GHGT-9

Experience with CO_2 capture from coal flue gas in pilot-scale: Testing of different amine solvents

Jacob N. Knudsen[a*], Jørgen N. Jensen[a], Poul-Jacob Vilhelmsen[b], Ole Biede[c]

[a]DONG Energy Power, A.C. Meyers vaenge 9, 2450 Copenhagen SV, Denmark
[b]DONG Energy Power, Kraftvaerksvej 53, 7000 Fredericia, Denmark
[c]Vattenfall A/S, Stoeberigade 14, 2450 Copenhagen SV, Denmark

Abstract

As part of the EU project CASTOR, a 1 t/h CO_2 absorption pilot plant has been erected at Esbjergværket (Esbjerg power station) in Denmark. The main purpose of the pilot plant is to demonstrate the post combustion capture technology in conjunction with a coal-fired power station. Additionally, the pilot plant has been used to test the performance of new energy efficient solvents and to validate modelling work. The pilot plant operates on a slipstream of flue gas from the power plant without any further pre-treatment. During the CASTOR project, four 1000-hours test campaigns have been conducted at the facility using conventional solvent, 30%-weight MEA as well as two novel amine-based solvents, CASTOR 1 and CASTOR 2. Among others, the test campaigns consisted of parameter variation tests and longer periods of continuous operation. This paper summarises the operation experience and some of the results obtained during the CASTOR project.

. . . .
Keywords: CO_2 capture; pilot-scale testing; coal flue gas, amine solvents

1. Introduction

As part of the EU project CASTOR (2004-2008), a 1 t/h CO_2 capture pilot plant has been erected and operated at a coal-fired power station. The main purpose of the pilot plant has been to demonstrate the post combustion capture technology in conjunction with a coal-fired power station. Additionally, the pilot plant has been used to test the performance of new energy efficient solvents and to validate modelling and laboratory results obtained by the different CASTOR partners. Within the framework of the CASTOR project, DONG Energy and Vattenfall Nordic have carried out the tasks of engineering, purchasing, installation and commissioning of the CO_2 capture pilot plant as well as planning and conducting tests at the facility. The CO_2 absorption pilot plant is placed at Esbjergværket (ESV). ESV is owned and operated by DONG Energy and is located at the west coast of Denmark. ESV is a 400MW pulverised coal-fired power station equipped with $deNO_x$ (high dust SCR), cold-sided ESP and FGD plants (wet limestone scrubber). The pilot plant operates on a slipstream of the flue gas, taken downstream the FGD plant. In the second half of 2005, the CO_2 absorption pilot plant was erected and commissioned. During the period of 2006-2007, a total of four test campaigns of approximately 1000 hours each were conducted using both

conventional and novel solvents. This paper presents selected results and experience obtained from the test campaigns conducted within CASTOR.

2. CO_2 absorption pilot plant at ESV

The design of the pilot plant is based on the design of a standard industrial amine-based CO_2 recovery plant with minor modifications. A flow diagram of the pilot plant is shown in Figure 1.
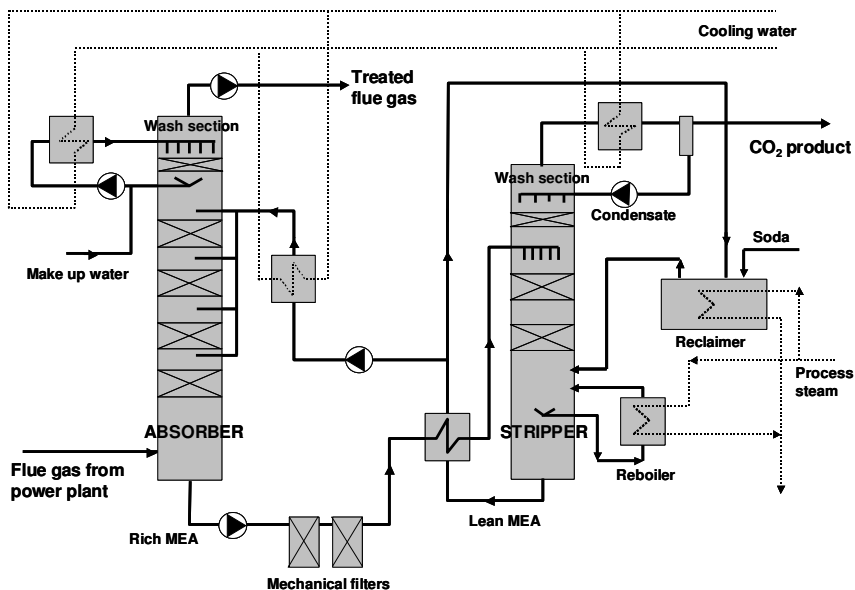

Figure 1. Simplified flow diagram of the CASTOR pilot plant at Esbjergværket.

A slipstream of the flue gas from ESV is taken at a position immediately after the SO_2 scrubber. The flue gas does not undergo any pre-scrubbing or cooling before supplied to the CO_2 absorber. The flue gas enters the absorber tower at the bottom in a counter current flow with the solvent. The fan is placed downstream the absorber, which implies that the absorber is operated at a pressure slightly below ambient. The CO_2 content of the absorber inlet and outlet is continuously monitored by IR analysers. The absorber tower consists of four consecutive packed-beds for CO_2 absorption and one water wash bed at the top. The absorber has an internal diameter of 1.1 metre. Each bed for CO_2 absorption is 4.25 metres in height and filled with IMTP50 random packing. The water wash bed is 3.0 metres in height and filled with structured packing. The water wash functions as a closed loop. The wash water from the bed is collected on a tray below the bed and is cooled in a water-cooler before returned to the wash section. Make-up water is added to the wash section, in order to control the amine build-up. The overflow from the wash section runs into the absorber. The rich solvent from the absorber is pumped through two mechanical filters in series and a plate heat exchanger (approximately 10°C delta T) before fed to the stripper. The stripper has an internal diameter of 1.1 metre and consists of two 5.0 metres beds filled with IMTP50 random packing and a water wash bed at the top (3.0 metres of random packing IMPT50). The stripper pressure is controlled by an overhead valve. The heat input to the stripper is supplied by a thermosyphon reboiler that is driven by utility steam (2.5 bar(g) saturated) from ESV. The overhead vapours from the stripper are quenched in a condenser. The condensate is returned to the stripper wash section and the resultant gas, essentially pure CO_2 saturated with water, is returned to the ESV flue gas duct. The regenerated solvent from the stripper is cooled to its final set point temperature by a water-cooler after it has been heat exchanged with the rich solvent. A slipstream of approximately 10% of the solvent flow is passed through a carbon filter in order to remove organic degradation products. Also part of the pilot plant is a reclaimer vessel where the impurities can be concentrated and removed from the solvent. In order to monitor energy and cooling water

consumptions as well as the general plant performance, the pilot plant is fitted with temperature sensors, pressure gauges and flow meters throughout. All of the measurements are continuously registered by a data acquisition system and logged on a PC. The key design and performance figures for the pilot plant are shown in Table 1. The flue gas purity criteria were defined in order to avoid excessive solvent degradation or other adverse impacts on the pilot plant operation, eg foaming and fouling.

Table 1: CO_2 absorption plant design specifications.

Parameter	Design value
Flue gas capacity	5000Nm^3/h ≈0.5% of ESV flue gas flow
CO$_2$ removal (at 12% CO$_2$)	1000kg/h
Capture percentage	90%
Max solvent flow	40m^3/h
Max reboiler steam flow	2500kg/h at 2.5 bar(g)
Max stripper pressure	2.0 bar(g)
Flue gas conditions	47°C (sat.), <10 ppm SO$_2$, <65 ppm NO$_x$, <10mg/Nm^3 dust (wet basis, actual O$_2$)

During the test campaigns, typical solvent analyses have been performed at the laboratory at ESV. The amine concentrations were determined by a standard titration procedure or GC analysis. The CO_2 loading was determined by the barium chloride method [1]. A number for the total acid equivalents, ie, heat stable salts, was determined by cation-exchange and subsequent titration. Selected solvent samples were analysed for inorganic constituents using ICP-OES.

3. CASTOR test program

During the CASTOR project, four test campaigns have been conducted at the pilot plant and more than 4000 hours of operation have been achieved in total. The test campaigns were:

1. 1000-hours operation on a reference solvent: 30% MEA
2. 1000-hours operation on a reference solvent: 30% MEA (similar to campaign #1)
3. 1000-hours operation on the novel solvent "CASTOR 1"
4. 1000-hours operation on the novel solvent "CASTOR 2"

CASTOR 1 and 2 are blended amine solvents developed in the CASTOR project. As the reference solvent, 30% MEA was chosen because of its well-known performance and the general availability of kinetic and thermodynamic data for simulations. During the first test campaign with MEA, it was discovered that some of the vital measurement devices, eg steam flow meter, were not working properly. Furthermore, the pilot plant was initially operated at conditions recommended by the supplier, which proved not to be optimal with respect to CO_2 capture from power plants [2]. Thus, it was decided to conduct a second test campaign using 30% MEA in order to improve the data quality and the overall process performance. Following the second MEA campaign, the CASTOR 1 and 2 solvents were tested back to back. The second test campaign with MEA and the test campaigns with the novel solvents CASTOR 1 and 2 were largely following the same outline. The first approximately 500 hours of the test campaigns were used to conduct a parametric study, whereas the last 500 hours were dedicated to one continuous test of 500 hours duration. The objective of the parameter variation tests was to identify the most feasible operation conditions for the capture plant in terms of energy efficiency. This was accomplished through individual tests where the absorber liquid-to-gas ratio (L/G), the stripper pressure and the CO_2 removal percentage were altered. The main objectives of the 500-hours test were to operate the plant at the optimised conditions and collect information on energy and solvent consumptions as well as corrosion rate and overall plant stability.

4. Test results and discussion

In this section selected results from the different CASTOR test campaigns are presented and discussed.

4.1 Optimisation of absorber liquid-to-gas ratio (L/G)

Tests were conducted to optimise the absorber L/G ratio at 90% CO_2 removal for all three solvents. The tests were carried out by operating the absorber at a fixed flue gas throughput ($\approx$5000Nm^3/h) and changing the solvent flow rate. The stripper pressure was held constant at 1.9 bar(a) and the CO_2 recovery was tuned to approximately 90% by adjusting the steam input to the reboiler. In Figure 2, the specific steam demand has been plotted as a function of the absorber L/G ratio (in kg solvent/kg flue gas) for each of the tested solvents. Because the CO_2 removal degree has been held constant, changing the L/G ratio also implies changing the solvent lean loading.
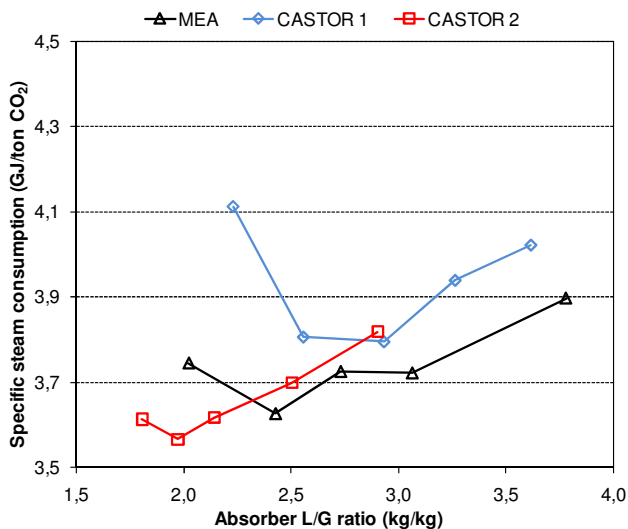

Figure 2. Optimisation of absorber liquid-to-gas ratio (L/G) at $\approx$90% CO_2 removal

With MEA, Figure 2 indicates that the lowest specific steam demand (3.6GJ/ton) was obtained at L/G ratio of approximately 2.5kg/kg. However, the specific steam demand is nearly constant for L/G ratios between 2.0 and 3.0kg/kg indicating that the optimum is quite broad for MEA. At the higher L/G ratio (3.8), the specific steam demand clearly increases. At L/G ratios below 2.0kg/kg, it was not possible to maintain the 90% CO_2 removal.

For the CASTOR 1 solvent, Figure 2 shows that the minimum specific steam demand is approximately 3.8GJ/ton CO_2 which is slightly higher than for MEA. Furthermore, the minimum reboiler duty is obtained at higher L/G ratios (2.5-3.0kg/kg) than with MEA. In addition, the increase in specific steam consumption is more pronounced at either side of the minimum. Altogether this indicates that the CASTOR 1 solvent has a lower cyclic CO_2 carrying capacity and is slightly less energy efficient compared to MEA. Based on the laboratory benchmark tests carried out in the CASTOR project, a somewhat better performance of CASTOR 1 was anticipated. The reason why this was not obtained in Esbjerg, was probably a lower reaction rate of CASTOR 1 than expected. This was also confirmed by the rich solvent loadings, which were substantially lower than expected.

For the CASTOR 2 solvent, Figure 2 indicates that the minimum steam demand is below 3.6 GJ/ton CO_2, which is slightly lower than that of MEA. In addition, the minimum steam demand is obtained at a significantly lower L/G ratio compared to that of MEA. This indicates that the cyclic CO_2 carrying capacity of CASTOR 2 is superior to that of MEA. Thus in addition to the lower regeneration energy, the pumping work for solvent circulation may also be reduced with CASTOR 2. Clearly the results in Figure 2 indicate that it is possible to develop new amine solvent that reduce the energy requirement of CO_2 capture compared to MEA. Moreover, it is believed that the regeneration energy of CASTOR 2 solvent can be further reduced by optimisation of its composition.

4.2 Reducing reboiler steam input at optimal L/G ratio

The purpose of this test was to determine the specific steam consumption at three different CO_2 capture percentages ($\approx$70, 85 and 95%) at the optimum L/G ratio. The test was carried out at a fixed stripper pressure of 1.9

bar(a) and at the nominal flue gas flow ($\approx$5000Nm^3/h). To change the CO_2 capture percentage, the steam input to the reboiler was adjusted.

In Figure 3, the specific steam consumption is depicted as a function of the CO_2 recovery percentage. For all solvents, the specific steam demand is relatively independent of the extent of CO_2 removal in the range $\approx$65-95%.
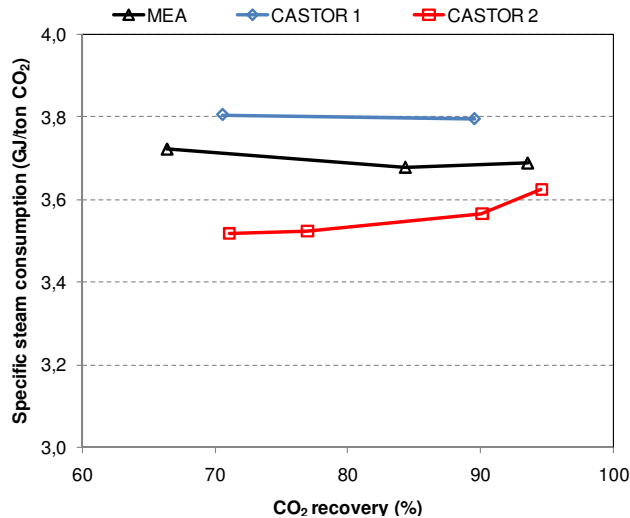

Figure 3. Reducing reboiler steam input at optimal L/G ratio.

For CASTOR 1 it was not possible to achieve 95% CO_2 removal at full load. For CASTOR 2, the specific steam demand is only increasing insignificantly as the CO_2 capture percentage is increased from 70 to 90%. However, if the CO_2 capture percentage is increased to 95%, the increase in specific steam consumption becomes more significant. Considering the small increase in the specific steam consumption when going from 65-70 to 90% CO_2 capture, 90% capture seems as a good target. This will of course to some extent dependent on the specific design of the capture plant, ie available mass transfer capacity of the absorber relative to the reaction rate of solvent. Since the absorber height at the pilot plant in Esbjerg is higher than required for MEA, the energy penalty by increasing the CO_2 capture percentage may be less significant for MEA.

4.3 500 hours of continuous operation at optimised conditions

Tests with 500 hours of continuous operation were conducted for all three solvents. The objectives of these tests were to operate the pilot plant continuously for 500 hours at the optimised conditions (identified in the parameter variation tests) and achieving 90% CO_2 removal on average. In addition, it was the aim to characterise the corrosion behaviour by installation of corrosion coupons as well as to gain information on solvent consumption and build-up of degradation products. The results of the corrosion studies have been reported elsewhere [3]. Finally, it was the objective to gain experience on the overall process stability.

In Figure 4, the history of the flue gas flow to the pilot, the CO_2 recovery and the specific steam demand are shown for the entire duration of the 500 hours test in the second MEA campaign. It appears that except from two short outages on 23 and 25 January 2007, the pilot plant has been in continuous and stable operation. The two outages were caused by incidents at the power station and not directly related to the CO_2 capture plant.

In addition, Figure 4 shows that the CO_2 recovery typically fluctuates between 85 and 95% throughout the test period. The fluctuations are responses to changing CO_2 concentrations in the flue gas caused by load changes at the power station. The average CO_2 removal for the entire 500-hours period is approximately 88%. Furthermore Figure 4 shows that the steam demand has been relatively constant around 3.7GJ/ton CO_2 with some narrow peaks reaching 4.2-4.3GJ/ton. The peaks appear to be related to a sharp increase in the CO_2 recovery. In fact, the peaks are caused by the sudden decrease in CO_2 production when the CO_2 concentration in the flue gas decreases, whereas the absolute heat input to the reboiler remains unchanged. The average steam demand for solvent regeneration during the entire test is approximately 3.7GJ/ton CO_2

The 500-hours tests with the CASTOR 1 and 2 solvents were performed in a similar way as with MEA. Initially foaming episodes with CASTOR 1 were experienced, which resulted in unstable operation. This could, however, be

solved by using an appropriate antifoam agent. Otherwise the 500-hours test confirmed that the regeneration energy of CASTOR 1 was slightly higher than for MEA.

In the beginning of the 500-hours test with CASTOR 2, the performance of the solvent was as expected and regeneration energy around 3.5-3.6GJ/ton CO_2 was achieved. However, as the 500-hours test progressed, unexpectedly high solvent losses were observed. This had adverse imp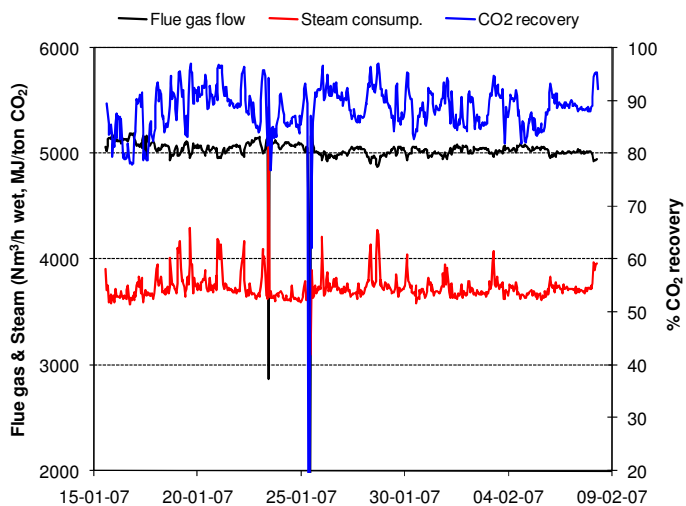act on the performance of the solvent, ie increased regeneration energy and reduced CO_2 removal. The performance of the CASTOR 2 solvent could be restored by periodically adding fresh solvent to the system. Nevertheless, the average steam consumption for the entire test was unfavourably affected by the solvent losses.

Figure 4. Pilot plant performance during 500-hours test on MEA.

4.4 Solvent consumption, degradation and flue gas pollutants

In amine based CO_2 capture processes, solvent is continuously consumed as results of physical solvent loss (evaporation & entrainment), solvent degradation and irreversible absorption of flue gas pollutants, eg SO_2. For the test campaigns conducted at the pilot plant in Esbjerg, the solvent consumption was quantified during the 500-hours tests. This was done by monitoring the decline in amine concentrations and keeping track of the amounts of make-up amines added. No solvent reclaiming was performed during any of the 500-hours test and no corrosion or oxidation inhibitors were used with any of the solvents. For the second MEA campaign, it has been estimated that approximately 720kg of MEA was consumed during the 500-hours test. During this test, 503 tons of CO_2 was captured, which resulted in a specific MEA consumption of 1.4kg/ton CO_2 captured. For CO_2 recovery from gaseous fuels (no SO_2), a MEA consumption of 1.6kg/ton CO_2 has been reported [4]. Considering the fact that the flue gas from ESV also contains a few ppm SO_2, the estimated MEA consumption is relatively low. This may be due to the fact that the solvent was relatively fresh, ie low content of degradation products, at the beginning of the 500-hours test, whereby the degradation rate was relatively low in the beginning. In addition, no reclaiming was performed, which is known to increase solvent degradation. With CASTOR 1 and 2, the solvent consumptions were in similar ranges as with MEA. This was in some way surprising as the degradation rates of these solvents are inherently lower. It is expected that the losses of CASTOR 1 and 2 were primarily related to physical mechanisms, ie foaming, mist formation, etc.

In the case with MEA, oxidative degradation and carbamate polymerization are very significant causes of MEA consumption [5]. The complex degradation mechanisms of MEA have been investigated in several publications [5, 6]. However, the relative importance of the different degradation mechanisms is still not completely clear. Among the more simple degradation products of MEA are ammonia, aldehydes and carboxylic acids. The degradation of MEA is also reported [5] to be catalysed by the presence of certain metallic elements, eg V, Fe and Cu. These species may enter the solvent due to the presence of fly ash, corrosion products, and corrosion inhibitors.

Part of the criteria that led to selection of the CASTOR 1 and CASTOR 2 solvents were increased resistance towards oxidative and thermal degradation. For this reason, it is expected that the degradation rates of CASTOR 1 and CASTOR 2 are lower than that of MEA. In Figure 5, the change in solvent concentration of heat stable salts (HSS) during the 500-hours tests with MEA and CASTOR 2 are depicted. The concentration of HSS can be used as a measure of the amount of degradation products in the solvent (including acidic gases absorbed from the flue gas). It appears from Figure 5 that, at the start of the 500 hours test, both solvents contain approximately 0.5 %w/w HSS. This represents the contents of HSS that have accumulated during the parametric testing phase. Figure 5 shows that the HSS concentration increases at a significantly higher rate for MEA than CASTOR 2 during the 500 hours test. This indicates that the CASTOR 2 solvent is much more chemically stable than MEA. Moreover, most of the growth in HSS for CASTOR 2 during the 500-hours test is a result of absorption of residual SO_2 from the flue gas. Based on Figure 5, the average HSS accumulation rates are estimated to 0.19 and 0.05kg/ton CO_2 for MEA and CASTOR 2, respectively.
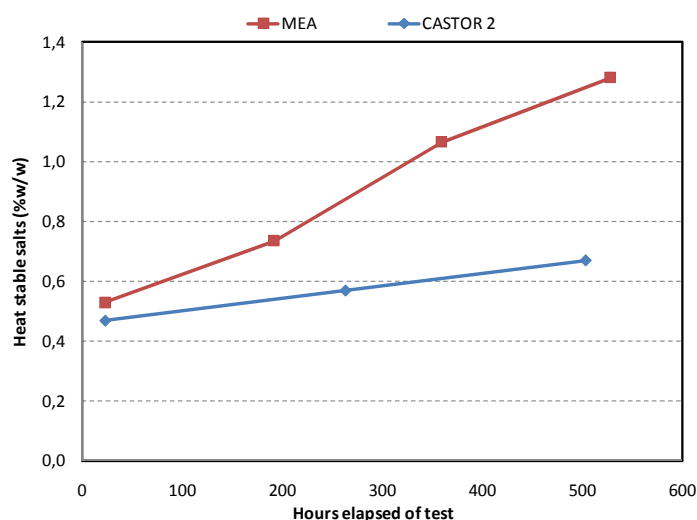

Figure 5. Development in heat stable salts during 500-hours test with MEA and CASTOR 2.

An attempt was made to close the sulphur mass balance during the 500-hours test. This was accomplished by monitoring the SO_2 concentration in the flue gas as well as analysing samples of solvent for the total sulphur content at the beginning and end of the 500-hours test, respectively.

It appears from Table 2 that the average sulphur concentration in the flue gas to the CO_2 capture plant has been similar ($\approx$6ppm) in the two test campaigns. However, for the MEA test, nearly all of the SO_2 in the flue gas was found to accumulate in the solvent as expected. In contrast, less than half of the sulphur input with the flue gas was found to accumulate in the CASTOR 2 solvent. It is not completely clear why this is the case. Perhaps it is related to a relatively high solvent loss of CASTOR 2 by some physical mechanism, ie carryover of sulphur containing solvent droplets, or perhaps SO_2 is to some extent reversible absorbed by CASTOR 2.

Table 2. Sulphur balance during 500-hours tests with MEA and CASTOR 2.

	2nd MEA test	CASTOR 2
Sulphur input with flue gas	21kg ($\approx$5.9ppm on average)	19kg ($\approx$6.0ppm on average)
Sulphur uptake in solvent	18kg	7.3kg
% accumulated sulphur	$\approx$85%	$\approx$40%

At the end of the 500-hours test with MEA, detailed emissions measurements were conducted on the flue gas leaving the absorber (after the wash section) and the CO_2 gas from the condenser. At the time of gas sampling, the pilot plant has been in stable and continuous operation for more than 300 hours. Both gas streams were analysed for MEA, ammonia, alcohols, aldehydes, ketones and carboxylic acids as well as the typical flue gas pollutants (CO, NO_x, SO_2, VOC and TOC). No MEA was detected (<0.01mg/Nm^3) in the flue gas from the absorber or the CO_2 product. However, the more volatile degradation products could be detected in both streams, eg ammonia,

formaldehyde, acetaldehyde and acetone. In particular, the emission of ammonia from the absorber ($25mg/Nm^3$) was rather significant. Ammonia is primarily formed as a result of oxidative degradation of MEA on a 1 to 1 mole basis. Based on the measured ammonia emission, it can be estimated that approximately 0.4kg MEA/ton CO_2 or ≈30% of the total MEA loss is consumed due to oxidative degradation. If it is assumed that 1 mole SO_2 reacts irreversibly with 2 moles MEA, Table 2 indicates that approximately 0.15kg/ton CO_2 or ≈10% of the total MEA loss is caused by SO_2. The remaining MEA loss (≈60%) may be caused by thermal degradation and to a smaller extent reaction with NO_x.

5. Conclusion

As part of the EU CASTOR project, a 1 t/h CO_2 absorption pilot plant has been erected at Esbjergværket, a coal-fired power station. During the CASTOR project, four test campaigns with both conventional (30% MEA) and novel amine solvents (CASTOR 1 and 2) have been conducted at the pilot plant in Esbjerg and more than 4000 hours of operation have been achieved in total. Among others, the tests have confirmed that it is possible to maintain stable and reliable operation of a post combustion capture unit on coal flue gas for extended periods of time achieving around 90% CO_2 capture. The steam requirement for solvent regeneration using 30% MEA was found to be 3.7GJ/ton CO_2 at 90% removal and the MEA consumption 1.4kg/ton CO_2. The tests with the novel solvent CASTOR 2 indicated that it is possible to develop amine solvents with lower regeneration energies and to have increased stability towards degradation. In the coming years, the pilot plant will be used to gain more experience on post combustion capture and to evaluate the performance of new solvents developed in the EU CESAR project. Furthermore, a series of process modifications that will reduce the regeneration energy and the environmental impact will be implemented.

6. Acknowledgements

7. References

[1] S. Ma'mun, R. Nielsen and H. F. Svendsen. J. Chem. Eng. Data. 2005; 50; 630-634.
[2] J. N. Knudsen, P.J. Vilhelmsen, J. N. Jensen, O. Biede. "CASTOR 1 t/h CO_2 absorption pilot plant at the Elsam Kraft A/S Esbjerg power plant - First year operation experience". 8th International Conference on Greenhouse Gas Control Technologies, 19-22 June 2006, Trondheim, Norway
[3] J. Kittel, R. Idem, D. Gelowitz, P. Tontiwachwuthikul, G. Parrain, A. Bonneau. Corrosion in MEA units for CO_2 capture: pilot plant studies, 9th International Conference on Greenhouse Gas Control Technologies, 16-20 November 2008, Washington D.C., USA
[4] D. Chapel, J. Ernest, C. Mariz. Recovery of CO_2 from flue gases: Commercial trends. Canadian Soc. Chemical Engineers annual meeting, Oct 4-6 1999, Saskatoon, Saskatchewan, Canada.
[5] G. S. Goff and G. T. Rochelle. Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. Ind. Eng. Chem. Res. 2004; 43; 6400-6408.
[6] A. Bello and R. O. Idem. Pathways for the formation of products of the oxidative degradation of CO_2 loaded concentrated monoethanolamine solutions during CO_2 absorption from flue gases. Ind. Eng. Chem. Res. 2005; 44; 945-969.