

## SELECTION AND PILOT PLANT TESTS OF NEW ABSORBENTS FOR POST COMBUSTION CARBON DIOXIDE CAPTURE

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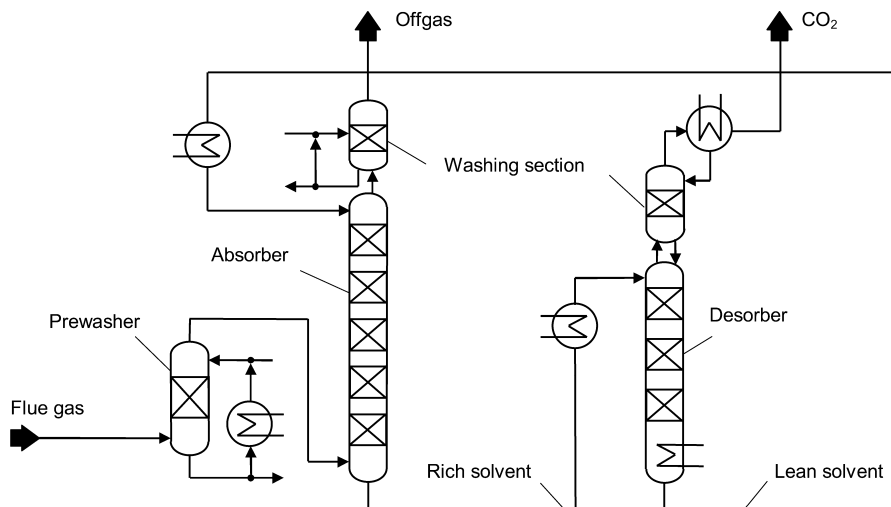
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### INTRODUCTION

Carbon dioxide is a green house gas with a major impact on global climate change. Technologies for reducing carbon dioxide emissions, especially from power plants, are therefore intensively being developed. Among these, only post combustion capture has the potential of being implemented quickly on a large scale. The best technology for post combustion capture of carbon dioxide is absorption with a suitable solvent and subsequent regeneration of the solvent in a desorber. Almost pure carbon dioxide is obtained on the desorber top for storage or further use. Several commercial processes of that type are being offered [1, 2, 3, 4], but most of them were initially developed for other purposes and there is only limited experience with their performance in flue gas cleaning. Furthermore, the cost of post combustion capture with these existing technologies is generally considered to be prohibitively high, for cost estimates, see, e.g., [1, 3, 4]. The key to better process economics is finding highly efficient solvents, tailored for post combustion capture. This is the task of the present work that was carried out in the frame of the Integrated European project CASTOR [5]. The paper gives an account of the achieved progress in this process.

A major challenge for the carbon dioxide removal using post combustion capture is the amount of the flue gas. In typical applications flue gas flow rates are of the order of thousands of tons per hour corresponding to millions of cubic meters per hour, and hundreds of tons of carbon dioxide per hour. The few existing plants for post combustion carbon dioxide capture are 1–2 orders of magnitude smaller [3]. It should be noted that abundant industrial experience with carbon dioxide removal is available in natural gas treatment, but even the largest realized plants in that area are small compared to the present application and the conditions differ significantly from the ones which are of interest here [3, 6].

The basic process concepts for carbon dioxide post combustion capture by absorption that are being discussed in the literature or offered by commercial vendors like Fluor or Mitsubishi Heavy Industries are all similar [1, 2]. A general scheme is shown in



**Figure 1.** Basic scheme of the absorption-desorption process for post combustion carbon dioxide capture

Figure 1. The flue gas is fed to an absorber operated at ambient pressure, eventually after having passed a prewasher that is mainly used for cooling. Carbon dioxide removal rates are typically 85–95%. The solvent is regenerated in the desorber operated at elevated pressure and, hence, temperature. Almost pure carbon dioxide is produced at the desorber top. On top of both absorber and desorber, additional washing sections are installed that allow reducing solvent losses.

The column diameters of the absorber and desorber and thus capital cost are mainly determined by the flue gas flow rate. In addition capital cost is also related to the column heights, which is strongly influenced by the kinetics of the absorption. Operating costs are mainly determined by the solvent flow rate and the regeneration energy. The absorption-desorption technology itself is well developed and major improvements can only be expected if new, improved solvents are found.

The flue gas mainly consists of nitrogen, water (vapor) and carbon dioxide. Typical values of the carbon dioxide partial pressure are 40 mbar for gas-fired power plants and 140 mbar for coal-fired power plants. Note that these low partial pressures are a major difference between carbon dioxide removal in the present application and that in natural gas processing. Due to the low carbon dioxide partial pressure and the fact, that a flue gas compression is not economic, application of physical absorption is not sufficient. Therefore, promising solvents are only those in which carbon dioxide is chemically bound.

In addition to the main components, the flue gas contains important impurities, namely oxygen as well as  $\text{NO}_x$  and  $\text{SO}_2$ . It is known that these components may react with solvents so that the carbon dioxide absorption capacity decreases and solvent make up is necessary. Therefore also solvent losses have an impact on operating costs.

For carbon dioxide capture by chemisorption especially solvents based on aqueous amine solutions are attractive candidates. Solvents from that class have successfully been used for carbon dioxide capture in various industrial applications for many years. All existing processes for carbon dioxide capture from flue gases are operated with amines. The class of amines is so wide that it offers plenty of opportunities for finding new tailor made solvents for the application studied here, especially if also amine blends are considered.

Even if the search for new solvents is restricted to amines, the selection task is tremendous. The key steps that are described here in some detail are: a) the development and application of a method for comparison of thermodynamic equilibrium data; b) screening tests for assessment of solvent degradation, and c) experiments in a gas-fired absorption-desorption mini plant built in the present project.

### **AMINE BASED SOLVENTS FOR CARBON DIOXIDE CAPTURE**

The group of aqueous amine solutions probably includes the most promising solvents for carbon dioxide capture from flue gases as amines seem to be a good compromise regarding absorption capacity and regenerability. Within this solvent group primary, secondary and tertiary amines can be distinguished. Only primary and secondary amines directly react with carbon dioxide to form carbamates. All amines lead to increased solubility of the acid gas carbon dioxide because they are bases. In general solvent capacity and reaction kinetics are determined by the molecular structure of the solvents. Within a specific solvent group, e.g. ethanolamines, usually it can be found that the overall reaction rates, that determine the overall mass transfer rate, are high for primary amines, somewhat lower for secondary amines and very low for tertiary amines. For the capacity, the opposite tendency is observed, i.e., tertiary amines are most favorable.

In the most important available processes for carbon dioxide post combustion capture, that of Fluor [3], the primary amine monoethanolamine (MEA) is used in an aqueous solution of about 0.3 g/g. That solvent is considered as a baseline against which new solvents have to be compared.

In looking for new solvents, it is especially attractive to combine the advantages of primary/secondary and tertiary amines in blends. Well known solvent blends of this type are activated MDEA solutions. A family of blends of different activator systems with MDEA is known as BASF's aMDEA. Those blends are successfully used in natural gas treatment and synthesis gas production. One example for an activated MDEA solution is an aqueous solution of the tertiary amine methyldiethanolamine (MDEA) which is blended with piperazine (PIP), a cyclic secondary diamine as activator. PIP increases the reaction rate while MDEA provides a high capacity.

### THERMODYNAMIC METHOD FOR SOLVENT SELECTION

Any procedure for solvent selection in an early stage of process development must be applicable using a very limited amount of thermodynamic data and must, therefore, be based on a simple process model. Here, an equilibrium stage model is used both for the absorber and desorber. It is assumed that only carbon dioxide and water take part in the mass transfer, but not the solvent itself due to its low vapor pressure. The solvent/water ratio in the liquid phase as well as the total mole flows of the gas and the liquid are assumed to be constant. Based on these assumptions only by using material balances, the operating lines for the absorber or desorber can be derived as straight lines in the coordinates carbon dioxide partial pressure in the gas phase in dependence of the carbon dioxide loading in a given solvent/water mixture. The operating lines can be determined by an equilibrium stage construction for which only equilibrium curves showing the partial pressure of carbon dioxide above the carbon dioxide loading for absorber and desorber conditions as well as process specifications are needed as input. Although this simplified model is not suitable for process design, the advantage is that it allows a relative comparison of the process behavior of different solvents.

Absorbers for removing carbon dioxide from power plant flue gases operate close to atmospheric pressure at temperatures which are determined by those of the input streams. Low temperatures are normally favorable for absorption, however in chemisorption processes, like the one studied here, elevated absorption temperatures may be desirable due to faster reaction kinetics and therefore enhanced transport into the liquid phase. For a first comparison of different solvents the absorber temperature is assumed to be constant and set to  $T^A = 40^\circ\text{C}$ , an operating temperature typically encountered in scrubbing carbon dioxide with amine solutions. For that temperature, the equilibrium line as described above is needed (absorber equilibrium line).

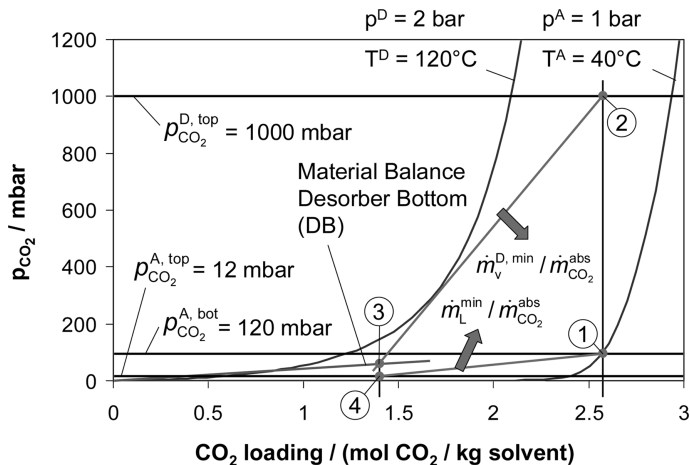
The choice of the operating conditions of the desorber is based on the following considerations: Generally, high desorber temperatures are desirable. However, most of the candidate solvents tend to thermally decompose or degenerate chemically at higher temperatures. Therefore, the maximum allowable temperature in the desorber is limited. For a first comparison, based on experience with different industrially used aqueous amine solvents, the maximum temperature was fixed to  $120^\circ\text{C}$ . As the vapor used for the desorption is generated in a reboiler at the desorber bottom, also the maximum pressure in the desorber is limited. The boiling temperatures of the aqueous solutions of low boiling solvents studied here are generally close to those of pure water. The maximum temperature of  $120^\circ\text{C}$  (in the desorber bottom at low carbon dioxide concentration) corresponds therefore roughly to a pressure of 2 bar. Due to the higher amounts of carbon dioxide in the upper sections of the desorber, the temperature will decrease, typically by about  $10\text{--}20^\circ\text{C}$ . Despite this, for the studies carried out here, a constant temperature of  $T^D = 120^\circ\text{C}$  is used for the desorber equilibrium line.

For comparison of different solvents, boundary conditions have to be defined, so that all solvents are treated in the same way. The purpose of the absorption-desorption process is to remove a specified fraction of the carbon dioxide from flue gases, for which the corresponding boundary conditions may depend on the type of power plant.

The specifications used as an example in the following are: 90% capture from a flue gas containing 0.12 mol/mol carbon dioxide at 1 bar, which is a typical number for coal fired power plants. This results in a reduction of the partial pressure of carbon dioxide in the absorber from  $P_{\text{CO}_2}^{\text{A,bot}} = 120$  mbar to  $P_{\text{CO}_2}^{\text{A,top}} = 12$  mbar. A rough estimate for the partial pressure of the water at the desorber top is used: the vapor pressure of pure water at the estimated temperature of the desorber top:  $p_{\text{W}}^{\text{D,top}} = p_{\text{W}}^{\text{s}}(100^\circ\text{C}) = 1000$  mbar. At a total pressure of 2000 mbar in the desorber this results in a partial pressure of carbon dioxide of  $P_{\text{CO}_2}^{\text{D,top}} = 1000$  mbar. For the scope of a first comparison of different solvents based on a limited amount of data that simple estimate is sufficient.

In the early stages of conceptual process design, it is often useful to study limiting cases. This reduces the number of design variables, so that comparisons of process variants are easier to make. In separation technology, the probably most important limiting case is that of infinite separation capacity, or, in terms of the equilibrium stage model, infinite number of stages. That assumption is adopted here. Then, with the specifications given above, the absorber and desorber operating lines are fully determined. The analysis following the well known ideas of McCabe-Thiele then yields the minimum solvent circulation rate  $\dot{m}_{\text{L}}^{\text{min}} / \dot{m}_{\text{CO}_2}^{\text{abs}}$  which is a measure for the size of key equipment like regeneration heat exchangers and pumps, and the minimum desorption vapor flow rate  $\dot{m}_{\text{V}}^{\text{D,min}} / \dot{m}_{\text{CO}_2}^{\text{abs}}$  which is proportional to the steam flow needed to heat the desorber. These two quantities are used here for a thermodynamic comparison of different solvents.

The method is illustrated in Figure 2 for the example of an aqueous MEA solution with 0.3 g/g MEA. The corresponding equilibrium lines at  $40^\circ\text{C}$  and  $120^\circ\text{C}$



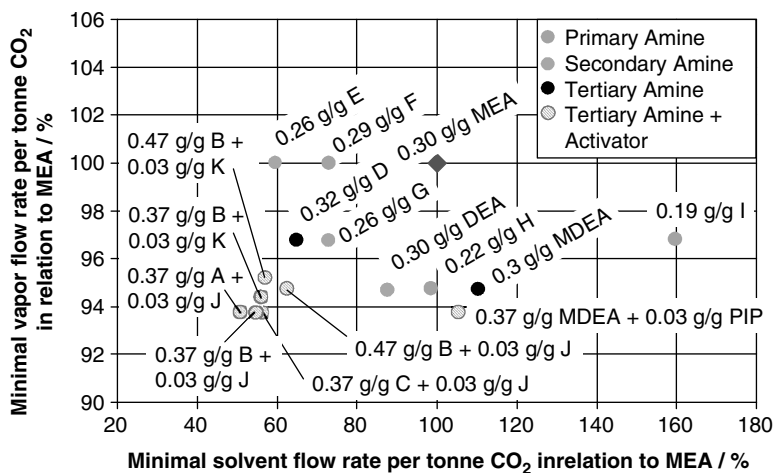
**Figure 2.** Illustration of thermodynamic method for solvent comparison based on the construction of the absorber and desorber operating lines for infinite number of stages

are given in a plot relating the partial pressure of carbon dioxide in the vapor phase to the carbon dioxide loading of the liquid phase in moles of carbon dioxide per kilogram of solvent. Based on the process specifications and the model assumption the operating lines of absorber and desorber are constructed as straight lines in this diagram. Starting with the assumption of equilibrium in the absorber bottom at the carbon dioxide partial pressure in the flue gas, one point of the operating line is known (Point 1). Thus the rich loading of the solvent is also known at the desorber top. Together with the estimated carbon dioxide partial pressure at the desorber top, the operating line is fixed at this point (Point 2). Due to the assumption of infinite number of stages in the desorber, the operating line is the tangent to the equilibrium curve, but the point in the desorber bottom is not yet fixed. A material balance around the desorber bottom shows that the lower end of the desorber operating line must lie on a curve DB. This corresponds to the well known construction of the lower end of the operating line for the stripping sections of distillation columns in the McCabe-Thiele diagram. So Point 3 is fixed and the desorber operating line is known. Therefore the lean loading of the solvent is taken to fix the operating line in the absorber top (Point 4). As result of this construction the slope of the absorber operating line yields the minimum solvent circulation rate  $\dot{m}_L^{\min}/\dot{m}_{\text{CO}_2}^{\text{abs}}$  and the minimum desorption vapor flow rate  $\dot{m}_V^{\text{D},\min}/\dot{m}_{\text{CO}_2}^{\text{abs}}$  can be calculated from the slope of the desorber operating line.

This method described above was applied to MEA and to a list of promising new solvents that were preselected based on general criteria like availability, price, safety and toxicity, and preexisting know how from related processes. From accompanying studies that were carried out in the group of Svendsen at NTNU, Trondheim, Norway [7], and that are not subject of the paper, it is known that all candidate solvents meet the basic demands on reaction rate. Equilibrium data were either calculated with validated models from literature, measured in the present work or supplied by the project partner NTNU, Trondheim [7].

As result a ranking of solvents in relation to the reference solvent monoethanolamine (MEA) is obtained. The minimum vapor flow rate is plotted versus the minimum solvent flow rate both related to MEA in Figure 3 for known solvents like methyldiethanolamine (MDEA), diethanolamine (DEA) and MDEA with Piperazine (PIP) as well as new solvents, details on which presently must remain undisclosed. It can be seen that several primary, secondary and tertiary amines show an improved behavior compared to MEA. But especially blends of tertiary amines with an activator show a high potential for reduction of solvent flow rate and regeneration energy. The absolute numbers for the reduction compared to MEA should not be over-emphasized, neither the small ones for the energy nor the very large ones for the solvent flow rate. The simple method proposed here can not yield correct absolute numbers, it is only suited for a relative ranking of solvents. Much of its charm comes from the fact that it can consistently be applied to many solvents and needs only very limited input data.

Based on these results, the next steps of the solvent selection procedure, namely the stability tests and the mini plant experiments can be carried out with a reduced list



**Figure 3.** Results of thermodynamic method for solvent comparison: ranking of solvent flow rate and desorber vapor flow rate in relation to MEA

of solvents. It is known from screening tests of project partners, that all selected solvent candidates show an acceptable reaction rate.

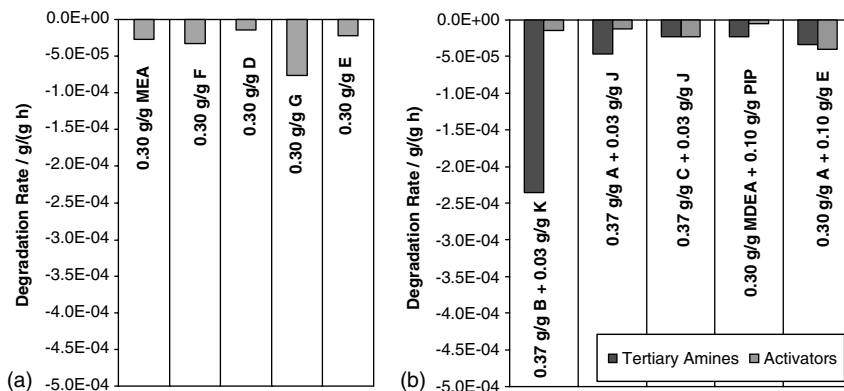
## DEGRADATION

Solvent degradation leads to a decrease of the amine mass fraction and thus to a reduced carbon dioxide removal. Chemical degradation and thermal degradation have to be distinguished. The flue gas in the absorber contains oxygen between 3 and 13 Vol % for different types of power plant. NO<sub>2</sub> and SO<sub>2</sub> are also present in concentrations in the ppm range that depend on the type of fuel and flue gas treatment in the power plant.

Upon the contact with the solvent in the absorber at temperatures of approximately 40°C to 60°C, oxidation of the amines may occur [8]. Furthermore NO<sub>2</sub> and SO<sub>2</sub> react as acid and will lead to solvent degradation by irreversibly blocking basic functions. The products of that process are often referred to as heat stable salts [1, 3]. In the desorber degradation may occur due to the high temperature and the presence of side products or oxygen radicals coming from the absorber.

In practical operation of carbon dioxide post combustion capture plants usually stabilizers are added to the amine solvents to reduce solvent degradation. The development of stabilizers is a challenging task and not addressed here.

Within a solvent selection procedure a quick method for solvent screening for degradation has to be applied. Since the irreversible reaction of the acid gases NO<sub>2</sub> and SO<sub>2</sub> with amine solvents to form heat stable salts is well known [3] and it is expected



**Figure 4.** Results from screening of solvent degradation: degradation rate for primary or secondary amines (a) as well as for amine blends (b) at identical conditions

that the behavior is similar for all amine solvents, the present work focuses on the analysis and the comparison of oxidative degradation for new promising solvents. For experimental analysis, a reactor is used, in which a defined gas stream is bubbled into the thermostated solvent. Solvent loss is avoided by use of an offgas cooler with recycling of condensate to the reactor. Since solvent degradation in the real plant is a long term effect, severe conditions have to be chosen in the laboratory experiments to obtain useful data in short time. The experiments were therefore run at 90°C under atmospheric pressure with a gas composition of 0,4 mol/mol N<sub>2</sub>, 0,3 mol/mol CO<sub>2</sub> and 0,3 mol/mol O<sub>2</sub>. Again all solvents are treated in the same manner with the aim of comparison rather than obtaining useful absolute numbers. Each experiment took two weeks.

For evaluation of solvent degradation, liquid samples were taken each day. The decrease of the amine mass fraction with duration of the experiment was evaluated using GC analysis. Since these results show a linear decrease of the amine mass fraction after some time, the slope of this curve is referred to as degradation rate here. The results are shown in Figure 4 a) for MEA and other primary or secondary amines, and in Figure 4 b) for blends of tertiary amines with an activator. The degradation rate for most studied amines and activators are found to be in a similar range as that of MEA. Only the primary amine G and the tertiary amine B show a much higher degradation rate. Thus, most solvents that are promising based on the thermodynamic comparison discussed above survived the degradation test.

### MINI PLANT EXPERIMENTS

The result of the solvent selection procedure described above is a list of solvents, which seem promising in application for post combustion carbon dioxide capture. In a next





**Figure 5.** Gas-fired mini plant for post combustion carbon dioxide capture at ITT, University of Stuttgart. Left: overall view with gas burner. Right: absorber and desorber

step the process behavior of most interesting candidates is studied in mini plant tests, which are presently under way. For that purpose a mini plant was set up at ITT, University of Stuttgart. The principle flow sheet is identical with the one shown in Figure 1, pictures of the plant can be seen in Figure 5.

The flue gas is produced by a gas burner,  $\text{SO}_2$  and other flue gas components can be added. The flue gas flow rate can be set between approximately 70 kg/h and 150 kg/h, corresponding to a carbon dioxide flow rate of 5–11 kg/h. The solvent flow rate can be chosen between about 50 kg/h to 350 kg/h. A carbon dioxide reduction of 90% in the flue gas can be reached easily with reasonable effort.

Absorber and desorber, including the washing sections, are equipped with the structured packing Mellapak 250 Y (Sulzer Chemtec). The diameter of the columns is 125 mm. The packing height in the absorber is about 4 m, arranged in five sections. The desorber has a packing height of about 2.5 m in three sections. Despite these dimensions, which exceed those of typical laboratory set-ups, we use the term mini plant here, as compared to equipment in power plants, the size of our plant is small. The diameter of the mini plant columns was chosen so, that the results allow a safe scale-up to very large dimensions, due to the similarity of the structured packings employed in both cases. The measurement

and control equipment of the mini plant allows taking all data which are necessary for the process analysis, including, e.g., temperature and liquid concentration profiles along the columns.

For the mini plant operation with different solvents, a high flexibility is provided by the installed equipment. Therefore, the process operation can be optimized by variation of the most important parameters like solvent flow rate or regeneration energy. By the time of the conference, data will be available from the plant operation with MEA and with a new solvent. These results will be discussed and directly compared.

Furthermore, a rate-based physico-chemical model of the process was developed and tested for MEA using the data from the pilot plant. The simulations for the process with the new solvent will be performed after the model is completely parameterized based on new physico-chemical data for that solvent.

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