Chapter 1

Gas Treating Processes

1.1 Treating methods

Acid gases such as carbon dioxide (CO$_2$), hydrogen sulphide (H$_2$S), carbonyl sulphide (COS) and mercaptans (RSH), are often present in industrial gas streams. They have to be removed in large amounts for several reasons:

- **To reduce corrosion**
  The presence of acid components and water may result in severe corrosion of process equipment;

- **To improve plant operation and economy**
  When these gases are present in large amounts, they lower the heating value of the gas or decrease plant or pipeline capacity;

- **For safety and the environment**
  H$_2$S, COS and RSH are toxic components and even small amounts may cause severe health problems. CO$_2$ is an important greenhouse gas and capture and storage of huge amounts of it are required to stop the global warming problem.
The process conditions for these gas treating (or sweetening) processes vary widely. For example flue gas from a coal fired power plant contains 12–15 % CO₂ at atmospheric pressure, while the main component is nitrogen. However, a typical natural gas stream has a high pressures and mainly contains CH₄, while acid components such as CO₂, H₂S, COS and RSH may be present up to 30 % of the whole.

Which kind of gas treating process is used depends on the specifications of the treated gas. These specifications can be determined by environmental regulations (total sulphur specification), the heating value of the gas (CO₂ concentration) or downstream process limitations. Typical specifications of the treated gas for the various applications are given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>H₂S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>2-3 % (v/v)</td>
<td>&lt; 4 ppm</td>
</tr>
<tr>
<td>LNG</td>
<td>&lt; 50 ppm</td>
<td>&lt; 4 ppm</td>
</tr>
<tr>
<td>Syngas (Oxo)</td>
<td>10-100 ppmv</td>
<td>&lt; 1 ppm</td>
</tr>
<tr>
<td>Syngas (ammonia)</td>
<td>&lt; 500 ppmv</td>
<td>-</td>
</tr>
<tr>
<td>Refinery streams</td>
<td>no specifications</td>
<td>4 – 150 ppm</td>
</tr>
<tr>
<td>Tail gas</td>
<td>None</td>
<td>&lt; 250 ppm</td>
</tr>
<tr>
<td>Flue gas</td>
<td>85-95 % removal</td>
<td>-</td>
</tr>
</tbody>
</table>

*Table 1 Typical gas specifications [1]*

The processes which are currently available for the removal of acid gases vary widely. Single wash operations can be used, but also complex multi-step recycle units may be required to meet the requirements. Below an overview of the different gas purification processes is given [2]:

- *Chemical absorption*
  
  The most important process for the removal of acid gases is the chemical absorption in an aqueous alkanolamine solution. In this process the acid gas is contacted with the solvent in an absorber. A reversible reaction takes
place and the solvent is regenerated in a stripper at an elevated temperature or lower pressure. The advantage of this process is the low partial pressure of the acid gas, that can be obtained in the absorber outlet. The main disadvantage is the high energy costs of regeneration. When the total sulphur content is very low and gas outlet concentrations are stringent, a scavenger can be considered as absorption liquid for the removal of sulphur components. The reaction between acid gas and a scavenger is irreversible, so regeneration is not possible. The loaded scavenger can be treated as waste or discharged to sea after treatment;

- **Physical absorption**
  Acid gas absorption in physical solvents (glycols or ethers) is normally used for bulk separation of carbon dioxide and/or hydrogen sulphide, when the acid gas is available at high partial pressure and deep removal is not required. Because no chemical reaction takes place between acid gas and the solvent, regeneration costs are low compared to those of chemical absorption. When the acid gas is available at a partial pressure higher than 15 bar, physical absorption is usually attractive. For acid gas partial pressures lower than 5 bar, chemical absorption tends to be more favourable;

- **Adsorption**
  Adsorption is the process of binding vapor molecules in the pores of a microporous solid. The acid components are concentrated on the solid surface by forces existing at this surface. Forces between the acid gas and adsorbent can be both physical and chemical. Commercial adsorbents mostly use physical adsorption, because they can be regenerated more easily. Molecular sieves based on zeolite structures, are commonly used as adsorbent in gas treating, because they have a high adsorption selectivity for polar components such as \( \text{H}_2\text{O} \), \( \text{CO}_2 \), \( \text{H}_2\text{S} \), \( \text{COS} \) and \( \text{RSH} \). In this way these components can be easily removed from the non-polar components such as \( \text{CH}_4 \) or \( \text{H}_2 \). Adsorption can be a suitable process, where \( \text{H}_2\text{S} \) has to be removed, the total amount of sulphur is very small, and also other...
sulphur components (such as mercaptans (RSH)) have to be removed. Normally, two parallel units are installed, where one unit is in the adsorbing mode and the other in the regeneration mode;

- **Membranes**
  Membrane technology is a new development in the gas treating industry. In a membrane separation process the components are separated by a difference in diffusion rates through a thin polymer barrier. The diffusion rate through the membrane is determined by the component and membrane characteristics and the partial pressure difference of the specific component across the membrane. Membranes are mostly used for bulk separation. However, when multiple stages, recycle streams or a combination with other technologies are used, also high purities are possible. The main disadvantage of membrane units is their tendency to become plugged, so normally a clean feed is required.

The processes described above are the most important unit operations used in gas treating. To combine the advantages also combinations of these processes are used. For example a hybrid solvent, which contains both a physical as a chemical absorbent, can be used for treating of gas streams where acid partial pressures are intermediate. The bulk separation is carried out by the physical absorbent while the deep removal is carried out by the chemical solvent.

### 1.2 Amine treating plant

One of the most common processes in the gas industry is absorption / desorption with an aqueous alkanolamine solution. Alkanolamines are chemicals which contain at least one nitrogen group and one alcohol group. The nitrogen group is responsible for the required alkalinity of the molecule and the alcohol group reduces the vapor pressure, and thus losses in the regenerator are minimised. Alkanolamines are classified by the number of non-hydrogen atoms attached to the
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nitrogen atom in primary, secondary and tertiary amines. In this work MDEA (N-methyldiethanolamine; a tertiary amine) is studied, because this is one of the most commonly used alkanolamines in the gas treating industry. The reaction between CO₂ and aqueous MDEA is relatively slow, compared to the reaction with H₂S. Therefore, this amine is commonly used in processes where H₂S has to be removed selectively from a gas stream containing both CO₂ and H₂S.

In Figure 1 the basic process flow diagram of a typical amine treating plant is shown.

![Gas treating processes](Image)

**Figure 1  Basic process flow diagram of a gas treating plant**

The acid gas stream, enters the absorber at the bottom and is contacted counter-currently with the aqueous alkanolamine solution. The absorber, which can be filled with trays or packing material typically has an operating temperature between 20 and 40 °C. The lower the operating temperature, the higher the acid gas solubility. However, the reaction rate between acid gas and amine decreases with decreasing temperature. For high pressure natural gas treatment, an intermediate flash step can be used to release dissolved hydrocarbons, which are co-absorbed in the absorber. The rich amine solution is flashed and heated in a heat exchanger by lean
solvent from the bottom of the regenerator. The heated rich solvent enters the regenerator at the top of the column. In the regenerator the acid gases are released from the liquid with steam as stripping agent. The lean solution in the stripper is cooled in the heat exchanger with cold rich amine and further cooled before it is sent back to the top of the absorber. The gas that is released in the regenerator is cooled to condense the water. The condensed water is sent back to the stripper; the concentrated acid gas stream can be sent to a Claus unit for sulphur removal or can be prepared for disposal.

1.3 Gas treating fundamentals

For the reliable design of equipment in gas treating plants the following information has to be available:

- Physical, thermal and transport parameters; such as. $k_G$, $k_L$ and $a$. Empirical correlations are available in the literature for these parameters;
- Reaction kinetics;
- Vapor-liquid equilibrium data (VLE).

In Figure 2 the parameters (according the film model) for the driving force in a countercurrent gas-liquid system without chemical reaction are shown:
Gas and liquid resistances are determined by the diffusion coefficients and the film thickness in both phases. In the film model it is assumed that equilibrium exists at the gas-liquid interface. For an acid gas-alkanolamine system, where a chemical reaction takes place in the liquid, mass transfer in the liquid may be enhanced by the chemical reaction. In this thesis the acid gas solubility in the aqueous alkanolamine solution (VLE) is discussed. The acid gas solubility is defined as the relation between the partial pressure acid gas (or more precisely the fugacity) and the concentration of acid gas in the liquid at equilibrium conditions for a specified temperature, pressure and amine liquid concentration. Many experimental VLE data have been reported in the literature at different process conditions. In Figure 3 some VLE data measured by different researchers are presented for the CO₂ solubility in 20 wt. % aqueous DEA.
The scatter in the reported experimental data is large, especially in the low loading regime. All these experimental data can be used for preliminary calculations, but thermodynamic models are required to develop a consistent VLE dataset, to interpolate and extrapolate the data to the required process conditions, and to predict VLE in flowsheet simulation programs.

The driving force for mass transfer as calculated in flowsheet simulators, is usually based on the difference in concentrations between the different phases. However, it has been shown that this approach results in inconsistencies and a more consistent approach is required to predict mass transfer. For example Haubrock [3] has shown that, when the kinetic relation is based on concentrations, the reaction between OH\(^-\) and CO\(_2\) is influenced significantly by the counter-ion, which does not take part of the chemical reaction. However when activities of each species are used (instead of concentrations) a unique activity independent kinetic correlation can be derived.
Therefore rigorous thermodynamic models are required in process simulators and the reaction rates should be based on activities instead of concentrations to make the process design more consistent.

1.4 This thesis

In this thesis the solubility of the acid gases CO₂ and H₂S in aqueous N-methyldiethanolamine is studied experimentally and theoretically. Also the influence of methane (the main component in natural gas) on the acid gas solubility is investigated quantitatively. Experimental solubility data of this system have been determined in a stirred cell and these data were compared with an electrolyte equation of state (E-EOS). This equation is used for both the vapor and the liquid. Below a short outline of the structure of this thesis is presented.

In Chapter 2 a review of the several thermodynamic models, which can be used to predict the acid gas solubilities is presented and discussed. The content of this chapter has been presented during:


In Chapter 3 the solubility of CO₂ in aqueous MDEA is discussed quantitatively. An electrolyte equation of state is developed to predict the solubility of CO₂ in aqueous MDEA. This thermodynamic model has been compared with experimental solubility data from open literature. Also a comparison with the experimental data (CO₂-MDEA-H₂O-CH₄) as presented in appendix A has been carried out. The content of this chapter has been published in:

In Chapter 4 the solubility of H$_2$S in aqueous MDEA is studied. The E-EOS developed in Chapter 3 is further developed to describe the solubility of H$_2$S in aqueous MDEA in the presence of methane. The model is compared with H$_2$S solubility data from open literature (H$_2$S-MDEA-H$_2$O) and from Appendix A of this thesis (for H$_2$S-MDEA-H$_2$O-CH$_4$). The content of this chapter has been published in:


In Chapter 5 the simultaneous absorption of CO$_2$ and H$_2$S in aqueous MDEA is studied. New experimental solubility data of CO$_2$ and H$_2$S in aqueous MDEA are presented at methane pressures up to 69 bar. These experimental data are compared with the E-EOS developed in Chapters 3 and 4. Only one new binary interaction parameter is required to describe the quarternary system CO$_2$-H$_2$S-MDEA-H$_2$O from the ternary systems discussed in Chapters 3 and 4. The content of this chapter has been published in:


In Appendix A several experimental CO$_2$ and H$_2$S solubility data are presented. The influence of the methane partial pressure (up to 69 bar) on the solubility of CO$_2$ and H$_2$S (single gas) in aqueous MDEA is presented. The content of this chapter has been published as:

References


