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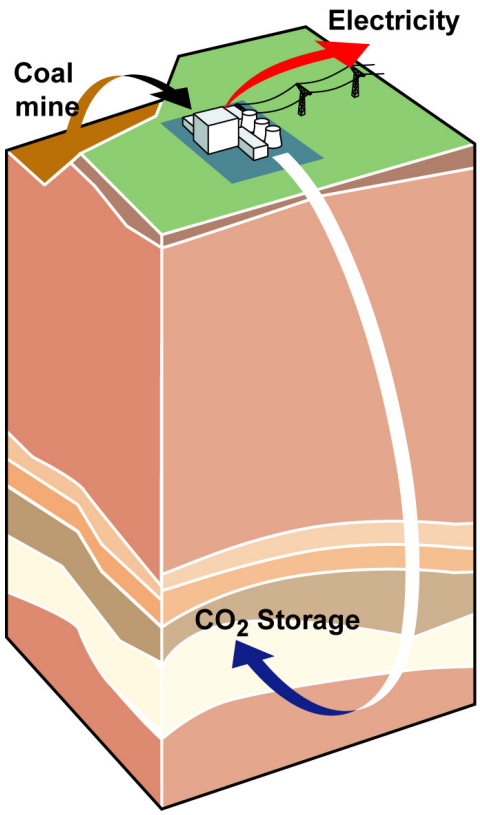
Performance and modelling of the pre-combustion capture pilot plant at the Buggenum IGCC - Summary report

A report within the CO_2 Free Power Plant Project

Kay Damen, Richard Faber, Radek Gnutek

Vattenfall Research and Development AB



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This report summarises the results of the CO_2 Catch-up project. For the complete report with all non-confidential results, please contact Kay Damen (kay.damen@vattenfall.com).

Dit project is uitgevoerd met subsidie van het Ministerie van Economische Zaken, Landbouw en Innovatie, regeling EOS: unieke kansen regeling uitgevoerd door Agentschap NL.

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CCS R&D Portfolio

Coal power will continue to be a cornerstone of Europe's energy system in the foreseeable future, due to its economic attractiveness and ability to contribute to secure and stable electricity generation. As such, it will remain part of Vattenfall's generation portfolio.

However, when fossil fuels are combusted in power plants, vehicles, or industrial plants, carbon dioxide (CO_2) is emitted into the atmosphere. The increased levels of carbon dioxide in the atmosphere is the dominating contributor to increased global warming - one of the greatest environmental challenges of our time.

Vattenfall intends to cut its CO_2 exposure from 90 million tonnes in 2010 to 65 million tonnes by 2020. By 2050, the vision is to have a carbon-neutral generation portfolio. Part of the strategy is to develop the Carbon Capture and Storage (CCS) technology to reduce CO_2 emissions into the atmosphere from coal-fired power plants. The idea is to capture CO_2 from a coal-fired power plant, transform it into a liquid, and store it deep underground. The storage repositories will be of the same kind as where oil and gas are extracted - formations of porous rock with a sealing cap on top. The aim is to develop a commercial concept operable by 2025-2030.

Political support, legal framework, and societal acceptance are crucial to make CCS possible, and Vattenfall is collaborating with various stakeholders to develop relationships and requisite conditions. In the long term, new sustainable energy sources will have to be deployed, but the development of emission free fossil fuel utilisation is considered as necessary bridging technology.

The CCS R&D project portfolio is providing options for Vattenfall's fossil based operations in its continental core markets. It has been running since 2001 and involves in addition to Business Unit R&D Projects, also specialists from BU Engineering, BU Production Lignite and a large number of external partners, including several major manufacturers, other power companies, engineering companies and research providers and leading universities in Europe.

The CCS R&D project portfolio consists of three elements:
- Development of concepts and technologies to capture carbon dioxide more efficiently and at less cost
- Investigations of CO_2 transport and geological storage options that are safe, reliable and cost effective
- Environmental assessments and acceptance building.

This report is one of several reports produced within the CCS R&D Portfolio. Any questions and inquiries concerning the report should be directed to the authors. Questions and inquiries concerning the Portfolio drivers and roadmap should be directed to R&D Projects/Sustainable Asset Development.

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CB&I	Michel Hagg	1 PDF-file
CB&I	Michiel van der Griendt	1 PDF-file
CB&I	Jaap van der Wouden	1 PDF-file
CATO-2		1 PDF-file

Table of Contents

1 Project rationale and objective

In 2005, Nuon started the development of a multi-fuel Integrated Gasification Combined Cycle (IGCC) power plant, the so-called Magnum project, in Eemshaven, the Netherlands. The application of gasification technology enables pre-combustion carbon dioxide (CO_2) capture in order to store the CO_2 in a geological formation. The original concept for Magnum was to construct the gasification section first, with the option to install the CO_2 capture unit afterwards ("capture ready retrofit").
In 2007, a study was performed by CB&I Lummus, an engineering company managing the EPC of the Magnum IGCC, to select the technology for a CO_2 capture retrofit. The energy consumption of the WGS reaction and CO_2 absorption is significant, comprising of the loss in heating value in the shift reaction, the steam to drive the shift reaction and the power to drive (mainly) pumps and compressors. Therefore, the main task for CB&I Lummus was to minimise the specific energy consumption and costs per tonne avoided CO_2.

Although CO_2 capture has never been applied in combination with an IGCC unit, many of the elements have been proven in the chemical industry, yet in a slightly different configuration as foreseen in Magnum due to the different purpose of CO_2 capture. Also the syngas composition when gasifying coal (and biomass) in the Magnum plant differs from that when gasifying natural gas or heavy oil residues as performed typically in the chemical industry (for which most experience exists). In addition, the mode of operation in the chemical industry is different than the power sector; in the latter the load of the WGS and CO_2 capture unit should be able to follow the ramping of the power plant. Therefore, it was decided to demonstrate and optimise the concept developed by CB&I Lummus on a small scale first before applying a full-scale commercial CO_2 capture unit at the Magnum plant. This resulted in the so-called CO_2 Catch-up project, encompassing the engineering and construction of a CO_2 capture pilot plant and operation at the site of the IGCC power plant in Buggenum, the Willem Alexander Centrale (WAC).

The objective of the CO_2 Catch-up project is to demonstrate pre-combustion CO_2 capture at the pilot plant in Buggenum in order to verify the technology performance and to generate knowledge in the form of validated models and operational experience that can be applied to optimise the design and operation of the full-scale CO_2 capture unit at the Magnum IGCC.

The CO_2 Catch-up project consists of 2 parts:

1. Engineering and construction of the pilot plant (finished in 2011)
2. Operation and execution of the test and R&D programme (2011-2013)[1]

[1] The PhD projects in the R&D programme last until 2014.

The test programme is the collection of test runs performed at the pilot plant. The results of the test programme are input to the overarching R&D programme aiming to understand and improve the process by means of process modelling and laboratory experiments. The test and R&D programme has been managed by Vattenfall R&D Projects and performed together with Delft University of Technology and Energy research Centre of the Netherlands (ECN) and involves a number of scientists and PhD students. This report summarises the results of the pilot plant operation and test and R&D programme of the CO_2 Catch-up project.

2 Pilot plant design

The pilot plant is a simplified, smaller version of the CO_2 capture plant for the Magnum IGCC power plant designed by CB&I Lummus. It was designed to capture 1.4 t /h of CO_2 from 1.2 t/h of syngas (=0.8% of the syngas flow from the Buggenum gasifier). In the pilot plant carbon monoxide is catalytically converted into carbon dioxide and hydrogen, the so-called water-gas shift (WGS) reaction (see below), after which CO_2 is separated from H_2 in the absorption-regeneration section.

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g), \quad \Delta H°298 = -41.1 \text{ kJ/mol}$$

The shift reaction can either take place in the sour syngas before sulphur removal (sour shift) or in the cleaned syngas after sulphur removal (sweet shift). Most IGCC + CCS concepts found in literature are based on sour shift. In the original Magnum concept, a sweet shift concept was foreseen due to its presumed compatibility for easy CO_2 capture retrofit and the ability to bypass the shift and CO_2 absorption unit (e.g. when CO_2 capture is not economically viable). Another advantage of a sweet shift is that both desulphurised syngas and H_2 can be delivered over the fence (which was one of the options considered for the Magnum plant). For these reasons, sweet shift catalysts have been considered in the project.
The WGS catalyst applied in the pilot plant is Haldor Topsøe's SK-201-2, a copper promoted iron/chromium based HTS catalyst. HTS catalysts are commonly applied in hydrogen and ammonia plants, mainly treating syngas from steam methane reforming, but also to shift syngas produced by gasification of heavy oil residues (typically in combination with a Rectisol unit and low-temperature shift catalysts). In those applications, the sulphur level to which the catalyst is exposed is very low (below ppm level) and many of the trace elements are removed in the Rectisol unit or upstream. There are, however, little references where iron/chromium catalysts are exposed to the sulphur levels and trace elements common in a coal gasification plant with a less stringent H_2S removal.

The (physical) solvent used to remove CO_2 is dimethyl-ether of poly-ethylene-glycol (DEPEG). DEPEG is commercially licensed by DOW under the trade name Selexol™

and by Clariant under the trade name Genosorb^{R} 1753. In the pilot plant, only the latter solvent has been tested (as the difference between these solvents is marginal). The Selexol process is a proven commercial process licensed by UOP to remove acid gases from synthetic or natural gas streams. It is ideally suited for the selective removal of H_2S, COS and CO_2. Sulphur levels below 1 ppmv can be achieved with variable and optimised CO_2 capture levels. Selexol is a stable and non-corrosive solvent and has a relatively low vapour pressure (i.e. solvent losses are acceptably low).

Figure 2-1 depicts a simplified process flow diagram of the entire process and the pilot plant.

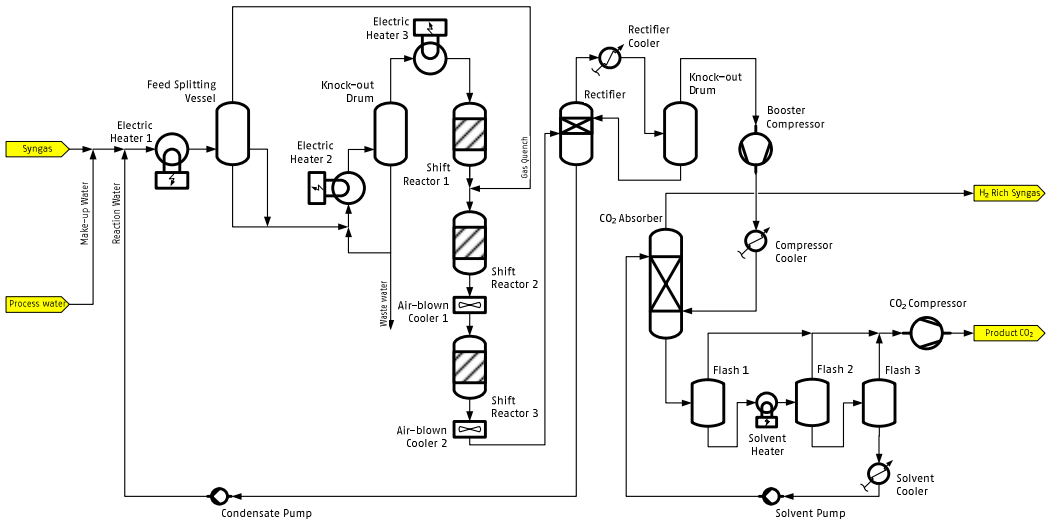

Figure 2-1: Simplified process flow diagram of the CO_2 capture pilot plant

There are a number of essential differences between the pilot plant and the (future) large-scale capture plant. The most important difference is the heat integration in the WGS section. To understand these differences, first the design rationale of the full-scale capture plant is explained.

As the MP/IP steam needed in the WGS reaction, which is either extracted from the syngas cooler or heat recovery steam generator (HRSG), cannot be expanded to produce electricity, reducing the steam consumption to a minimum is the key to minimise the efficiency penalty of CO_2 capture in IGCC applications. In a conventional scheme with several reactors in series, the temperature rise in the first reactor would determine the steam requirements. Coal syngas from a Shell dry quench gasifier typically contain 60 mol% CO, which results in high reaction rates and temperature rise. Ideally steam with only part of the syngas is to be fed to the first reactor. As steam and CO are consumed in equal quantities the H_2O:CO ratio increases, thereby allowing part of the

syngas feed (containing less steam) to be fed directly to the second reactor. This can be achieved by splitting the syngas flow, which has been applied by CB&I Lummus to optimise the flowsheet of the full-scale capture plant. As a result, the overall H_2O:CO ratio (and hence overall steam demand) is reduced drastically. Basically, the minimum steam demand is set by the inlet conditions of the second reactor, which equals the minimum to prevent carbide formation. In order to further reduce the efficiency loss in the water-gas shift reaction, maximum heat integration has been applied. Instead of using steam from the syngas cooler or the HRSG directly, steam is generated internally, which is the most efficient way to generate the required steam. In this concept steam is produced by evaporating make-up water and recycled excess water condensed downstream the reactors using the hot syngas outlet from the WGS reactors.

In the pilot plant, water is evaporated/condensed by means of electrical heaters and forced-draft air coolers, respectively, instead of shell and tube feed-effluent heat exchangers as foreseen in the Magnum plant. In this way the temperature dependency of two streams (feed-effluent) is avoided and the precise control of the temperature becomes possible. This simplifies the operation, extends the operational flexibility and prevents process fluctuations that could influence the reliability of the test runs in the test programme. As a consequence specific energy consumption figures of the pilot plant are non-representative and incomparable with figures from literature for large-scale plants (and are therefore not discussed).

Figure 2-2: CO_2 capture pilot plant. The tall column in the middle of the picture is the CO_2 absorber.

3 Pilot plant operation

The pilot plant has been operated from January 2011 to March 2013, with two major (initially unforeseen) interruptions during summer in which the IGCC was shut down for several months. Total operating hours are 5886 hours and the cumulative CO_2 captured is 4478 ton. After an initial period with 24/7 manned operation, it was decided to change the operating regime to fully automatic with manned supervision during the work-days only.

The pilot plant has been operated without major problems after some (relatively minor) hardware and control modifications, most of them being specific for the pilot plant design. The sampling conditioning system and analyzers have been the largest point of concern. Condensation in the sampling lines caused inaccurate composition measurements in the shift section. Fortunately, the dry gas composition measurements were reliable and these were used to evaluate the WGS performance. It also took some time to produce reliable results from the analyzers.

Corrosion and material issues

In the pilot plant, corrosion probes were installed and wall thickness measurements were performed at several locations before, during and after operation. One of the main corrosion mechanisms that could occur is wet CO_2 corrosion. Most equipment, piping and tubing susceptible to wet CO_2 corrosion are made of stainless steel (SS304(L) or SS316(L)), which are completely resistant against CO_2 corrosion. DEPEG will protect the surface of piping and equipment and wet CO_2 corrosion will be strongly reduced. Therefore carbon steel with 3 mm corrosion allowance is selected for wet DEPEG piping and equipment. If not a continuous DEPEG film is formed (e.g. for equipment top sections and top outlet piping or flashing conditions), stainless steel is applied. Generally it was observed that corrosion rates (for carbon steel as indicated by the corrosion probes) were below the expected values.

Traces of some unidentified substance (possibly DEPEG) deposited on CO_2 compressor pistons in the second stage downstream of the intercooler were found during maintenance activities. Attempts by the equipment supplier to identify and explain the cause of the problem were not successful. This issue needs to be investigated in more detail for the design of the full-scale plant.

HSE

During pilot plant operation, no incidents occurred (zero lost time incidents). The HSE risks identified relate mainly to the chemicals present in the plant. Throughout the plant no large volumes of flammable gas/liquid are present. Therefore the fire hazards within the pilot plant are low. To detect CO (toxic and flamable), CO_2 (asphyxiation)

and H_2 (flammable) in an early state of release, detectors were installed at locations where the specific gas is the major component.
The solvent used to capture CO_2, Genosorb 1753 (or DEPEG) is a low-viscous, colourless to yellowish liquid. Genosorb 1753 has a high boiling point/low vapour pressure and therefore solvent losses to the environment via the treated gas are minimal. No spills occurred during operation.
The catalyst applied in the WGS section, SK-201-2, is a copper promoted iron/chromium catalyst. After the final plant shut down, the catalyst needs to be oxidized in a controlled manner to avoid that the catalyst will heat up during unloading (as the oxidation is an exothermic process). During oxidation, some amount of the Cr(III) present in the catalyst will be transferred into Cr(VI), which is recognized as a human carcinogen. This means that workers should wear proper protection gear in order to avoid getting in contact with the catalyst pellets and to inhale catalyst dust. The normal procedure prescribed by Haldor Topsøe is to purge the catalyst with steam until the temperature is 200-250°C, after which the airflow is gradually increased and controlled such that the catalyst temperature does not exceed 300°C. For operational reasons and the fact that catalyst sampling was planned, it was decided to perform the oxidation in nitrogen. Due to fact that the air flow could not be controlled carefully and the lower heat capacity of nitrogen, the catalyst at the centre of the bed has been exposed to temperatures (peaks) between 600 and 800°C.

4 Mass balances and pilot plant performance

Mass balances were calculated to check the quality of the raw measurement data from the plant and to see if these can be used for model validation. The overall mass balance as well as the mass balances for the individual plant sections close very well. For the overall mass balance the relative deviation between input and output is only 0.11% at reference state (i.e. normal operating conditions close to original design point), which is significantly below the measurement accuracy of the individual measurement devices. Also for the sub-sections the mass balances close well (between 2 and 4%).

The main performance parameters of the plant are the efficiencies for converting CO into CO_2 in the shift section and the CO_2 absorption efficiency in the absorption section as these determine the overall carbon capture efficiency of the plant.
Both Haldor Topsøe and CB&I Lummus calculations indicate a 92-93% overall CO conversion for the entire WGS section. Similar overall CO conversions are measured in the pilot plant (see Table 4-1). However, reactor 3 catalyst activity is insufficient i.e. not reaching equilibrium at the specified inlet temperature. In the pilot plant reactor 3 (and 2) indeed contribute less to the overall conversion efficiency in the pilot compared to the CB&I and Haldor Topsøe calculations. The poorer performance of reactor 3 is completely compensated by the much higher contribution of reactor 1 to

the overall conversion due to a higher split flow of the syngas going towards reactor 1. In conclusion, the achieved CO conversion can be easily reached, especially if the unusual reactor 3 deactivation is avoided.

According to the heat and mass balances from CB&I Lummus, the absorption efficiency is 90.8%. The pilot plant average absorption efficiency is around 86% at the reference state. However, the results are incomparable as the design from CB&I Lummus was based on a Mellapak 350 Y structured packing at the bottom and a Mellapak 750 Y packing at the top whereas Raschig Super-Ring 0.6 and Raschig Super-Pak 250Y were tested in the pilot plant (which have a lower surface area).

The carbon capture efficiency (carbon in minus carbon out divided by carbon in) measured in the pilot plant is roughly 78%. As a check, the overall capture efficiency can be estimated by the product of the CO conversion efficiency and the CO_2 absorption efficiency. Using the CO conversion and CO_2 absorption efficiency mentioned above, the overall capture efficiency is approximately 80% (in reference state).

Table 4-1: Pilot plant reactor performance (reference state)

Parameter	Unit	Reactor 1		Reactor 2		Reactor 3	
		in	out	in	out	in	out
T	°C	334	486	338	470	336	346
H_2	%wet	7.81	23.11	20.45	33.54	33.54	34.80
N_2	%wet	1.87	1.87	2.82	2.82	2.82	2.82
CO	%wet	16.42	1.12	16.20	3.11	3.11	1.84
CO_2	%wet	0.70	16.00	9.70	22.78	22.78	24.05
Ar	%wet	0.25	0.25	0.38	0.38	0.38	0.38
H_2O	%wet	72.94	57.64	50.46	37.37	37.37	36.10
S/CO=	mol.mol-	4.44		3.12		12.03	
Flow=	kmol.h-1	59.24		104.76		104.76	
Xco	**%**		**93.2%**		**80.8%**		**40.7%**
∑ Xco, Ri	**%**		**34.9%**		**52.7%**		**5.1%**
∑ Xco	**%**		**34.9%**		**87.6%**		**92.7%**

Xco = CO conversions per reactor, ∑ Xco, Ri = progressive conversion per reactor, ∑ Xco = cumulative progressive conversion.

5 Pilot plant test programme

The test programme is subdivided into test campaigns covering a period in which a number of test runs are performed.

- TC-I: trial period to understand the operating window and limits of the pilot plan and to define reference state. No analyzers available (Jan 2011 – April 2011)
- TC-II: execution of main parametric tests of shift section and absorption section with random packing in absorber (September 2011 – April 2012, September 2012 - November 2012)
- TC-III: repetition of several parametric tests with structured packing in absorber (November 2012 – February 2013)

5.1 Parametric tests syngas conditioning and water-gas shift section

Several parametric tests were performed to evaluate the impact on the catalyst performance. The axial temperature profiles in the WGS reactors give a good indication whether and at which coordinate equilibrium is reached and how it moves in time and upon changes in process conditions. An optimal operation of the shift reactors could be achieved by adapting the reactor inlet temperatures such that equilibrium is just reached at the end of the catalyst bed. The first test run indicated that the inlet temperature of reactor 1 could be lowered to 315°C. For reactor 2 the reaction front at reference condition is well within the catalyst bed and hence the inlet temperature of reactor 2 can also be decreased. For reactor 3 the inlet temperature had to be increased to at least 355°C to boost the reaction rate and reach equilibrium.
In addition, a dynamic test has been performed with the purpose to study the dynamic behaviour of the 3rd reactor during a rapid variation in the inlet temperature. Starting at steady-state operation, a rapid temperature drop resulted in the expected inverse temperature response at the reactor outlet. The subsequent rapid temperature increase resulted in a dynamic response corresponding with a reactor start-up.
Changing the syngas composition to mimic gasifier part-load operation or biomass co-firing hardly influences the CO conversion and adiabatic temperature rise.
The variation of the syngas mass flow results in changes of the pressure losses along the process. For the reactors a clear almost linear relation between pressure loss and mass flow is observed whereby increasing mass flow leads to higher pressure loss. This was not apparent for other components in the syngas conditioning and water-gas shift section.

5.2 Catalyst stability and selectivity

Analysing the reference state operation throughout the entire operational period for the WGS reactors by means of modelling of the axial temperature profile yielded insights into the rate of decay of the catalyst activity. Initial rapid deactivation during the first 500 hr operation is observed for reactor 1 and reactor 2. Subsequently, the reactor 1 catalyst activity decreases at a much slower rate than expected. The reactor 2 catalyst first restores its activity after which a decrease in activity is observed at a slower rate

compared to reactor 1. The reactor 3 catalyst has a much lower activity than anticipated. Repeated chemical analysis of reactor 3 catalyst samples hinted towards catalyst damage due to an over reduction as being the probable cause for the observed lower activity. This over reduction might result from steam condensation upstream of the reactor during start-up (large heat losses in between reactor 2 and 3 were observed in the commissioning phase), exposing the catalyst to hot dry syngas.

The high and stable activity directly following the rapid initial catalyst deactivation allows reduction of the reactor feed temperatures and lowering of the pilot steam consumption. For reactor 1 the lower overall temperature and lower steam content likely results in a more stable operation, prolonging catalyst lifetime. For reactor 2 the lower overall temperature is similarly beneficial and a prolonged catalyst lifetime is also expected for reactor 2. On the contrary, the increased pressure foreseen for the Magnum plant most likely leads to an increase in deactivation rate, which is not compensated by an increased pellet activity. Unfortunately, these effects cannot be quantified.

For FeCr-based catalysts, the catalyst CH_4 production is an indication of the catalyst selectivity. During the entire operating period, the CH_4 production by the catalyst is low (<50 ppm) and stable in time.

5.3 Catalyst coking (and the potential for reduced steam consumption)

This test run aimed to study the effect of reduced steam content on the catalyst resistance to iron carbide formation. Operation at a reduced steam/CO ratio would allow reducing the steam requirement for the WGS section and thus the CO_2 capture penalty, but can lead to reduction of the magnetite phase, Fe_3O_4, to FeC, which is active in hydrocarbon formation, noticeably CH_4. This so-called carbiding of the catalyst is reversible if the extent of carbide formation is not too severe. Severe carbiding can lead to permanent loss of catalyst activity and/or selectivity and even to physical damage of the catalyst pellets.

Compared to reference state operation at steam/CO=3.1 mol/mol (for reactor 2), operation at reduced ratios of 2.6 down to 1.5 leads to step-wise increases in the catalyst CH_4 formation while no continuous increase or light-off of the CH_4 content is observed. This indicates that at the conditions tested the catalyst does not display progressive carbiding. Other indications that excessive catalyst carbiding did not occur are i) the lower steam/CO testing does not appear to have influenced catalyst activity, ii) the absence of C_2+C_3 hydrocarbons in the reactor 2 effluent and iii) the uncompromised reactor 2 pellet strength measured after the entire campaign. It is concluded that the catalyst, which had more than 5000 h of operation, is stable at the reduced steam/CO ratios tested. Note that each set point representing a lower

steam/CO ratio was performed for 10 up to 116 hours. The effect of prolonged operation at reduced steam content on the catalyst performance remains uncertain. Therefore, on-line monitoring of the CH_4 content is crucial: at the moment an exponential increase of the CH_4 content is observed, the steam content should be increased to stabilize the CH_4 content. As the CH_4 content of the entering syngas has the same order of magnitude than the CH_4 production by the catalyst at reduced steam/CO ratio operation, an accurate indirect measurement of catalyst carbiding is possible in entrained flow gasifier systems. Using this characteristic, the steam content of the quench flow can be controlled by means of the measured CH_4 content in the reactor 2 effluent over the catalyst lifetime.
A trial and error procedure, in which the "carbiding turning point" for the first catalyst batch in the large-scale plant is used to anticipate carbiding in the next catalyst batch needs to be developed. Applying such procedure allows building up a strategy for the required steam content throughout the catalyst lifetime, such that the catalyst is always operated outside the carbiding regime. Note that increasing the operational pressure from 20 bar for the Buggenum pilot to 40 bar as the Magnum design will result in an increased tendency for catalyst carbiding. It is estimated that the steam/CO ratio for safe operation would increase by about 8% relative.

A reduction in reactor 2 steam content can lead to a significant energy saving at the expense of a slightly lower CO conversion. Lowering the reactor 2 steam/CO ratio from reference state conditions to 2.06 mol/mol results in a decrease of the overall conversion by 3.6%-points, while the overall steam/CO ratio decreases by 26%. This means that a small decrease in CO_2 capture ratio saves a significant amount of steam, thereby decreasing the efficiency penalty for CO_2 capture. For the most aggressive set point, the steam feed decreases by 35% resulting in a 9.2%-points drop in CO conversion. These results suggest that the increase in CO slip per amount of steam saved becomes larger at lower steam contents. Note that besides reactor 2, reactor 1 can also be operated at a reduced steam content of the feed. These aspects need to be investigated in an optimisation study for the full-scale plant.

5.4 Parametric tests CO_2 absorption section

Several parametric tests were performed to evaluate the impact on the CO_2 absorption efficiency, validate the mass transfer coefficients and the thermodynamic model developed for the solvent and the gas components. Most parametric tests were performed for both random packing Raschig Super-Ring 0.6 and structured packing Raschig Super-Pak 250Y, which enables a comparison between those packings.

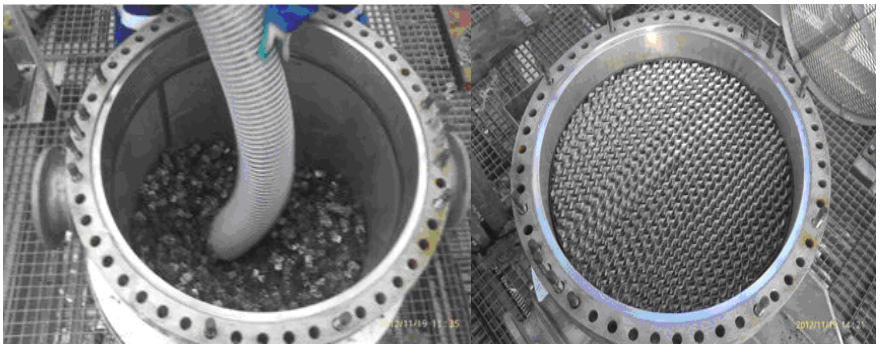

Figure 5-1: Raschig Super-Rings 0.6 (left) and Raschig Super-Pak 250 Y (right) in the CO_2 absorber of the pilot plant

All trends observed in the parametric tests are in line with expectations. The CO_2 absorption efficiency is slightly decreasing (0.6% absolute) with increasing water content from 1 to 4 wt%. The CO_2 absorption efficiency is increasing with decreasing solvent and shifted syngas temperature and with increasing absorber pressure, due to the higher partial pressure in the gas phase. Decreasing shifted syngas mass flow at constant solvent mass flow significantly increases the CO_2 absorption efficiency. Results also indicate that Raschig Super-Ring 0.6 has a better performance than Raschig Super-Pak 250Y. Decreasing solvent mass flow (while keeping shifted syngas mass flow constant) has the reverse effect. In addition, tests were done with extremely high solvent mass flows (240 $m^3/m^2/h$) as anticipated in the CB&I Lummus design for the full-scale capture plant. No experiments have been performed at such hydraulic conditions for structured packings. The main objective is to test the column hydraulics and the separation efficiency under these conditions. The test run showed a clear and expected relation between the solvent flow rate pressure drop and that flooding of the column can be identified based on the measured pressure drop for Raschig Super-Ring 0.6. For Raschig Super-Pak 250Y, the pressure drops show a much smoother behaviour and no sign of flooding of the packing or the distributor can be identified. Towards higher solvent flow rates, the CO_2 concentration at the absorber outlet levels out, indicating that the process becomes limited by mass transfer and no more CO_2 can be absorbed at these conditions.
Finally, the pressure of the 1st flash vessel was varied. The CO_2 concentration in the gas outlet is reduced significantly with increasing flash pressure, as less CO_2 is evaporated from the DEPEG solution. As a result, the H_2 concentration in the gas outlet increases.

After the test programme was finished, a sample of fresh and spent solvent was taken for analysis by Clariant. The analysis indicates that the spent solvent is still in good conditions, which is confirmed by the fact that the solvent performance was not deteriorating in time and the solvent physical appearance did not change in time.

6 Process modelling

For a better understanding of the CO_2 capture process and explanation of observed performance a series of process models (described below) have been developed. By validating the pilot plant models against real operational data, more reliable and accurate models applicable to the large-scale capture plant can be obtained. For this purpose, the pilot plant models are to be extended and extrapolated to the full-scale operational range based on theoretical scale-up rules and physical insights. The developed process models serve multiple objectives:

- Verify overall pilot plant performance
- Evaluate the performance of a specific technology component (e.g. assess catalyst activity, mass transfer coefficients in the absorber, etc.)
- Identify measurement errors in the data obtained from the pilot plant
- Simulate different operation scenarios in order to perform energy optimisation with respect to input process variables.
- Evaluate the dynamic response of the system in order to improve the controllability and modifying/improving the control system.
- Develop methods for (automated) process and control optimisation

6.1 WGS reactor model

The WGS reactor model is a heterogeneous adiabatic plug-flow reactor using intrinsic reaction kinetics in the form of a power-law rate equation. Using 2 parameters, being the catalyst activity factor and the length of the dead zone, the axial temperature profiles for all variations are accurately predicted. The model has been validated successfully. Up-scaling the model for Magnum implies adjusting the geometrical parameters of the reactors, while no other parameters need adjustment.

6.2 Steady-state model of the WGS section

A simulation model for the syngas conditioning and WGS section has been developed in Aspen Plus V7.3 and validated against 20 experimental data sets obtained from the pilot test programme. The quantitative model validation has been carried out as simultaneous data reconciliation and parameter estimation using the contaminated Normal distribution in order to decrease the influence of gross errors affecting the measurements. The model predictions for mass flows, temperatures and compositions

show good agreement with the measured values and 90% of the reconciled estimates are within ± 3.34σ (gross error cut point). It can be concluded that the steady-state model of the shifting section is capable of predicting the pilot plant performance throughout the entire operational range, and it can be used for the development of a large-scale model of the capture unit.

6.3 Steady-state model of the CO_2 absorption section

A simulation model for the absorption and regeneration section has been developed in Aspen Plus V7.3. The model was validated on seven sets of experimental data during which the shifted syngas and solvent flow rate were changed. The model parameters were multiplied constants (C_L and C_V) of the Billet and Schultes mass transfer coefficient correlation. The optimized values of the parameters for random packing Raschig Super-Ring 0.6 are $C_L = 0.1471$ and $C_V = 0.1085$. The absorber outlet molar fractions are on average fitted with an error of 0.72% absolute. The optimized values of the parameters by using objective for structured packing Raschig Super-Pak 250 function f_2 are $C_L = 0.1179$ and $C_V = 0.06242$. The absorber outlet molar fractions are on average fitted with an error of 0.86% absolute. The CO_2 absorption efficiency is predicted with a standard deviation of 0.016 for both packings. The accuracy of the concentration measurements is sufficient in order to get reliable C_L value. The C_V value is much more sensitive to a change in the concentrations used for parameter estimation and is therefore not so reliable.

The optimization results show that the parameter C_L is about 25% higher for Raschig Super-Ring 0.6 than for Raschig Super-Pak 250. As the resistance against the mass transfer is concentrated in the liquid phase, Raschig Super-Ring 0.6 seems to be a more suitable packing for the physical absorption of CO_2 for the specific hydraulic conditions tested in the pilot plant.

However, the fitted values for C_L and C_V are approximately a factor 10 lower than the default values used in Aspen/Winsorp (Raschig's simulation tool). In other words, the pilot plant performance is below expectations. One explanation can be the occurrence of foaming in the absorber. A second possibility can be gas back-mixing as the gas velocity is very low and liquid can entrain the gas. As no clear evidence for either of these hypotheses is present, it may be recommended for the design of the large-scale plant to apply a higher gas velocity to avoid the risk of back-mixing and add some anti-foam to ensure that the mass transfer is optimal. Because the structured packing is more sensitive to foaming, the expected performance increase by adding anti-foam is higher for the structured packing. The mass transfer performance should improve similarly for both packings by increasing the gas velocity because the back-mixing is packing independent. Assuming approximately two times higher gas velocity for the large-scale plant design versus the pilot plant, the hydraulic limit (loading point) of the random packing Raschig Super-Ring 0.6 is reached. Hence it is recommended to use structured packing Raschig Super-Pak 250 for the large-scale plant.

The trends in CO_2 absorption efficiencies with the change of the process variables (mass flows, concentrations, temperatures, pressures) are predicted correctly by the model. The CO_2 absorption efficiency is slightly underestimated (in reference state) which results in a safe prediction for up-scaling. For the full-scale plant, the process conditions may be outside the validated range e.g. absorber pressure up to 40 bar and solvent temperatures down to 10°C. The CO_2 absorption efficiency at higher pressure is overestimated which can be resolved by refitting the VLE data for the right pressure range. The CO_2 absorption efficiency at lower temperature is slightly under predicted by the model. In conclusion, the full-scale capture plant performance can be predicted within similar accuracy as for the pilot plant (CO_2 absorption efficiency ± 1.6% absolute).

6.4 Dynamic model of the WGS section

A dynamic model has been developed following an object-oriented, lumped parameter modelling approach using the Modelica language to study transient behaviour. The subsystem models and the entire system model are validated by comparison with experimental data obtained from various open-loop and closed-loop transient tests performed on the pilot plant. The validated models provide a reliable basis for the development of large-scale system models of the pre-combustion capture process which can be used to design control strategies. This requires the assembly of the respective process and the adaptation of the available component models according to the commercial-scale equipment sizing. With the pilot plant system model it has been demonstrated that such a large-scale model can be used to investigate the load-following potential of the capture unit with respect to the power producing process. The models allow to easily determine the system time constants, responses of the integrated streams and any process limitations.

6.5 Dynamic model of the CO_2 absorption section

An equilibrium-based dynamic absorber model using the Modelica language is validated by comparison with experimental data obtained from two open-loop transient tests in which the shifted syngas and solvent mass flow are perturbed. Satisfactory agreement between the experimental data and model predictions considering absorber pressure and temperature and H_2-rich gas flow rate is achieved. The adopted holdup correlation can be used for predictions of the dynamic performance of the pilot plant absorber column. Hence, the validated model provides a reliable basis for the analysis of the transient performance of a large-scale absorber.

7 Value of the R&D and application of the results

With the exception of the combustion of H_2-rich gas in state-of-the-art gas turbines, the components of pre-combustion capture are in fact proven on an industrial-scale, which is also indicated by the ZEP technology matrix (http://www.zeroemissionsplatform.eu/). As is indicated in the ZEP studies, integration of already proven blocks is essentially the main challenge for IGCC and pre-combustion capture. The initial study performed by CB&I Lummus was a first attempt to develop an optimally integrated design for the Magnum IGCC using state-of-the-art capture technology. The specific objectives (and therefore conventions and assumptions in design and operation) of WGS and CO_2 absorption technologies in the chemical industry are slightly different in comparison to power generation. In most chemical plants, for instance, the objective is to maximise the H_2 production regardless of the steam production, as H_2 is a valuable commodity (e.g. in refinery or as feedstock for ammonia). This results in a design where the catalyst is operated at relatively high steam/CO ratios. These conventions and assumptions for use in the chemical industry have been challenged in discussion with the vendors and new ideas verified in the pilot plant test programme. The results of the test programme clearly show that there is still improvement potential in conventional WGS and absorption technologies, and for some components even larger than anticipated by CB&I Lummus. Although several improvements have been suggested throughout this report, the implications are not yet quantified in detail for the large-scale capture plant. A study to calculate the impact of the improvements in the WGS section for the full-scale plant (in terms of overall plant efficiency and specific energy consumption per ton of capture CO_2) is ongoing together with Delft University of Technology. Next, more detailed economic evaluations are needed to assess the trade-off between CAPEX and OPEX. This is one of the tasks in the feasibility study for a future large-scale IGCC. It must be realised that by that time, the assumptions that determined the design of the Magnum IGCC (choice of gasifier etc.) may be outdated. The impact of some of the changes (e.g. higher gasifier pressure, different feedstock and hence syngas composition) could be predicted using the process models. More fundamental design changes would make part of the results obsolete though. It may also happen that the 2nd generation technologies may have been tested in demonstration plants and are commercially available. The work in this project represents the current state-of-the-art to which the new developments can be benchmarked. In addition, there may be opportunities to apply some lessons learned and insights to a wider spectrum of technologies/applications.

In summary, the project objectives to verify the technology performance and to generate knowledge in the form of validated models and operational experience are

clearly achieved. However, the knowledge generated in the CO_2 Catch-up project will not be applied directly, as the investment decision for the gasification and CO_2 capture unit in the Magnum project has been postponed beyond 2020, after it was decided earlier to separate the development and realisation of the power plant in two phases. Phase 1 comprises the construction of three 400 MW_e M701F4 combined cycle units operated on natural gas. At the moment of writing the report, the three combined cycle units are in operation. Phase 2 comprises the coal gasification based system with integrated CO_2 capture, transport and storage (CCS) to provide a synthetic gas as fuel for one of the combined cycle units, including the replacement of the dry low NO_x burners for natural gas combustion installed in Phase 1 by diffusion burners to enable the combustion of (hydrogen-rich) syngas.

The commercial outlook for phase 2 and IGCC+CCS in general remains uncertain. According to the Global CCS Institute, a total of 34 large-scale integrated CCS projects using the pre-combustion technology are known at the time of writing this report. Of these 34 projects, 11 are power generation projects (IGCC), the rest being natural gas processing, fertiliser, SNG, hydrogen and Fischer-Tropsch liquids production. The only project under construction is the Kemper country IGCC. The other projects in the USA also aim to sell their CO_2 for EOR (which may increase the chance of realisation). The European projects are all in the UK and with the announced preferred bidders for the UK's £1bn Carbon Capture and Storage Commercialisation Programme Competition (Peterhead Project in Aberdeenshire, Scotland, and the White Rose Project in Yorkshire), the future of the IGCC projects is rather uncertain. Apart from GreenGen, the Chinese projects are in the feasibility phase.

The main concern for IGCC plants remain the relatively high costs (both in terms of CAPEX and OPEX). The results of the CO_2 Catch-up project, basically promising an optimised design for the WGS and CO_2 absorption unit with reduced specific energy consumption (and hence OPEX) and possibly CAPEX, are not expected to change much to this problem. Although the CO_2 avoidance costs can be reduced, they are still far higher than the current ETS price.

Although direct application in the Magnum plant is not foreseen on the short term, the gasification projects under development in other parts of the world as well as new future projects may benefit from the achievements made in this project. Knowledge dissemination is aimed for by means of (scientific) publications of the researchers involved in the project. Papers in peer-reviewed journals are currently being prepared on the steady-state and dynamic pilot plant modelling work, as well as the results of the WGS reactor modelling and low steam/CO ratio test run. As the suppliers of catalyst, solvent and packing all have been heavily involved in the project to learn on the outcome of the test programme, hopefully the generated insights will be followed up and potentially discussed/offered in any new IGCC + CCS project. Finally, several seminars have been organised with Elcogas and J-Power, which operate(d) similar pre-combustion capture pilot plants, to exchange results.