Development of an Economic Post-Combustion Carbon Capture Process

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Abstract

Siemens develops an improved CO\textsubscript{2} capture process with minimized energy demand, optimized for integration in conventional coal-fired power plants. The solvent based on an amino-acid salt solution features low absorption enthalpy and near-zero vapor pressure, permitting an economic and environmentally friendly capture process. Optimized process configuration and power plant integration significantly reduce the energy demand and result in an efficiency penalty of approx. 9 \%-points. The process will be tested with real flue gas in a pilot plant linked to an E.ON power plant in Germany. Commissioning is planned for August 2009 for subsequent process validation and further solvent optimization.

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1. Introduction

Climate change is one of this century’s most serious challenges, and most European energy suppliers accept their particular responsibility to contribute to combating climate change because of the obvious opportunity to significantly reduce carbon emissions in the power generation sector.

However, low carbon emission is not the only requirement the energy supply has to fulfill from now on. Requirements such as immediate availability at any time, careful use of resources, security of supply and low price of electricity are still valid. Renewable energies can contribute to a low-carbon power generation, but the lack of ready availability, limited capacities and rate of growth as well as high prices have to be considered. Nuclear power generation also has advantages regarding CO\textsubscript{2} emissions, but faces other challenges.

The long-lasting resources of fossil fuels (especially coal) and the worldwide still increasing use of this primary energy source suggest that fossil fuels will continue to play an important role for the world’s energy supply for decades. To comply with global emission reduction targets, the development of carbon capture and storage technologies (CCS) is obligatory and represents a ‘no regret’ option - independent from the future role of fossil fuels in Europe or other industrialized economies.

By giving CO\textsubscript{2} emissions an economic value, the European Emission Trading System (ETS) is a driver towards low-carbon power generation technologies, unless the CO\textsubscript{2} caps can be achieved just by switching fuels and by realizing efficiency-increasing retrofit measures within the existing generation fleet. As the modernization of the European generation fleet is ongoing while CCS is not yet mature for commercial use, the operators can decide to prepare capture-readiness of coal-based new-built power plants, so that later retrofit of CCS can be done smoothly and without heavy additional investments.

It is therefore essential to bring CCS to commercial maturity as soon as possible – focussing on retrofittable capture technology options. E.ON and Siemens are committed to this goal and preparing the large-scale demonstration phase with their cooperation in the POSTCAP project, which is part of the German COORETEC programme.
2. POSTCAP targets for Siemens and E.ON

The POSTCAP project of Siemens and E.ON is funded by the German Federal Ministry of Economics and Technology and pursues the development of an economic post-combustion CO₂ capture process for coal-fired steam power plants. The overall project target is to obtain an optimally-integrated advanced capture process based on an improved solvent that shows major advantages compared to MEA¹-based processes in terms of energy efficiency, solvent slip and life-cycle costs. The POSTCAP research activity is characterized by an integral approach. Development targets are:

- Optimization of a CO₂ capture solvent for application in steam power plants, with advantages regarding performance, environmental aspects (solvent slip, safety), costs and stability in coal flue gas.
- Development of an advanced capture process design that is focused on power consumption and well-adapted to the solvent.
- Optimal integration of CO₂ capture process into power plant regarding steam/power extraction and operational flexibility.
- Pre-selection of suitable equipment for the capture process in a steam power plant.
- Erection and operation of a pilot plant at an E.ON power plant site for process validation. Pilot plant commissioning is scheduled for August 2009.

With the development activities on the carbon capture process, Siemens will keep and extend its competence and business as a major solution provider for power plants. Siemens masters the whole chain from process development to project implementation thanks to in-house competencies for project execution, chemical process development, flue gas treatment and CO₂ compressor technology.

E.ON’s commitment is driven by the expected future role of coal and low-carbon power generation from coal in the E.ON portfolio. Therefore E.ON’s activities concentrate on achieving technical maturity of capture, transport and storage technologies to enable commercial application of coal-fired power plants with CCS under market conditions until 2020. As there is limited time to reach high capacity and reliability for commercial application, E.ON relies on a partnership with a powerful partner like Siemens with competence and experience in plant engineering and supply of power plant components as well as chemical engineering. E.ON is fully in line with the goals of the Siemens development of a new capture process based on an environmentally friendly and at the same time most energy effective process and solvent. Regarding the ongoing power plant projects within E.ON and the uncertain future development of CO₂ prices within the EU ETS, post-combustion capture technologies are of great interest and need to be developed to a competitive alternative to other capture pathways.

3. Solvent characterization, lab plant and development of simulation model

3.1. Chemical structure and properties

Solvent selection is an essential step because the solvent directly influences the energy demand and the environmental impact of the CO₂ scrubbing process. Mastering the environmental risks of CCS is a precondition for its implementation because the advantage of decelerated global warming through reduced CO₂ emissions should not be impaired by other environmental risks that might result from CO₂ capture.

Beyond minimized environmental impact, Siemens’ priorities for solvent choice are high selectivity for CO₂, low degradation, low energy demand, high CO₂ capture rate and high purity of the CO₂ stream. This is why Siemens uses an amino-acid salt solution for the chemical absorption process because this substance group has the advantage of negligible vapor pressure so that, given an appropriate demister on top of the absorption column, the solvent emissions will be nearly zero. The molecular structure is illustrated in Fig. 1; R representing an organic group.

![Figure 1: Molecular structure of an amino-acid salt](image)

Amino-acid salts have ionic structure and are less sensitive to oxygen. As salts have no vapor pressure, they are not inflammable. Furthermore, the solvent exhibits low thermal sensitivity, so that refill requirements are expected to be very low, which has a direct impact on the operating costs of the CO₂ capture plant. Thermal stability of the solvent also gives more flexibility to the process design, i.e. the absorption and desorption process can be run at a wide range of temperatures and pressures.

This second-generation solvent is well-adapted to operational needs because handling for operation and storage is easy, i.e. it is not inflammable, not hazardous, and nontoxic and has a good biodegradability. In addition, it is a registered chemical substance with available safety data. Tests have shown that the heat requirement for solvent regeneration is considerably lower than for MEA. This is due to a lower heat of absorption and advantageous partial pressures ratios in the absorber and desorber column respectively. The absorption enthalpy measured was approx. 10% below the MEA value.

With these benefits, the Siemens solvent is well adapted for CO₂ capture from the flue gas of fossil-fired power plants.

¹ monoethanolamine
3.2. Lab plant and simulation model

A successful process development requires reliable data for the process synthesis, optimization and the equipment design. Therefore Siemens has developed a rigorous simulation model for the process and erected a fully-automated absorption plant in lab scale for an extensive test and validation of the simulation model. Besides the model validation, the lab plant has delivered valuable information on the behavior of the different flue gas by-components with the solvent. In long-term investigations the superior stability of the amino-acid salt against oxygen has been confirmed. Since the lab plant is driven with a synthetic flue gas, the influence of gases such as NO₂ and SO₂ has been investigated separately in order to get a deeper understanding of the underlying absorption mechanisms of these sour gases. Furthermore, corrosion experiments with the potential plant materials were carried out inside the columns. Due to the fact that the plant is partly made of glass, process behavior can be easily observed during operation. Last but not least, much operational experience could be gained during approx. 5,000 plant operating hours.

The lab plant (Fig. 2) consists of a stainless steel desorber with a diameter of 80 mm that can also be equipped with a 50 mm inner tube for increased gas velocities. The desorber is made of glass with 50 mm inner diameter. Both columns are equipped with a structured packing. The flue gas capacity of the lab plant is about 5 m³/h. In order to achieve a sufficient energy balance the equipment is carefully insulated, and most parts are equipped with electrical heat jackets. The lab plant is fully automated and due to the comparatively harmless properties of the solvent, the plant can be run overnight without any personnel. The content of carbon dioxide in gas outlet streams of the column is measured online. Solvent samples are analyzed offline.

![Figure 2: Siemens carbon dioxide absorption plant in laboratory scale](image)

Two prerequisites were necessary for the simulation model development. At first a rough but sufficiently reliable model had to be available in order to ensure an early start of the process synthesis. In a second step a more rigorous model was developed. This model can give precise data for the energy requirement and the equipment design. Therefore the necessary phase equilibria (e.g. gas solubilities, solid liquid equilibria and vapor pressures) were measured in the relevant pressure, temperature and concentration range. Caloric data and transport properties (e.g. heat capacities, enthalpy of absorption, viscosities and surface tensions) were experimentally determined for both lean and loaded solvent. All these data were used to parameterize a comprehensive thermodynamic model within ASPEN Plus. Furthermore, the underlying chemical reaction (Fig. 3) was investigated in order to consider kinetic limitations.
Occurring mass transfer limitations are considered within the ASPEN Plus mass transfer model RATESEP. The comparison of the measured mass balance and the simulation results matched well. In Fig. 4 some examples of measured and calculated carbon dioxide concentrations are compared at different solvent pump-around quantities, while other operating parameters like reboiler duty, flue gas composition and flow were kept constant.

4. Process development, power plant integration and economics

4.1. Process design

Besides the identification and improvement of a suitable capture solvent, the Siemens development focuses on determining an optimum capture process configuration considering the given boundary conditions and interfaces from the underlying power generation process (e.g. defined flue gas properties).

It is known that operating costs of the capture plant, which are mainly caused by the energy demand for stripper heating, strongly contribute to the overall separation costs. The energy demand for solvent regeneration can be reduced by applying mature technologies that have been used for absorption and distillation systems in the chemical industry (e.g. heat integration).
concepts, withdrawal of side streams). Therefore, the identification of suitable process configurations was supported by an extensive survey in the open literature and in databases. The development of an optimal process configuration was done in a systematic manner:

1. Identification of starting points for process improvements and development of process ideas based on own process expertise and a continuous literature survey.

2. Analysis and rating of identified process improvements according to POSTCAP boundary conditions. The process variants were rated according to three grades of accuracy:
   - Qualitative rating based on process expertise, used for pre-selection of the variants,
   - Determination of energy consumption through process simulation
   - Economic evaluation of the most promising options, i.e. calculation of cost of CO2 avoided

3. Combination of most promising variants

Steps 2 and 3 were repeated in an iterative manner until an optimum absorber/desorber configuration with the lowest possible CO2 separation costs was found. In order to fully exploit the potential for saving separation costs, both the capture plant and the possible energy integration in the power plant were considered (see Section 4.2).

During process development, approx. 50 different improvement options of the flow scheme were identified and rated according to qualitative criteria. From these 50 options, about 30 promising process variants were selected and calculated using the simulation model, and the operating conditions were optimized for each process scheme. The results were put into a ranking regarding energy consumption, investment and operation costs. In a further step, combinations of the most promising process variants were evaluated. As a preliminary result, the energy consumption of the process can be decreased from 3.5 GJ/ton (for a standard flow scheme as shown in Fig. 5) to 2.3 GJ/ton of separated CO2 by using an advanced process configuration. At the same time, costs per ton of CO2 avoided can be decreased by about 15%.

4.2. Power plant integration

Due to the high thermal and electrical energy demand as well as cooling requirements of the capture unit, a material integration between the capture unit and the power plant, i.e. the utilization of the power plant infrastructure for the capture unit, is an imperative in terms of efficiency and economics. The need for low-pressure steam for thermal regeneration of the loaded solvent has the main impact on power output and plant efficiency.

Since the amounts of required media (steam, electricity, cooling water) are interdependent and additionally depend on the considered capture process variant, an integrated evaluation and optimization of the complete system incorporating the power plant and the capture unit is necessary. The detailed cycle modeling of the power generation and CO2 capture process requires different modeling tools, which are implemented and optimized for the corresponding simulation tasks. Therefore, the evaluation and optimization of the complete system is done by aligning the interface values between the different simulation models. To avoid numerous iterations, it is possible to derive evaluation functions, which quantify the impact of single interface streams on the power output and efficiency. For example, the influence of the required reboiler steam temperature or of the reachable temperature level for the low-temperature waste heat from the capture process can be described as a characteristic function that can be used as an input for modeling different variants of the capture unit.

Compared to the reference case without capture, the latest preliminary performance calculations for a power plant (hard coal, 800MW class steam power plant, net efficiency 45.7% (LHV) without CCS) with Siemens CO2 capture process show an...
efficiency drop of 10.4 %-pts. with standard capture process layout including CO₂ compression. With an optimized capture process layout and power plant integration, the process simulation even yields an efficiency drop as low as approx. 9 %-pts. Beside the capture process optimization itself, the considered variants also feature low-temperature heat integration between the power plant and the CO₂ compressor as well as appropriate steam desuperheating for further reduction of efficiency drop. The evaluation of single possible integration measures in terms of economics, i.e. their respective influence on the CO₂ avoidance costs, will be conducted in the next phase of the project, once the capture process layout will have been fixed.

As a further important consequence, the definition of the capture process and the appropriate integration measures enable the determination of necessary capture-ready features, which allow for a later retrofit of a power plant with a CO₂ capture unit. Because of the high relevance of climate protection, future new-built steam power plants should be ready for incorporation of a carbon capture plant at a later date, i.e. to be “capture ready”. Siemens reviews exemplarily the plant layout of a state-of-the-art 800 MW steam power in order to fulfill post-combustion capture readiness based on chemical absorption. The underlying capture ready definition is based on the following topics:

- Enable or ease later integration of a carbon capture plant,
- Avoid lock-ins that exclude or hinder use of future capture developments,
- Delete aspects that make retrofit of capture plant impossible.

This results mainly in space and access for additional equipment and auxiliaries, necessary energy supplies and provisions for cooling requirements.

Relevant power plant areas with different impact on readiness for a later retrofit of a capture plant are:

- Whole plant layout with rearrangement of components and sufficient space for whole capture plant (mainly absorption / desorption columns and heat exchangers) as well as CO₂ compressor set according to technological requirements.
- Steam turbine building with space for future modifications on steam turbine, routing of different large piping as well as space for heat exchangers for low-grade heat utilization (e.g. from CO₂ compressor intercoolers).
- Steam turbine able to be rebuilt for requirements of future capture plant requirements.
- Flue gas system ready for incorporation of additional or modified blower, additional or enlarged desulphurization plant and tie-in for the capture plant.
- Cooling system expandable for additional waste heat loads and preparation for additional circulating water pump.
- Electric auxiliary power supply and cable routing prepared for enlargement.
- Preparation for enlargement of raw water intake and treatment/demineralization as well as provisions for waste water disposal.

Resulting steam power plants in capture-ready design will consequently be able to incorporate later a wide range of possible post-combustion carbon capture processes.

4.3. Economic figures

The currently estimated CO₂ capture costs (including CO₂ compression, without transport and storage) are approx. 30 €/t CO₂ in the early commercial phase (>2020) and approx. 20 €/t CO₂ in the mature commercial phase (>2030). The price of a carbon capture plant including CO₂ compression and plant integration is estimated to be in the range of 300 to 400 million € for an 800 MW steam power plant, depending on the train concept selected (price base 2008). Fig. 7 shows an example how the carbon capture plant is integrated into the power plant and gives an indication of the space requirements for the capture plant.
5. Pilot plant and next steps

5.1. Preparation of pilot plant

In a further step, the process will be validated in a slip-stream pilot plant under real operation conditions. The projected pilot plant will be installed at an E.ON hard-coal fired power plant site in Germany. Start of pilot plant operation was initially scheduled for January 2010, but as the market asks for earlier research results, the planning and erection have been accelerated by fast track measures, so that pilot commissioning is scheduled already in August 2009.

The main components of the pilot plant are flue gas cooler, absorption and desorption column, heat exchangers, top condensers, steam-driven reboiler etc., as shown in Fig. 8. At the E.ON site, the flue gas is extracted after the FGD; CO₂ stream and lean flue gas from the CO₂ capture plant are fed back into flue gas duct. The column size is approx. DN 200 and 35m height. The pilot plant operation and record of all measurements will be controlled by “Siemens DCS”, placed in the control container close to the test facility. In a first step, the standard process configuration is used for the pilot plant design in order to obtain comparability of test results with already existing research results in the field of post-combustion carbon capture. During pilot plant operation, the lab plant at the research center in Frankfurt-Hoechst will continue to run for trials with improved solvent compositions and process configurations for further enhancement of process efficiency.

Figure 8: Process flow diagram of pilot plant
Pilot plant operation is planned for a period of 16 months and starts with pilot plant commissioning in August 2009. Tests will be carried out with the following objectives:

- Gain detailed information on solvent stability with realistic flue gas composition from a coal-fueled power plant
- Prove low solvent emission level
- Gather data sets of operating and solvent parameters to validate the developed simulation model and refine the model
- Check corrosion interactions
- Analyze the operating behavior of the process design regarding part load and maximal load change gradients
- Test solvent behavior with various \( \text{SO}_2 \) concentrations in the flue gas by injecting \( \text{KOH} \) in the flue gas cooler to catch \( \text{SO}_2 \)
- Test advanced solvent compositions and improvements derived from Hoechst lab plant tests performed in parallel.

5.2. Next development steps

Basically the vast experience in the engineering of absorption columns will allow a large scale-up factor. Even a direct scale-up from the above-mentioned pilot plant size to a demo plant size seems feasible. However, it is presently planned to have a scale-up step in between, i.e. a larger pilot after successful completion of the POSTCAP project, in order to gain more experience in operational behavior and power plant interaction.

Due to the fact that Siemens Sector Energy business is focused on combined cycle gas turbine power plants, Siemens is striving to provide as soon as possible a commercial carbon capture process for natural gas flue gas, too. Low carbon dioxide and high oxygen content require an advanced process and further improved solvent stability regarding \( \text{O}_2 \) degradation. The Siemens post-combustion process will therefore be adapted to typical flue gas compositions and operating conditions of combined-cycle plants. A major development focus will be to maintain the high flexibility of combined-cycle plants with carbon capture, i.e. to reduce start-up time and consider stand-by operation of the capture plant.

Further development is also planned for the assessment of using the precipitation potential of amino-acid salts in a next-generation carbon-capture process. The current design does not involve precipitation.

6. Conclusions

As fossil fuels are expected to remain the backbone of worldwide electricity production in the next decades, Carbon Capture and Storage will play a significant role for the reduction of \( \text{CO}_2 \) emissions. Currently available post-combustion capture technologies lack the desired energy efficiency and show a potentially high amount of solvent loss due to chemical and thermal degradation as well as some solvent slip to the atmosphere.

In an integral approach, Siemens has been developing a proprietary solvent-based post-combustion capture process and optimized solvent with the objective to obtain an economic process with minimized environmental impact that can be optimally integrated into the power plant. This optimal integration can be achieved because Siemens masters the whole chain from process development to project implementation thanks to in-house competence power plant project execution, chemical process development, flue gas treatment and \( \text{CO}_2 \) compressor technology. The process has been developed and will continue to be improved at laboratory scale. Process validation with real flue gas will be done in a slip-stream pilot plant at an E.ON hard-coal fired power plant site in Germany from August 2009 on.

The efficiently designed and optimally integrated \( \text{CO}_2 \) capture process based on an improved solvent shows major advantages compared to MEA-based processes in terms of energy efficiency, solvent slip and costs. The advantages of Siemens’ process rely on an amino-acid salt solution as a solvent that has been optimized for high selectivity, high absorption capacity, low chemical and thermal degradation, low energy demand for solvent regeneration and near-zero solvent slip. Comprehensive measurement data from extensive trials have been used for detailed thermodynamic and chemical process modeling with state-of-the-art engineering tools to obtain an enhanced capture process with significantly reduced thermal and electrical energy demand. Considering the project results obtained so far, the Siemens process with optimized process configuration, power plant integration and solvent achieves an efficiency loss of approx. 9 % points, including \( \text{CO}_2 \) compression, compared to a standard coal-fired power plant.