EVALUATION OF NOVEL POST-COMBUSTION CO_2 CAPTURE SOLVENT CONCEPTS

Technical Study

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Evaluation of Novel Post-Combustion CO_2 Capture Solvent Concepts

Background to the Study

The IEA Greenhouse Gas R&D Programme (IEA GHG) has been monitoring the progress of the development of post-combustion CO_2 capture technologies especially looking at the various different solvent alternatives to the standard monoethanolamine (MEA) process.

It was proposed in the study voting round of the 30th ExCo meeting (Vaasa, Finland), that a technical review of some of the more novel capture processes should be undertaken. The review which is reported here looked at solvents other than MEA that could be used for post-combustion CO_2 capture in the near term.

The purpose of this review was to outline the current state of knowledge and provide an assessment of the following aspects:

- Process chemistry and kinetics,
- Operational issues and major development issues,
- Qualitative evaluation of the performance of absorber and stripper column,
- Safety and Environmental Impact considerations.
- Technology maturity and reported time scale for commercialisation.

For this study, SINTEF Material and Chemistry, Norway was employed to do the technical review on three different solvents namely: Alstom's Chilled Ammonia Process, the CANSOLV Amine Process and Praxair's MEA-MDEA solvent.

Assessments were made to identify the potential benefits, challenges, and uncertainties regarding the three processes described. Also included in this report is a brief review of the current state of knowledge of Flour's Econamine FG+ process which was used as a baseline case for performance comparison.

All assessments made in this report were based on information made available in the open literature, supported by kinetic evaluations made at SINTEF's laboratory.

Summary of Discussion

Summary of the Assessment of the Chilled Ammonia Process

Alstom's Chilled Ammonia Process is a carbonate / bicarbonate process which could be considered analogous to the Benfield Hot Carbonate Process developed during the 1950's. In comparison to the Benfield Process, there are many similarities but also with significant differences.

The idea behind Alstom's process is to use a high concentration of aqueous ammonium carbonate solution and form an ammonium bicarbonate solution for the absorption of CO2 from the flue gas. It has been reported that the solvent loading could be increased in this process compared to a standard MEA process therefore reducing the solvent recirculation rate.

For this process, the absorber should operate between 0 -10°C. This process would therefore require the flue gas to be pre-cooled in two stages by 2 direct water contact coolers (DCC's).

The regeneration of the solvent primarily consists of the main stripper with a reboiler and a condenser. It is expected that the regeneration unit would be similar in principle to an amine desorption tower. The key assumption should be that there will no carbonate solids present in the stripper and reboiler section. This is achieved by dissolution of the solids in a regenerative heat exchanger.

The process flow diagram is shown in Figure 1.

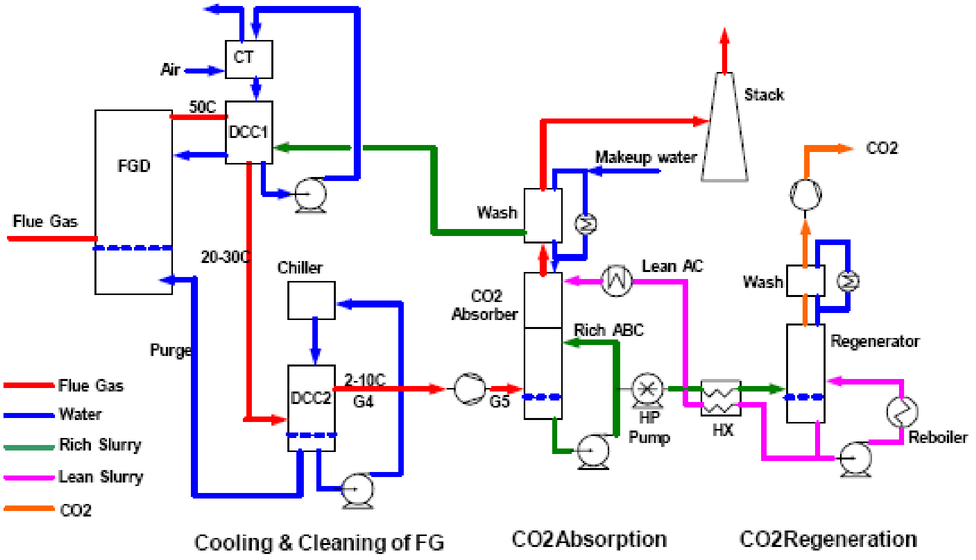

Figure 1: Simplified schematic diagram of Chilled Ammonia Process

The report presented the detailed description of each process unit and identified various potential advantages, disadvantages and challenges which remain to be addressed.

Some of the potential advantages identified for the Chilled Ammonia Process are as follows:

- Low regeneration energy requirement: the heat of absorption of CO_2 with ammonium carbonate to form bicarbonate is about 30% lower than that of MEA. Regeneration occurs at high pressure, which could potentially reduce compression costs and reduces the size of the regenerator considerably. As noted the energy requirement will be about one fourth of that for the compression stage compared to the typical compression requirement of the CO_2 captured from standard MEA or Flour Econamine process.
- Operation with slurry potentially enhances the CO_2 carrying capacity of the solvent which is far greater than that of MEA.
- Pre-cooling of the inlet flue gas reduces the volumetric flow rate to the absorber, which could potentially reduce the absorber diameter and pressure drop significantly.
- Process waste heat and heat rejection can possibly be re-used in other part of theCO_2 capture process. Heat removed in the pre-heating stage can be reused as well as cool sources such as the overhead cleaned flue gas.

- Ammonia is cheap and does not degrade like MEA.
- The extensive cooling of the flue gas will be an effective particle wash, effectively removing trace SOx and other particulate matters that remains in the flue gas

Some of the potential disadvantages identified for this process are as follows:

- Operational disadvantages:
    - A slurry type of solvent significantly complicates the process which will require an absorption tower that could handle solids. Concern has also been raised with regard to the particle distribution in the absorption tower and its impact to the reliability of the process.
    - The absorber will probably have to be of a spray tower type, which will reduce the performance of a liquid film controlled reaction.
    - More unit operations and piping and narrower operational interval implies increased requirement on process control.
    - A high pressure slurry pump is needed.
- Lean solution pressure:
    - The lean solution pressure exiting the desorber is about 30 bars. Flashing of steam and CO_2 might occur when reducing pressure to ambient prior to the absorber.
- The solid formation:
    - High energy of dissolution,
    - The exothermic precipitation reaction will require additional cooling/refrigeration in the absorber to keep the temperature low as well as mechanical agitation,
    - A complicated regenerative heat exchanger is needed for providing the additional energy required for the rich solvent consisting of solids to dissolved and become a liquid solution. Therefore there is a need to control solvent dissolution and flashing. Mechanical stirring will probably be necessary to provide uniform heat transfer to the solution in the heat exchanger.
- Reaction rate and absorber chilling:
    - Operation of absorber at a low temperature is required to provide sufficient driving force for the absorption and to minimise overhead slip of ammonia.
        - At this low temperature the carbonate/bicarbonate reaction kinetics are very slow (this is confirmed by experiments performed at SINTEF). It should be noted that absorption of CO_2 by the ammonium carbonate system might not be possible without a significant presence of free ammonia working as an activator. This makes the process more energy intensive and puts higher demands on slip reduction control of ammonia.
    - The separate coolers and refrigeration system required for cooling of the flue gas inlet stream, inter-cooling of the absorber and cooling of the lean stream implies considerably larger CAPEX and OPEX compared to the corresponding cooling system of an MEA based processes.
        - Pre-coolers will have similar diameters as the absorber.
- CO_2 removal efficiency
    - It is unclear if the process can absorb 90% of the CO_2 in the flue gas without free ammonia being present at the absorber.

Some of the remaining challenges needed to be addressed are as follows:

- Ammonia slip:
  - Is it practically feasible to retain the ammonia in the system?
- Absorption rate:
  - Is the carbonate/bicarbonate rate of reaction sufficiently fast at the low operational temperature or is significant free ammonia a necessity?
- Slurry:
  - Are the particle sizes of the solid bicarbonate manageable so it can be effectively handled in the hydro cyclone and cross-flow heat exchanger and other unit operations?

Summary of the Assessment of the Cansolv Amine Process

The main feature of the Cansolv Amine Process is the use of specific proprietary solvent (DC101^{TM}) which was described as a solvent with (a.) low oxidative degradation potential, (b.) low volatility of the solvent and (c.) low energy consumption for regeneration.

Although the composition of the solvent (DC101^{TM}) is not specifically mentioned in the patent, some indications have been given that this solvent comprises a blend of various types of amine (mostly secondary amine) and constitutes at least one type of tertiary amine and an oxidative inhibitor. Primarily the secondary amine acts as the activator to the tertiary amine to increase its mass transfer rate for capturing the CO_2.

Figure 2 below presents the simplified schematic diagram of the CANSOLV CO_2 capture process.

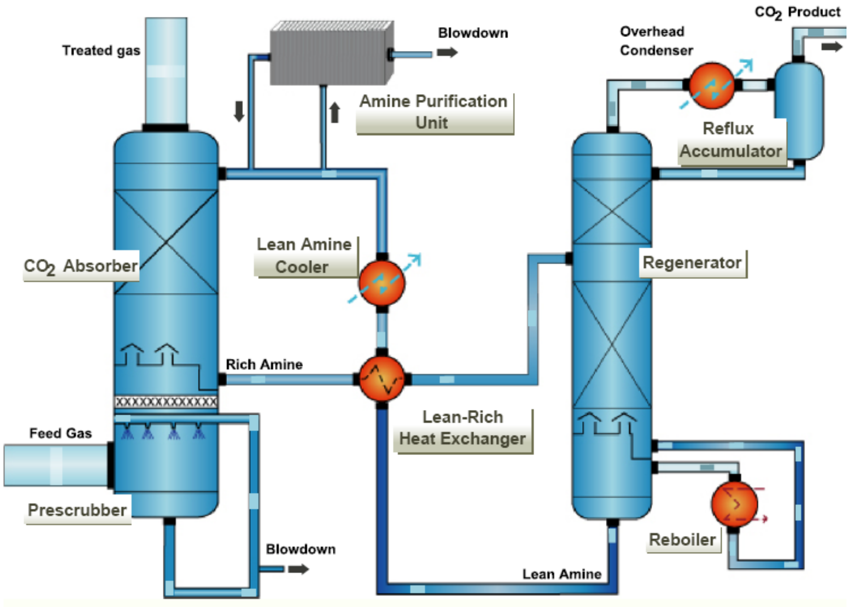

Figure 2: Simplified schematic diagram of CANSOLV CO_2 Capture Process

The key features of the CANSOLV solvent have been identified in the report and include:

- By using a tertiary amine, the pH range 6.5 – 8.5 has been claimed to be the optimal with respect to lowest energy consumption and highest absorption capacity for CO_2 capture.
- The tertiary amine has a vapour pressure less than 1 mmHg (approx. 1.3 mbar) at 120°C and a water-wash treatment is not required for this solvent. Due to the presence of a secondary amine a water-wash section is however, needed, but this section is smaller in volume compared to the standard MEA process.
- The solvent comprises an aqueous solution consisting of 10-50 wt% of the tertiary amine, 0-8 wt % of piperazine, 1-30 wt% of N-(2-hydroxyethyl) piperazine, and with the remainder comprising water.

The second key feature of this process is the ppossibility of integrating the CO_2 capture process with the NOx and SOx removal process. Figure 3 present the simplified schematic diagram of the process.

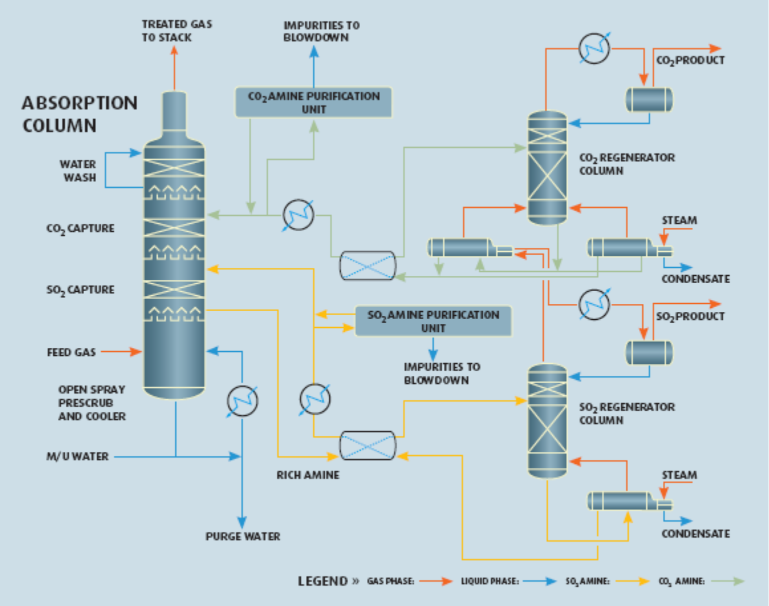

Figure 3: Simplified schematic diagram of CANSOLV CO_2 Capture Process with integrated SO_2 removal process

The report presented the detailed description of each of the process units and identified various potential advantages, disadvantages and challenges which remain to be addressed.

Some of the potential advantages identified for the CANSOLV process are:

- Low regeneration energy requirement: CANSOLV has claimed that energy consumption is 40% lower than the Flour Economine process. But it should be noted that clarification is still necessary for this claim. Firstly, it has not been specified in the literature which Flour Economine configuration is used as reference case for CANSOLV's claim. Secondly, it is not clear to the authors if this lower energy requirement is applicable to the CO_2 capture process alone or also to include the integrated SO_2 removal process as well.

- The integrated SO_2 and CO_2 removal could provide potential capital cost savings since both gases could be removed in a single absorption column.

One of the key concerns raised by the authors of this review is the potential implication of the effluent which consists of piperazine derivatives, which are known for their low biological degradability rating.

Some of the key challenges identified for the CANSOLV process are:

- The operation of the integrated CO_2 and SOx removal process could be more complex than the MEA process. Primarily, it has been noted that one solvent will be used to capture both gases; however, the solvent is required to be operated at two different pKas. This could also be further complicated by the effect of varying load which is normal to a coal fired power plant.
- The authors also raised the issue of the synergetic advantage of capturing both CO_2 and SO_2 species. The key issue is whether the accumulation of SOx in the solvent circulating through the absorption column could adversely affect the capture of CO_2. This is an outstanding question that needs to be answered.

Summary of the Assessment of the Praxair MEA-MDEA Process

Praxair has recently developed a common amine absorption configuration using a proprietary solvent consisting of a blend of MEA and MDEA with the following key features:

- The specific handling of oxygen content in the CO_2 captured gas prior to its regeneration in the stripper column.
- The possibility of the addition of an organic component to the aqueous solvent to reduce energy consumption.

Figure 4 presents the basic schematic diagram showing the absorption and desorption process and indicating the application of specific Praxair technology (i.e. solvent and vacuum pump).

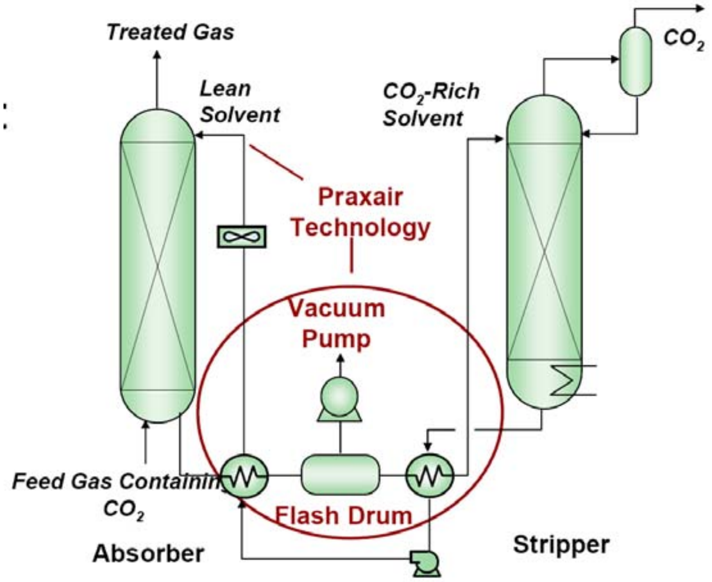

Figure 4: Simplified schematic diagram of Praxair Amine Blend Process

The first key feature of this process is the handling of the problems with oxidative degeneration of amine. This is achieved by removing the dissolved oxygen from the rich solution, before it is heated prior to regeneration, through a process modification. It is claimed that there will be no need for inclusion of inhibiting agents. The dissolved oxygen would otherwise cause amine degradation leading to corrosion of steel piping and equipment and other operational problems. To overcome this issue, the modified process incorporates a vacuum flash tank downstream from the absorber, operating at a pressure of 0.2-0.4 bar_a. The depressurization stage is claimed to remove the oxygen from the rich solution to less than 2 ppm. Some CO_2 may be released here also. Alternatively, it is noted in the patent that the rich solvent can be moderately heat exchanged to a temperature within 60-71^oC prior to the vacuum flash deoxygenation. The oxygen can also be removed by contacting the solution with an oxygen scavenging gas such as nitrogen or a portion of the stripped CO_2 in a packed column or a similar mass transfer device. The resulting oxygen free rich solvent then passes through a (second) heat exchanger and is heated to a temperature of about 105^oC before entering the stripper as in a traditional process configuration.

The second key feature of this process is the use of a proprietary concentrated alkanolamine blend, up to 50wt% using a larger concentration of one or more slow reacting amines (from 5 to 50 wt%) and a smaller concentration of one or more fast reacting amines (from 5 to 35 wt %). As an example, in a preferred blend one fast reacting amine is chosen, 20wt% MEA, with a second higher capacity and slower reacting amine such as 20-40 wt% MDEA also included. Other fast reacting amines suggested include DEA, Piperazine and diisopropanolamine and other slow reacting amines include TEA and sterically hindered amines such as 2-amino 2-methyl 1-propanol (AMP) could also be used.

The third key feature to this process is the addition of an organic component to improve its energy efficiency. This component is suggested, among others, to be a C_1-C_3 alcohol, ethylene glycol or similar chemical. This addition is thought to reduce the sensible and latent heats that are required for regenerating the amine.

The report presented the detailed description of each process units and identified various potential advantages, disadvantages and challenges which remain to be addressed.

Some of the potential advantages identified for Praxair process are:

- The addition of the organic component provide significant reduction in energy consumption It was noted in this review that by adding the organic component this could potentially reduce steam consumption down to 2.98 GJ/ton of CO_2 (as compared to 4.2 GJ/ton of CO_2 from a standard MEA plant).
- The handling of oxygen prior to regeneration of the solvent could reduce, but not totally remove, the use of the inhibitors. The authors noted that oxidative degradation of the solvent could also occur in the absorber and absorber sump (i.e. it should be noted that occurrence of the degradation of solvent is not only limited in the desorption tower)

Some of the potential disadvantages identified for Praxair process are:

- The use of an organic solvent could increase the operating temperature of absorber due to increased vapour pressure contributed by the organic components. This could result in higher thermal degradation of the solvent and carbamate polymerisation.

- Concern has also been raised with regard to the potential environmental impact caused by the effluent due to the presence of organic components, which are alcohol based.

Conclusions

SINTEF Chemistry and Materials has extensively evaluated and assessed three novel solvents in this report. The assessment has been made based on publicly available information and supplemented by kinetic data gathered in their laboratory.

The assessments made were aimed to identify the potential benefits, challenges, and uncertainties regarding the three processes described. Also included in this report is a brief summary of a standard MEA based process which is used for performance comparison. The standard MEA process is based on Fluors Econamine technology.

It was agreed during the 35th Executive Committee meeting at Brisbane, Australia that prior to distribution of this report to the members; the report will be given to the various stakeholders of these technologies (i.e. providers and users) for their comments. SINTEF Chemistry and Materials would further evaluate any new material provided and incorporate any validated new results and information to this report. In this regard, the next section, presents the various comments of independent experts and technology providers.

Expert Review Comments

The Expert Reviewers' noted that this study was undertaken based on a broad review of the open literature for the three types of absorbent based on aqueous ammonia (Alstom's Chilled Ammonia Process) and "advanced amines" (CANSOLV and Praxair solvent) with limited validation of the claims of the literature.

This study brings out the pitfalls and benefits of the processes in a structured manner and where possible also in a quantitative manner. Overall, all the expert reviewers agreed that this document is a good report and useful as a reference. Furthermore, they have concluded, as recorded in various part of this section, on how to extend and improve this work for future studies.

In the aspect of capture costs and the potential for reductions of these costs with any of the three technologies, the reviewers noted that this was not well documented in the report and perhaps also difficult to analyse, because of the technology status. However, it was suggested for future work, a baseline cost should be established for the standard MEA technology which goes one level further than the regular vendor information. For MEA, the costs could be established using information in the public domain and the reviewers' experience noted that these estimates do compare well with vendor's information. This would allow an assessment of the possible impact of alternative amine technologies on e.g. cost of electricity and avoided CO_2 costs.

Specific Reviewers' Comments Relevant to the Chilled Ammonia Process

The reviewers noted that the thermodynamics of the aqueous ammonia are well documented and suggested that the report could have benefitted from a deeper analysis of the energy requirement of the aqueous ammonia process. They have suggested that a future study should evaluate particularly the trade-off between the lower energy requirements for regeneration as against to the additional energy requirements due to the cooling.

The reviewers noted that the authors of this report did point out precisely the challenges of limiting the ammonia emissions and the lower mass transfer rates. In addition to this comment, the reviewers also agreed with the report that instead of a packed column, a more intensified reactor where liquid side mass transfer will be much improved should be used for any aqueous ammonia application. An obvious candidate for such technology is now widely used in FGD where the promotion of oxygen transfer to calcium-carbonate slurries to aid the conversion of sulphite into sulphate is an essential element of the design. However, the reviewers noted that it is unlikely that absorption rates similar to MEA could be achievable with a chilled ammonia process, as the authors also imply.

Specific Reviewers' Comments Relevant to the CANSOLV and PRAXAIR Process

The reviewers noted that the benefits of the CANSOLV process are clearly described. The integrated SO_2/CO_2 removal can lead to advantages, but the magnitude of these advantages must be related to the SO_2/CO_2 ratio. With respect to the energy consumption as claimed by CANSOLV, the reviewers also agreed with the report that the patent claims as regards to the energy consumption can be substantiated.

The reviewers noted that the relevant aspects of the Praxair technology were also well described in the report. The technology encompasses a method to reduce the impact of oxygen on the solvent and the use of organic additions to the solution which should have benefits in lowering the energy requirement. Again it is difficult to assess the validity of the claims by the vendor because the technology has not been demonstrated even in small scale. The reviewers also noted the lack of information regarding the reaction kinetics in the absorber, which might be of major concern in relation to the size of the columns. This should be further investigated in future studies.

TECHNOLOGY PROVIDERS' COMMENT

Comments from Alstom Power

Alstom provided additional information in response to the findings of SINTEF in this report. Furthermore, they have provided an updated version of the process flow diagram, updated the process description, and the process chemistry overview. This information was included in Appendix B (Part 1).

Some of their key discussion addressed and providing clarity to the following issues:

- operational issues related to solid handling, solid formation,
- lean solution operating pressure
- reaction rate of the chilled absorber
- CO_2 removal efficiency
- ammonia emissions

Comments from CANSOLV

In addition to the technical comments provided by CANSOLV which have all been included in the report, they have also indicated the various projects currently underway to further improve their solvent. This includes their participation in the SaskPower CCS Activity in Canada, where they were requested to provide a proposal for the 1050MW unit with 90% capture for the Boundary Dam Power Station near Estevan, Saskatchewan. Additionally, there are plans to construct a 100 tonne/day CO_2 capture pilot plant in collaboration with E.ON Energie at the Heyden power station, Germany.

Furthermore, they have also indicated development of a new solvent, Cansolv Absorbent DC-103, which offers faster absorption kinetics, greater cyclic loading and lower energy consumption, while retaining the advantages of DC-101. Some information regarding the new solvent was briefly presented during the 12th International CO_2 Capture Meeting held at Regina, Canada (as shown in Appendix C).

Comments from PRAXAIR

PRAXAIR agreed to the stated assessment for the first 3 criteria - potential performance, challenges related to operation and technology maturity. However, they have disagreed with the assessment for environmental impact and suggested that it should be neutral (0) instead of negative (-).

They have also commented on the fact that the stated steam consumption of 3.1 GJ/tons of CO_2 could be achieved through the use of amine blends alone, where no organic components were added to achieve this level of energy consumption.

With regards to technology maturity, they have noted that this report rightly points out that the process "must be tested on a larger scale pilot plant". Similarly, it is pertinent to note that heat loss is usually a bigger issue at small scales, e.g. the pilot plant scale of 0.2 tons/day. Thus, the 3.1 GJ/tons is considered a conservative estimate of what can be achieved at a bigger scale. It is conceivable that the steam consumption could reduce to 2.6 GJ/tons or lower at a larger scale. At a fundamental level, use of amine blends offer another parameter for optimization at the bigger scales. The report, as written, does not recognize this critical feature of the process.

SINTEF F9109 – Confidential

REPORT

Evaluation of post-combustion CO2 capture solvent concepts

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ABSTRACT

An assessment study is made of three processes for post-combustion CO_2 capture that is currently under development. The technologies assessed are Alstom’s Chilled ammonia process, the Cansolv amine process and the Praxair amine process. Potential benefits, challenges and uncertainties regarding the three processes are described.

There are particularly large uncertainties related to the chilled ammonia process. This, since the process is a less mature technology. The available data are too limited to draw confident conclusions on the overall viability of the process.
While the process has a potentially low heat of absorption and high capacity, the process is complex and the slow reaction kinetics would appear to be a challenge.

The Cansolv and Praxair processes are based on more mature technologies. These processes are therefore almost certainly viable for large-scale CO_2 recovery. Some of the improvements proposed in these processes have however not been demonstrated, and potential efficiency gains are uncertain. For many of the proposed improvements it is not clear whether the benefits are greater than the disadvantage of added complexity.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Process Technology	Prosessteknikk
GROUP 2	Absorption	Absorpsjon
SELECTED BY AUTHOR	CO_2 Capture, Post-combustion	CO_2 separasjon, Eksosgass
	Process evaluation	Prosessevaluering

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1 Executive summary

A technology comparison has been conducted in order to assess three alternative absorption processes intended for large-scale post-combustion CO_2 capture for near future applications. These three processes are the Alstom Chilled Ammonia Process, the Cansolv amine process and Praxair's MEA-MDEA (mono-ethanol amine/ methyl-di-ethanol amine) solvent process.

Assessments were made to identify the potential benefits, challenges, and uncertainties regarding the three processes described. Also included in this report is a brief summary of a standard MEA based process which is used for performance comparison. The standard MEA process is based on Fluors Econamine technology.

It should be noted that all the assessments made in this report were based on information made available in the open literature, supported by kinetic evaluations made at SINTEF's laboratory. There might be issues the authors are not aware of, which could have changed the results of the present assessments. The technologies are in general assessed based on the following criteria. Due to lack of available data, not all these criteria are compared for the three processes.

- Potential performance
    - Heat requirements, capture rate, cyclic capacities, kinetics, costs
- Challenges related to operation
    - Process complexity (level of heat and process integration)
    - Operating conditions
- Technology maturity
    - Major development issues
    - Timescale for commercialization
- Safety and environmental impacts and considerations
    - Solvent characteristics
    - Slip of solvents and effluents

The main results from the assessments of each process are summarized in Table 1-1.

Table 1-1: Assessment of the Fluor Econamine FG+ process, the Alstom Chilled Ammonia Process (Alstom), the Cansolv amine process (Cansolv) and Praxair's MEA-MDEA solvent process (Praxair)

Criteria	-	Fluor Econamine FG+	Alstom	Cansolv	Praxair
Main feature	Standard MEA	Improved MEA	Solvent precipitate	Promoted amines	Promoted amines
Potential performance	0	+	+	+	+
Operational challenges	0	-	--	--	0
Technology maturity	0	0	--	-	0
Environmental impact	0	0	+	-	-

“0” indicates similar potential to a standard MEA process. ”+” indicates potential improvement over a standard MEA process. “-“ indicates greater challenges than for a standard MEA process. “--“ indicates substantially greater challenges than for a standard MEA process.

2 Scope of work and objectives

2.1 Background

Solvent technologies for post-combustion capture are considered one of the most feasible options for large scale CO_2 removal in the next 10-20 years.[1] The most important reasons for this are the capture efficiencies of these systems even for low CO_2 partial pressure streams where 90% capture can readily be achieved from flue gases (around 4% CO_2 from natural gas fired and 10-15% from coal fired power stations at ambient pressure), and because this is proven and commercially available technology although not yet applied at the scale required for full scale CO_2 capture from power stations. One key advantage of post-combustion capture is that it can be installed on existing power plants as retrofits. Furthermore, these units are similar to Flue Gas Desulphurization (FGD) units already installed at power plants. Manufacturers are therefore not required to develop completely new power plants. There is significant ongoing work for improving these processes in order to reduce the relatively high capital cost and high thermal energy demand. Research is also ongoing to identify and reduce possible environmental side-effects of the process.

Today, two leading processes for separating CO_2 from flue gases with low CO_2 partial pressure are the processes from Fluor (Fluor Econamine FG+) and MHI/Kansai Electric (KM-CDR). Quite significant information as well as some operational data is available for these processes. Some performance comparisons have also previously been made.[2] These processes are developed commercially; however, the experience is limited to sizes less than about 800 tons/day.

Alternative solvent scrubbing processes are currently being developed intended for low pressure exhaust gas CO_2 removal. In the present work the Alstom Chilled Ammonia process, the Cansolv CO_2 capture process and the Praxair amine process are considered.

There are also other processes being developed such as the Aker Clean Carbon process. This process is presently under active development. Another is the process being developed by HTC Purenergy/Doosan Babcock and the ECO_2 process being developed by Powerspan.[13] In the present work these have not been included in the evaluations due to the need to limit the number of processes studied.

There is a need for an assessment of these new processes in terms of performance costs, safety, and environmental impacts for use for CO_2 separation from post-combustion gas streams. This can be done by comparison towards a base case technology, such as amine absorption with MEA.

2.2 Objective

The objective of this study is to make a technological assessment of new processes which have been developed beyond bench scale, but which have not yet been widely assessed for CO_2 capture.

2.3 Scope of work

The amine processes that will be assessed for post combustion CO_2 capture are the Alstom Chilled Ammonia system, the Cansolv amine system and the MDEA/MEA process currently under development from Praxair.

The Chilled Ammonia process is described in much greater detail since it differs significantly from the traditional amine absorption plants. The process is also significantly more complex than conventional amine processes.

It is beyond the scope of the present project to conduct a complete benchmarking involving both quantitative and qualitative criteria of these processes. The assessment will involve comparisons based on information available in the open literature. For assessment of the Alstom Chilled Ammonia process kinetic measurements were performed.

2.4 Report outline

Firstly, a general description of the methodology that was applied for the comparative study is given in Chapter 3. Then a reference technology for comparison is described, a basecase MEA process. This process is described in Chapter 4. Then the other processes are presented in the consecutive chapters (5-7) and compared to the base case (Chapter 8). Finally some conclusions are drawn (Chapter 9).

2.5 Note to reader

The evaluations and discussions set forth in this report are based on publicly available literature, including patents, publications, reports, press releases and some in-house laboratory experiments. The report draws on the judgment and experience of the present authors and thus represents a best effort to make a non biased technology comparison and evaluation based on the available data.

This report was submitted to IEA April 30th 2009. It has been withheld from publication until November 2009 in order to give the technology developers sufficient time to provide feedback.

The cut-off for inclusion of material in this report was April 2009.

3 Qualitative comparison methodology

3.1 Selection of criteria and limitations

3.1.1 The generic amine absorption plant and it’s most important features

The most important unit operations for a CO_2 absorption process with amines are the absorber and stripper columns, shown in Figure 3-1. These are normally columns with random or structured packing. In these columns counter-current vapor and liquid contact throughout the tower, with optimum absorption or desorption conditions, large interfacial areas at a minimum pressure drop are desired.

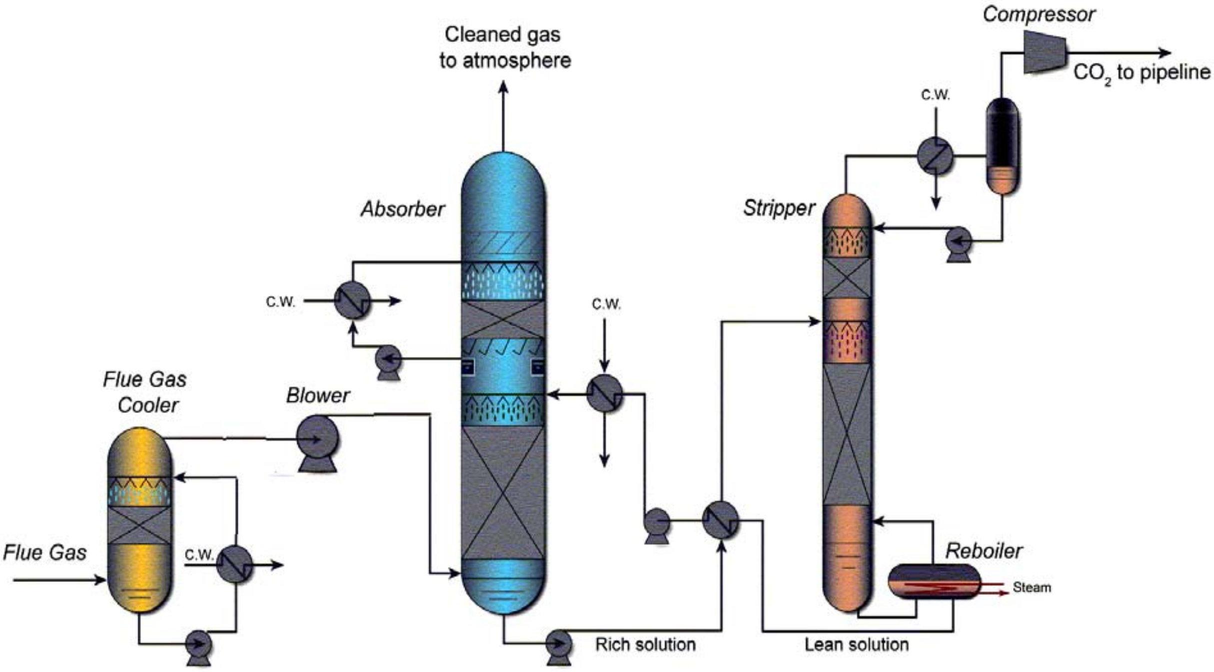

Figure 3-1: Schematic diagram of a typical amine plant.

Other important unit operations are the cross flow heat exchanger, the reboiler and the condenser. The rich/lean cross flow heat exchanger facilitates heating of the rich CO_2 solution prior to the regeneration units, while the lean solution is cooled in order to enter the absorber again for a new absorption cycle. The reboiler is a special heat exchanger where low-pressure steam is used to heat and partially vaporize the loaded absorbent that exits the stripper column.

The most important unit, which adds to the capital cost of the capture plant, is the absorber column. The column consist of one or more packed sections, where the CO_2 absorption takes place, and a water-wash section at the top which minimizes the amount of solvent being released to the atmosphere. The most important solvent properties, which determine the absorber column height and thus the cost, are the kinetics of the solvent and the volatility of the solvent (which determines the height of the washing section).

The energy requirement which mainly determine the operating cost of the absorption plant, is the steam required in the reboiler for solvent regeneration and the duty required for compression of the CO_2 to supercritical transport pressure. This total energy requirement is dependent on several specific properties such as the solvent cyclic capacity, the solvent vapor-liquid equilibrium properties, the CO_2 capture rate, the operating pressure of the stripper and so forth.

3.2 Criteria used in the assessment

Based on the statements given in the previous section, the following criteria were chosen as a basis in the process comparison:

- Performance assessment
    - Steam requirements, capture rate, kinetics and costs
- Challenges related to operation
    - Process complexity (level of heat and process integration)
    - Operating conditions
- Technology maturity
    - Major development issues
    - Timescale for commercialization
- Safety and environmental impacts and considerations
    - Solvent characteristics
    - Slip of solvents and effluents

4 Reference case: the Fluor Econamine process

4.1 Description of the process

The Fluor Econamine SM process is used as reference in the qualitative comparison of the processes.
It represents a commonly used basecase when comparing CO_2 absorption processes and will also be used as basis of comparison in this study, referred to as the MEA reference case. It must be noted that Fluor has further developed their process, the Fluor Econamine FG+ process, which is described in Section 4.2.5.

Fluor's Process experience, The Fluor Econamine SM Process:
The process uses a 30wt% MEA solution in which inhibitors are added to the solvent to reduce oxidative degradation of the absorbent. Inhibitors are also needed to reduce equipment corrosion.[3] It was developed in the 1970's primarily for the purpose of producing CO_2 for enhanced oil recovery (EOR). Several plants were built in West Texas to recover CO_2 from boiler flue gas for EOR purposes between 1982 and 1986.[3] Some were also built for the food industry. A total of 16 commercial plants were built, as of 1999, including 9 plants that produce more than 60 ton/day[3], 7 of which are still in operation. Among these, a 320 ton/day CO_2 plant in Bellingham, Massachusetts, USA for Northeast Energy Associates, a 150 ton/day plant for Sumitomo Chemical in Chiba, Japan, and a 90 ton/day plant for Prosint Produtos Sintéticos in Rio de Janeiro, Brazil. The plant in Chiba, Japan treats flue gas from a variety of fuels including heavy fuel oil, while the other plants process flue gas resulting from combustion of natural gas. The Bellingham plant is no longer in operation. Three plants have been built for demonstration purposes using flue gas from combustion of coal. These include a 4.5 ton/day plant in Yokosuka, Japan, a 2 ton/day unit in Alberta, Canada and a 4 ton/day unit at the Boundary Dam Power plant in Saskatchewan, Canada.[4]

4.2 Assessment of the process

4.2.1 Steam requirement for regeneration

The established Econamine SM process has a steam consumption value of about 3.7 GJ/t,[9] which has also been measured at the CASTOR/CESAR EU pilot plant in Esbjerg, Denmark, which independently investigated the simple process configuration with 30 wt-% MEA.[5]

4.2.2 Challenges related to operation

Issues related to operation of amine plants with oxygen content in the flue gas are production of heat stable salts that must be handled properly. This is in particular a problem with MEA. Fluor uses a low-temperature reclaiming technology that apparently has reduced the quantity of reclaimer waste.[6] Fluor is the technology vendor with the most long-term commercial operating experience in CO_2 recovery from flue gas with a very high oxygen concentration.

4.2.3 Technology maturity

According to Reddy et al.[9] large-scale carbon dioxide sequestration projects are currently being planned with absorber diameters of up to 15m and with removal rates up to 8,000 ton/day. The Fluor technology (Econamine SM) has also, as noted, been demonstrated in commercial applications with several plants over the past 20 years. They are actively working, through laboratory and field testing, on ways of lowering the steam consumption. Recently, (July 2008)

Fluor formed a partnership with E.ON to build a pilot plant for CO_2 removal from a coal fired power plant with a gas volume flow of about 16,000 Nm^3/h (corresponding to about 4 tons/h assuming 12 % CO_2 content).[7]

4.2.4 Safety and environmental impacts and considerations

With regard to environmental impacts of amine scrubbing technology, this will be an issue for all amine systems. The known sources of concern for solvent scrubbing processes for CO_2 capture should be studied further. Major issues should be studied in more detail, such as determination of effluent volume and its degradation products, as well as determination of emissions to air, amount and toxicity of these products and degradation products. There has been significant emphasis recently in Norway regarding the degradation products of amines that escapes through the absorber vent gas. Specific concerns have been raised regarding the possibility of formation of nitrosamines. [8] This issue is however beyond the scope of the present work. Technology developers argue that amine emission to vent gas can be reduced to very low levels by adequate water wash system design.

4.2.5 Further developments of the Econamine process

In 2003, Fluor announced an improved version of this process called the Fluor Econamine FG+, [9] but no plants have yet been built. The process configuration is similar to the generic absorption process shown in Figure 3-1 and the main process units are the same.

Today, Fluor claims that the Econamine FG+ process uses a steam consumption of 2.8 GJ/ton CO_2 removed for a typical coal combustion flue gas.[10] Similar values are reported for the Mitsubishi KS-1 process. [11] It is however not clear if these numbers have been demonstrated in CO_2 capture plants or are estimated values.

5 The Alston Chilled Ammonia Process

5.1 Introduction

There are two new processes under development based on Ammonia, the Chilled Ammonia Process being developed by Alstom[12] and the ECO_2 process being developed by Powerspan.[13] Of these processes the Alstom Chilled Ammonia Process has been chosen in this study. The authors have considered evaluating the Powerspan process; however, very little information is available to perform a process evaluation. The data available for the Alstom process are also limited. The evaluation has been based on the available data from literature as well as additional in-house experiments for measuring reaction kinetics. The final report has been commented by Alstom and this comment is enclosed in the Appendix.

5.2 Description of the process and process units

5.2.1 Process description

The Alstom Chilled Ammonia Process bears a resemblance to a carbonate process such as the Benfield Hot Carbonate process developed in the 1950s.[14] There are similarities, but there are also some significant differences, both which will be discussed below.

The idea behind Alstom's process appears to be to use a high concentration of aqueous ammonium carbonate solution and form an ammonium bicarbonate solution in the absorption of CO_2 from the flue gas. An increased CO_2 loading is possible in these systems compared for example to the reference MEA process, as a result lower solution circulation rates are required. As the ammonium bicarbonate is formed in the absorber, it will precipitate at the operating conditions. This introduces a solid phase that complicates the process and must be carefully considered in the process design. In such a process there will be a circulating solvent consisting of aqueous ammonium carbonate, aqueous ammonium bicarbonate, and solid ammonium bicarbonate. It appears that Alstom has selected as absorber design a spray tower type that is able to handle solids formation.[15]

The main chemical reactions in the liquid phase can be written in the following form:

$$CO_2(g) + H_2O(aq) + NH_3(aq) \longleftrightarrow HCO_3^- + NH_4^+ \tag{1}$$

$$CO_2(g) + 2NH_3\left(aq\right) \longleftrightarrow NH_2CO_2^- + NH_4^+ \tag{2}$$

$$CO_2(g) + CO_3^{2-}(aq) + H_2O(aq) \longleftrightarrow 2HCO_3^- \tag{3}$$

$$NH_3 + H^+ \longleftrightarrow NH_4^+ \tag{4}$$

$$CO_3^{2-} + H^+ \longleftrightarrow HCO_3^- \tag{5}$$

In addition there the reactions of solid formation:[16]

$$NH_4^+ + HCO_3^- \longleftrightarrow NH_4HCO_3(s) \qquad (6)$$

$$NH_4^+ + NH_2CO_2^- \longleftrightarrow NH_2CO_2NH_4(s) \qquad (7)$$

$$2NH_4^+ + CO_3^{2-} + H_2O \longleftrightarrow (NH_4)_2CO_3.H_2O(s) \qquad (8)$$

$$4NH_4^+ + CO_3^{2-} + 2HCO_3^- \longleftrightarrow (NH_4)_2CO_3.2NH_4HCO_3(s) \qquad (9)$$

As shown in equations (1) to (3), there are three competing reactions for CO_2 binding. Equation 1 is a direct reaction of aqueous ammonia with water and CO_2 to form ammonium bicarbonate. In reaction (2) the aqueous ammonia reacts with CO_2 to form ammonium carbamate, whereas in reaction (3), carbonate formed via reaction (5) further reacts with CO_2 and water to form bicarbonate. Based on the standard heat of formation (at 25^{o}C), reaction (3) requires the least energy for regeneration, $\Delta H_{Rx} = 26.4kJ/mol$, where as for reaction (1) it is $\Delta H_{Rx} = 63.7kJ/mol$ and reaction 2 it is $\Delta H_{Rx} = 74.1kJ/mol$. In comparison the heat of absorption for MEA at 25ºC and 1 atm is $\Delta H_{Rx} = 80kJ/mol$. From Alstoms patent it would appear that reaction (3) is intended to be the main reaction used to absorb CO_2. If the process can not be operated using mainly reaction (3) to absorb $CO_{2,}$ due to thermodynamic and/or kinetic limitations, free ammonia is needed through reactions (1) and (2). This requires increased energy because of the need to regenerate the ammonium bicarbonate and carbamate to free ammonia (see reactions 1 and 2).

The reaction between ammonium carbonate and bicarbonate is reported to be best maintained at solvent temperatures below 15ºC.[15] Above this temperature reactions (1) and (2) are prevalent. Also, the solid formed are unstable and will dissolve at elevated temperature. Since the desired reaction, equation (3), and solid precipitation require such low temperature, a large flue gas cooling system is integrated into the capture plant prior to the absorber.

As noted, various solid compounds, presented with equations (6)-(9), can be present in the absorber. The solid increases the absorption capacity, but the precipitation reactions are exothermic and increase the cooling requirements in the absorber and the heating requirements in the stripper. For reactions (6) and (7) the energy needed to dissolve the solids are 28.4 and 15.9 kJ/mol respectively (calculated from the heat of formation data at 25^{o}C). The main solid phase present after the absorption is ammonium bicarbonate.[16,17]

Increased precipitation gives a potential for high absorption capacity since the solid does not contribute to the equilibrium backpressure, thus facilitating large carrying capacities. Conversely, operating the absorber in a slurry flow causes operational issues and requires special contactor design considerations as will be discussed below. The increased carrying capacity causes reduced circulation rates that again cause reduction in the sensible heating requirements of the regeneration energy as well as smaller equipment sizes and pump loads. If the system was operated with no solid precipitation occurring, the theoretical carrying capacity is claimed to be less than that for MEA[18] . In Figure 5-1 a simplified flow diagram of the system is shown.

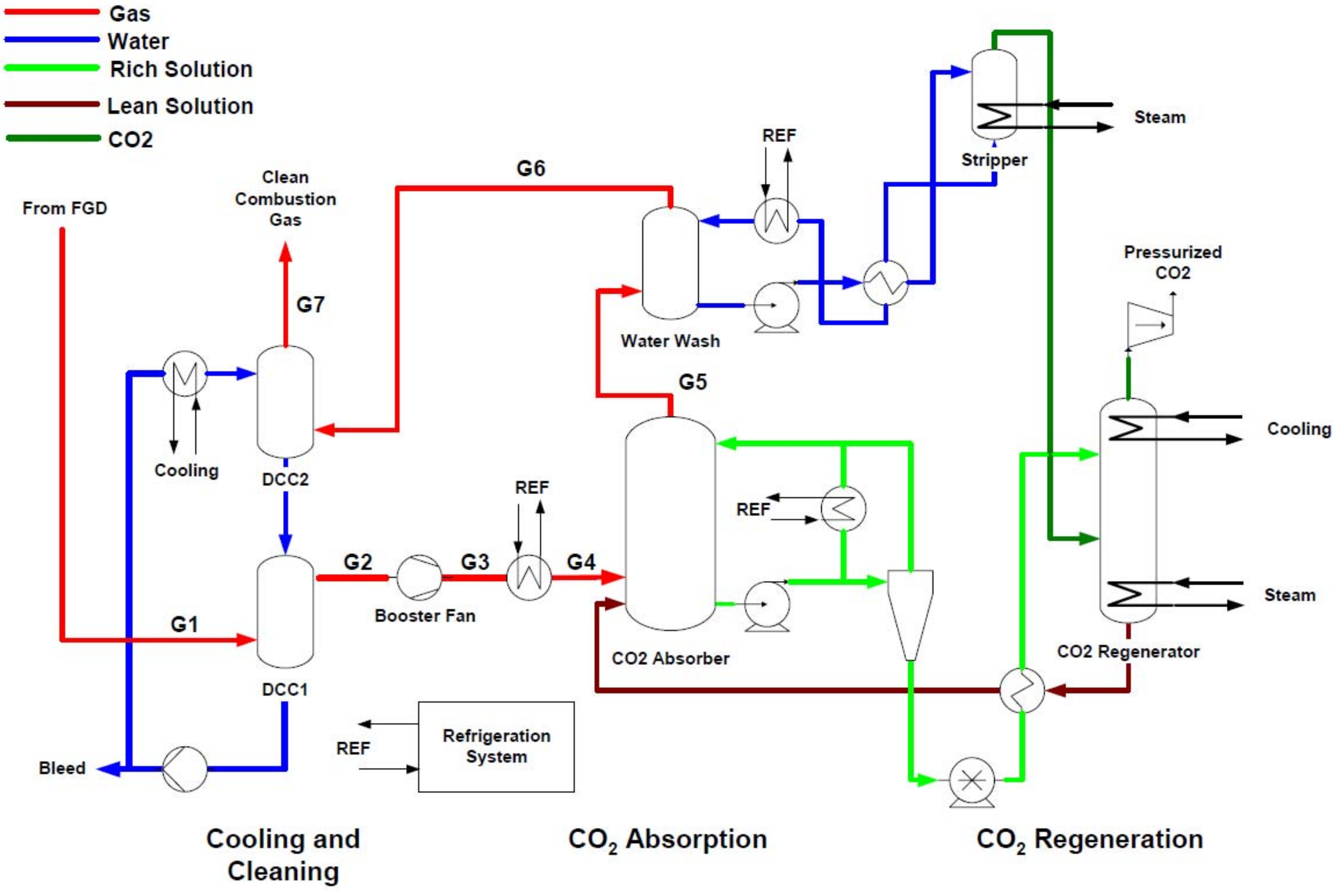

Figure 5-1: Simplified schematic representation of the Chilled Ammonia Process[19, 20]

5.2.2 Flue gas cooling and refrigeration

Since the chilled ammonia capture plant is reported to operate at 0-10 ºC, the flue gas must be pre-cooled. The flue gas is cooled in two stages by direct contact with water, DCC1 and DCC2.[15] In the coolers large amounts of water is condensed out as the gas is cooled below the adiabatic saturation temperature. The exit temperature of DCC1 is 20-30ºC.[15] It is claimed that other acidic contents of the flue gas will be removed to practically zero in this wash process.[15] In the second cooling stage, the flue gas is contacted with a chilled cooling medium at 3ºC, cooling it to about 5ºC.[21] It is unclear if the chiller is a direct contact cooler with an internal water loop, or one or more heat exchangers operating with a cooling medium. In any case the chiller requires a separate refrigeration system. After cooling the flue gas in DCC1 the cooling water is cooled further in a heat exchanger before further cooling in an air-cooled cooling tower (this is not shown in Figure 5-1 but is shown in ref 15). At the cooling tower exit the temperature of the cooling water is about 25ºC before entering DCC2 where the stream is further cooled with the cold exit gas of the absorber water wash system, down to 20.5ºC before it is transferred back to DCC1. This also serves to further wash the flue gas. Sulphuric acid is added to the cooling water to remove ammonia slippage and the ammonia goes with the cooling water which can react with SOx in the incoming flue gas. The ammonia thus can work as a SOx remover also. It is claimed that even though most of the water in the flue gas is removed, heat rejection from the cooling tower and chillers cause major evaporation of water resulting in a net water consuming operation of the cooling section.[15] The DCC units must be constructed with a non-corrosive material to withstand acidic compounds that are condensed out from the flue gas stream. The gas volume at the DCC1 outlet is 15-20% lower than at the FGD outlet which will reduce the size of the downstream booster fan and also the diameter of the absorber. The booster fan is probably placed after the DCC1 and before the chiller. The size of the two DCCs will have a similar or even larger diameter compared to the absorber, while the height will be significantly shorter.

5.2.3 CO_2 absorption units

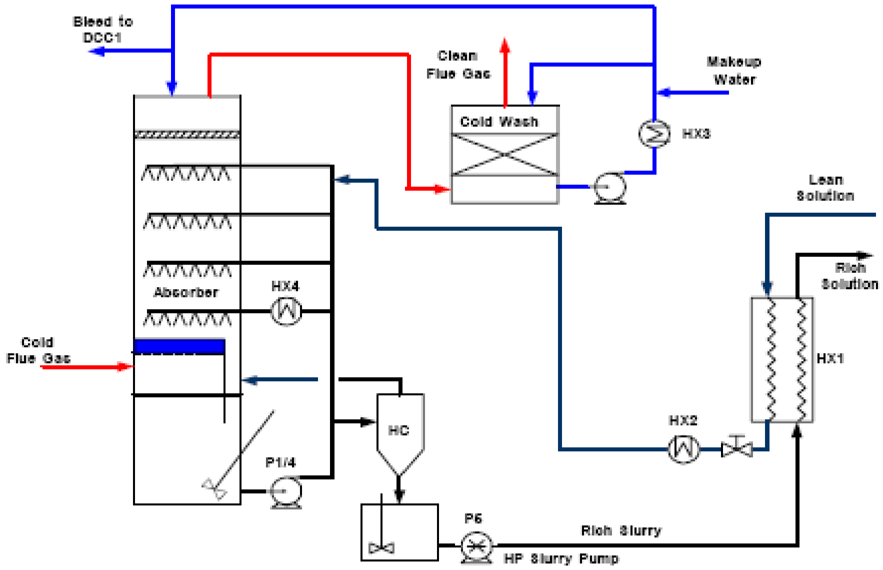

Figure 5-2: The absorber system[15]

Figure 5-2 shows a schematic of the absorber system. It can be noted that this schematic differs somewhat from the overall schematic given in Figure 5-1. We are assuming that Figure 5-2 gives the correct picture of the streams. The schematic in Figure 5.2 includes an absorber that can handle slurries and large volumes of gas in a single vessel, for example an open or packed spray type. It includes recycle streams with cooling heat exchangers, to remove heat released in the absorption reaction. After passing through the absorber, the CO_2 rich stream goes to a hydro cyclone (HC) that concentrates the slurry to a solid content from 10-15% to 30-50%wt and continues to a slurry retention tank. A minimum amount of water is transferred to the regeneration section to reduce the sensible heat required for heating the solution. As noted the resulting slurry must be such that it can be manageable in the pumps and other equipment. The overflow from the HC is returned to the absorber. The key parameters for success of the absorber operation are sufficient mass transfer, CO_2 removal capacity, slurry content and optimum liquid/gas ratio. Due to the slow carbamate/bicarbonate kinetics large L/G rates are probably necessary which facilitates the use of the internal recycle piping to increase flow and L/G retention times. The large recirculation of liquid makes the absorber acts more as a mixing tank with maximum one theoretical stage. Using a spray column will also reduce the liquid phase mixing, thus the liquid film resistance will be higher compared to a packed column.

Downstream from the retention tank a high pressure slurry pump increases the slurry pressure to about 30bar before the slurry enters the regenerative (rich/lean) heat exchanger.[15] The heat exchanger(s) must be able to handle slurry, and as the concentration of solids is reduced due to gradually heating, it must most probably be designed in such a way that it is able to remove gas due to stripping of CO_2 occurring while heating. Thus both the design and operation of this heat exchanger will be challenging as discussed later (section 5.3)

5.2.4 Water wash system

An extensive water wash section is required at the top of the absorber since the exit flue gas contains large amounts of ammonia slip even at the low operating temperature of the absorber (reported to be 0-10ºC). A wash unit of this type contains several sections of packing with several stages. The resulting bleed from the wash is reported to be at pH9-9.5 and contains ammonia and CO_2.[15] This bleed is transferred to the DCC1 where traces of SO_2 are captured. In a last stage, to remove ammonia to below 5ppm, an acid wash is needed where sulphuric acid is used.[15] This requires regeneration of the ammonia and CO_2. This is also discussed in the section assessing the process, section 5.3.

5.2.5 Regeneration

The regeneration units of the carbonate solution consist of a main stripper with reboiler and a condenser. This section is similar in principle to traditional amine desorption units. Since the solids in theory should dissolve in the regenerative heat exchanger, no solids are present in the stripper and reboiler. The temperature at the top of the stripper is 110-115ºC, and in the reboiler 115-120ºC at 30bar, which is caused mainly by the CO_2 partial pressure. Since the pressure is caused by CO_2, the high pressure results in a low volumetric gas flow rate resulting in a cross sectional area less than half of an atmospheric regenerator (at around 2 bar). The three main factors contributing to lower steam consumption in the reboiler are:

1. The lower heat of reaction for the carbonate/bicarbonate reaction (equation 3)

2. The significantly decreased amount of water needed for evaporation[15]

3. The higher CO_2 cyclic capacity possible per unit mass of solvent reducing the sensible heat required in the regeneration to one third of that for MEA[15]

Since the desorber operation is at 30bar the required compression duty to compress CO_2 up to 120bar will be about one fourth of that for compression from atmospheric pressure.

5.3 Assessment of the process

5.3.1 Performance

Steam requirement for regeneration
In absorption/regeneration systems, the CO_2 rich solution is regenerated by addition of heat in order to reverse the absorption reaction and strip the CO_2 from the solution. The regeneration energy can be separated into three contributions, the sensible heating of the solution, the heat of reaction and the stripping steam required for providing a driving force for desorption throughout the column. Since the rich solution contains solid slurry, an additional energy sink involves the energy required for phase change. This dissolution energy is determined by the weight percentage of solids formed in the slurry solution. Since the desorber operates at a high pressure, the stripping steam is very low or negligible. In a NETL report it was estimated that the *steam* energy required to heat a 46.5%wt slurry solution to regeneration temperatures and, to reverse the absorption reaction, is 2.1 MJ/ kg CO_2 removed, which is about a 40% reduction over MEA.[18] This does not account for the energy required for phase change (from solid to liquid) since all solids are

assumed to be dissolved within the rich/lean heat exchanger. It is also unclear what removal efficiency is assumed. It is not known how these numbers above were calculated. In the Alstom patent,[22] it is claimed that the steam consumption required is less than 15% of that for MEA.

Rigorous process calculation and experimental data are required to make a quantitative estimate of the costs of operating such a plant compared to an MEA process. The authors do not have access to such data and therefore are not able to make a quantitative energy requirement analysis, but it is clear that this constitutes the largest potential advantage of the process. If one could achieve absorption/regeneration using only equation 3, the process will require much less regeneration steam.

CO_2 cyclic capacity

The CO_2 cyclic capacity is as noted dependent of the percentage of solid ammonium bicarbonate present in the slurry transferred to the desorber. If no solids were allowed to form, the maximum capacity, for a lean solution with a minimum concentration of 8.5wt% ammonium carbonate (forms a saturated solution of ammonium bicarbonate), would be 0.039kg CO_2/kg solution, which is slightly less than for 30wt% MEA, according to the internal distribution by NETL.[18] When solids can form, the carrying capacity of the solution is 0.1-0.2 kg CO_2/kg of solution with a lean solution of 24-28 wt-% ammonium carbonate assuming full regeneration of the ammonium bicarbonate. This corresponds to a solid concentration of 22.5% to 66.5% ammonium bicarbonate (theoretical amount of solid in the slurry after the absorber).[18]

CO_2 capture rate

It is reported in the literature that with the ammonium bicarbonate – ammonium carbonate reaction it is difficult to achieve high levels of CO_2 removal. It is therefore of importance to determine if it is possible to reach 90% removal efficiency without jeopardizing the potential process benefit of the lower required steam duties compared to traditional amine systems.

The theoretical maximum removal efficiency from an equilibrium point of view, is 76% if the lean solution is pure ammonium carbonate with a NH_3/CO_2 mole ratio of 2.0 (according to NETL, it is not known what the flue gas content is here).[18] However, in order to maximize CO_2 uptake in the absorber, the absorbing solvent might have to contain additional free ammonia, i.e. there should be a given percentage of free ammonia to absorb CO_2 via direct reaction (reaction (1) and (2)). Therefore, the NH_3/CO_2 mole ratio should be higher than 2.0. This will, however, cause reduced performance since additional cooling in the absorber and regeneration of the ammonia is expensive. Thus, because more ammonia is needed in the absorber, a portion of the bound ammonia (bicarbonate or carbonate) must be stripped back to ammonia. An additional consequence of this will be increased ammonia slip due to the high vapor pressure of free ammonia.

5.3.2 Reaction kinetics

CO_2 can be absorbed by reactions (1)-(3). Reaction (1) is relatively slow.[23, 32] The direct reaction of ammonia with CO_2 (reaction 2) is relatively fast and the rate of reaction is:

$$r = k_{NH3}\left[NH_3\right]\left\{\left[CO_2\right]-\left[CO_2\right]_{eq}\right\} \tag{10}$$

Reaction (10) shows that the reaction rate is dependent on the rate constant, the free ammonia concentration and the distance from the equilibrium (giving the reaction driving force). According to Dankwerts (1970) the k_{MEA} is 17 times higher than k_{NH3} at 25 C.[24]

According to Derks et al. (2009) this reaction is in the same order of magnitude as MEA.[25] However, in the process, the amount of ammonium carbonate and free ammonia is small. Reaction (3) is an overall reaction that also takes place in equivalent potassium and sodium carbonate systems. This reaction is normally divided into the following two reactions:

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (11)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \qquad (12)$$

Hydration of CO_2 (Reaction 11) is of second order, i.e. first order with respect to both CO_2 and OH^- ions. Reaction (11) is rate determining, since reaction (12) is a proton transfer reaction thus having a very much higher rate constant compared to reaction (11).[26]

Reaction (11) is a quite fast reaction[27], but in solutions where carbonate and bicarbonate ions are present (where pH is low) the concentration of OH^- -ions is still very small and the overall reaction (reaction 1) becomes slow especially at low temperatures. The rate of reaction 5 is well defined for systems containing, OH^-, Na^+, K^+, Li^+, CO_3^{2-} [27]. The absorption rate for the overall reaction (reaction 4) has also been studied for sodium and potassium carbonates by Comstock and Dodge (1937)[28], Roper (1955)[29] and Knuutila et al., (2008).[30]

Thus in the process free ammonia reacts to produce carbamate with reaction (2) however the production of bicarbonate via reactions (1) and (3) is slow. Since the key factor in the process is to absorb CO_2 by producing bicarbonate, reactions (1) and (3) have an important role for the feasibility of the process.

Motivated by concerns of slow reaction kinetics for reaction (3), SINTEF performed kinetic measurements of this system at the proposed operation conditions found in the patent describing the process.

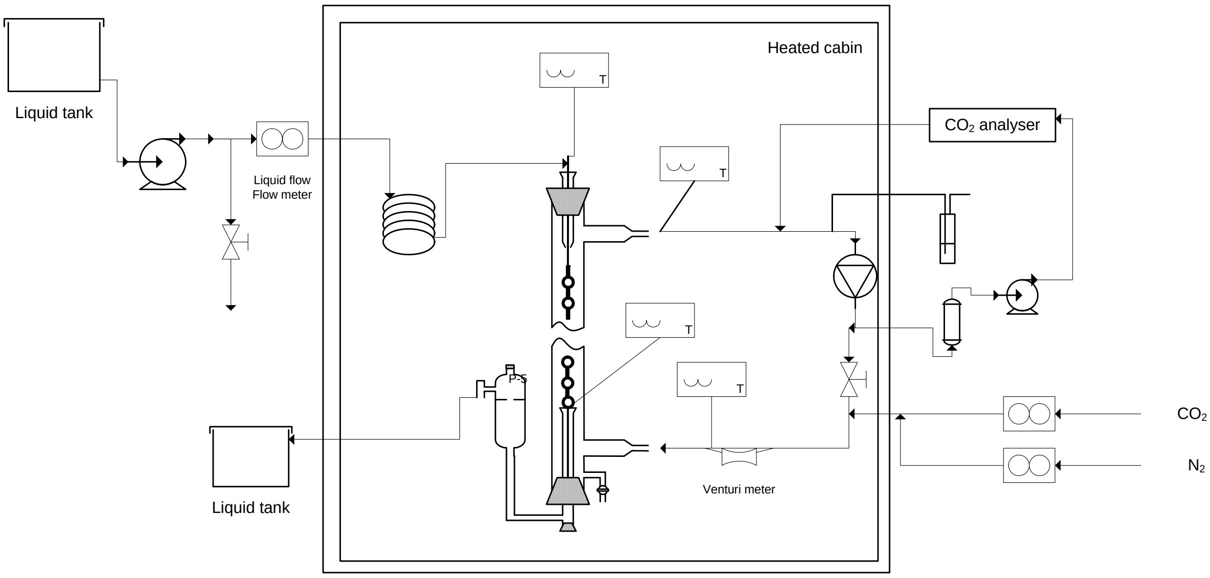

Figure 5-3: Experimental set-up of the string of discs apparatus

Measurements and results

To determine the overall mass-transfer coefficient of ammonium carbonate a string of discs apparatus, shown in Figure 5-3, was used. In the apparatus an ammonium carbonate solution is passed through the column and a known mixture of CO_2 and N_2 is fed into the column. When the CO_2-analyzer showed a constant value the process was terminated. Ammonium carbonate temperatures of 25 and 30^oC and carbonate concentrations of 5 and 10 wt% were used. The high equilibrium partial pressure of CO_2 over the ammonium carbonate solution combined with a low absorption rate made it impossible to measure the absorption rates with this set-up. In the study partial pressures of CO_2 2-4vol% were used in the gas phase. It was noted that much higher partial pressures of CO_2 in the gas phase must be used to be able to quantitatively measure the overall mass transfer coefficient of this system because of the low absorption rate and the high equilibrium CO_2 pressure over the carbonate solution.

The order of magnitude of the absorption rates can be estimated by analogy. The apparatus was therefore used to measure absorption rates of CO_2 into 20 wt% *potassium carbonate* and 30 wt% MEA solutions at 31^oC. The results are presented in Figure 5-4. The results in Figure 5-4 are for unloaded solutions. In potassium carbonate solution the absorption of CO_2 is based on the overall reaction (3). The rate of reaction for reaction (3) is dependent on the cations in the solution and for potassium carbonate the absorption rate is reported to be 10 % higher than for sodium carbonate.[28] But *even if ammonium carbonate was twice as fast compared to potassium the absorption rate would significantly lower than for a 30 wt% MEA solution.* In ammonium carbonate solutions the rate of reaction for reaction (3) is most likely close to the values of potassium carbonate and therefore is can be concluded that the production of bicarbonate via reaction (3) is slow.

The absorption capacity of ammonium carbonate solution was also tested using the screening apparatus. The apparatus, designed to operate at atmospheric pressure, is shown in Figure 5-5. During the experiments a CO_2-N_2 gas mixture containing 10 vol-% CO_2 was passed through a water saturator and then to the bubble absorber containing ammonium carbonate solution. The gas phase leaving the absorber was cooled and the CO_2 content directly determined by IR analysis. The process was terminated when the concentration of CO_2 in the outlet reached 9.5 vol-%. The results are shown in Figure 5-6. The ammonium carbonate is able to absorb more CO_2 at temperature of 15^oC compared to 40^oC. This can be explained by the equilibrium behavior of the system. At 15^oC the equilibrium of reactions (1)-(6) provides better driving force compared to higher temperatures. Nevertheless when compared to 30 wt-% MEA the rate of absorption and the absorption capacity of ammonium carbonate solutions is much lower.

The slow reaction kinetics of ammonium carbonate systems have been also shown by Danckwerts and McNeil (1967)[32] who measured the absorption rate of CO_2 in 2M ammonia solution with stirred cell. The results are shown in Figure 5-7. From the figure it can be seen that the absorption rate is first quite high because of the high amount of free ammonia. The absorption rate decreases fast with increasing CO_2 loading since the amount of carbonate and carbamate in the system increases. At loading 0.5 mol_{CO2}/mol_{NH3} the absorption rate is only 1/8 compared to a loading of 0.2 mol_{CO2}/mol_{NH3}. There is also no enhancement by the chemical reaction at avloading of 0.5 and the reaction kinetics could be described by physical absorption. The operating range of the chilled ammonia process is reported to be in a loading interval of about 0.25-0.67 $mol_{CO2}/mol_{NH3.}$[16]

In chilled ammonia process low temperatures are needed to minimize the loss of ammonia and to have high driving force towards bicarbonate (reaction 3). For the reactions (1)-(3) the kinetic rates increases with increasing temperature[27,23] and the low temperatures used in the process will have a negative effect to the absorption kinetics increasing the required size of the absorption tower.

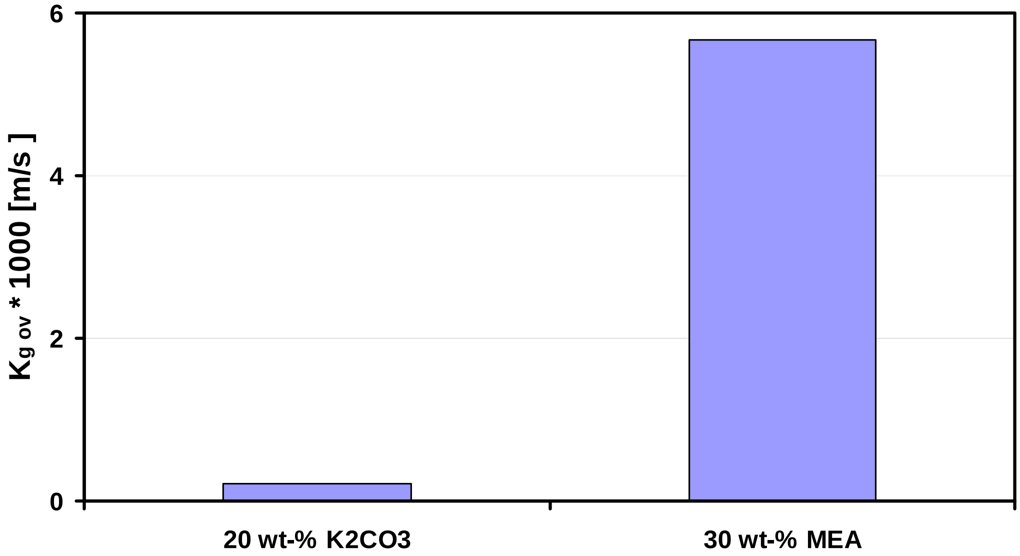

Figure 5-4: The overall mass transfer coefficients for unloaded 20 wt-% K_2CO_3 and 30 wt-% MEA solution at ~3 ^oC.

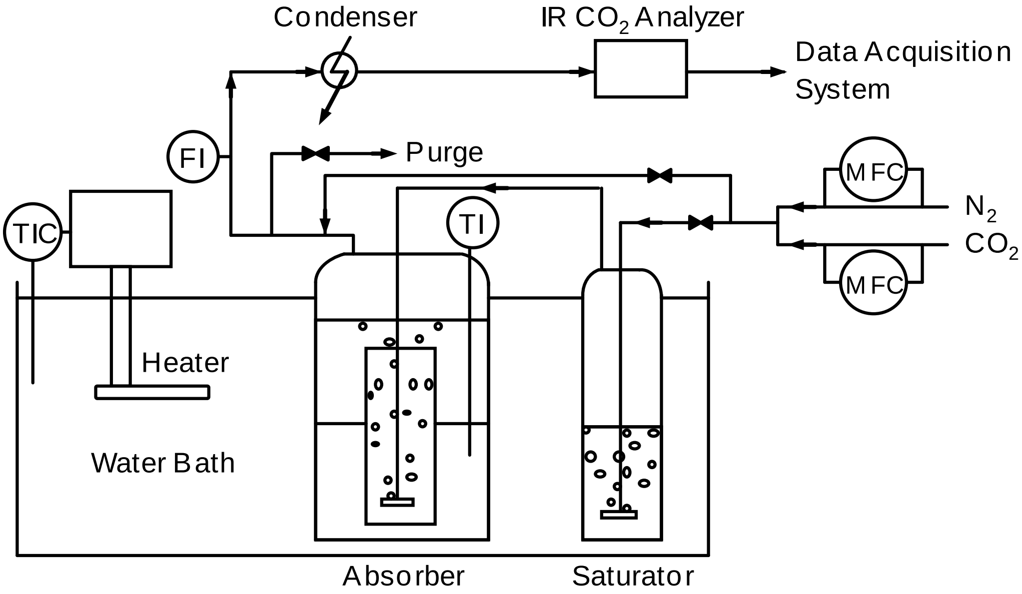

Figure 5-5. Screening apparatus for CO_2 capture.[31]

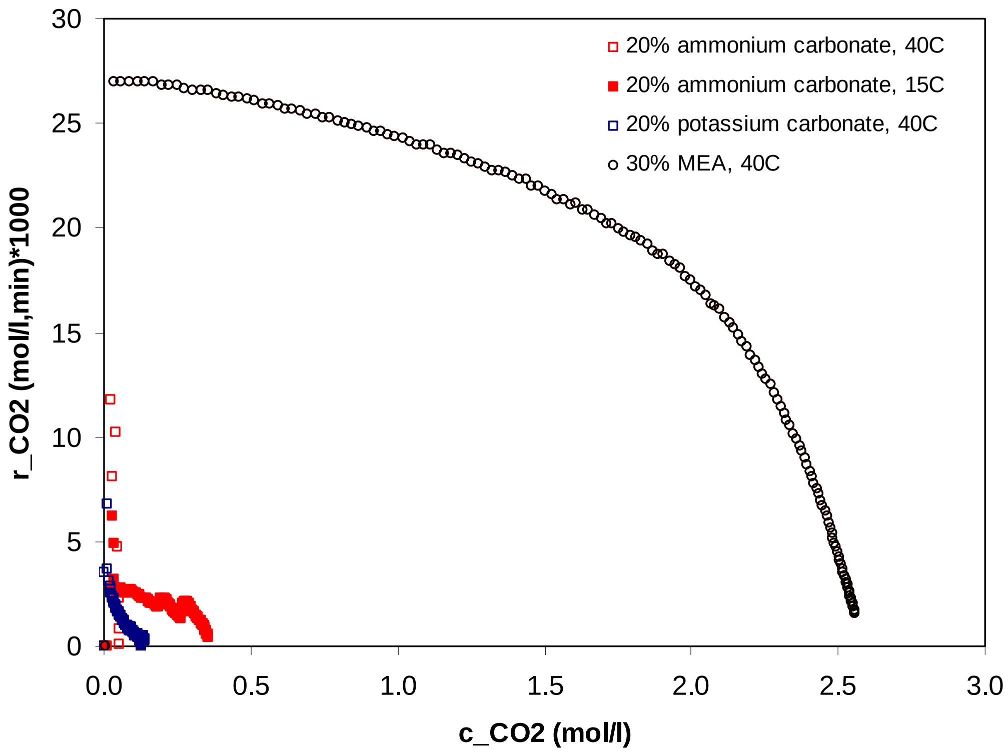

Figure 5-6: Screening test results.

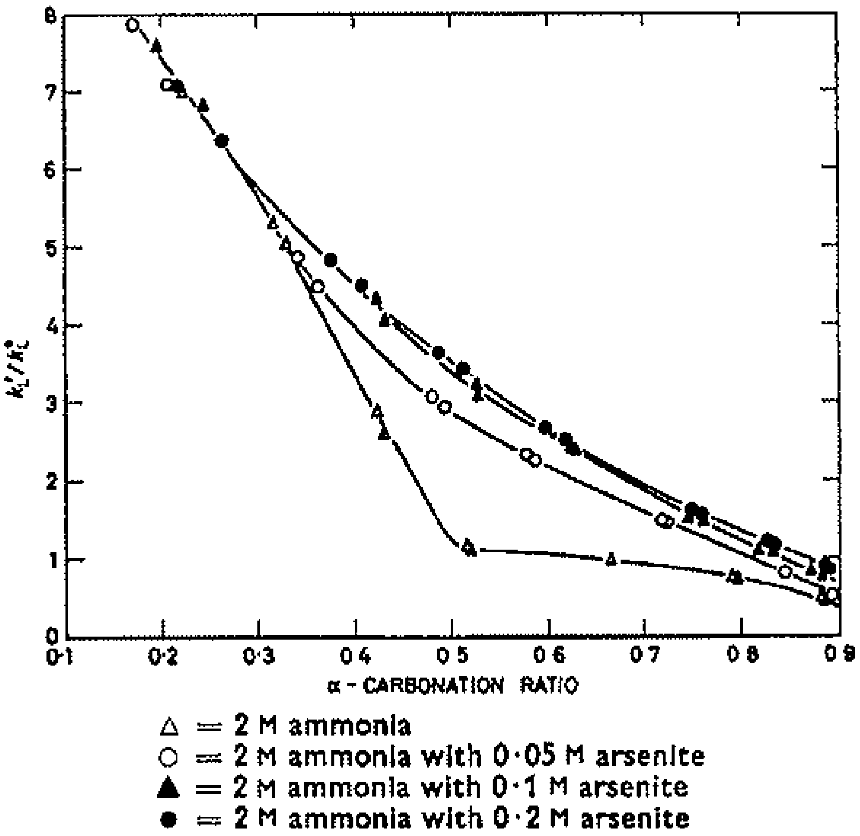

Figure 5-7: Ratio between liquid-side chemical mass transfer coefficient and liquid side physical mass transfer coefficient as a function of CO_2 loading (mol absorbed CO_2/original NH_3) at 18°C.[32]

5.3.3 Challenges related to chemical kinetics

The rate of absorption of CO_2 into ammonia solution is relatively fast as has been shown by Derks and Versteeg (2009)[25] as can also be seen from Figure 5-7. But the absorption rate decreases fast as the amount of free ammonia decreases and the amount of carbamate and bicarbonate in the solutions increases. At CO_2 loadings of 0.5 and higher the absorption rate is almost equal to physical absorption. Because of the slow kinetic rates an absorber design with high solution retention times, recirculation loops and volumetric flow rates will be needed and a major issue concerning the viability of this process is therefore if absorber can successfully absorb 90% of the flue gas CO_2 content.

It is thus of importance to determine how much free ammonia, acting as an “activator” that must be used to accomplish 90% capture. This will increase the demand on the water wash system and make the process more expensive since a portion of the ammonia must be regenerated via reaction pathway 1 and 2.

5.3.4 Challenges related to operation

The present authors do not know if the regenerative heat exchanger and desorber is capable of converting all solid bicarbonate back into solution at high ammonia concentration and high solid bicarbonate concentration. This is a particularly interesting question since the slurries in theory can contain a very high percentage of solids (maybe more than 40-60 wt %). This will be an issue that depends on the dissolution time and retention time in the heat exchanger and connecting units. If solids are returned back to the absorber, the desorber too will have to handle solids, resulting in both reduced solvent efficiency and more difficult operation. The heat exchanger must gradually increase the temperature of the solution throughout the solvent. If the solvent is heated too fast or if it is not mixed properly during heating, CO_2 will start flashing out. Maybe more heat is needed in addition to that available from the sensible heat from the lean solvent from the stripper for this section, because of the additional energy required for dissolving the solid. It is difficult to predict what effect this flashing might have. In the process description it is suggested that waste heat from other units can be used for dissolving solids.

Slurry particle size

The solids must not have too small particle sizes since the slurry must be separated in an efficient manner in the hydro-cyclone/thickener unit and can therefore not be a paste or pulp. The particle size is therefore an important parameter in the practicalities of the process.

5.3.5 Technology maturity according to Alstom

The chilled ammonia process is targeted for limited commercialization by 2011 and full commercialization by 2015.[33] However, based on the information publicly available the impression is that these targets seem very uncertain. Their field pilot plant is currently under operation (from fall 2008) for validation of key performance parameters. The testing is scheduled to continue into late 2009.[33]

5.3.6 Safety and environmental impacts and considerations

Ammonia slip, absorber and desorber

The rate of ammonia slip is determined by the free ammonia concentration in the solvent, the operation temperature at the top of the absorber, the solvent concentration and the CO_2 loading.

The low operation temperature 0-10^{o}C minimizes the vapor pressure. It is also important to minimize the amount of free ammonia in the solvent thereby maximizing the concentration of less volatile carbonate (and bicarbonate). However, this parameter is as noted dependent on the ability of the system to achieve the specified removal rate, for example 90%. The last two factors, solvent concentration and CO_2 loading are determined by the specific operation of the column.

Slip from the Absorber

High CO_2 removal efficiencies causes a higher degree of ammonia slip since a higher solution loading (higher NH_3/CO_2 ratio) yields more free ammonia in the solution that results in a significantly higher ammonia vapour pressure. The vapour pressure is orders of magnitude larger than in an MEA plant, and requires a complex wash system. As already noted, it is most likely that some free ammonia will be required in order to approach 90% removal efficiency. Minimum slip rate is according to NETL obtained at a partial loaded solution with a NH_3/CO_2 ratio of 1.7.[18] At lower CO_2 loading, meaning higher NH_3/CO_2 ratio than 1.7, the vapour pressure of NH_3 increases significantly. Again, according to NETL, a maximum removal efficiency of 65% is possible at this loading-ratio, where the slip rate is at a minimum, demonstrated in an experiment using a bubble reactor.

Slip from the desorber

It is unknown what the degree of slippage will be from the desorber. It is expected that this is much lower than the slippage from the absorber due to the lower temperatures appearing here after the condenser units. However, since the ammonia carbonate and bicarbonate decomposes at the high temperature found in the desorber it would seem likely that the gas phase will always have significant concentrations of ammonia in the stripper, which will precipitate in the overhead cooling system and give some practical challenges as well.[34]

The water wash sections and DCC

It is estimated that significant ammonia will slip from the absorber even at NH_3/CO_2 mole ratios below 1.7, in the 900-3000 ppmv range. This means that a water wash unit, which includes additional supply of an acid in addition to DCC2, is required. The cost and complexity of operation of this system is therefore a major consideration.

Degradation

Compared to amine solvents ammonia is a much simpler molecule. It is unlikely that it forms undesired degradation products. The environmental risk presented by ammonia is perhaps therefore more readily quantifiable than for an amine solvent. Ammonia is as already noted a volatile compound and controlling evaporation losses will in general be a greater challenge than for amine solvents.

6 The Cansolv amine process

6.1 Introduction

The Canadian company Cansolv Technologies Inc. was formed in 1997 to commercialize and market the CANSOLV® SO_2 scrubbing system. They now also offer an amine based CO_2 capture process as well as an integrated process for simultaneous capture of CO_2 and SO_x.

Two demonstration plants of the Cansolv CO_2 capture system have been built. One in Montreal, Canada, for capture of CO_2 from flue gas of a natural gas fired boiler, and one in Virginia, for CO_2 capture from flue gas of a coal fired boiler. No commercial plants have yet been built, however, according to their webpage, Cansolv is developing a project to build, own and operate a 5000 ton per day unit in Western Canada. The flue gas is from a coal fired power plant and the CO_2 will be compressed and transported to oil fields for EOR.[35]

Cansolv Technologies, which is also located in China, has recently been bought by Shell Global Solutions.[36]

6.2 Process description

The main features of the Cansolv CO_2 capture process is the specific solvent used as well as the possibility of integrating the SO_x + CO_2 capture units.

Simplified flowsheets for the CO_2 capture plant and the integrated CO_2 and SO_2 capture plants are given in Figure 6-1 and Figure 6-2, respectively. The CO_2 capture process is similar to the generic absorption based systems using amines (see Section 3.1.1), while the integrated system is more complex.

A short description of each key feature is given in the following sections.

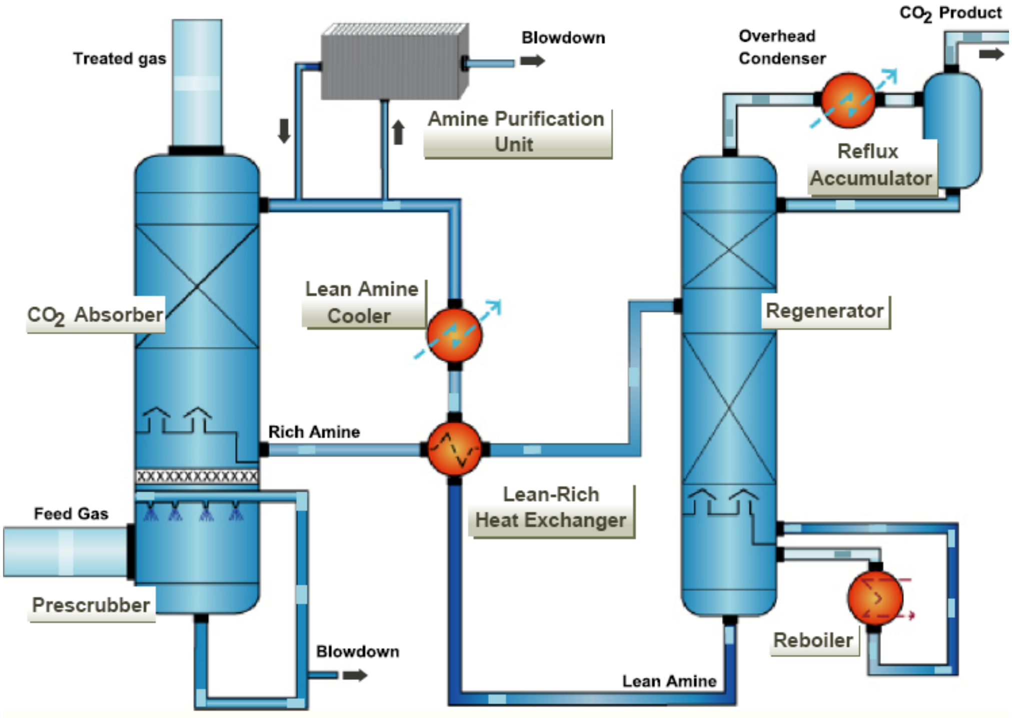

Figure 6-1: Cansolv® CO_2 capture system (taken from Cansolv's webpage).[35]

6.2.1 The solvent

Cansolv has developed a proprietary solvent named Absorbent DC101™ which, according to the patent, is based on the following three criteria:[37]

1. Low oxidative degradation of the amine
2. Low volatility of the amine
3. Low energy consumption in the process

It is not mentioned specifically in the patent which components are involved in the solvent blend, however some indications are given. They indicate that the solvent constitutes at least one tertiary amine including an oxidation inhibitor. In order to increase the generally poor mass transfer rate of tertiary amines a secondary amine is added to act as an activator for the CO_2 capture. Furthermore, they claim the following features:

- By using a tertiary amine, the pH range 6.5 – 8.5 is the optimal with respect to least energy consumption and high absorption capacity for CO_2 capture.
- The tertiary amine has a vapour pressure less than 1 mmHg (app. 1.3 mbar) at 120°C and a water-wash treatment is not required for this solvent. Due to the presence of a secondary amine a water-wash section is however, needed, but this section is less than for MEA.
- The solvent comprises an aqueous solution consisting of 10-50 wt% of the tertiary amine, 0-8 wt % of piperazine, 1-30 wt% of N-(2-hydroxyethyl)piperazine, and with the remainder comprising water.
- The steam consumption will be reduced with 40 % compared to the MEA basecase. (Please see the discussion regarding energy requirements below).
- The right buffering pH for SO_2 capture is 3-6 and thus by using a proper diamine absorbent, the SO_2 capture is achieved by having the stronger amine function in a "half-salt" form. The same amine can be used for CO_2 capture in the integrated process, but the pH must be adjusted accordingly by having the diamine in free base form.
- The SO_2 lean stream from the SO_2 capture part must contain a concentration of SO_2 as to maintain a concentration of sulphite in the CO_2 scrubbing loop sufficient to prevent the oxidation of the absorbent by molecular oxygen. (To the present authors it thus seems that this claimed advantage of low oxidative degradation holds only with integrated SO_2-CO_2 capture).

Further details about the chemistry and possible components are given in Appendix A.

6.2.2 The integrated CO_2 and SO_2 capture plant

The second key feature of this process is the possibility of combining SO_X- and CO_2-capture, directly integrated in the CO_2 plant, as shown in Figure 6-2.With this integrated feature, the same solvent and absorber column is applied, but CO_2 and SO_2 are absorbed in different sections of the absorber and two different solvent cycles are required

Brief description of the process

Prior to the absorption, the feed gas containing both components is saturated with a spray of water and cooled to approximately the adiabatic saturation temperature. The pre-treated gas then flows through a chimney tray to the SO_2 removal section, where it flows counter-currently to a suitable lean diamine absorbent, wherein the diamine is in so-called "half salt" form. As such the buffering pH is kept in the right range (3-6) for SO_2 capture. The majority of the SO_2 is removed and leaves the tower in the SO_2 rich stream. This SO_2 is regenerated by indirect steam stripping in the SO_2 regenerator. Approximately 80 % of the heat used for the SO_2 regeneration is used for the CO_2 stripping process as the regenerated SO_2 overhead steam is led to one of the two reboilers for the CO_2 regenerator. The remaining heat for the CO_2 stripping process is provided by the indirect steam fed to the second reboiler. The SO_2 lean gas stream from the SO_2 absorber section flows through a chimney tray before it is treated in a CO_2 scrubbing loop with a second absorbent stream to obtain a CO_2 rich liquid stream. This absorbent stream contains the same diamine in free base form meaning a pH range of 6-9 suitable for CO_2 capture. Most of the remaining SO_2 is also captured in this section. The CO_2 rich liquid stream is regenerated in the CO_2 regenerator column. Both a slip stream from the SO_2 loop and the CO_2 loop is treated separately to avoid accumulation of heat stable salts (HSS) in the system.

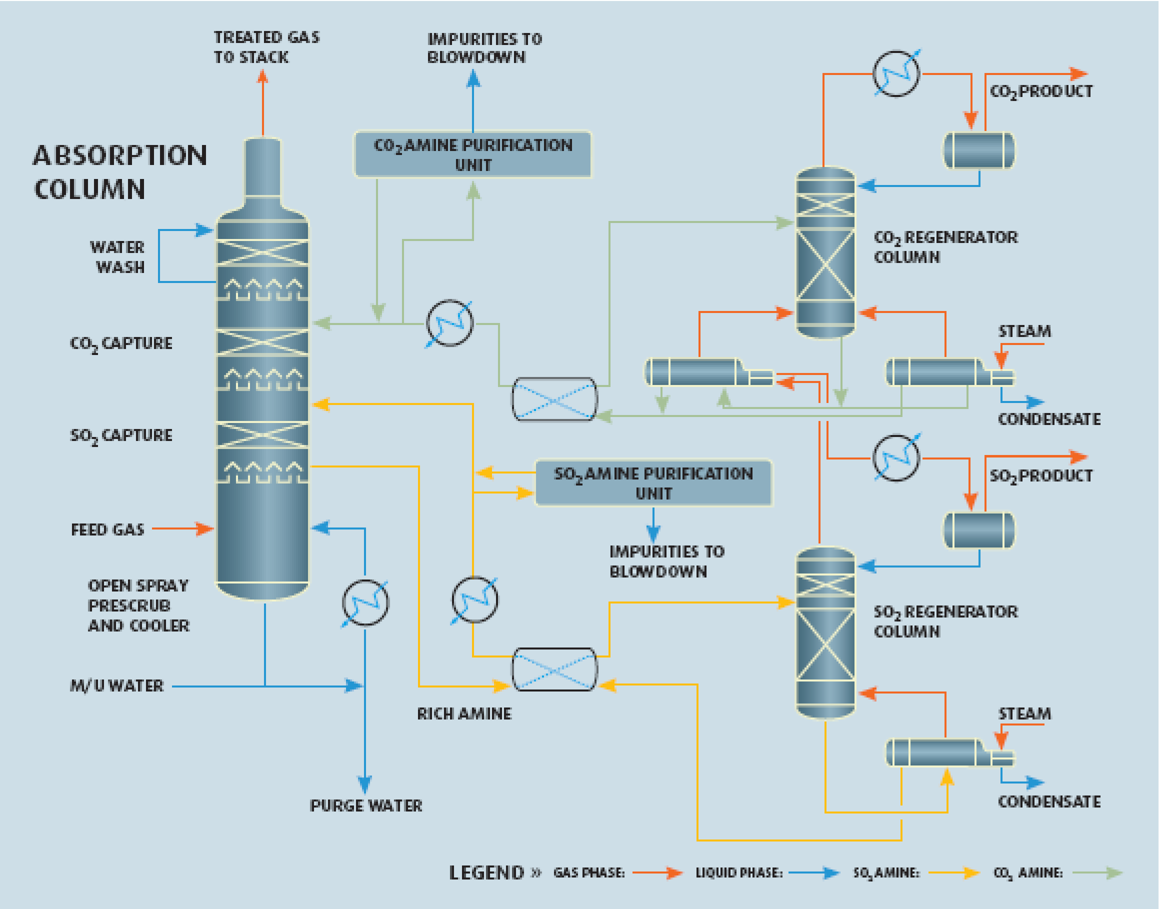

Figure 6-2: The Cansolv® integrated SO_2-CO_2 capture system (taken from Cansolv’s webpage).[35]

6.3 Assessment of the process

6.3.1 Performance

Cansolv claim that the formulated amine will reduce the steam consumption with 40 % compared to the reference MEA process. It has, however, not been specified which configuration of the MEA-process that has been used as reference. It is also not clear to the authors whether this concerns the integrated process or the CO_2 capture process only. If the baseline MEA is 4.2 GJ/ton, this means a steam consumption of 2.5 GJ/ton. Whether the solvent is capable of achieving sufficient removal with the claimed steam consumption is not known to the authors and for a confirmation of these numbers pilot plant data or equilibrium data is required.

Without knowing specific details of the solvent formulation it is hard to draw conclusions on the performance of the system. Tertiary amines do however tend to have low capacity to bind CO_2 and slow kinetics when the CO_2 partial pressure is low (as they are in exhaust gases). Our concern would therefore be that the solvent might not readily achieve 90% capture.

It is also claimed that the amine degradation is very low compared to MEA and that the kinetics are comparable to primary amines.[38]

The integrated plant means that significant capital expenditures can be cut since only one absorber is used for both SO_2 and CO_2 capture as well as operational costs due to the heat integration. Another issue is the synergic effect of the captured acids. Will accumulation of SO_2 adversely and negatively affect the CO_2 capture and vice versa?

6.3.2 Challenges related to operation

The combined process is very integrated both with respect to heat and process streams. This implies generally a more challenging operation and the process is apparently vulnerable based upon the strict requirements for control of pH and salt concentration in two separate but still integrated solvent loops. The same solvent captures both SO_2 and CO_2, but will have to operate at different pK_as depending on the specific capture sections. This seems difficult in practice, especially at varying loads, but most probably manageable.

6.3.3 Technology maturity

The Cansolv process was evaluated in competition with the concepts offered by Fluor and Mitsubishi for the now terminated Halten CO_2 project in 2006/2007. Pilot testing in a portable container based rig was performed at the Risavika Gas Technology Center. Since the Halten project was terminated due to an expected prohibitive high cost of CO_2 capture, it is assumed that the process did not indicate a *significant* improvement. The process itself with all its complexities seems rather conceptual, and it should be verified on a demonstration scale to prove feasibility. A pilot unit was commissioned on coal fired industrial boiler to run filed testing from 2004 to 2007. A 50 ton/day demo plant was according to Hakka et al.[38] designed in 2007 with construction and start-up in 2008. Full commercial project engineering was planned for start-up in 2007.[38] The recent acquirement by Shell indicates a continued effort and it is expected that both the solvent and the process configuration are being continuously evaluated.

6.3.4 Safety and environmental impacts

The piperazine derivatives described as preferred solvent components according to the Cansolv patent, are likely to have very low biological degradability. Such chemicals do present a potential environmental issue and their use may be restricted by environmental authorities.

The extent of emissions to air and the amount of degradation products or reclaimer waste formed is not known.

7 The Praxair Amine process

7.1 Introduction

Praxair has recently filed a patent for a process that is based upon a common amine absorption configuration but with certain specifics (Int. Pat No WO 2007/075399).[39] Previous patents have also been filed from Praxair describing parts of this process (US Patents 6,174,506 B1 6,146,603 and 6,165,433).[40,41,42]

7.2 Description of the process and process units

The following are key features of this process:

- The specific handling of oxygen in the flue gas
- The amine blend
- The possibility of addition of an organic component to the aqueous solvent.

The process is, except for the mentioned specifics, similar to a typical amine absorption plant like the base case MEA plant (see section 3.1.1).

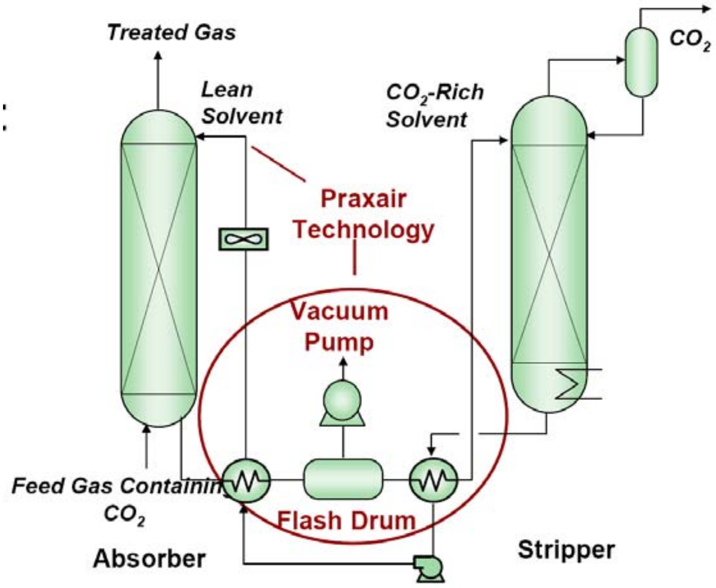

Figure 7-1: Schematic of the Praxair process (Figure taken from Praxair's webpage).[43]

7.2.1 Specific handling of oxygen

The idea for handling the problems with oxidative degeneration of amine is to remove the dissolved oxygen from the rich solution, before it is heated prior to regeneration, through a process modification. It is claimed that there will be no need for inclusion of inhibiting agents. The dissolved oxygen will otherwise cause amine degradation leading to corrosion or steel piping and equipment and other operation problems. To overcome this issue, the modified process includes incorporation of a vacuum flash tank downstream from the absorber, operating at a pressure of 0.2-0.4 bara. The depressurization is claimed to remove the oxygen from the rich solution to less than 2 ppm oxygen. Some CO_2 may be released here also. Alternatively, it is noted in the patent that the rich solvent can be moderately heat exchanged to a temperature within 60-71^oC prior to the vacuum flash deoxygenation. The oxygen can also be removed by contacting the solution with an oxygen scavenging gas such as nitrogen or a portion of the stripped CO_2 in a packed column or a similar mass transfer device. The resulting oxygen free rich solvent then passes through a (second) heat exchanger and is heated to a temperature of about 105 ^oC before entering the stripper as in a traditional process configuration.

7.2.2 The amine composition

In the patents (US Patent 6,165, 433 and 6,174,506 B1) it is suggested to use concentrated alkanolamine blends up to 50wt% using a larger concentration of one or more slow reacting amines (from 5 to 50 wt%) and a smaller concentration of one or more fast reacting amines (from 5 to 35 wt %). As an example, in a preferred blend is chosen one fast reacting amine, 20wt% MEA, with a second higher capacity and slower reacting amine such as 20-40 wt% MDEA. Other fast reacting amines suggested include DEA, Piperazine and di-isopropanolamine and other slow reacting amines include TEA and sterically hindered amines such as 2-amino 2-methyl 1-propanol (AMP).

The faster reacting amine is used in a relatively low concentration which, among other issues, avoid problems with corrosion without use of inhibitors, but a concentration sufficient to enable fast CO_2 absorption from the flue gas. The slower reactive amine, with higher absorption capacity, is included in sufficiently large concentrations to provide absorption at an acceptable rate in presence with the primary fast reaction amine.

7.2.3 Organic component

As an element in the process, it is described in Int. Pat No WO 2007/075399 that a water-soluble liquid (at 25 ^oC and atmospheric pressure) organic component is to be added to the solvent in addition to the amine. This component is suggested, among others, to be a C_1-C_3 alcohol, ethylene glycol or similar. This addition is thought to reduce the sensible and latent heats that are required for regenerating the amine. It is claimed that the latent heat is reduced since less steam is needed for vaporization and the heat capacity of the solution is reduced at least 10%.

Due to addition of such an organic component, additional complicating factors need be considered, such as flammability (since there is significant oxygen in the flue gas), health hazards as well as environmental considerations. Special considerations may need to be addressed to the wash water sections due to increased solvent vapor pressure. The organic component must also be chemically compatible with the amines and the plant equipment. Furthermore, it should not negatively alter the chemical reaction rates.

7.3 Assessment of the process

7.3.1 Performance

Steam requirement for regeneration

It is claimed that this process requires less energy per unit of CO_2 treated, due to the lower energy required to evaporate the organic component and thus less amount of water necessary for evaporation. It is also claimed that the circulation rate of solutions containing the organic phase can remain the same as the rate of a solution without the organic component. To illustrate, the following example is given: A 30 wt% MEA solution typically has a specific steam consumption of 4.2 GJ/ton CO_2 removed (an early estimate for Fluor's Econamine process) while a blend of 30wt% MEA and 20wt% MDEA and 30wt% diethylene glycol and remaining water, potentially has a specific steam consumption of 2.98 GJ/ton CO_2. The specific heat capacity of an aqueous blend of 30wt% MEA and 20wt% MDEA at 93^{o}C is in the patent reported to be 3.64 kJ/kg where as by inclusion of 30wt% diethylene glycol the value is reduced to 3.11 kJ/kg. Furthermore, it is mentioned that the inclusion of an organic components such as ethylene glycol, can increase the absorption reaction rate and reduce foaming tendencies, which can possibly reduce the required size of the absorber and less operational difficulties. The increased kinetics seems improbable since previous work has shown that the introduction of glycol to an aqueous solution will have negative impacts on reaction rates.[44]

Since the oxygen absorbed in the solvent is removed straight after being absorbed by the vacuum flash downstream from the absorber, it is claimed that there will be no need for inhibitors of oxidative degradation of the amine.

According to the patent, an optimized operation of the Praxair process will require about 3.1 GJ steam per ton CO_2 removed but it is unclear what the CO_2 concentration is in the flue gas for this example, it is probably intended to be a coal combustion stream. As a comparison, using a 30wt% MEA aqueous solvent, the reference basecase, requires 4.2 GJ steam per ton CO_2 removed. With specific process optimizations etc, it could be possible to further reduce specific steam requirement. Among the assessed processes this would seem the be one which involves the smallest risks of implementing on a large scale, since it is the closest one to a traditional MEA based system. This is, if one can safely handle the addition of the organic component.

Handling of oxygen and solvent degradation

The way O_2 is handled might still require inhibitors to prevent oxidative degeneration of the amine solvent. In a previous study, it was claimed that the oxidative degradation was most severe in the absorber and absorber sump. The extent depends on the solvent temperature and retention time in the sump due to the relationship between the O_2 solubility and the kinetics of the oxidative degradation reactions. The extent to which the O_2 is stripped from the solution depends on the O_2 solubility and will increase with a pressure reduction and increased temperature, it seems logical to have a vacuum flash tank downstream the absorber as well as minimizing the retention time in the absorber sump by rather having the solvent storage in or prior the vacuum flash, but away from the absorber. If the increased pressure downstream from the rich pump (needed for the hydrostatic pressure drop to the top of the stripper) accelerate degradation, (decreased ratio of solubility to rate of reaction for oxidative degradation) the oxidative degeneration will become significantly larger and the vacuum flash will be way of reducing the degradation. If there is no accelerated degradation downstream from the pump, the O_2 will in any case flash off at the top of the stripper after being heated in the crossflow heat exchanger. In this case the vacuum flash will be of now use.

In addition to oxidative degradation, thermal degradation can be significant at elevated temperatures. This occurs primarily in the reboiler and stripper (where the temperature is the highest in the process). The flash will not work for these phenomena.

The organic component addition might cause operating temperatures to be larger in the absorber as well as the desorber at the same operating pressure (due to the increased vapor pressure of the organic components), which may cause increased thermal degradation and carbamate polymerization.

Following the discussion concerning the handling of oxidative degradation, it is clear that specific concerns must be taken in the design of the absorber and following flashing of the O_2. It is also not known how much steam will be lost with the vacuum flashing of O_2 and CO_2, (nor the parasitic energy load of operating the vacuum flash). The flashing might also alter the water balance of the process and reduce the temperature of the rich stream thereby reducing the efficiency of the overall process (that is, if the waste steam cannot be re-used).

In regards to the organic addition it is difficult to estimate the overall benefits of adding an organic component to the solvent circulation, without the necessary process data. It is clear that the addition will produce additional concerns that will have to be handled. Proper operation might reduce the total steam consumption.

7.3.2 Technology maturity

This process is claimed to have a steam consumption of around 3.1 GJ/t and there might be some potential for further reductions if other process improvements are included. The underlying process is more or less mature; but must be tested on a larger scale pilot plant. The inclusion of the proposed organic component to the solvent might cause problems with respect to safety and environmental impacts as well as performance and must be shown on a pilot plant. Praxair have operated a small pilot test rig that cleans 0.2 tons/day and has been in operation since 2000. The current authors have not been able to find information concerning the current status of the development.

7.3.3 Safety and environmental impacts

Emission and pollution preventative needs must be addressed, especially with regards to the addition of organic components. Otherwise, the safety and environmental issues are the same as for other amine systems.

8 Comparison

Each of the three processes is compared to the base case and then and overall comparison of the processes is given.

8.1 The Alstom Chilled ammonia process

8.1.1 Advantages

The potential advantages of the Chilled Ammonia process are:

- Low regeneration energy requirement: The heat of absorption of CO_2 with ammonium carbonate to form bicarbonate is much lower than that of MEA, about one third.
- Regeneration occurs at high pressure, which reduces compression costs and reduces the size of the regenerator considerably. As noted the energy requirement will be about one fourth of that for compression from Fluor’s desorber (approx. 2 bar pressure) to 120bar.
- Operation with a slurry potentially enhances CO_2 carrying capacity far greater than that of MEA
- Pre-cooling of the inlet reduces the volumetric flow rate to the absorber, which might reduce the absorber diameter and pressure drop significantly.
- Process waste heat and heat rejection can possibly be re-used somewhere in the process. Heat removed in the pre-heating stage can be reused as well as cool sources such as the overhead cleaned flue gas.
- Ammonia is cheap and does not degrade.
- The extensive cooling will be an effective particle wash, effectively removing trace SO_X etc.

8.1.2 Disadvantages

The potential disadvantages of the Chilled Ammonia process are:

- Operation
    - A slurry type of solvent significantly complicates the process
    - Requires units that can handle slurries.
    - Particle distribution must be one that can be handled in the process
    - Absorber will probably have to be of a spray tower type, which will reduce performance of a liquid film controlled reaction.
    - More unit operations and piping and narrower operational interval implies increased requirement on process control.
    - A high pressure slurry pump is needed
- Lean solution pressure

    - The lean solution pressure exiting the desorber is about 30 bar. Flashing of steam and CO_2 might occur when reducing pressure to ambient pressure prior to the absorber.
- The solid formation
    - High energy of dissolution
    - The exothermic precipitation reaction will require additional cooling/refrigeration in the absorber to keep the temperature low as well as mechanical agitation.
    - Complicated regenerative heat exchanger needed for providing the additional energy required for the rich solvent phase change of the solids to bring into solution. Must control solvent dissolution and flashing. Mechanical stirring probably necessary to provide uniform heat transfer to the solution.
- Reaction rate and absorber chilling
    - Operation of absorber at a low temperature required for sufficient driving force for the absorption and minimizing overhead slip of ammonia.
    - At this low temperature the carbonate/bicarbonate reaction kinetics is very slow (this is confirmed by experiments performed at SINTEF).
        - Might not be possible to accomplish the goals without a significant presence of free ammonia working as an activator. This makes the process more energy intensive and puts higher demands on slip reduction.
    - The separate coolers and refrigeration system required for cooling of the flue gas inlet stream, inter-cooling of the absorber, cooling of the lean stream, implies considerably larger CAPEX and OPEX compared to the corresponding cooling system of MEA based processes.
        - Pre-coolers will have similar diameter as the absorber.
- CO_2 removal efficiency
    - It is unclear if the process can absorb 90% of the CO_2 in the flue gas without free ammonia present

8.1.3 Potential challenges

1. Ammonia slip:
    - Is it practically feasible to retain the ammonia in the system?
2. Absorption rate:
    - Is the carbonate/bicarbonate rate of reaction sufficiently fast at the low operational temperature or is significant free ammonia necessary?
3. Slurry:
    - Are the particle sizes of the solid bicarbonate manageable so it can be effectively handled in the hydro cyclone and cross-flow heat exchanger and other unit operations?

8.1.4 Overall evaluation of the technology

The Alstom Chilled Ammonia process includes process improvements but also requires a very complex operation, with extensive refrigeration requirements as well as slurry handling and ammonia slip prevention. It is not known if all these issues have been resolved by Alstom. It is also unknown if sufficient absorption capacity is possible with an acceptable ammonia slip, and if the process has the potential to perform better than an MEA process.

As mentioned earlier the chilled ammonia process is targeted for limited commercialization by 2011 and full commercialization by 2015.[33] Due to the complexity of the process, and the current early stage of development the authors believe it will take longer time for this process is ready for commercialization.

8.2 The Cansolv Process

8.2.1 Advantages

The potential advantages of the Cansolv process are:

- The chosen solvent system implies lower amount of steam for the regeneration process than the MEA based base case (Cansolv claim 40 % lower).
- The degradation rate is lower than MEA
- Integrated SO_2 and CO_2 capture:
  - Heat integration means lower required external heat
  - Integrated capture means lower capital costs

8.2.2 Disadvantages

The potential disadvantages of the Cansolv process are:

- It is questionable if a proper CO_2 capture rate is obtained with the solvent system
- The piperazine derivatives used in the solvent system are expected to have low biological degradability. As a result their use may be restricted, unless proper water-wash in the top of the absorber and desorber columns is secured
- Integrated SO_2 and CO_2 capture:
  - Possibly very complex operation due to integrated process
  - SO_2 in the captured CO_2 stream is most likely more difficult to control than a system with stand-alone sulphur removal

8.2.3 Overall evaluation of the technology

The main advantage of this process seems to be related to the combined CO_2 and SO_2 removal process. However, this process is very complex and it is very difficult to control the operation, which relies on having different pH levels in the same absorber column.

8.3 The Praxair amine process

8.3.1 Advantages

The potential advantages of the Praxair process are:

- Regeneration steam is claimed to be about 3.1 GJ/ton CO_2 removed, which is lower than the basecase MEA system.

- The specific handling of oxygen in the flue gas could remove the need for corrosion inhibitors
- The process seems to be the one, which involves the smallest risks of implementing on a large scale, since it is the closest one to a traditional MEA based system.
- The underlying process is more or less mature.

8.3.2 Disadvantages

The potential disadvantages of the Praxiar process are:

- It is not known if one can safely handle the addition of the organic component.

8.3.3 Overall evaluation of the technology

The Praxair process is based on traditional amine technology and as such, it is the most mature technology among the three that are assessed. This also involves smaller risks, but does not offer a significant advantage over a basecase MEA system.

9 Conclusions

In this report a technological assessment of three post-combustion CO_2 capture processes is made. These are processes which have been developed beyond bench scale, but which have not yet been widely assessed for CO_2 capture. The processes have been discussed based on publicly available literature. The Chilled Ammonia under development by Alstom has been discussed more elaborately since it is a more complicated process involving slurries. Two amine processes are discussed. The processes have been described and discussed based on technical complexity, costs and some environmental issues.

The Chilled ammonia process is a technology under development. The process has both advantages and short-comings when compared to more conventional amine processes. There are a number of challenges and uncertainties in operating a chilled ammonia process. Based on the data that has been available to the present authors it is hard to judge to which extent these challenges have been resolved by Alstom. All in all, this technology seems to need much more research before it is technologically mature for large scale operation.

The amine processes considered are closer to technology currently in use. In this sense these processes can be regarded as technically more mature than the chilled ammonia process. Both processes offer innovations that may reduce energy consumption, but at the cost of a somewhat more complex process.

Acknowledgement

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Appendix A: Chemistry for the Cansolv solvent

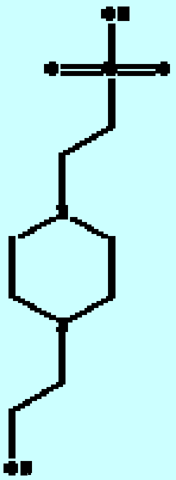
CO_2 capture plant

According to the patent by Hakka and Ouimet,[37] the absorbent should at least contain one tertiary amine and most likely this is either methyldiethnolamine (MDEA) or triethanolamine (TEA) or a combination. Additionally the absorbent could contain the following piperazine derivates, diamines, and tertiary alkylamine sulfonic acids:

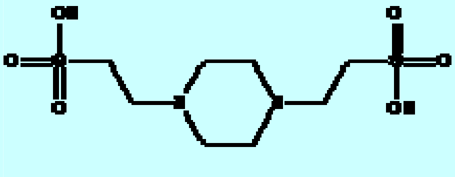
N,N'-di-(hydroxyalkyl)piperazine, N,N'-di-(2-hydroxyethyl)piperazine, N,N'-di-(3-hydroxypropyl)piperazine

N,N,N',N'-tetrakis(hydroxyalkyl)-1,6-hexanediamine, N,N,N',N'-tetrakis(2-hydroxyethyl)-1,6-hexanediamine, N,N,N',N'-tetrakis(2-hydroxypropyl)-1,6-hexanediamine

Examples of the alkylamine sulfonic acids are:



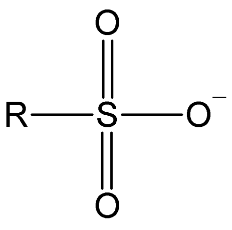
4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (MW 238.3, mp 234-238, white chrystalline powder, soluble)



1,4-piperazinedi(ethanesulfonic acid)

Sulfonic acids are a class of organic acids with the general formula *R*-S(=O)2-OH, where *R* is usually a hydrocarbon side chain. Sulfonic acids are typically much stronger acids than their carboxylic equivalents, and have the unique tendency to bind to proteins and carbohydrates tightly; most "washable" dyes are sulfonic acids (or have the functional sulfonyl group in them) for this reason. They are also used as catalysts and intermediates for a number of different products. Sulfonic acid salts (sulfonates) are important as detergents, and the antibacterial sulfa drugs are also sulfonic acid derivatives. The simplest example is methanesulfonic acid, CH3SO2OH, which is a reagent regularly used in organic chemistry. *p*-Toluenesulfonic acid is also an important reagent.Note that the sulfonic acids and sulfonates are analogous to carboxylic acids and carboxylates; in both cases, -C(=O)- is replaced by -S(=O)2-. Chemical properties are similar as well, although sulfonic acids are often even stronger acids than carboxylic acids, the hydrogen being easier to leave than in most compounds, and they readily form esters.

General structural formula sulfonates:



The sulfonic acid and sulfonate functional groups, -SO2OH and -SO2O-, are found in many chemical compounds, e.g. certain detergents and dyes as well as in strongly acidic cation exchange resins.

Primary and secondary amines produce carabamate salts in the 1:2 ratio of CO_2 to amine. Since tertiary amines do not have a hydrogen atom attached to the nitrogen, they cannot form carbamates, but they do form bicarbonate salts in the 1:1 ratio of CO_2 to amine. Thus tertiary amines will potentially achieve higher loading than the primary and secondary amines.

Since tertiary amines have relatively slow mass transfer rates, a secondary amine can be utilized as an activator to increase the rates. The carbamate salts produced from secondary amines tend to hydrolyze to bicarbonate salts. The protonated secondary amine and the tertiary amine equilibrate with each other thereby catalyzing the hydration of CO_2 and the formation of the tertiary amine bicarbonate salt:

$$R^1R^2NCO_2^-H_2N^+R^2R^1 + H_2O \Leftrightarrow R^1R^2NH_2^+ + HCO_3^- + R^1R^2NH \tag{1}$$

$$R^1R^2NH_2^+ + R^3R^4R^5N \Leftrightarrow R^1R^2NH + R^3R^4R^5NH^+ \tag{2}$$

Tertiary amines are more stable than primary and secondary amine meaning they are less prone to chemical degradation. Even though tertiary amines also are more resistant to oxidative degradation than primary and secondary amines, oxidation inhibitors are added. Hakka and Oiment[37] has determined that the combination of an oxygen scavenger, such as sulfite and a free radical scavenger, such as thiosulphate act as the best protection to oxidation. Chelating agents such as amine or polyaminepolycarboxylic acids may be added to the solvent to inhibit metal ion catalyzed oxidation.

Integrated SO_2 and CO_2 capture process

Hakka and Oiment[37] states that the most preferred components in the absorbent are:

N,N’-di-(2-hydroxyethyl)piperazine (DIHEP) as tertiary amine

N-2-hydroxyethylpiperzine (HEP) as secondary amine activator

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APPENDIX B – Part 1

Response of Alstom to the SINTEF Report

Alstom Response to SINTEF Report

Please note that an updated process flow diagram, updated process description, and process chemistry overview are enclosed as Exhibits A, B, and C to this document.

Alstom first provides general rebuttal to the technology weaknesses and key challenges noted in Sections 8.1.2 and 8.1.3 of the SINTEF report. Following this are specific clarifications to the main portion of the report.

The potential disadvantages of the Chilled Ammonia process that were identified by SINTEF are identified in the section headings below followed by the Alstom rebuttal for each section.

SINTEF Comment:

- Operation:
    - A slurry type of solvent significantly complicates the process
    - Requires units that can handle slurries.
    - Particle distribution must be one that can be handled in the process
    - More complicated operation compared to an amine plant.
    - Absorber will probably have to be of a spray tower type, which will reduce performance of a liquid film controlled reaction.
    - More unit operations and piping and narrower operational interval implies increased requirement on process control.
    - A high pressure slurry pump is needed

Alstom Response:

The Chilled Ammonia Process ("CAP") involves the use of packed absorption vessels that can be operated with and without solids. The primary advantage of operation with solids is an increased CO_2 loading (kg CO_2/liter solvent) of the solvent to the regenerator resulting in reduced sensible heat loss and lower capital costs. The higher CO_2 loading of the regenerator feed stream will result in a lower solvent (rich stream) flow rate. This will reduce the sensible heat needed to raise the rich stream to the desired regeneration temperature and allow for smaller sized equipment. The CAP does have more equipment than a conventional amine process. However, our experience at both the We Energies Pilot and the EON Karlshamn Pilot have proven that the CAP is easily operated and controlled using instrumentation and control loops that are commonly utilized within the power generation steam cycle and flue gas desulphurization systems. The ammonium bicarbonate solids that are precipitated in the CAP absorption stages have been shown to dewater readily in the laboratory using conventional and low cost solids-liquid separation equipment.

Alstom has operated the CAP at our We Energies Field Pilot for over 7,000 hours. The system has recently reached the design solution molarity without solids and has demonstrated high CO_2 removal efficiency. To date, we have operated the field pilot with solids for short durations and experienced solids deposition on internals that interfered with the test program. While we have found that the solids depositions can easily be resolved with the unit in service, we have intentionally operated the pilot under conditions where solids will not form until testing is completed at the design solution molarity. Now that the testing is completed under these conditions, we are presently focused on a test program to operate the field pilots at We Energies and E.ON Karlshamn with solids. The We Energies field pilot will be decommissioned at the end of this month but it is our goal to achieve reliable operation with solids at the E.ON Karlshamn pilot in the coming months. The lessons learned will continue to be transferred to the operation of our validation pilots at AEP Mountaineer and TCM Mongstad.

With regard to slurry pumps, Alstom has been working with suppliers to select commercially available pumps that can achieve the desired process duties of the CAP. Alstom has been working closely with manufactures for several decades in the development of slurry pumps for its wet flue gas desulphurization technology and is confident that slurry pumps are available to achieve the desired conditions. Although limited operating data is presently available with solids at our pilot plants, there have been no signs that the solids are erosive in nature. We are presently conducting tests with slurry pump suppliers to determine the characteristics of the solids in a pumping environment.

Additional responses to SINTEF comments pertaining to operation of the CAP are summarized below:

- The absorption columns are not spray towers. Instead, the design involves the use of packed columns in a proprietary Alstom design; first evaluated at SRI International and validated at We Energies with over 7,000 hours operating experience.
- The ammonium bicarbonate solids formed in the CAP are observed to be light and relatively, non abrasive, no issues have been observed with excessive wear or erosion of any components;
- In some aspects, operation of the CAP is more complex because of additional equipment required, but the process has proven to be very controllable; the field pilots at We Energies and E.ON are each operated reliably using two full-time operators for each shift, with additional support for pilot testing and maintenance. As a result of the experiences at both We Energies and E.ON Karlshamn, robust operating procedures are being developed to account for start-up, shutdown, steady state and transient conditions.
- Process is flexible given higher liquid inventory and liquid recirculation in absorber system. The design has demonstrated the ability to accommodate excursions in flue gas, boiler load fluctuations, and variations in steam conditions.

Alstom has successfully operated the field pilot at We Energies for over 7,000 hours with high levels of reliability. Many of the control loops involve instrumentation and control logic similar to that used in flue gas desulphurization systems. Since September 2008, the field pilot has reliably operated 24 hours per day, 7 days per week. There have been a total of eleven outages, described as follows:

- Two forced outages of the power plant (unrelated to the field pilot);
- One planned outage to provide the pilot operations and validation teams a break over the Christmas and New Year holiday;
- Six planned outages to support additional modifications to the pilot plant; and
- Two forced outages to: a) to perform maintenance on the mechanical chiller; and b) inspect and troubleshoot a malfunctioning electric heater for the ammonia stripper.

SINTEF Comment:

- Lean solution pressure:
    - The lean solution pressure exiting the desorber is about 30 bar. Flashing of steam and CO_2 might occur when reducing pressure to ambient pressure prior to the absorber.

Alstom Response:

Heat from the hot lean solution is transferred to the rich regenerator feed prior to the return to the absorbers. At We Energies, the lean solution is returned at temperatures that are low enough to prevent flashing. Because of this heat exchange, we currently observe no flashing across the control valve that reduces the lean solution stream to atmospheric pressure. Future operations and designs are intended to improve upon this heat transfer such that there will be additional margin (further away from flashing) in future designs.

SINTEF Comment:

- The solid formation:
    - High energy of dissolution
    - The exothermic precipitation reaction will require additional cooling/refrigeration in the absorber to keep the temperature low as well as mechanical agitation.
    - Complicated regenerative heat exchanger needed for providing the additional energy required for the rich solvent phase change of the solids to bring into solution. Must control solvent dissolution and flashing. Mechanical stirring probably necessary to provide uniform heat transfer to the solution.

Alstom Response:

Operation with solids will require additional energy to precipitate solids and in the dissolution of solids in the regenerator feed as it is heated. These energy demands are offset by the reduced amount of sensible heat required to increase the regenerator feed stream temperature needed for regeneration. It is important to understand that the energy associated with the heating of the rich stream is performed primarily with the heat from the lean solution and at low temperatures allowing for the use of waste heat from sources that are available in the power generation facility. Therefore, little or no external heat is required for the dissolution of solids in our process.

The configuration at of the field pilots at We Energies and E.ON Karlshamn is a standard series of feed/bottoms exchangers that transfer heat from the hot, lean solution leaving the regenerator with the cold, rich solution leaving the absorbers. For the pilot, the rich feed system consists of one pump followed by a feed/bottoms exchanger leading to a second pump and feed bottoms exchanger. In this configuration, flashing (if it occurs) is not seen until the latter part of the second exchanger. As the exchangers are designed to handle this condition, no adverse operating consequences have been noted with two pumps in series.

From this basic configuration, the heat transfer mechanism can be evaluated and provides a basis for designing an improved system which would include utilization of reject heat from different sources, both within the CAP, as well as from external sources.

Alstom does use mechanical agitation in the process. The design draws upon the Alstom experience with flue gas desulphurization systems to deliver a robust and reliable process.

SINTEF Comment:

- Reaction rate and absorber chilling:
    - Operation of absorber at a low temperature required for sufficient driving force for the absorption and minimizing overhead slip of ammonia.
    - At this low temperature the carbonate/bicarbonate reaction kinetics is very slow (this is confirmed by experiments performed at SINTEF).
    - Might not be possible to accomplish the goals without a significant presence of free ammonia working as an activator. This makes the process more energy intensive and puts higher demands on slip reduction.
    - The separate coolers and refrigeration system required for cooling of the flue gas inlet stream, inter-cooling of the absorber, cooling of the lean stream, implies considerably larger CAPEX and OPEX compared to the corresponding cooling system of MEA based processes.
    - Pre-coolers will have similar diameter as the absorber.
- CO_2 removal efficiency:
    - It is unclear if the process can absorb 90% of the CO_2 in the flue gas without free ammonia present

Alstom Response:

The field pilots at We Energies and E.ON Karlshamn were designed using mass transfer data obtained from the SRI bench-scale pilot. At the operating temperatures reported for the CAP, high CO_2 capture (90% removal efficiency) with ammonia emissions below 10 ppmv in the flue gas leaving the plant have been achieved. The field pilot at We Energies has operated for over 7,000 hours, incorporating the absorber design based upon the data obtained from the SRI bench-scale pilot. The pilot at E.ON has now been operating for several months. The reaction kinetics of the NH_3 – CO_2 reactions are slower than conventional and advanced amine-based, CO_2 capture technologies. As such, the absorption tower velocities and mass transfer equipment must be designed accordingly. Alstom's pilot facilities have demonstrated that the mass transfer equipment and absorption tower sizing considered for the technology are capable of simultaneously and reliably achieving high CO_2 capture and low ammonia emissions at the desired absorption temperatures. The capital cost associated with this equipment on a commercial plant is expected to be within expectations with significantly lower energy consumption than amine based CO_2 capture technologies. The equipment installed at our pilot facilities to capture ammonia vapor present in the flue gas has performed better than expected. On that basis, the capital costs anticipated for the CAP are in line with Alstom's initial projections. One important feature of the CAP involves the use of cooler ambient temperatures or available cold water to reduce the electrical demand associated with maintaining the flue gas at design temperatures. This feature allows for a significant reduction in OPEX associated with the CAP, compared to other amine-based technologies.

The CAP uses a "pre-cooler" to condense water vapor in the flue gas stream, capture residual ammonia leaving the process, and to transfer heat to the residual flue gas stream for stack buoyancy. One of the side benefits of this design is the removal of SO_2. Amine processes are also considering this technology to remove SO_2 and to condense flue gas water vapor to prevent dilution of the amine solution. The 'pre-cooler" design to accomplish these objectives is well known to Alstom with a number of units commercially supplied. Based on Alstom's experience, the pre-cooler can be operated successfully at much higher velocities than the CO_2 absorption stages resulting in significantly smaller diameters than the absorber vessels. The pre-cooler units have operated successfully at our pilot facilities. Another advantage of this pre-cooler design is that the inlet requirements to the CAP for SO_2 are higher than can be tolerated with amine-based technologies and can be met using conventionally accepted FGD technologies. The result is that the CAP can be retrofitted downstream of existing FGD systems, with little or no required performance enhancement. In contrast, conventional and advanced amine processes may require significant and expensive upgrades to the existing FGD system to adapt them for operation with amine-based CO_2 capture systems.

When comparing the CAP against amine processes, it is clear that the reaction kinetics and approach to equilibrium are slower with the CAP. However, our experience (supported by data at the field pilots) has shown this to be more than offset by the more favorable kinetics and thermodynamics in the regeneration column. This difference results in the CO_2 being released more readily from the CAP than for amine processes. Furthermore, it enables the CO_2 to be released at an elevated pressure (approximately 20 Bar) resulting in significant savings both in capital and operating costs of the CO_2 compressor.

The lower temperature selected for CO_2 absorption within the CAP will minimize the amount of ammonia in the vapor phase and allow for the precipitation of ammonia bicarbonate solids. The reaction kinetics at the temperatures selected for the CAP are sufficient to allow high levels of CO_2 capture which can be accomplished with cost competitive absorption towers. The driving force for CO_2 capture is defined largely by the R value (mol NH_3/mol CO_2) in the scrubbing liquor and CO_2 concentration rather than the flue gas temperature at the temperature range considered for CO_2 capture projects. Operating data from the We Energies pilot plant (**Figure 1)** demonstrates an average CO_2 capture efficiency of the CAP of 87%. As the figure illustrates, this average removal efficiency was maintained over a one-month period at 100% design gas flow.

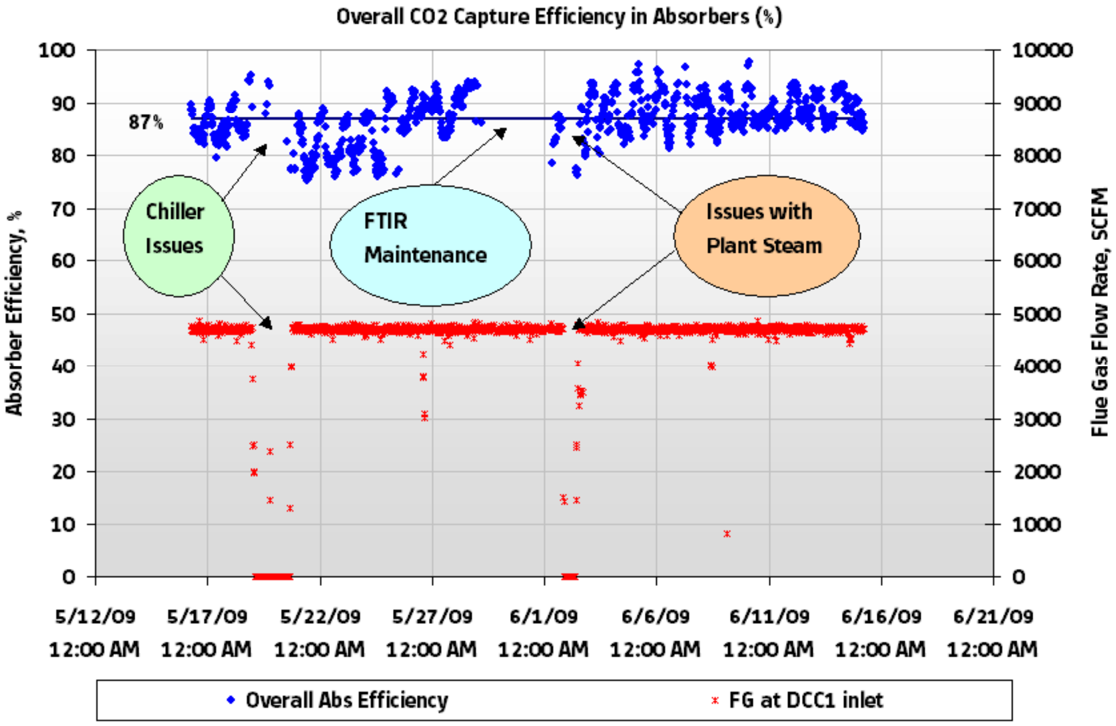

Figure 1 – CO_2 Removal Efficiency at We Energies Field Pilot

SINTEF Comment:

- Ammonia slip:
    - Is it practically feasible to retain the ammonia in the system?
- Absorption rate:
    - Is the carbonate/bicarbonate rate of reaction sufficiently fast at the low operational temperature or is significant free ammonia necessary?

Alstom Response:

Figure 2 provides data measured by EPRI during 2009 in their various sampling campaigns at the We Energies field pilot. This chart shows: a) the total ammonia loss from the process (bleed stream is shown in dark green, the ammonia slip is shown in light green) measured in lb/hr; and b) the ammonia slip in the flue gas measured in parts per million volume (ppmv). Two of these campaigns were conducted during the same period of time in which the data on CO_2 removal from **Figure 1** was obtained. This data is consistent with Alstom's measurements that demonstrate ammonia slip being controlled to less than 10 ppm. The data from **Figure 1** and **Figure 2** demonstrate that Alstom has been able to capture CO_2 at removal efficiencies of 90%, while maintaining ammonia losses at levels that are both commercially and environmentally acceptable.

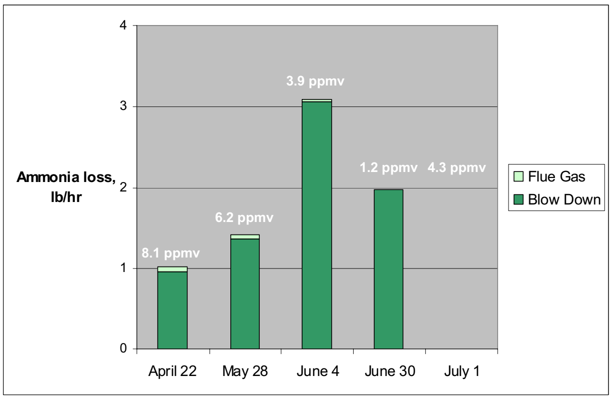

Figure 2 – Measured ammonia losses from We Energies Pilot (data courtesy of EPRI)

SINTEF Comment:

- Slurry:
    - Are the particle sizes of the solid bicarbonate manageable so it can be effectively handled in the hydro cyclone and cross-flow heat exchanger and other unit operations?

Alstom Response:

Alstom performed extensive testing of capturing and dewatering ammonium bicarbonate solids at the SRI bench-scale pilot. The testing at SRI involved settling tests, particle size distribution analysis, density measurements, and dewatering characteristics using equipment similar to that used in our larger scale pilots and validation facilities. Alstom has found the ammonium bicarbonate solids to dewater readily using hydro cyclones, which are commercially available liquid–solid separation equipment (**Figure 3**). We have been able to operate without plugging heat exchangers at the SRI bench-scale pilot and the We Energies and E.ON Karlshamn field pilots.

Figure 3 - Solids captured in hydro cyclone operating at SRI pilot.

Exhibit A – Simplified Process Flow Diagram

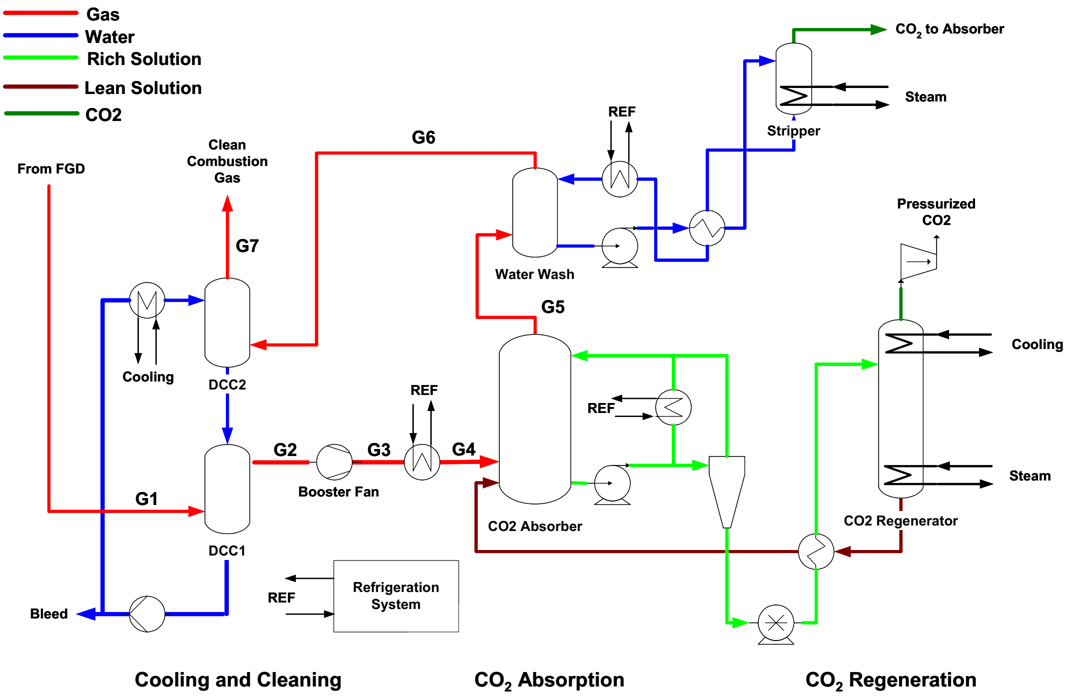

Exhibit B – Chilled Ammonia Process Description

While the following process description assumes application on a utility, coal-fired boiler, the Chilled Ammonia Process (CAP) can be applied to achieve high removal of CO_2, as well as reduction of residual emissions of SO_2, HCl, SO_3, and particulate matter (PM) from different utility and industrial processes. Exhibit A provides a simplified process schematic.

Flue gas from the boiler is first cooled in a direct contact cooler to condense water and residual emissions that reduce the volume of gas to be treated and the size of the downstream equipment. The flue gas then enters the bottom of the CO_2 absorber. As the gas flows upward through the absorber column, it flows counter-currently to an ionic solution consisting of ammonium-based salts to absorb CO_2 and form an ammonium bicarbonate solution. The treated flue gas then passes through a water-wash column and direct contact cooler to recover ammonia vapor and heat the gas, prior to venting a clean flue gas to the stack. The ammonium bicarbonate solution, which is now rich in CO_2, is heated with a cross exchanger, pressurized and pumped to the top of a regenerator column. Energy from steam is added to the bottom of the column and the absorption process is reversed to release the CO_2. The 'lean' ammonium carbonate solution - lean in CO_2 - leaves the bottom of the regenerator column where it is pumped back to the absorber. The CO_2 leaves the top of the regenerator column where it is further compressed and purified to client specifications to facilitate transportation or storage.

A key advantage of this process is the ability to regenerate CO_2 at high pressure with low steam energy requirements. This process produces a CO_2 product stream of very high purity and significantly reduces the energy requirements for CO_2 compression.

Exhibit C – Process Chemistry Overview

The overall chemical reactions associated with the carbon capture process are defined in Equations 1–4:

CO_2 (g) ←==→ CO_2 (aq) (1)

$(NH_4)2CO_3$ (aq) + CO_2 (aq) + H_2O (l) ←==→ $2(NH_4)HCO_3$ (aq) (2)

$(NH_4)HCO_3$ (aq) ←==→ $(NH_4)HCO_3$ (s) (3)

$(NH_4)2CO_3$ (aq) ←==→ $(NH_4)NH_2CO_2$ (aq) + H_2O (l) (4)

The reactions in the process are all reversible and their direction depends on pressure, temperature and concentration in the system. Equations 1-4 are exothermic reactions in the left to right direction requiring removal of heat from the process in order to maintain the desired CO_2 absorption temperature. Equations 1-4 are endothermic reactions in the right to left direction that require energy to produce the desired products.

Overall chemical reactions associated with removal of residual SO_2 in the flue gas in the cleaning and cooling stage of the CAP process are provided below in Equations 5 and 6:

SO_2 (g) + $2NH_3$ (g) + H_2O (aq) $\Rightarrow$ $(NH_4)2SO_3$ (aq) (5)

$(NH_4)2SO_3$ (aq)+ $1/2O_2$ (g) $\Rightarrow$ $(NH_4)2SO_4$ (aq) (6)

Other minor acid gases, including sulfur trioxide, hydrogen chloride, and hydrogen fluoride, are also removed in the CAP cleaning and cooling stage, but equations are not listed in this document.

APPENDIX B – Part 2

An Overview to the AEP Mountaineer Chilled Ammonia Process Large Scale Pilot Plant Demo Project

CCS with Alstom’s Chilled Ammonia Process at AEP’s Mountaineer Plant

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Abstract:

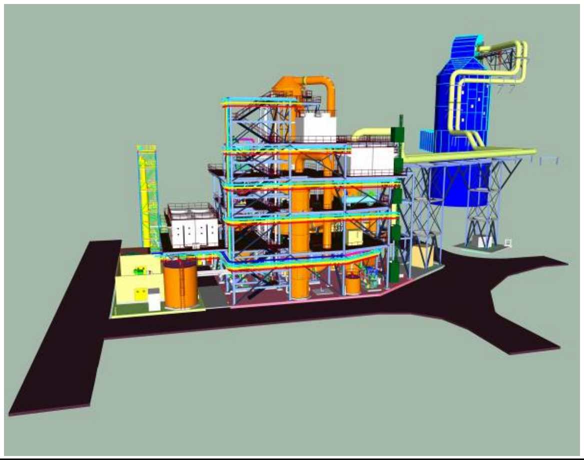
Alstom and American Electric Power are jointly participating in the installation of a carbon dioxide (CO_2) capture Product Validation Facility at AEP's Mountaineer Power Plant. The CO_2 capture technology to be installed at Mountaineer is Alstom's Chilled Ammonia Process; AEP is also working with Battelle to develop a saline formation geologic storage system. The Product Validation Facility is approximately 20 megawatt electric (MWe) in size and involves the treatment of a slipstream of combustion flue gases from an existing coal-fired boiler. A flue gas slipstream will be taken from a location downstream of the Mountaineer's existing selective catalytic reduction (SCR) and wet flue gas desulfurization (WFGD) systems. The project is presently in the construction phase with scope that includes CO_2 capture, compression, and storage in

two geologic reservoirs with injection wellheads located on the plant property. The following paper summarizes Alstom's Chilled Ammonia Process technology and describes the scope and objectives of the CO_2 Capture Product Validation Facility and Geologic Storage Project.

INTRODUCTION

American Electric Power's (AEP) Mountaineer Power Plant is a coal-fired power generation facility that is presently equipped with an air quality control system (AQCS) consisting of low NOx burners, SCR, and WFGD. Alstom and American Electric Power are jointly participating in the installation of a Carbon Capture and Storage (CCS) Product Validation Facility (PVF) at the Mountaineer site for capture and storage of approximately 100,000 metric tons of CO_2 annually. Validation of Alstom's Chilled Ammonia Process (CAP) CO_2 capture technology and CO_2 injection and storage in two geologic reservoirs beneath the site are key objectives of the project. AEP is working with Battelle to develop the geologic storage and monitoring, mitigation, and verification (MMV) systems.

Figure 1. PVF at AEP's Mountaineer Power Plant, New Haven, WV



The Mountaineer PVF is designed to remove carbon dioxide from a slipstream of flue gas taken downstream of the existing WFGD system. The PVF is designed to treat approximately 50,000 SCFM of flue gas. This represents a scale-up of over ten (10) times of Alstom's CAP pilot plant facility at We Energies Pleasant Prairie Power Plant. The CCS Product Validation Facility at Mountaineer is presently in the construction phase with commissioning on schedule to commence in September, 2009.

Plant Background

Located on the Ohio River near New Haven, West Virginia, the Mountaineer Plant complex consists of one 1,300 megawatt (MW) net super-critical coal-fired unit that began service in 1980. The plant was initially equipped with an electrostatic precipitator (ESP) and was later retrofitted with more advanced AQCS equipment including SCR, WFGD, and a sulfur trioxide (SO_3) Mitigation System. Mountaineer Plant is one of AEP's best operating plants having the distinction of 607 days of

Figure 2. AEP's Mountaineer Power Generating Station, New Haven, WV

continuous operation in 1985-1987. AEP chose to demonstrate the CAP technology at Mountaineer due to the existing pollution control equipment on the Mountaineer unit and an existing 9,200-foot geologic characterization well dug on site.

Under direction of Battelle, with sponsorship from the U.S. Department of Energy (DOE), AEP, and several other entities, a characterization well was drilled on the site in 2003 with reservoir testing completed during 2004 as part of the Ohio River Valley project. Since that time, the data have been analyzed and a multi-phase flow model completed for the site. The results of the study indicate that the Rose Run Sandstone and Copper Ridge B Zone, located at 7,800 and 8,200 feet below ground surface, respectively, are acceptable reservoirs for geologic storage. CO_2 will be trapped in the reservoir layers due to the excellent containment conditions. In total, there are several thousand feet of very low-permeability caprock layers above the storage formations.

Project Overview

In September 2007, Alstom, Battelle and AEP started the CCS project with preliminary engineering, project planning, and permitting activities. Procurement of long lead time items started in December 2007.. Preliminary site activities started in March 2008 with utility tie-ins during a scheduled Mountaineer unit outage. Detailed engineering started in April 2008, followed closely by relocation of ancillary facilities and site preparation starting in May 2008. Construction of the CAP and shallow drilling for the storage system started in June 2008 with mechanical completion scheduled for summer 2009 and system startup in third Quarter 2009.

AEP and Alstom are sharing the costs for the capture project. AEP is responsible for all costs associated with the storage system. RWE has joined the project as a funding partner and AEP is in discussion with other organizations interested in participating in the project, including funding. While the estimated cost of the project is not publicly available, it is important to note that this is an experimental project with additional costs for testing, monitoring, and validation that may not be required for a commercial project. In addition, full heat integration with the power generation facility will not be implemented for the Mountaineer PVF. Finally, it is a relatively small project and neither the capture nor storage systems have been optimized with respect to both capital and operating costs. However, the results of the PVF will be used to refine preliminary techno-economic studies for commercial-scale projects.

Outreach and communication are important parts of the project. In addition to having dedicated personnel with experience in retrofit projects, the Mountaineer Plant has an excellent environmental record and a good relationship with the community. In order to maintain this relationship and gain support for this effort, the team developed an outreach plan at the beginning of the project. AEP initially held a series of internal informational meetings at its corporate office, Mountaineer Plant site, and operating companies followed by meetings and presentations with other key stakeholders including the West Virginia Department of Environmental Protection, other permitting agencies, public officials, local residents, and universities. AEP and Battelle completed the second round of Mountaineer Plant staff meetings in May 2008 and AEP conducted the first two public informational meetings in early June 2008 at local town hall meetings with community leaders.

Project Structure

AEP, Alstom, and Battelle are the three main entities involved in the Mountaineer CO_2 Capture and Storage Project. Alstom and AEP are developing the Mountaineer Product Validation Facility (CO_2 Capture Project) with Alstom as the project leader. Alstom is responsible for the design, supply and installation of the CAP equipment. AEP is responsible for the utilities to and from the CAP and the compressed CO_2 discharge stream.. AEP has subcontracted the utilities to and from the PVF to local construction companies for civil, electrical and mechanical services. AEP has contracted with Battelle to perform engineering, procurement, and construction services for the storage system (CO_2 Storage Project), and Enerteq Engineering Company for engineering and procurement services for the CO_2 transport system. Additionally Battelle has contracted with several firms for the various aspects of well drilling, well completion, and well monitoring systems.

Scope of Work

The following is a high-level work breakdown structure for the project, including the primary party responsible for the work:

CO_2 Capture Project:

1. Flue gas handling (Alstom)
2. Utilities to and from the PVF (AEP)
3. Monitoring and control system (Alstom)
4. PVF island steel (Alstom)
5. Cooling and cleaning system (Alstom)
6. CO_2 absorption system (Alstom)
7. CO_2 regeneration system (Alstom)
8. CO_2 compression for CO_2 transportation (Alstom)
9. Handling of PVF bleed stream (AEP)

CO_2 Storage Project

1. CO_2 transport pipeline (AEP)
2. Pump to reach injection pressure (AEP)
3. Finish existing well for injection (Battelle)
4. Install second injection well (Battelle)
5. Install monitoring wells (Battelle)
6. Monitoring, mitigation, and accounting (MMA) system (Battelle)

Obtaining the plant permits and legal approval along with communication and public outreach programs for the CO_2 Capture and Storage project are the responsibility of AEP.

Technology Overview

The Mountaineer carbon capture PVF will involve the treatment of a flue gas stream using Alstom's Chilled Ammonia Process. The flue gas is taken from a location downstream of an existing WFGD system. The PVF is designed to capture and store approximately 100,000 metric tons of carbon dioxide annually and treats approximately 50,000 SCFM of flue gas, or 1.5% of the total plant flue gas flow. The features of the Chilled Ammonia Process CO_2 technology include:

- Regeneration of a low-cost reagent (ammonia), that is tolerant to oxygen and flue gas impurities, resulting in low reagent consumption costs;
- Ammonium sulfate byproduct stream that can be used commercially as fertilizer;
- Low heat of regeneration; lower energy consumption than other CO_2 removal technologies;
- High-purity CO_2 product stream containing low moisture and ammonia at elevated pressure, resulting in reduced costs and energy consumption for CO_2 compression;
- A flexible process that can be retrofitted to units with conventional air quality control systems (AQCS), without the need for additional flue gas treatment; and utilize low grade, reject heat.

The flue gas leaving the WFGD system is cooled and sent to the CO_2 absorber, where the CO_2 in the flue gas will react with ammonium carbonate to form ammonium bicarbonate (ABC). The flue gas slip stream, with most of the CO_2 removed, will be returned to the existing stack for discharge, and the PVF bleed stream will be sent to the plant waste water treatment system for processing. The rich ammonium bicarbonate (ABC) solution is sent to a pressurized regenerator column. Heat will be added in the regenerator to separate the CO_2 and return the ammonium carbonate (AC) solution to the CO_2 absorber for re-use. The CO_2 stream will be scrubbed to remove excess ammonia and excess water will be condensed. The CO2 will then be compressed and transported to the storage system. The storage system will use a pump to boost the pressure to the appropriate pressure for each of the injection zones. The system will inject approximately 100,000 metric tons of CO_2 per year into one or both of two geologic reservoirs: the Rose Run Sandstone or Copper Ridge B Zone. There will be three monitoring wells and an extensive MMV program to monitor the injection and migration of the CO_2 within the reservoirs.

Process Chemistry

The overall chemical reactions associated with the carbon capture process are defined in Equations 1–4:

$$CO_2\ (g)\ \leftarrow\!==\!\rightarrow\ CO_2\ (aq) \tag{1}$$

$$(NH_4)_2CO_3\ (aq) + CO_2\ (aq) + H_2O\ (l)\ \leftarrow\!==\!\rightarrow\ 2(NH_4)HCO_3\ (aq) \tag{2}$$

$$(NH_4)HCO_3\ (aq)\ \leftarrow\!===\!\rightarrow\ (NH_4)HCO_3\ (s) \tag{3}$$

$$(NH_4)_2CO_3\ (aq)\ \leftarrow\!===\!\rightarrow\ (NH_4)NH_2CO_2\ (aq) + H_2O\ (l) \tag{4}$$

The reactions in the process are all reversible and their direction depends on pressure, temperature and concentration in the system. Equations 1-4 are exothermic reactions in the left to right direction requiring removal of heat from the process in order to maintain the desired CO_2 absorption temperature. Equations 1-4 are endothermic reactions in the right to left direction that require energy to produce the desired products.

Overall chemical reactions associated with removal of residual SO_2 in the flue gas in the cleaning and cooling stage of the CAP process are provided below in Equations 5 and 6.

$$SO_2(g) + 2NH_3(g) + H_2O(aq) \Rightarrow (NH_4)_2SO_3(aq) \qquad (5)$$

$$(NH_4)_2SO_3(aq) + 1/2O_2(g) \Rightarrow (NH_4)_2SO_4(aq) \qquad (6)$$

Other minor acid gases, including sulfur trioxide, hydrogen chloride, and hydrogen fluoride, are also removed in the CAP cleaning and cooling stage, but equations are not listed in this document.

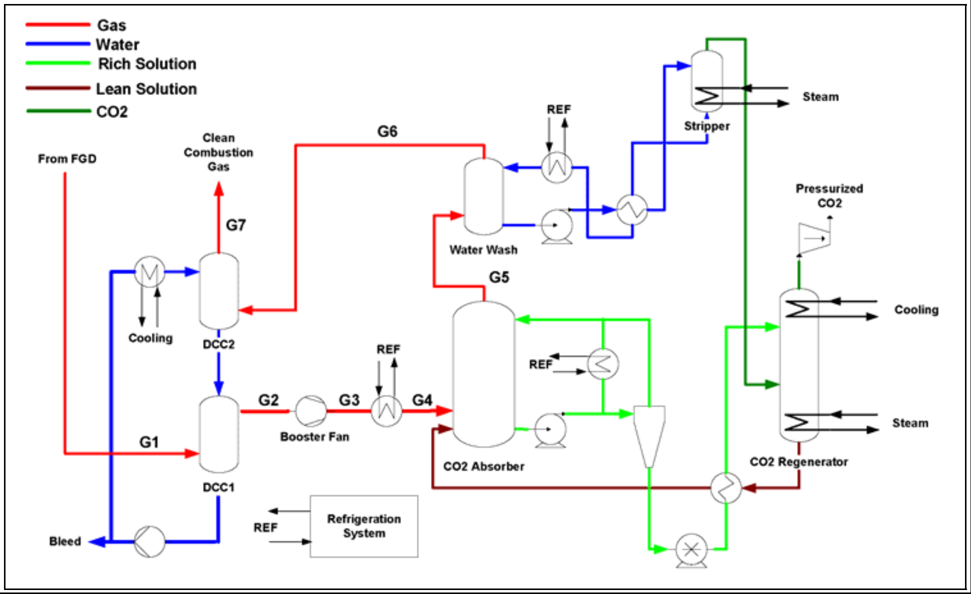
In the CAP, CO_2 is absorbed in an ammoniated solution at temperatures lower than the exit temperature from the flue gas desulfurization system. Therefore, cooling of the flue gas is a necessary step within the process, resulting in condensation of moisture from the flue gas. Gaseous ammonia (NH_3) is released from the ammoniated solution during absorption of CO_2. To minimize gaseous NH_3 emissions, CO_2 absorption is carried out at lower flue gas temperatures. Generally, a lower absorption temperature results in lower ammonia emissions from the CAP absorber and higher power consumption for the cooling process equipment. The formation of aqueous ammonium carbonate ($(NH_4)_2CO_3$) and ammonium carbamate ($(NH_4)NH_2CO_2$) with the precipitation of ammonium bicarbonate ($(NH_4)HCO_3$) solids is conducted at a temperature that optimizes cooling energy demand, carbon dioxide removal efficiency, and minimizes ammonia vapor in the flue gas. Ammonium bicarbonate contains about 55% CO_2 by weight and thus the formation and precipitation of ammonium bicarbonate solids dramatically increases the CO_2 loading capacity of the system. The formation of ammonium bicarbonate solids is a reversible reaction. With the required amount of heat, the ammonium bicarbonate solids are dissolved with eventual evolution of ammonia, water, and carbon dioxide gases. A regeneration vessel that operates as a distillation column is used to produce the gaseous CO_2 product stream. The CO_2 product stream leaves the CAP regenerator vessel at a higher pressure than other CO_2 processes which results in fewer stages of downstream CO_2 compression equipment. The ammonia and water reaction products are stripped and condensed from the resulting gas stream for use as reagent and flue gas wash solvent, respectively.

The Chilled Ammonia Process equipment can be divided into the following systems:

1. Flue gas cooling and cleaning
2. CO_2 absorption
3. Water wash and CO_2/NH_3 stripping
4. High-pressure regeneration and compression
5. Chiller system

An overview of the Mountaineer PVF is illustrated in the following schematic (Figure 3) and is described in the following sections.

Figure 3. Chilled Ammonia Process – Process Flow Diagram



A booster fan diverts flue gas from a location downstream of the WFGD absorber to the PVF. The flue gas first enters the cooling and cleaning stages of the process. In the CAP, the purpose of cooling the flue gas is to:

- Operate at a flue gas temperature that minimizes ammonia slip from the absorption process
- Operate at a temperature that enables the formation of ammonium bicarbonate solids, which significantly increase the CO_2 capacity of the rich solution sent to the regenerator
- Condense the moisture in the flue gas, which reduces the volumetric gas flow, increases the CO_2 concentration and reduces the size of CO_2 absorber vessels.

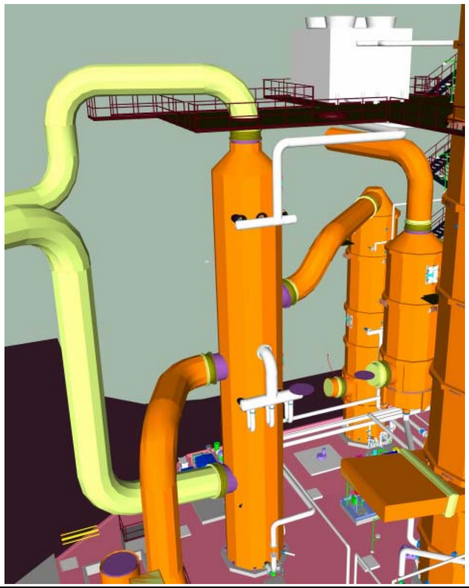
In the process of cooling the flue gas, other benefits are realized, including:

- Residual pollutants are condensed from the flue gas making CAP operation less susceptible to variance in boiler combustion and FGD operation, and
- Clean combustion gas temperature leaving the CAP (from DCC2: refer to Figure 3) is increased prior to entering the flue gas to the existing chimney.

The flue gas enters a direct contact cooling tower (DCC1) to reduce the temperature of the flue gas and to remove residual acid gases. The DCC vessel is illustrated in Figure 4; support steel and other ductwork are hidden for clarity. The flue gas design basis for the project is provided in Table 1. The direct contact cooler is a conventional packed tower with liquid recirculation through a cooling tower that uses ambient air to lower the recirculation liquid temperature.

Flue gas enters the DCC1 inlet at the bottom and flows upward through the packing. Cool water is sprayed at the top of the packing and flows downward, counter to the flue gas flow. As the gas flows upward through DCC1, it is forced into contact with the water. Direct cooling of the saturated flue gas results in the condensation of most of the water in the flue gas stream. In addition, the residual acid gases and particulate present in the flue gas leaving the WFGD system, including SO_2, SO_3, hydrogen chloride, and hydrogen fluoride gas, are removed from the flue gas in DCC1. As such, the CAP technology can accommodate acid gases present in flue gases downstream of typical wet and dry FGD systems without the need for additional SO_2 control technology.

Figure 4. Direct Contact Cooler



A bleed stream containing primarily dissolved ammonium sulfate is purged from the DCC1 tower for possible commercial use as fertilizer or disposal.

Table 1

Mountaineer PVF CO_2 Capture Design Basis		
Parameter	**Unit**	**Value**
Flue Gas Temperature	°F	129
Flue Gas Pressure	In H_2O	-1.5 to 1.0
Flue Gas Flow Rate	Scfm	50,584
Total Mass Rate	lb/hr	240,336
Particulate	lb/hr	3.8
CO_2	lb/hr	39,472
CO_2 Concentration	Vol%	10.61
SO_2	lb/hr	28.5
SO_3	lb/hr	26.9
H_2O	lb/hr	22,874
N_2	lb/hr	163,087
O_2	lb/hr	14,904
NOx	lb/mmbtu	0.47
NH_3 Concentration	Ppmv	2

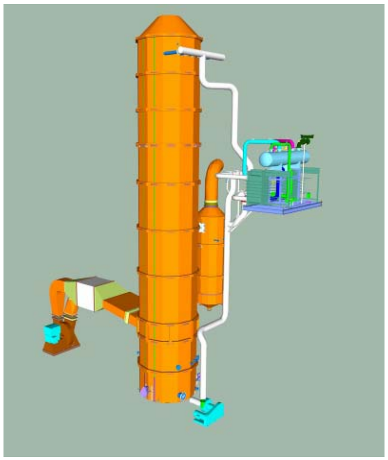
The flue gas leaves DCC1 and is directed through flue gas cooling coils to further reduce the flue gas temperature prior to entering the CO_2 absorbers. The flue gas cooling is accomplished with the use of a mechanical chiller system. Additional moisture is condensed from the flue gas in the cooling coils and is collected for use within the process or discharged from the CAP for use as WFGD make-up water. The quality of the condensed water from the cooling coils is suitable for use as make-up without further treatment.

CO_2 Absorption

Carbon dioxide absorption occurs in the absorber system using an ammonium carbonate/bicarbonate scrubbing liquor. As the flue gas flows upwards through the column, it is contacted with the scrubbing slurry solution containing dissolved ammonium carbonate and ammonium bicarbonate suspended solids that flow in a countercurrent direction to the flue gas, and the CO_2 is absorbed.

Lean (low CO_2 concentration) ammonium carbonate solution from the regenerator is returned to the absorber. A small amount of fresh ammonium carbonate reagent is added to replenish ammonia losses from the CAP system and is used to control the ratio of ammonia to CO_2 in the flue gas.

Figure 5 CO_2 Absorber



The CO_2 absorber (Figure 5) system design is optimized using an Alstom proprietary design that minimizes the packing volume while maintaining the ability to form ammonium bicarbonate solids and minimize the ammonia slip from the absorber. The absorption of CO_2 and reaction with ammonia is an exothermic reaction. As such, heat exchangers remove heat from the process and control the temperature at the desired set point. The cooling medium for these heat exchangers comes from a mechanical chiller.

Water Wash and CO_2/NH_3 Stripping

The flue gas exits the CO_2 absorption system and enters a water wash system to further reduce the ammonia vapor from the flue gas. The water wash system (WW) is a packed column that utilizes water to absorb ammonia from the flue gas (Figure 6). The temperature of the flue gas is maintained using heat exchangers and a mechanical chilling system. The ammoniated water is sent to a stripper column (CO_2/NH_3 Stripper, Figure 7) where the ammonia is stripped and returned to the process as reagent.

Figure 6 Water Wash Column

The clean water from the CO_2/NH_3 stripper is re-used within the water wash column to remove additional ammonia. Energy for the CO_2/NH_3 stripping column is provided by steam from the power generation facility.

The flue gas exits the water wash column and enters the direct contact cooler (DCC2) for removal of residual ammonia, using a proprietary design before entering the chimney as clean combustion gas.

Chiller System

The Chilled Ammonia Process includes a mechanical chiller system to remove heat from the following process streams:

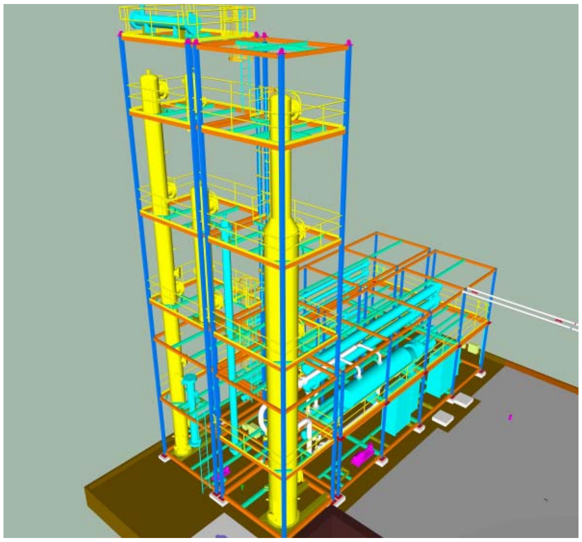
- The flue gas downstream of the direct contact cooler # 1 (DCC1) to further reduce the flue gas moisture and to lower the flue gas temperature
- The absorber (ABS 1 & 2) recirculation streams to remove the heat of reaction generated by the absorption of carbon dioxide with ammonium carbonate solution
- The water wash recirculation stream to reduce the amount of ammonia vapor in the flue gas

Both chiller system compressors are screw type. The heat transferred from the process streams to the chiller system refrigerant is dissipated from the system using evaporative condensers.

Because of the short-term nature of this project and small scale, the chiller system chosen is not optimized, as it would be for a commercial scale plant. The chiller system refrigerant was selected based upon its efficiency and compatibility with the mechanical chiller compressor system. Ammonia is the most efficient refrigerant for the chiller system as it results in the lowest energy consumption. It can be efficiently used with screw-type chiller compressors. However, site restrictions prohibited the use of ammonia as a refrigerant for the chiller system, so the team selected the hydrofluorocarbon (R410A), even though hydrofluorocarbon (difluoromethane and pentafluoroethane) is slightly less efficient than ammonia.

CO_2 Regeneration

Figure 7 Regenerator and CO_2/NH_3 Stripping Column



The CO_2-rich solution in the absorber system contains ammonium bicarbonate solids in an aqueous carbonate/bicarbonate solution. The solution is pumped through a hydrocyclone, where the solids content is increased, before being sent to the regenerator. A regenerator feed pump then pumps the solution under pressure through a series of heat exchangers. There, the heat is recovered against the lean solution from regenerator bottoms and the CO_2/NH_3 stripper reboiler condensate.

The regenerator vessel is a stripper column that contains mass transfer elements. The feed to the regenerator is introduced at several stages. Flashed CO_2 in the feed proceeds up the column to the overhead. Rich solution, containing CO_2, is flashed by heat introduced in the regenerator reboiler. The regenerator reboiler is designed to maintain the temperature of regenerator bottoms as needed to evolve CO_2 at a pressure resulting in fewer compression stages than other CO_2 removal technologies. As the rich solution falls through the lower regenerator bed, CO_2 is separated and rises to the regenerator overhead, and the solution becomes leaner as it reaches the bottom of the column. The lean solution is then returned to the CO_2 absorber for re-use.

The CO_2 exits the top of the regeneration column and flows to a receiver at the top of the regenerator to condense residual moisture and ammonia. At these conditions, there is a significant difference in the vapor pressure between CO_2 and ammonia and water. Because of this difference, a very low concentration of water vapor and ammonia are present in the regenerator overhead. The CO_2 product stream enters the CO_2 compressor, which compresses the stream to a pressure of 1500 psia (103 bar).

The CO_2 compressor is a two-stage, reciprocating type with intercooler and aftercooler to produce the desired pressure and temperature for CO_2 handling prior to storage. The CO_2 compressor is designed with CO_2 stream bypass to the chimney if required. The CO_2 compressor is carbon steel construction with stainless steel inlet scrubber, intercooler and aftercooler.

CO_2 Handling & Storage

Taking control of the supercritical CO_2 at the outlet of Alstom's compressor is one of the key interface points between AEP and Alstom. AEP will install the 4-inch carbon steel pipe at Alstom's compressor outlet. Carbon steel is an acceptable material for the transport system due to the low moisture content ($\leq$ 600 ppm) and low ammonia levels ($\leq$

50 ppm) in the CO_2 product stream. Moisture or ammonia concentrations above these values could lead to corrosion or erosion issues over time requiring specialized materials of construction and frequent maintenance. The subcritical CO_2 will be transported via pipeline approximately 1,200 feet to the injection wells. A pump will then increase the CO_2 pressure to approximately 2,000–2,800 psi for injection into one or both of two injection wells. The project team evaluated having one compressor that would achieve injection pressure versus a compressor and pump or two compressors. In the end, the team selected a compressor and pump system to give maximum flexibility to inject the CO_2 into two different reservoirs at the same time with varying pressures.

The key objective of the storage project is validating CO_2 injection and storage in the geologic reservoirs. Geologic formations need to be both porous and permeable in order to serve as storage reservoirs. In general, sandstone formations make excellent geologic storage reservoirs, whereas dolomite, shale, and limestone formations are excellent caprock for geologic storage. At Mountaineer, the CO_2 will be injected into one or both of two reservoirs: the Rose Run Sandstone, approximately 7,800 ft below ground; and the Copper Ridge B-Zone, approximately 8,200 ft below ground. At the Mountaineer site, the Rose Run Sandstone, an interbedded sandstone and dolomite layer, has approximately 114 ft gross thickness with porosity (8–13%) and permeability (up to 35-70 mD), and the Copper Ridge B-Zone consists of several thin but high permeability zones within a 250 ft thick interval of dense dolomite. The reservoir properties have been evaluated using both laboratory and field tests and published in peer-reviewed literature. *(Battelle)* However, these reservoirs would not be acceptable storage zones without caprock above these layers to contain the CO_2.

Formation fluids in the Rose Run Sandstone and Copper Ridge B Zones are contained vertically with confining caprock consisting of thick layers of dense and impermeable dolomite, shale, and limestone formations. The confining layer above the Rose Run Sandstone begins with the Beekmantown Dolomite, which is approximately 550 feet thick at a depth of 7,160 to 7,710 feet below ground. The Ohio River Valley Project core samples from this interval showed very low porosity and permeability. The confining layer above the Copper Ridge B Zone is the upper Copper Ridge Dolomite, which is approximately 310 feet thick at a depth of 7,840 to 8,150 feet below ground. Additionally, there are several thousand feet of dolomites, shales, and limestone formations above these layers that provide very substantial additional layers of containment for the injected CO_2 *(Battelle).*

Data collected from the storage efforts of this project will be compared with modeling results and predicted CO_2 behavior. Battelle's modeling simulations based on the seismic survey, well logging, and core and reservoir testing data from the existing well, AEP-1, will be validated and tuned based on this real-world information. This project offers a rare opportunity for authenticating a large pool of data collected during characterization. Following the active injection period, the CO_2 placed below ground will continue to be monitored for migration and confinement. The duration and extensiveness of this monitoring program is still under development.

Permitting this first-of-a-kind CO_2 storage project with the appropriate West Virginia agencies is another key task for the storage project. The list of known or anticipated permits for the project includes:

- Underground Injection Control (UIC) – WV DEP
- Well work permits for drilling deep wells– WV DEP
- NPDES permit modification – WV DEP
- Storm Water Construction Permit – WV DEP
- Public Lands Permit – WV DNR
- Corps permit notification – Corps of Engineers
- Periodic seismic survey – Local/county engineer

The two most significant permits for the storage project are the well work permits needed to drill the monitoring and injection wells and the Underground Injection Control (UIC) Permit needed to operate the CO_2 injection wells. Well work permits are needed in West Virginia for deep wells that are used for geologic characterization or other non-producing deep wells. AEP submitted the monitoring well work permit applications in March 2008 and received them in June 2008. AEP submitted the injection well work permit applications in July 2008 and received them in August 2008.

The UIC Permit for this project is a Class V experimental well permit. It is important to note that the permitting activities for this project were undertaken prior to establishment of a new permitting classification for CO_2 injection. AEP filed the project UIC permit application on February 8, 2008 and received the permit in April 2009. The Department of Energy (DOE)-sponsored Ohio River Valley Project provided most of the information needed for this permit. The UIC permit also includes modeling data from Battelle's proprietary STOMPCO$_2$ model, including a map showing the 3,490 ft radius which indicates the extent of the CO2 plume projected on the surface ("Area of Review"), which was based on several conservative assumptions. This area assumes that all of the CO2 is injected in to one zone at the maximum capture rate.

For geologic storage of CO_2, there are several questions and concerns that need to be addressed before programs are implemented on a commercial scale basis, such as:

- Who owns the rights to the pore space in the geologic reservoirs thousands of feet under ground? How can those rights be acquired and /or utilized to support commercial storage projects?
- Are uniform federal standards needed to govern storage requirements in order to facilitate the use of interstate formations?
- How will liability protection be handled during project operation, post-closure, and ultimately during the long-term stewardship period?
- What are the risks and liability complications for situations when CO_2 or pressure effected zone from one source combines underground with CO_2 or pressure effected zone from other source(s)?

For the Mountaineer CO_2 storage project, AEP owns most of the property and mineral rights within the Area of Review. AEP is researching pore space usage mineral rights issues for the property not owned by AEP and is working with West Virginia to craft language that addresses corrective action during the term of the UIC permit. Questions regarding third party liability and insurance coverage are also still being reviewed.

Construction Progress

Figures 8 and 9 taken in February and April 2009 provide an perspective of the recent progress of construction of the CAP

Figure 8 APCom setting part of the CO_2 absorber, 2-22-09

Figure 9 Overview of the CO_2 Capture Facility

Alstom's Chilled Ammonia Process Operating Experience

Given the promising results in the laboratory, Alstom embarked on a multi-phase development program. In the first step of this program, a large bench pilot was constructed and operated at SRI International from November 2006 through June 2008 and used to demonstrate both CO_2 absorption and regeneration. The bench-scale regenerator demonstrated CO_2 product stream quality of greater than 99.9%, with ammonia emissions below 10 ppm and water emissions well below 1,000 ppm. The data from the bench scale pilot was used to develop an equilibrium and thermodynamic model of the process. This model was initially applied in the process development and sizing of equipment for the initial field validation pilot plants at WE Energies' Pleasant Prairie Power Plant ("P4") and E.ON Karlshamn.

Field Pilots at We Energies and E.ON Karlshamn

Figure 9 Field Pilot at We Energy's Pleasant Prairie Power Plant

The field pilot at P4 illustrated in Figure 10 was sized to capture over 15,000 metric tones/year of CO2 at full capacity and commenced operations in June 2008. The pilot has been operating in seven day per week, twenty-four hours per day continuous shifts since September 2008 and to date has logged over 4,000 hours of operation. The operating experience at the pilot facility has resulted in a greatly improved understanding of the process and the numerous interactions with the power plant. While some modifications have been applied, no material changes to the overall concept have proven necessary. Parametric testing of the P4 pilot facility is underway with continued operations planned throughout 2009.

A second field pilot was commissioned at E.ON Karlshamm in April of 2009 that will capture CO_2 emissions from a boiler combusting a high sulfur fuel oil. The boiler unit is equipped with an existing AQCS to control PM, SOx and NOx emissions. This pilot will operate into 2010. The two field pilots were designed as 'proof of concept' facilities with considerable operating flexibility to test the different unit operations. Four of the key criteria to validate the chilled ammonia process were initially identified as follows (to be met at the design conditions):

- CO_2 removal efficiency (90%);
- Low ammonia slip;
- High CO_2 quality (with low ammonia slip and low moisture content);
- Low system pressure drop.

Validation of Process Energy Consumption

Another important consideration is to validate the process energy consumption. In parallel to these pilots, additional work has been performed at Alstom's Global Technology Center in Vaxjo, Sweden to fully evaluate solution heat capacities and other physical properties. This information has been applied to further validate Alstom's equilibrium model that was developed to size the process for future applications. Particular focus has been given to validating the process energy consumption for CO_2 regeneration.

The heat of regeneration includes all the heat required to take the rich solution from the absorber to the regenerator and separate the CO_2 and is further categorized into: 1) sensible heat; 2) heat of dissolution; 3) heat of reaction; and 4) heat of vaporization.

While the flow schemes appear similar, the regeneration of rich ammonium bicarbonate solution in the CAP is very different than regenerating CO_2 from conventional amine process. The key differences are the following:

- For amine-based CO_2 capture technologies, there are no solids so the heat of dissolution is zero;
- The heat of reaction for conventional amine technologies is higher; furthermore, additional heat is required to generate and maintain a major stripping steam fraction in the gas phase throughout and out of the column;
- In the CAP, CO_2 is regenerated under pressure and the residual moisture and ammonia content in the CO_2 product is extremely low. Combined with the resulting lower CO_2 compression energy requirement (about 30% of what is required to compress CO_2 from atmospheric pressure), regeneration under pressure is a significant feature.
- While ammonium bicarbonate solids must be dissolved, the resulting heat of dissolution is more than offset because: a) concentrating the CO_2 in solids reduces the water content of the solution being regenerated which reduces the sensible heating requirement, as well as pumping energy requirements and size of regeneration equipment (piping, heat exchangers, etc.); and b) solids dissolution occurs at relatively low temperatures which means that, if available, low grade reject heat can be used to offset this incremental energy requirement.

In conclusion, the heat of regeneration for the chilled ammonia process is estimated to be less than half of what has been reported for conventional amine-based, CO_2 capture technologies. Alstom has since commenced internal studies to evaluate a commercial scale-up of the CAP. These initial studies currently estimate the average energy penalty at around 20% of net boiler output (e.g., net after deducting the parasitic load of the plant and traditional AQCS equipment). Under ideal site conditions, initial studies suggest the process can potentially be designed to operate with an energy penalty that is well below 20%.

SUMMARY

Alstom and American Electric Power are jointly participating in the installation of a CO_2 capture Product Validation Facility at AEP's Mountaineer Power Plant. The CO_2 capture Product Validation Facility is designed to capture and store 100,000 metric tons of CO_2 annually. The CO_2 capture technology to be installed at Mountaineer is Alstom's Chilled Ammonia Process. The project targets include:

- Energy consumption that is lower than conventional, amine-based, CO_2 capture technologies
- Ammonium sulfate byproduct stream with a potential commercial value
- Inlet flue gas conditions that are tolerant of acid gases at levels consistent with outlet conditions of modern FGD systems
- Regenerable reagent requiring low reagent make-up

The CO_2 storage portion of the project involves validation of CO_2 injection and storage in the geologic reservoirs located beneath the site. At Mountaineer Plant, the CO_2 will be injected into one or both of two reservoirs: the Rose Run Sandstone at approximately 7,800 ft below ground, and the Copper Ridge B-Zone at approximately 8,200 ft below ground. These formations are representative of geologic reservoirs in the Ohio Valley region and should be good indicators of the feasibility of CO_2 geologic storage in the region.

Acknowledgements

1. Battelle, *Section XVI Support Material – Class 5X25 Underground Injection Control Permit Application for Geologic Carbon Dioxide Storage Demonstration for the AEP Mountaineer Plant New Haven, West Virginia, February 2008.*

APPENDIX B – Part 3

Alstom's and EPRI's Presentation on the Chilled Ammonia Process during the 12th International CO_2 Capture Network Meeting held at Regina, Canada on the 29th/30th September 2009

Chilled Ammonia - Pilot Testing at the We Energies Pleasant Prairie Power Plant

12th IEA Post-Combustion Meeting

Regina, Saskatchewan

Sean Black, Alstom
Richard Rhudy, EPRI

30th September 2009

ELECTRIC POWER RESEARCH INSTITUTE

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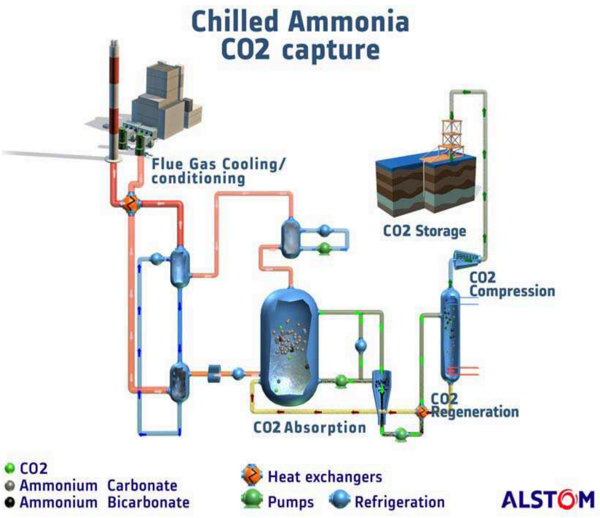
Chilled Ammonia Process

Principle

- Cooled flue gas is treated with ammonium carbonate in solution, which reacts with CO_2 to form ammonium bicarbonate
- Raising the temperatures reverses the above reactions – releasing pressurized CO_2

Advantages

- Energy-efficient capture of CO_2
- High CO_2 purity
- Tolerant to oxygen and flue gas impurities
- Stable reagent, no degradation possible, no emission of trace contaminants
- Low-cost, globally available reagent



A promising technology!

Alstom's development program of carbon capture technologies

Running

We Energies Pleasant Prairie
USA - 5 MWth
Chilled Ammonia - Coal

Vattenfall Schwarze Pumpe
Germany - 30 MWth
Oxy - Lignite

EoN Karlshamn
Sweden - 5 MWth
Chilled Ammonia - Fuel/Gas

Total Lacq
France - 30 MWth
Oxy - Gas/Fuel

Commissioning

AEP Mountaineer
USA - 30 MWth
Chilled Ammonia - Coal

Dow Chemical Co.
USA, West Virginia
Advanced Amines

Study / Engineering

TCM Mongstad
Norway - 40 MWth
Chilled Ammonia - Gas

Transalta
Canada - >200 MWe
Chilled Ammonia - Coal

PGE Belchatow
Poland – 260 Mwe
Adv. Amines - Lignite

Vattenfall Jänschwalde
Germany - 250 MWe
Oxy - Lignite

Pre-selected for European Energy Programme for Recovery funding

A pioneer in developing Post and Oxy combustion capture technologies

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Chilled Ammonia Process
Field Pilot at We Energies

Pleasant Prairie Power Plant ("P4")

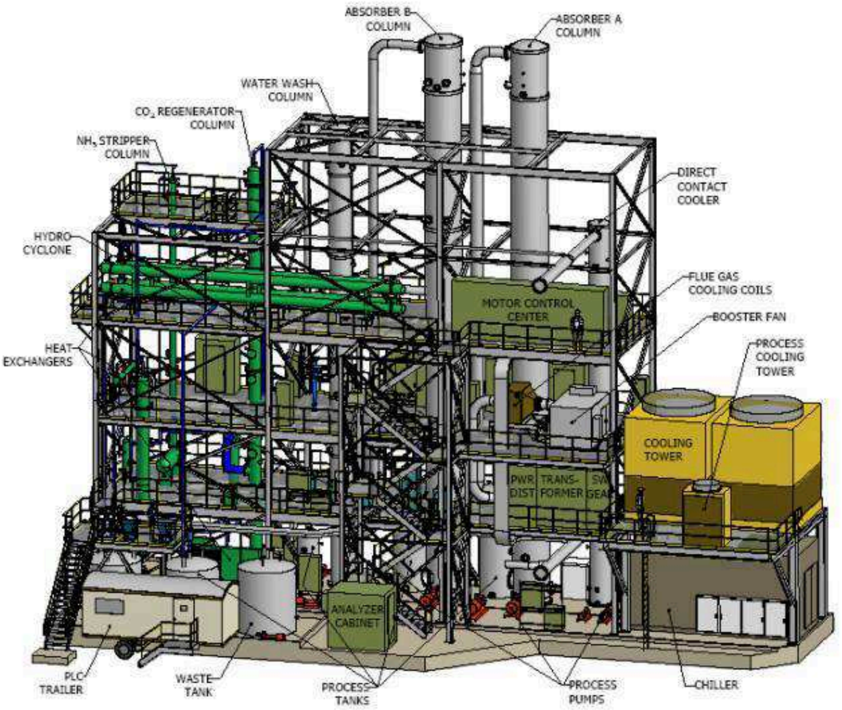
CO_2 Field Pilot at Pleasant Prairie

Validation Pilot Program

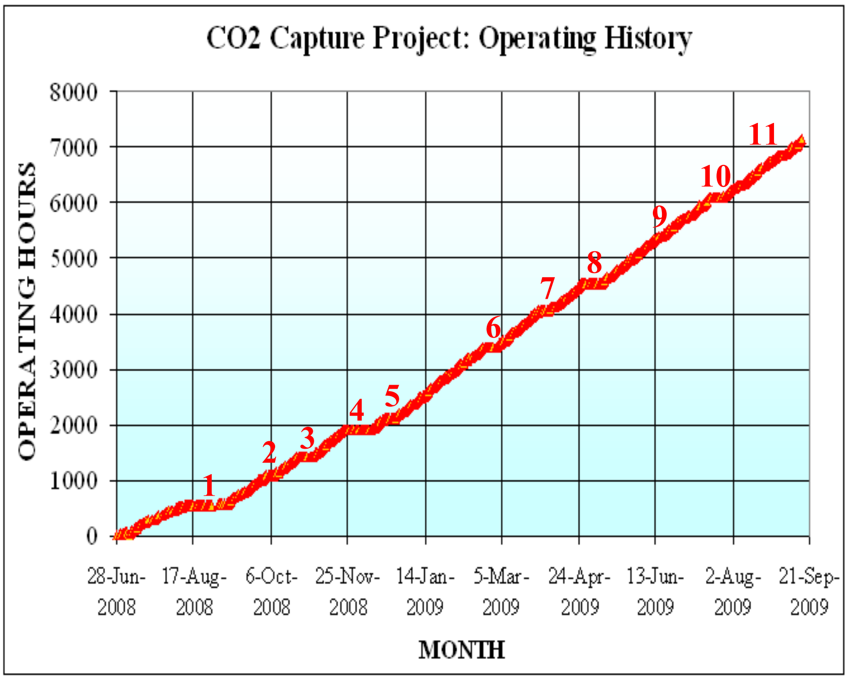
- Project participation through EPRI by 37 US and international utilities
- Designed to capture 1,600 kg CO_2/hour
- Operations commenced in June 2008
  - Over 7,000 hours operation
  - Achieved 90% capture in continuous operation at full load
  - Empirical data collected from pilot to date supports "proof of concept"
  - Initial data on steam and electrical energy consumption is consistent with expectations

A great technical success!

Validation Pilot at We Energies
3-D View of Pilot



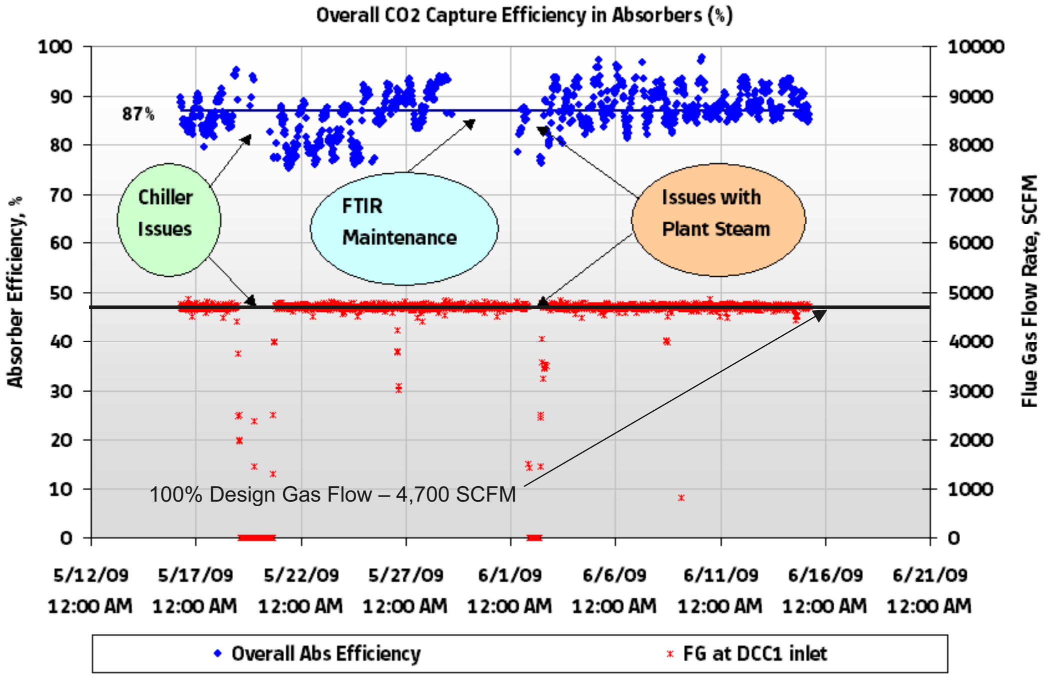
Field Pilot Activities
Operating History



Total operating hours through Sept 16, 2009: 7,136

1. **Planned outage to support pilot modifications**
2. **Power Plant Forced Outage**
3. **Planned outage to support pilot modifications**
4. **Thanksgiving + Planned outage to support modification**
5. **Christmas Holidays**
6. **Power Plant Forced Outage**
7. **Planned outage for pilot maintenance**
8. **Unplanned outage for pilot maintenance (chiller)**
9. **Unplanned outage for pilot maintenance (stripper)**
10. **Planned outage to support piping modifications for Hydro cyclone and Absorbers**
11. **Planned outage to install additional instrumentation**

Validation Pilot at We Energies
CO_2 Capture Efficiency



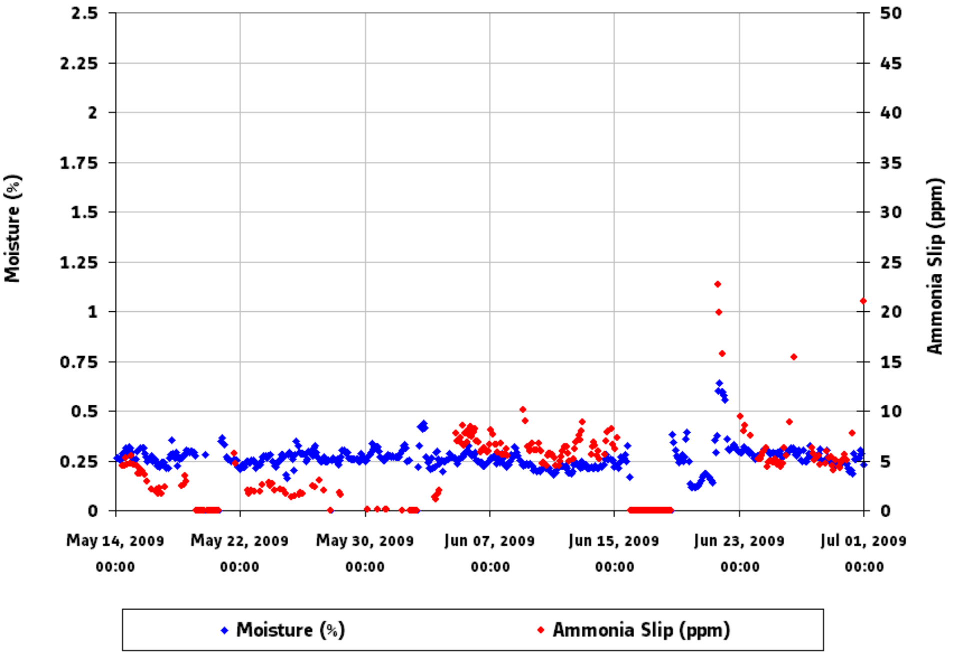
Chiller Issues

FTIR Maintenance

Issues with Plant Steam

100% Design Gas Flow – 4,700 SCFM

Validation Pilot at We Energies
CO_2 Quality



EPRI Material Monitoring Approach - 2009

- Every-day activities
  - Routinely collect and analyze liquid samples for NH_4^+, HCO_3^-, CO_3^{2-}.
  - Log FTIR gas analyzer data for CO_2, SO_2, NOx, NH_3.
  - Log other continuous data; T, P, F
- Multiple “mini-campaign” tests for material and energy balances:

Flue gas inlet	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
Flue gas outlet	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
CO_2 produced	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
DCC blowdown	NH_3, Flow
Thermal / electrical / CW utilities	

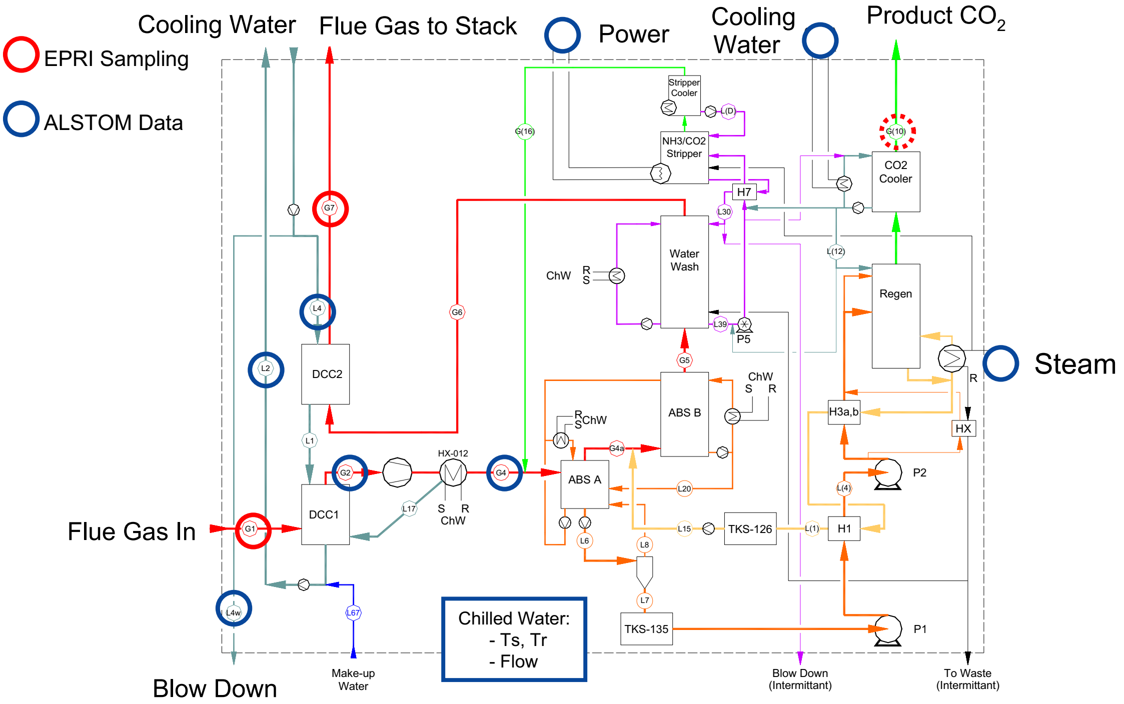
- One **campaign test** for material and energy balances around selected control volumes: (Manual) Gas, Liquids, and Solids sampling – Late Summer 2009.

EPRI Mini-Campaign Testing

Testing Objective – Accumulate high-reliability data on process performance.

- Independent Parameters:
  - Flue Gas Flow rate
  - Solution Strength
  - Process Temperatures, Pressures, Flows
- Dependent Parameters
  - CO_2 Removal, Quality
  - Utilities usage (Heat, electrical, cooling water)
  - Materials usage/disposal
    - Water CW blowdown / CW make-up
    - NH_3 loss / make-up

Mini-Campaign Sampling

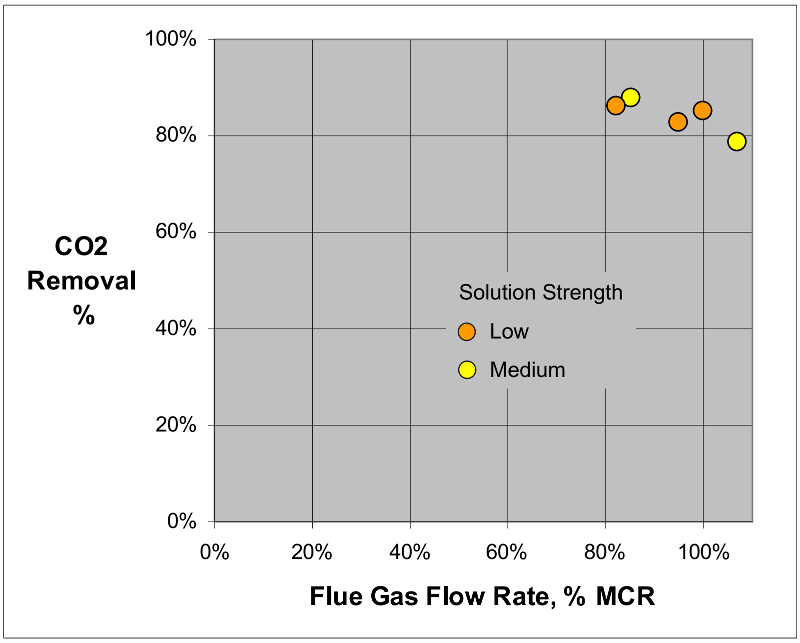


Mini-Campaign Test Conditions

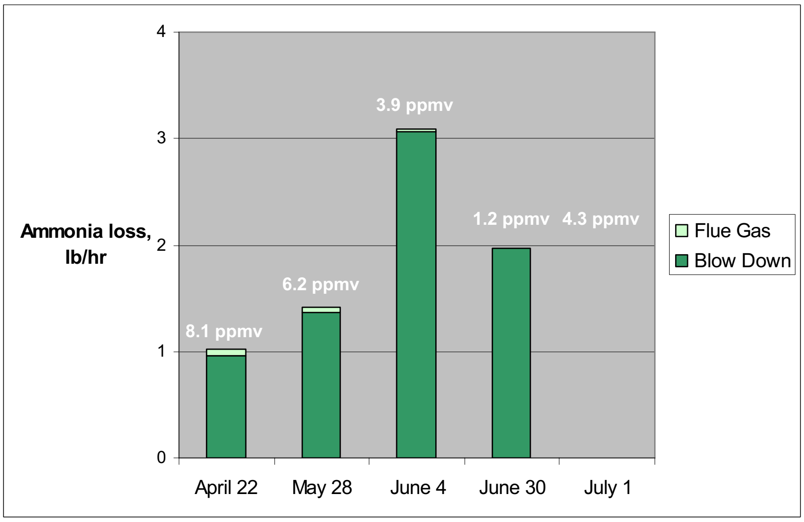
Date	Inlet Flue Gas Flow	Inlet Flue Gas Temperature	CO_2 content vol %, wet	Solution Strength
April 22	85.1%	127°F 53°C	11.9%	Low
May 28	94.8%	128°F 53°C	12.3%	Medium
June 4	100.1%	130°F 54°C	13.0%	Medium
June 30	82.4%	130°F 54°C	11.5%	Low
July 1	106.9%	132°F 55°C	12.0%	Low

Overall CO_2 Removal Performance

Date	Inlet Flue Gas Flow	CO_2 Removal
April 22	85.1%	87.9%
May 28	94.8%	82.7%
June 4	100.1%	85.0%
June 30	82.4%	86.2%
July 1	106.9%	78.5%



Ammonia Losses (Measured by EPRI)



Ammonia loss streams

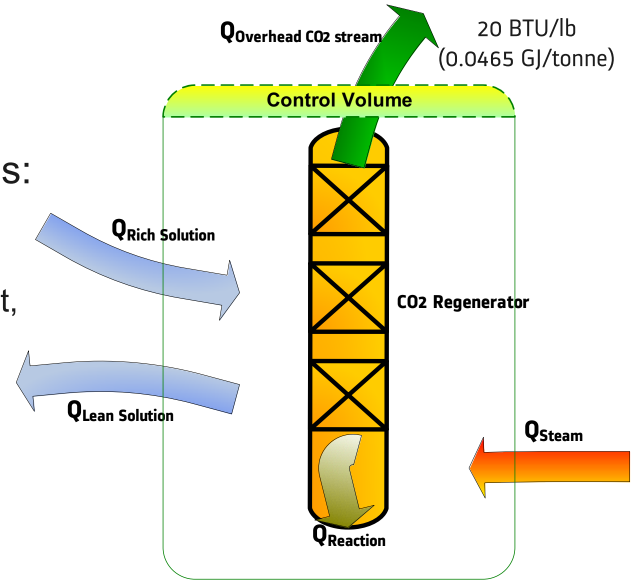
- DCC blow down
- Slip in flue gas
- Product CO_2
  much less than flue gas loss
- Cooling tower exhaust
  Insignificant when DCC cooling water pH is adequately controlled

Design blow down NH_3 loss is ~1 lb/hr.

July 1 blow down data still under review

Chilled Ammonia Process
Steam Energy Consumption

- Steam Consumption
  - Heat of Regeneration
  - $NH_3\backslash CO_2$ Stripping
- Heat of Regeneration includes:
  - Heat of reaction
    - Heat required to drive the reactions, regenerate reagent, produce pure CO_2 stream
  - Solids dissolution
  - Sensible heat requirements
  - Heat in overhead stream leaving the regenerator



$$Q_{\text{Heat of Reaction}} = Q_{\text{Heat Input (steam)}} - Q_{\text{Overhead CO}_2\text{ stream}} - Q_{\text{Liquid Sensible Heat Losses (Lean/Rich solution)}}$$

Validation Pilot at We Energies
Summary – Thermal Energy

- Total steam energy consumption must be validated on an efficiently designed system that is demonstrated at a commercial scale and fully integrated with the power plant.
- In contrast, heat of reaction is dictated by the process chemistry and can be validated at the pilot scale.
- Heat of reaction measured at We Energies compares favorably with values determined in the laboratory setting;
  - Validates the figure used to size the validation pilots;
  - Validates the figure being used in commercial studies and FEEDs.
- The results extrapolated to a commercial scale system support Alstom’s original estimate for total steam consumption

Validation Pilot at We Energies
Summary – Electrical Energy

- Chiller system is primary component
  - Electrical demand varies with ambient conditions
  - Use of cold water source can eliminate chillers
  - Free cooling to minimize electrical consumption
  - Chiller load dependant on cross exchanger performance
- Estimated energy consumption for the pumps in line with expectations
- Booster fan draft loss lower than expected
- Total electric power consumption consistent with expectations, after adjustments to reflect a commercial design
  - Pump power demand based on typical efficiency for larger pumps
  - Refrigeration Coefficient of Performance (CoP) based upon levels provided by refrigeration suppliers for a commercial design versus the unit installed at We Energies

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Accomplishments

- Unit operations have been successfully integrated as a complete process
- Achieved high levels of CO_2 removal at design gas flow
- Accomplished high pressure regeneration
- Achieved low ammonia emissions
- Achieved high purity CO_2 with low concentrations of ammonia, water and other impurities.
- Steam and electrical energy consumption in line with expectations

Next Steps

ALSTOM

- Complete parametric testing program for absorber
- Support completion of EPRI’s gas and liquid analysis test series
- Conduct long-term test at stable operating conditions
- Continue program at 10 x scale at AEP Mountaineer

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APPENDIX C

Cansolv Presentation
during the 12th International CO_2 Capture Network
Meeting held at Regina, Canada on
29th/30th September 2009

Cansolv Technologies :

The Value of Integration

P.E. Just, Cansolv Technologies
Montréal, Canada
Y. Mirfendereski & F. Geuzebroek, **Shell Global Solutions**
Amsterdam, The Netherlands

12th MEETING of the INTERNATIONAL
POST-COMBUSTION CO2 CAPTURE NETWORK
29th September 2009
Regina, Canada

Presentation Outline

- Cansolv Carbon Capture
- Integration 1- CO_2/SO_2 integration
- Integration 2 – USC boiler + Cansolv

Cansolv Technologies at a Glance

- 1997 : Founded as Union Carbide spin-off
- 2008 : Acquired by Shell Global Solutions
- Located in Montreal, Canada and Shenzhen, P.R.C.

Global leader in **amine based regenerable** scrubbing

- A leading regenerable **SO_2 control** technology
- A cutting edge **CO_2 capture** technology

11+ Years of Worldwide Success

- A flexible technology for **a variety of industries**
  - **Industrial combustion applications : coal and bitumen boiler power plant off-gas**
  - Oil & Gas applications : Sulfur plants, FCCs, Cokers
  - Smelter applications : lead/zinc furnaces, copper anode furnaces
  - Others: acid plant tail gas, incinerator off-gas
- Experience in delivering large commercial scale Amine Plants Worldwide
- Modularized plants & engineered solutions

14 plants in operation Worldwide

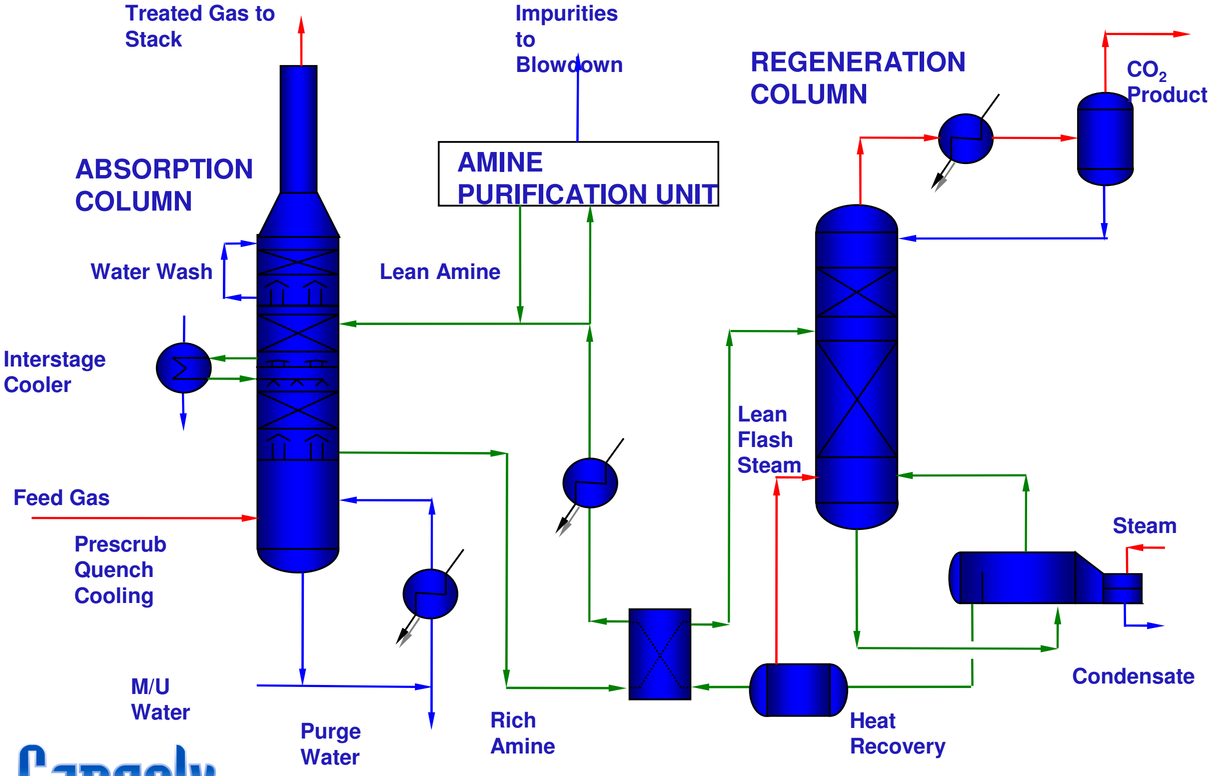
APPLICATION	LOCATION	GAS FLOW (Nm3/h)	INLET SO2	FINAL EMISSIONS (ppmv)	START-UP DATE
Sulfur Recovery unit	Belgium	12,000	1%	10	2002
Sulfur Recovery unit	USA	20,000	4%	< 140	2006
Sulfur Recovery unit	Canada	18,000	2%		2009
Fluid Catalytic Cracking unit	**USA**	**740,000**	**800 ppmv**	**25**	**2006**
Fluid Coker	**USA**	**430,000**	**0.20%**	**25**	**2006**
Zinc Smelter	Canada	4,000	7% – 10%	30 - 45	2002
Lead Smelter	India	35,000	0.1% – 11%	150	2005
Lead Smelter	China	30,000	0.1% – 10%		2009
Copper Smelter	China	40,000	0.09% – 2%		2007
Coal-Fired Cogen Boiler	**China**	**960,000**	**0.40%**	**<120**	**2009**
Sulfuric Acid plant	USA	40,000	0.50%	< 15	2002
Sulfuric Acid plant	China	35,000	0.40%		2009
Spent catalyst	Canada	50,000	0.90%		2007
Acid Plant Tail Gas	USA	157,000	0.5%	<100	2009

***Large Amine plants operating in oxidative environments**

CANSOLV

CO_2 Capture Process

Cansolv CO_2 Flowsheet



Cansolv CO_2 Technology Development Strategy

- Designed on Cansolv SO_2 control platform
- SO_2 compatible
  - Minimum Oxidative and Thermal Degradation
  - Low Specific Regeneration Energy
  - Minimum Effluent
  - High CO_2 product purity

CO_2 CAPTURE EXPERIENCE

Over 6000 hours of CO_2 Piloting

CO_2 CAPTURE EXPERIENCE - Piloting

Application	Date	Site	CO_2 in the gas	Removal
Natural Gas Fired boiler	2004	Paprican, Montreal, Canada	8%vol	75%
Coal fired Boiler	2004	Pulp Mill Boiler, US	11.5%vol	65%
Coal fired Power Plant	July – Sept 2006	Saskpower, Poplar River, Canada	12% vol	90%
Blast Furnace	April 2007 - 2008	Japan	22% vol	90%
Natural Gas Fired Boiler	May - Sept 2007	Shell-Statoil, Norway	4.5%vol	85%
Cement Kiln	2008	North America	20%vol	90% and 45%

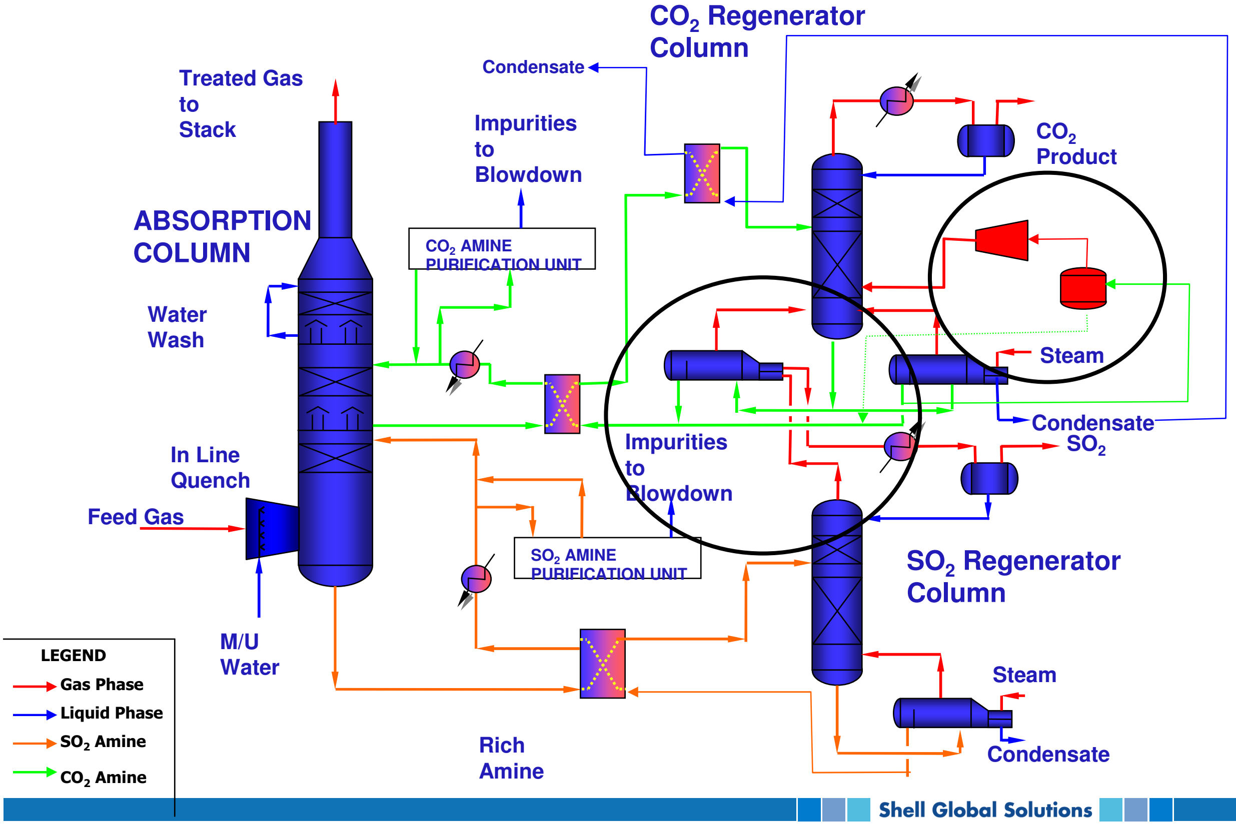
Value of SO_2 / CO_2 Capture Integration

Heat Recovery / Integration Concepts

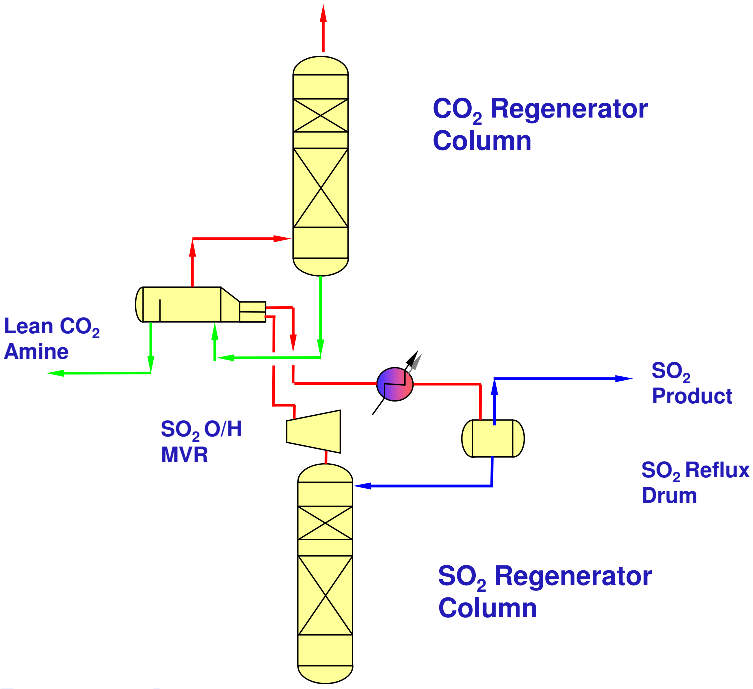
- Latent energy available in the Lean Amine exiting the Regenerator
- **Lean Flash MVR** allows for high coefficient of performance heat recycling internal to the process

- Heat Integration **with CANSOLV SO_2** FGD process
- Heat recycle from FGD **by-product conversion** (SO_2 to acid) Better CO_2 heat performance with higher sulfur fuel combustion gases

CANSOLV SO_2 - CO_2 CAPTURE INTEGRATED FLOWSHEET



SO_2 Overhead Compression



-SO_2 Overhead Compression

-Offsets CO_2 Regeneration Steam requirements

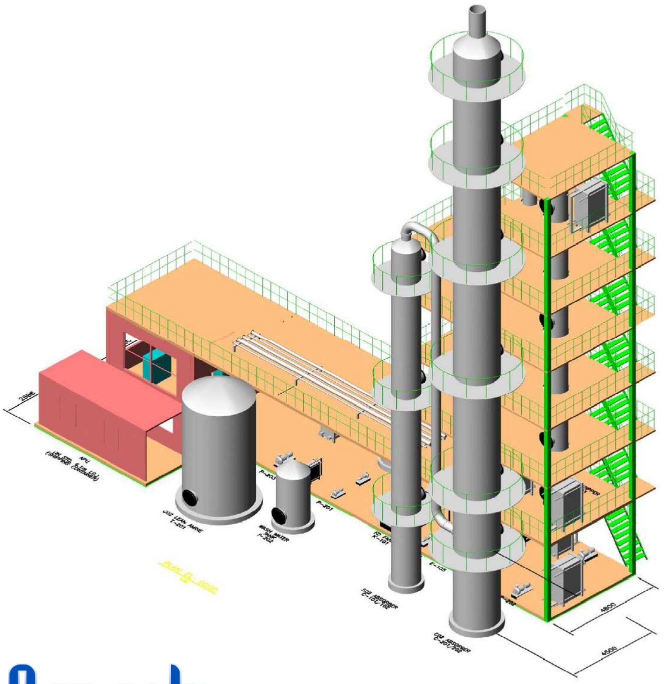
SO_2 / CO_2 Capture Demonstration Plant

- 50 ton/day CO_2 capture (~3 MW)
- Currently in Detailed Engineering and Procurement Phase
- Start-up beginning 2011
- CANSOLV-SO_2 Control and CANSOLV-CO_2 Capture Process

Objectives

- confirm specific heat consumption
- evaluate scale-up effects
- prove SO_2 compatibility of CO_2 solvent

SO_2 and CO_2 capture Demonstration Plant



SO_2 Control
and
CO_2 Capture

Demonstration Plant

Demo Plant Performance

- CANSOLV CO_2 Capture Process designed

  for 1.18 tons steam per ton CO_2

  (with Lean flash MVR heat integration used)

- Demo plant instrumented for **operating and capital cost** optimization

- **CANSOLV DC-103 and New solvents under development** in order to lower the regeneration energy

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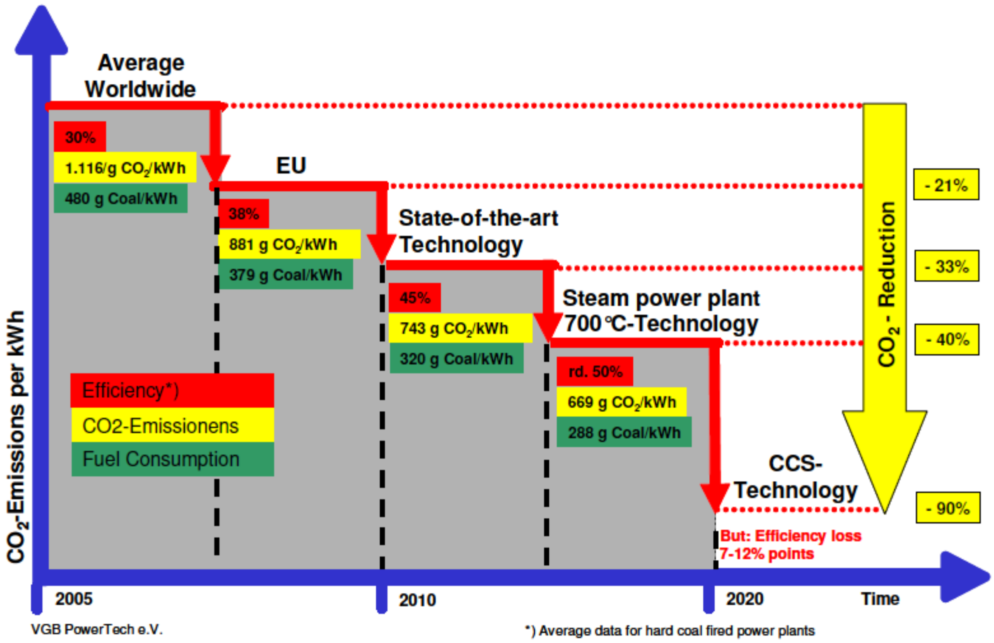
CO_2 Capture and
Ultra Supercritical Boiler

Acknowledgement

This study has been done in cooperation with Pierre Ploumen and Hans Kamphuis from **KEMA Consulting BV**.

Achieving reduction of CO2 emissions in a Power plant



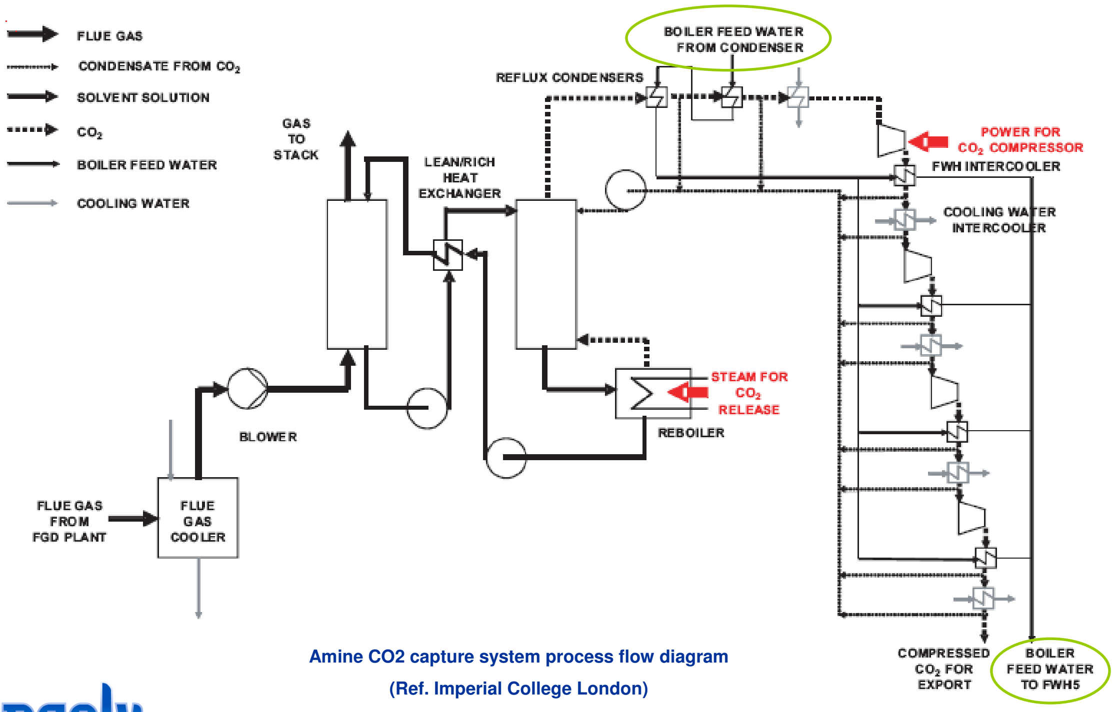
VGB PowerTech e.V.

*) Average data for hard coal fired power plants

Parameters used for CANSOLV CO_2 scrubbing

Parameter	Unit	Cold case	Hot case
Inlet temperature of flue gas CO_2 absorber	ºC	36.5	53.0
Specific steam consumption without Lean Flash and MVR	MJ(thermal) / kg CO_2 captured	2.97	3.18
Specific steam consumption with Lean Flash and MVR	MJ(thermal) / kg CO_2 captured	2.33	2.41
Energy consumption MVR **efficiencies: polytropic = 0.85 & mechanical = 0.95*	kJ(electric) / kg CO_2 captured	72.8	81.7

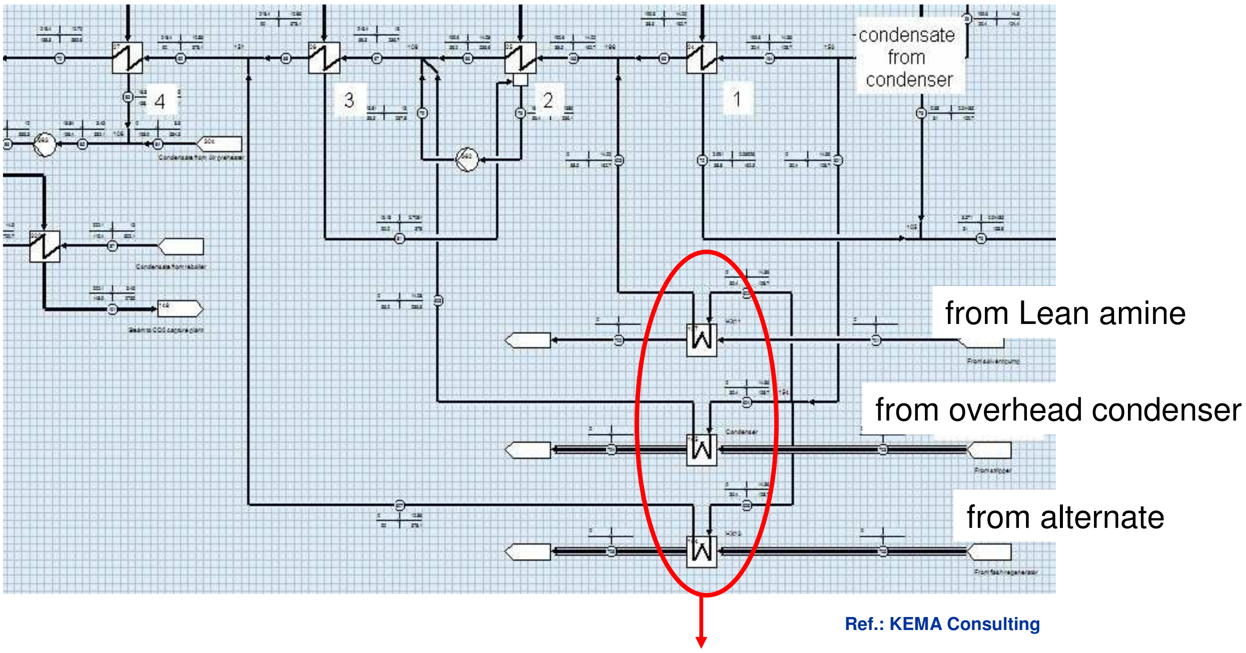
Integration of USC with the capture process



Amine CO2 capture system process flow diagram

(Ref. Imperial College London)

Integration of available heat of CO_2 capture plant



condensate from condenser

from Lean amine

from overhead condenser

from alternate

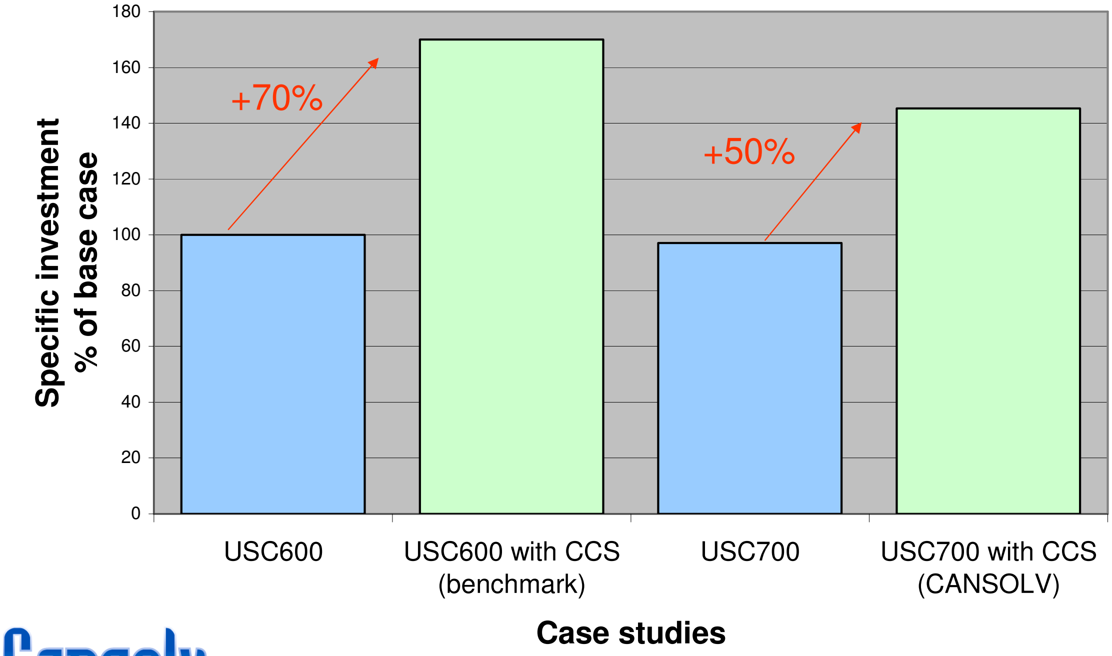
Ref.: KEMA Consulting

Heat from CO_2 capture system used for **condensate pre-heating**

Main results of KEMA case studies

Case	USC 600	USC 600	USC 700	USC 700
Capture technology (90% capture)	-	Benchmark	-	**Cansolv**
Reheat	Single	Single	Single	Single
Steam conditions: live steam press & temp / reheat temperature	29MPa / 600C / 620C	29MPa / 600C / 620C	35MPa / 700C / 720C	35MPa / 700C / 720C
Condenser pressure [kPa]	2.5	2.5	2.5	2.5
Integrat. with steam cycle	-	Yes	-	Yes
Fuel input (MWth)	2143	2143	2400	2400
Net output (Mwe)	994	789	1213	1016
Net Efficiency (%)	**46.4**	**36.8**	**50.5**	**42.3**
Cooling water req. (MWth)	997	1337	1029	1165
Efficiency drop due to capture(%)	-	9.6	-	8.2
CO2 captured(kg/s)	-	179.8	-	201.4
CO2 emission(kg/s)	199.8	20.0	223.8	22.4
Benefit heat integration(%)	**-**	**0.4**	**-**	**0.2**

Relative specific investment costs
USC600 + Benchmark vs. USC700 + Cansolv



Thank you!

Questions…?