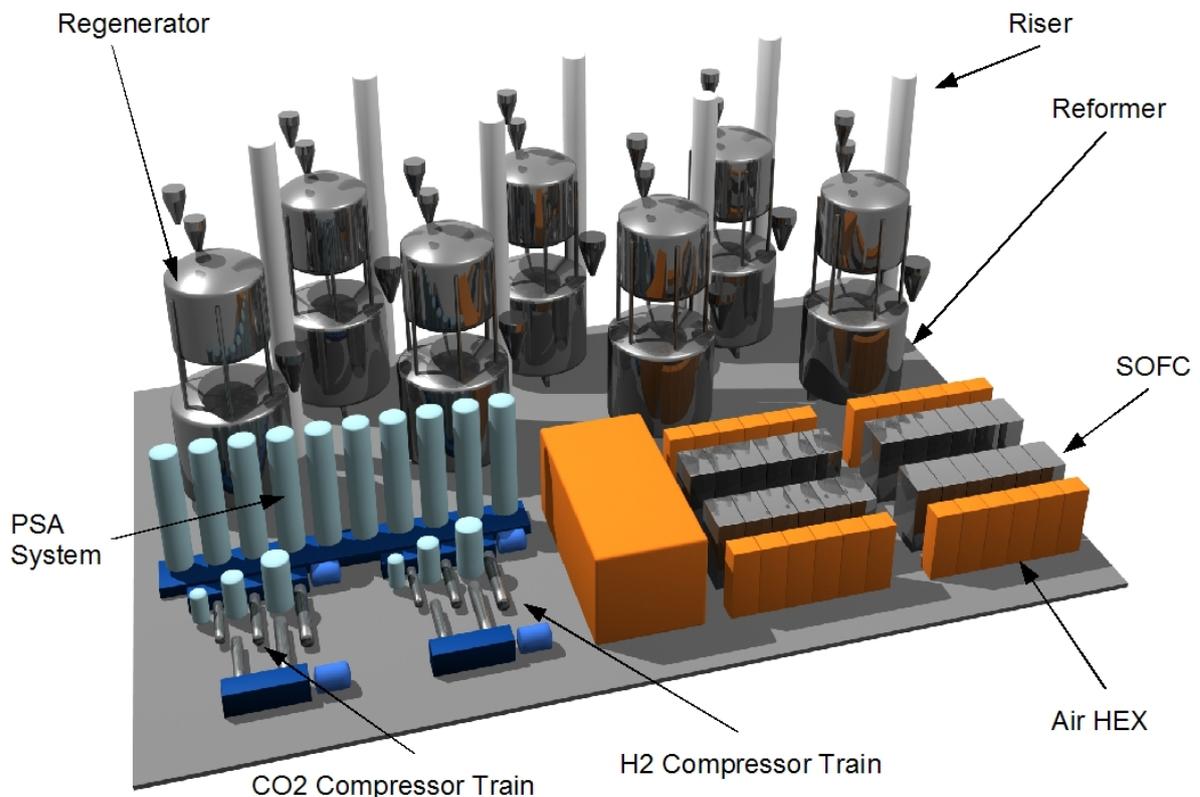


Figure 4.2 Possible arrangements of the process components

4.2 SOFC module and heat transfer

The heat produced in a fuel cell stack will be in the same order of magnitude as the electrical energy, and has to be made available for the regenerator through a heat transfer loop. High temperature heat exchangers are expensive, and represent significant cost elements in the analyses. Further work will focus on optimization of identified innovative solutions, and it is expected that the cost can be further significantly reduced.

4.3 Results

The ZEG-technology has a potential for a very high efficiency, and previous system studies have shown overall net efficiencies exceeding 90%. In order to achieve these high efficiencies, a very good thermal integration is required. The 2 cases evaluated are based on a reactor concept using a dual fluidised bed reactor system with circulating solids. The solids (CO₂-sorbent and reforming catalyst) from the regenerator enter the reformer at 880°C, and the solids from the reformer enter the regenerator at 600°C. The main advantages of this system are that it is compact, solids can be purged and refilled continuously, and no solid/solid heat exchanger is required. The disadvantage is that the overall efficiency is reduced by 5-8% compared to a more closely thermally optimized system. The latent heat that could be recovered from the solids is in the order of 100 MW. If this heat is recovered in a heat exchanger, the efficiency would increase by 5-8%.

Power consumptions and efficiencies are given in Table 4.2, and even without a solid/solid heat exchanger the overall net efficiencies are impressively high.

Table 4.2 Process efficiencies

	ZEG- Case 1 (700MW H ₂ + 400MW EL)	ZEG-Case 2 (50MW H ₂ + 400MW EL)
Thermal input NG (MW)	1401	621.2
Power output (MW)	515.5*	503*
Thermal output H ₂ (MW)	702.2	49.8
Process auxiliaries (MW)	117.7	47.8
Net power output (MW)	397.8	455.2
Overall gross efficiency (%)	86.9	89.0
Overall net efficiency (%)	78.5	81.3
CO ₂ captured (kmole/h)	6532	2897
CO ₂ capture (%)	100	100

*Including power from steam turbine and gas expander

The efficiencies are defined as follows:

$$\text{Overall gross efficiency \%} = \frac{\text{power output} + \text{thermal output } H_2}{\text{thermal input NG}}$$

$$\text{Overall net efficiency \%} = \frac{\text{net power output} + \text{thermal output } H_2}{\text{thermal input NG}}$$

The profitability of the two cases is strongly dependent on energy and CO₂ prices. ZEG case 1 produces large amounts of hydrogen and shows the highest sensitivity to a general increase in all energy prices (natural gas, hydrogen and electric power). Moreover, the co-production case producing relatively small amounts of hydrogen shows the highest sensitivity to electric power price, mainly due to its very high efficiency. With high energy prices for both natural gas, electricity and hydrogen, and keeping a CO₂-sales value equal to zero, the ZEG co-production cases show very good economy with net present values (NPV) in the range 6 000 MNOK to 12 000 MNOK.

Since the two technologies are relatively new and not demonstrated at pilot scale, the cost estimates for capital expenditure (CAPEX) are rather difficult to define for large scale applications and are still rather high compared to conventional available technology. Therefore, it is believed that with technology development and plant optimisation, the CAPEX can be reduced, leading to even better economy.