Optimization of CO$_2$ capture from flue gas with promoted potassium carbonate solutions

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Abstract

The studies aim to develop detergents which show similar reaction kinetics to the reference sorbent 2-aminoethanol (MEA) 30 mass-%. Furthermore the solvent properties and the energy requirement for regeneration can be improved. Apart from the lower desorption enthalpy, it is necessary that the solutions show low corrosiveness, a low vapour pressure, no toxicity and a low degradation rate. These requirements can be achieved by employing carbonate solutions. The challenge is the improvement of the reaction kinetics by using additives which enhance the performance to or above the level of the reference sorbent. In addition to the detergent investigation a detailed understanding of the two-phase system of flue gas and wash solution is required also.

Keywords: Carbonate; Energy demand; Packing height; Mass transfer; Solubility; Enthalpy

1. Introduction

Concerning the potentially increasing prices for CO$_2$ certificates, retrofitting a CO$_2$ capture plant to existing power plants might become an attractive option for power plant operators. This retrofit provokes a loss of efficiency for the power plant. For profitable retrofitting solutions researches still have to achieve a substantial increase of the efficiency of the CO$_2$-capture process [1].
2. Laboratory measurement

For the evaluation and characterization of various sorbents, different laboratory equipments are available. With these experimental setups, it is possible to determine the interaction between CO₂ and the detergents like absorption kinetics, CO₂ solubility and enthalpy of dissolving.

To study the interaction of gas molecules on a geometrically well defined liquid surface a wetted wall column reactor is used [2]. Carbon dioxide is mixed with N₂. Mass flow controllers are used to create a simulated flue gas of defined concentration. The gas is heated up to the preset experimental temperature before entering the wetted wall column reaction chamber. In the chamber the gas counter currently contacts the falling liquid film on the surface of the stainless steel rod. Depending on the experimental parameters, CO₂ is either absorbed or desorbed into the gaseous phase. A continuous and simultaneous documentation of the CO₂ concentration at the entry and exit of the reactor is realized with a FTIR-spectrometer. Out of chemical equilibrium we are mostly able to examine mass- and heat-transfer processes and reaction-kinetics in the phase-boundary and in the condensed phase.

A bubble column reactor [2] is used to determine the thermodynamic equilibria data of the sorbate and sorbent. In this reactor the gas mixture flows through the examined sorbents via a porous glass frit to create the gas bubbles. At the end of the reactor a non-dispersive IR gas analyzer is used to determine the CO₂-concentration after the absorption- or desorption-process. An upstream gas cooler avoids cross-axis sensitivities and disturbances by water vapour. Due to the high surface to volume ratio a sorbent saturation can be reached within a short time and the determination of chemical equilibrium data is possible.

To measure the reaction enthalpy a similar setup is used. By using a dewar as the reactor vessel quasi adiabatic conditions can be achieved. For the determination of the energy balance of the entire reaction system the gas inlet, outlet and the sorbent temperature are measured. By knowing the gas flow rates and heat capacities of all components within the system the heat of CO₂ absorption can be calculated.

All measurements were performed using a large variation of parameters such as temperature, partial pressure, concentration and carbonate/amine ratio.

These studies have shown that potassium carbonate has the greatest potential among the carbonates. The addition of amines to a carbonate solution has the greatest effect on its performance improvement. These solutions combine the fast absorption kinetics of amines and the low desorption enthalpy and the positive solvent properties of carbonates (lower toxicity and corrosiveness). By a widely spread additive screening, the following amines have been found to be most promising.

Table 1, Used additives for the CO₂-capture with carbonates

<table>
<thead>
<tr>
<th>Amine</th>
<th>Code</th>
<th>Amine</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Methylaminoethanol</td>
<td>MAE</td>
<td>Pyrrolidine</td>
<td>Py</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>DETA</td>
<td>Morpholine</td>
<td>MI</td>
</tr>
<tr>
<td>Piperazine</td>
<td>Pz</td>
<td>Meglumine</td>
<td>Mg</td>
</tr>
<tr>
<td>Reference: 2-Aminoethanol</td>
<td></td>
<td>MEA</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1 shows the absorption rates of the unloaded solutions plotted as the mass transfer rate (continuous bars) and the CO₂ absorption capacity (shaded columns) of amine (light grey) and carbonate/amine mixtures (dark grey). For each amine a pure amine solution [1 mole/l] and a carbonate/amine solution in an equimolar ratio [each 1 mole/l] is illustrated. The experiments were carried out at 30 °C and a CO₂ partial pressure of 0.14 bar.

![Absorption Rates](image)

Fig. 1, CO₂ absorption rates and solubility's of amines and carbonate/amine mixtures

It can be seen that piperazine (Pz) and pyrrolidine (Py) demonstrate the highest absorption rate. In comparison with the reference MEA the measured absorption rates of all amine and amine/ potassium carbonate blends, shown in Fig 1, are higher. It should be noted that the interaction between carbonate and amine affects the rate of absorption. Depending on the chemical structure of the amine, the initial absorption rates of the amine/carbonate mixtures (dark grey) are, other than the morpholine/carbonate blend, more or less slightly decreased. Furthermore, the graph clearly demonstrates that the CO₂-capacity can be significantly increased by carbonate presence. Due to the larger amount of reactive substance in the solution more CO₂ can be absorbed.

Another big advantage of carbonates in contrast to the amines is the lower energy requirement for the desorption. Thus with carbonate/amine mixtures it is possible to use the faster absorption kinetic of the amines and the lower desorption enthalpy of the carbonate. Additionally the CO₂-capacity rises when increasing the amount of carbonate. Fig. 2 shows the solvation enthalpies of potassium carbonate and the amine selection when unloaded at 25 °C.
In comparison to the amines potassium carbonate has a significantly lower reaction enthalpy of about 28 kJ/mole. Furthermore you can see that the reaction enthalpies of the examined amines are in the range of about 80 kJ/mole except for pyrrolidine (Py) with a measured desorption energy of more than 100 kJ/mole. Within the amines morpholine (Ml) and meglumine (Mg) show the lowest reaction enthalpies.

The behaviour of the reaction enthalpy as a function of loading is shown in Fig. 3. The dark grey curve presents the enthalpy of a pure piperazine (Pz) [1.0 mole/l] solution. The two gray stepped curves display each one molar carbonate solutions with piperazine adding [0.5 mole/l and 0.8 mole/l]. The measurements were performed at a temperature of 30 °C. For comparison the reference MEA [1.0 mole/l] is illustrated (black discontinuous line).
Fig. 3. Desorption enthalpy depending on the mole fraction

It can be seen that the pure piperazine solution proves a constant enthalpy up to high loadings. MEA presents a similar trend, which decreases earlier at lower CO₂ mole fractions. This is characteristic for pure amine solutions. Compared to the pure MEA solution the carbonate/piperazine mixtures prove lower reaction enthalpies, whereas the enthalpy decreases by decreasing the amine to carbonate ratio. Furthermore, the enthalpy is decreasing at lower CO₂-loadings. This drop can be explained by an increased hydrogen carbonate formation. Since these lower reaction enthalpies are attended by an almost identical absorption rate of the correspondent amine and its concentration, they can be explained by the hydrolysis of the corresponding carbamate. The stronger base CO₃²⁻ hydrolyses the piperazine carbamate forms back to the reactive amine, which results in such a high affinity to CO₂.

3. Up scaling to the industrial process of the CO₂ capture

To characterize the solvents efficiency with various properties, like sorbent structure, concentration and binary compositions, in a technical process, continuative simulations were performed. This model describes the capture process by defined general requirements. The calculations are based on the lab-measured parameters like the chemical equilibrium, the absorption kinetics, the reaction enthalpy and the heat capacity. For the calculations the power plant parameters of the reference power plant NRW [3] were used. The relevant flue gas parameters and other conditions are summarized in Table 2.
Table 2. General requirements of the calculations

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flue gas mass flow</td>
<td>543.7 kg/s</td>
</tr>
<tr>
<td>CO₂-concentration</td>
<td>14.2 vol.-% (58.9 kg/s)</td>
</tr>
<tr>
<td>Separation rate</td>
<td>90 %</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.013 bar</td>
</tr>
</tbody>
</table>

**Absorber parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter</td>
<td>15 m</td>
</tr>
<tr>
<td>Sorbent feed temperature</td>
<td>40 °C</td>
</tr>
<tr>
<td>Sorbent loading</td>
<td>L/G is set that the sorbent get loaded above the work capacity (under conditions)</td>
</tr>
</tbody>
</table>

**Specific surface**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface</td>
<td>250 m²/m³</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.970 m³</td>
</tr>
</tbody>
</table>

The following assumptions for the calculations are to be adopted:

- Flue gas contains only CO₂ as harmful gas component
- Heat exchanges operate without loss
- Saturation in the flue gas is not considered
- No intercooling, no reclaimer provided

With the measured data from the laboratory and the general requirements it is possible to calculate separation rate profiles in the absorber. One can determine the need of reaction surface, which is reflected in the packing height.

Furthermore it is possible to calculate the energy requirement for regeneration $E_{\text{reg}}$. This consists of the sum of the needed heat for the striping vapour $Q_{\text{vap}}$, the desorption $Q_{\Delta H_R}$ and sorbent heating $Q_{\text{heat}}$ [5].

$$ E_{\text{reg}} = Q_{\text{vap}} + Q_{\Delta H_R} + Q_{\text{heat}} $$

(1)

$$ Q_{\text{vap}} = m_{H_{2}O,g} \cdot \Delta H_{\text{vap}} $$

(2)

$$ Q_{\Delta H_R} = \frac{\Delta H_R}{M_{CO_2}} $$

(3)

$$ Q_{\text{heat}} = m_{\text{sorbent}} \cdot \Delta T \cdot c_p,\text{sorbent} $$

(4)

The dependence of the energy demand with the required packing height in the absorber is directly linked to the following values:

Desorber temperature $\rightarrow$ sorbent pre-loading $\rightarrow$ packing height

The desorber temperature determines the degree of regeneration of the washing media. The higher the temperature, the lower the sorbents pre-loading at the absorber feed. A higher temperature requires more
Heat for stripping under isobaric conditions. A lower sorbent pre-loading results in a faster absorption kinetic and thus the required packing height in the absorber decreases. Fig. 4 displays the separation rate profiles in the absorber column for MEA 30 mass-% for three different pre-loadings. The distinct pre-loadings ranging from 0.20 mole/mole to 0.25 mole/mole results from various desorber temperatures at constant atmospheric pressure.

The flue gas and the detergent flow counter currently through the column. Fig. 4 demonstrates that the same separation rate of 90% can be achieved for the three different pre-loadings whereas the required packing height decreases at lower pre-loadings. From the slope of the curves we are able to distinguish between two different absorption kinetics. The fast carbamate formation at the top of the absorber, followed by the slower bicarbonate formation at lower packing heights. The three curves clearly demonstrate that the fraction of carbamate/bicarbonate formation depends on the inserted pre-loadings. Higher pre-loadings are associated with an increased bicarbonate formation.

According to the Fig. 3, the required energy for desorption is a function of the sorbent loading. At lower washing media loadings the energy requirement for the desorption process increases. On the other hand a lower demand of thermal energy for the sorbent heating at identical desorber temperatures is necessary. These relationships are shown in Fig. 5 on the example of MEA 30 mass-%.
The diagram in Fig. 5 displays the energy demand for the total regeneration, including the desorption, the sorbent heating and the stripping vapour as a function of the packing height. The results have been calculated based on the conditions shown in Table 2. It can be seen that the energy demand for the stripping vapour decreases with increasing packing height. Since at lower packing heights, the required preload is lower and the corresponding desorber temperature is higher. At higher temperatures the vapour loss increases because more water vapour is present and dragged by the constant desorber atmospheric pressure.

The energy requirement for desorption decreases slightly with increasing packing height. For smaller sorbent pre-loadings, lesser absorber packing heights are needed. The higher the preloading, the greater is the required formation of bicarbonate in relation to the formation of carbamate to absorb the same amount of CO₂ in the washing media.

Due to the lower reaction enthalpy less energy is required for the regeneration of the bicarbonate. In contrast to the desorption energy demand, the energy demand for heating up the washing media increases for higher levels of the absorber packing. There are two conflicting steps to consider. On the one hand, in the range of lower packing heights, the detergent warming increases, because at low sorbent pre-loadings the more exothermic carbamate formation dominates. On the other hand a higher desorber temperature is needed to achieve these pre-loadings. The sum of both steps is the slight incline of the energy demand with the packing height, which can be observed in the diagram.

The sum of the three components of energy demand represents the total energy requirement for regeneration (black curve). It can be seen that the curve has a minimum. It is located approximately at the absorber packing height of 36 m and a regeneration energy demand of 3.4 GJ/t CO₂. The feasibility of
packed columns of these dimensions is questionable. Realistically packed heights are about than 25
meters. Thus, the energy requirement for a pack of 25 m is 3.9 GJ/t CO₂ for MEA 30 mass-%.

The comparison of the total regeneration energy demand for different carbonate solutions with amines
as additives in comparison to MEA 30 mass-% is shown in Fig. 6. In each case, a lower concentration
(dashed curves) and higher concentrated carbonate/amine solution (continuous curves) are illustrated.

![Energy demand of regeneration for different washing media](image)

Fig. 6, Energy demand of regeneration for different washing media

It can be seen that the various solutions have different flat minima. In contrast to the low concentrated
solutions, the higher concentrated carbonate/amine solutions are able to undercut the regeneration energy
requirement of the 30 % MEA solution. The shape of the carbonate [2.0 M] + Ml [96 mole-%] curve
shows the lowest energy consumption with packing heights up to 30 m. Generally higher concentrated
solutions have the advantage that they can be use at lower L/G ratios due to high molar flux. This means
that less scrubbing solution needs to be heated. Additionally carbonate solutions show low desorption
enthalpies, especially when morpholine (Ml) is used as an additive. Table 3 gives an overview of the
regeneration energy demands for different sorbents at a packing height of 25 m.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Energy demand [GJ/t CO₂]</th>
<th>Sorbent</th>
<th>Energy demand [GJ/t CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate [1.0 M] + Pz [1.0 M]</td>
<td>4.0</td>
<td>Carbonate [1.5 M] + Pz [1.0 M]</td>
<td>3.2</td>
</tr>
<tr>
<td>Carbonate [1.0 M] + Ml [1.0 M]</td>
<td>5.0</td>
<td>Carbonate [2.0 M] + Ml [1.9 M]</td>
<td>3.1</td>
</tr>
<tr>
<td>MEA 30 mass-% [4.9 M]</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The higher concentrated carbonate solutions with amine additives undercut the energy requirement of MEA 30% as displays in Fig. 6, and listed in Table 3. Carbonate [2.0 M] + MI [1.9 M] proves an energy requirement reduced by 0.8 GJ/t CO₂ at a packing height of 25 m compared to MEA 30%. Furthermore carbonates imply the following benefits compared to MEA or other amines:

- Reduced corrosiveness
- Reduced vapour pressure
- Thermal resistance
- No or very low degradation
- Non-toxic

4. Summary

In summary, the results prove that washing media based on carbonates and amine additives are a promising alternative to MEA scrubbing. This optimization of the CO₂ scrubbing requires a by far smaller proportion of amine in comparison to MEA scrubbing. The most significant feature of these solvents is that it is possible to replace a large amount of the previously used amines by carbonates. This carbonate-amine blend method design implies a significantly lower environmental impact comparable to pure amine solutions and in some cases even significantly better performance and lower energy demand than the reference method.
Nomenclature

\[ c_p \] heat capacity \[ \text{[J/kg·K]} \]

DETA diethylenetriamine

\[ \Delta H_R \] reaction enthalpy \[ \text{[J/mole]} \]

\[ \Delta T \] temperature difference \[ \text{[K]} \]

\[ E_{Reg} \] energy demand for regeneration \[ \text{[GJ/t CO}_2] \]

\[ H_{evap} \] evaporation enthalpy \[ \text{[J/kg]} \]

\[ m \] mass \[ \text{[kg]} \]

\[ M \] molarity \[ \text{[mole/l]} \]

\[ M_{CO2} \] molar mass of CO\(_2\) \[ \text{[g/mole]} \]

MAE 2-methylaminoethanole

MEA monoethanolamine

Mg meglumine

Ml morpholine

\[ Q_{HR} \] heat for desorption \[ \text{[GJ/t CO}_2] \]

\[ Q_{heat} \] heat for sorbent heating \[ \text{[GJ/t CO}_2] \]

\[ Q_{vap} \] heat for striping vapour \[ \text{[GJ/t CO}_2] \]

Py pyrrolidine

Pz piperazine

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References
