**Characterization and Modelling of Aerosol Droplet in Absorption Columns**

Hammad Majeeda Hanna Knuutilaa Magne Hillestada Hallvard F. Svendsena\*

aNorwegian University of Science and Technology, Trondheim 7491, Norway

First Author:

Hammad Majeed

Norwegian University of Science and Technology

E-mail address: [hammad.majeed@ntnu.no](mailto:hammad.majeed@ntnu.no)

**Second Author:**

Hanna Knuutila

Norwegian University of Science and Technology

E-mail address: hanna.knuutila@ntnu.no

**Third Author:**

Magne Hillestad

Norwegian University of Science and Technology

E-mail address: magne.hillestad@ntnu.no

**Fourth and Corresponding Author:**

\*Hallvard F. Svendsen

Norwegian University of Science and Technology

E-mail address: [hallvard.svendsen@ntnu.no](mailto:hallvard.svendsen@ntnu.no)

Corresponding author. Tel.: +47-95141784

Characterization and Modelling of Aerosol Droplet in Absorption Columns

Hammad Majeeda Hanna Knuutilaa Magne Hillestada Hallvard F. Svendsena\*

aNorwegian University of Science and Technology, Trondheim 7491, Norway

**Abstract**

Formation of aerosols can cause serious complications in industrial exhaust gas cleaning processes. Small mist droplets and fog formed can normally not be removed in conventional demisting equipmentbecause their submicron size allows the particles or droplets to follow the gas flow (Schaber et al., 2002)*.* As a consequence of this aerosol based emissions in the order of grams per Nm3 have been identified from PCCC plants (Khakharia et al., 2015).

In absorption processes aerosols can be created by spontaneous condensation or desublimation processes in supersaturated gas phases or as a result of droplets or particles entering with the exhaust gas. Undesired aerosol formation may lead to amine emissions many times larger than what would be encountered in a mist free gas phase in PCCC development. It is thus of crucial importance to understand the formation and build-up of these aerosols in order to mitigate the problem.

This paper presents a rigorous model of aerosol dynamics leading to a system of partial differential equations. In order to understand the changes taking place with a particle entering an absorber an implementation of the model is created in Matlab. The model predicts the development in droplet size, droplet internal variable profiles and the mass transfer fluxes as function of position in the absorber, and thus also at the outlet. The Matlab model is based on a subclass method of weighted residuals for boundary value problems named, the orthogonal collocation method.

The model comprises a set of mass transfer equations for transferring components and the necessary diffusion reaction equations to describe the droplet internal profiles for all relevant constituents. Also included is heat transfer across the interface and inside the droplet.

This paper presents results describing the basic simulation tool for the characterization of aerosols formed in CO2 absorption columns and gives examples as to how various entering droplets grow or shrink through an absorber and how their composition changes with respect to position.

**Keywords**: Post combustion CO2 capture, Absorption columns, Aerosol formation, Amine emissions, Internal droplet profiles, Orthogonal collocation method, Simulation

# Introduction

Global climate change is the most prominent environmental and energy policy issue of the current era. Burning of fossil fuels, several industrial processes, and various land use practices are contributing greatly to the accumulation of greenhouse gases (GHGs) and in particular CO2 in the atmosphere.

Carbon capture and storage (CCS) is globally under immense research and development in order to reduce CO2 emission to the atmosphere (Wall, 2007). Post Combustion CO2 Capture (PCCC) by chemical absorption is one of the most developed and promising technologies for capturing the CO2 emitted from large scale fossil fuel based power plants (Abu-Zahra, 2009; MacDowell et al., 2010; Rochelle, 2009; Sanchez-Fernandez et al., 2013)

Monoethanolamine (MEA, 30 wt% aqueous solution) has often been considered as the base solvent for CO2 capture by absorption because of its relatively high capacity, absorption rate and low price (Abu-Zahra et al., 2007; Ahn et al., 2013; Puxty et al., 2009). The entire process is energy demanding and reduces the overall power plant efficiency up to 12 % (Abu Zahra, 2009). There has been an increasing concern about solvent emissions from absorption columns (Mertens et al., 2012). Prevention of amine emissions is also of high importance for the overall sustainability and performance of absorption based Post Combustion CO2 Capture facilities. High amine emissions encountered have partly been attributed to aerosol formation in the absorption columns. The loss of amine solvent leads to higher operating costs as well as affects the environment (IEAGHG, 2010). In a typical PCCC pilot plant, 147 mg/Nm3 of MEA emissions in the treated flue gas stream has been measured based on volatility of amine (Nguyen et al., 2010). In the presence of sulphuric acid aerosols these emissions can increase to 600-1100 mg/Nm3 (Khakharia et al., 2013) and without water wash and demisting equipment, around 3000 mg/Nm3 MEA emissions have been reported (Mertens et al., 2014). BASF, Linde and RWE Power have tested BASF’s innovative, amine-based capture technology at the post-combustion capture pilot plant at Niederaussem and have also tested and amine mitigation system using wet ESP. The campaign results are described in (Moser et al., 2015, 2014) .

Aerosols are systems of particles or droplets suspended in gases. Undesired aerosol formation is a well-known industrial phenomenon in gas–liquid contact devices in which absorption or condensation processes take place. It has been described and explained in various literatures (Ehrig et al., 2002; Neiburger, 1968; Schaber et al., 2002)*.* In gas-liquid contact devices like absorbers, quench coolers, or condensers, aerosols can be formed by spontaneous condensation or desublimation in supersaturated gas-vapour mixtures. Supersaturation is an essential precondition of spontaneous phase transitions and aerosol formation. The degree of saturation S in a multicomponent mixture of an inert carrier gas and condensable vapour components K can be defined by (Gretscher and Schaber, 1999);

Where Px is the actual partial pressure of any vapour component (x = 1,.., K + 1, component K+1 being the inert gas) and Pxs is the equilibrium pressure at the dew point of the vapour mixture.

Supersaturation (S >1) can appear in absorption and condensation processes by two different mechanisms:

* Chemical reactions in the gas phase followed by desublimation of the generated substances. For example the reaction of ammonia with hydrogen chloride can be mentioned.
* Simultaneous heat and mass transfer processes can cause an intersection of the phase equilibrium line by the process trajectory, describing the change of state of the gas phase.

The saturation has to surpass the critical barrier before nucleation and consequently aerosol formation can take place (Schaber et al., 2002).

These aerosol droplets may form before the gas enters the absorber column and may be of various compositions. In order to understand the formation and build-up of these aerosols, to compare with experimental data and to mitigate this problem by better design and operation of gas cleaning equipment, a detailed simulation tool is required that is able to predict aerosol droplet development as function of aerosol droplet characteristics and gas parameters.

This paper focuses on the behaviour of a single aerosol droplet entering an absorber. When modelling aerosol dynamics, governing equations for growth of aerosol droplets lead to a system of partial differential equations which has to be solved numerically. In order to predict the fate of a particle entering an absorber an implementation of the model is created in Matlab. The model predicts the size, the particle internal variable profiles and the mass and heat transfer fluxes as function of position in the absorber, and thus also at the outlet.

The model comprises a set of mass transfer equations for transferring components and the necessary diffusion reaction equations to describe the droplet internal variable profiles for all relevant constituents. Also included is heat transfer across the interface and inside the droplet.

# Modelling

In order to understand aerosol characteristics in absorber columns mechanistic model is required as physical scenarios in gas-liquid contact devices are very complex and detailed explanations are needed to understand results acquired on a more aggregate level.

In order to model the transfer processes between an aerosol and its surrounding gas and liquid phase. The work starts with a single aerosol droplet. In typical CO2 capture absorption columns two streams are flowing counter-currently through the packing with a large interfacial area. The aerosol droplet is moving upwards with the flue gas in the column while amine solution is flowing oppositely as sketched in Figure 1. In the current work it is assumed that mass and heat transfer to and from the aerosol phase does not influence the main gas and liquid flows in the column because of the small aerosol volume. In further development of the model, possible depletion of components in the gas phase will be taken into account. Variation in gas phase component partial pressure and temperature through the absorber leads to transport of components and energy between gas and droplet and also within the aerosol droplet. The modelling used is analogue to the membrane contactor models given in (Hoff et al., 2004, 2002; Hoff and Svendsen, 2014) apart from the geometry which in the droplet case is spherical, and the fact that the droplet changes size. A model on a more aggregate level is presented by (Schaber et al., 2002).

M:\1.tif

Figure 1: Schematic illustration of aerosol phenomena in absorption column

### Mass Balance

The general balance equation in terms of flux for spherical particles (Bird et al., 2002) can be written as;

|  |  |
| --- | --- |
|  | 1 |

WhereCx indicates concentration of any component, Dx denotes diffusivity, rx characterizes reaction rate and r, represent radial, polar and azimuthal angles. Density and diffusivity have been assumed constant.

Considering angular symmetry the general balance equation can be further simplified as;

|  |  |
| --- | --- |
|  | 2 |

Slightly rearranging equation (2) will give;

|  |  |
| --- | --- |
|  | 3 |

Dimensionless equations can reduce the complexity of the problem. These equations provide insight into fundamental scales and represent the behaviour of the dynamic system. In this case only dimensionless radial position, based on the outer radius is introduced:

|  |  |
| --- | --- |
|  | 4 |

Here R is the droplet radius and ξ is the dimensionless internal position. In this case the outer radius varies and any component produced or transported will be distributed over a changing volume. Taking this into account the final equation becomes:

|  |  |
| --- | --- |
|  | 5 |

### Energy Balance

The general energy equation for pure Newtonian fluid in terms of spherical particles (Bird et al., 2002) can be written as;

|  |  |
| --- | --- |
|  | 6 |

Where and Cp indicate density and heat capacity of any component, k denotes thermal conductivity and r, represent radial, polar and azimuthal angles. µ and characterize viscosity and the viscous dissipation function. The term is usually negligible, except in systems with large velocity gradients.

Considering only the radial direction the general balance equation will then be;

|  |  |
| --- | --- |
|  | 7 |

In order to make equation (7) dimensionless in terms of radius.

|  |  |
| --- | --- |
| In order to solve the partial differential equations (5) and (8) initial and boundary conditions are required. As initial condition the concentration and temperature profiles in the droplet are flat, corresponding to equilibrium. Boundary Conditions **Droplet Center**   * At dimensionless radius =0, change in concentration of component will become zero. * At dimensionless radius =0, change in temperature will become zero.   **Interface**   * At dimensionless radius ξ=1, at the gas-droplet interface, the flux on the gas side is equal to the flux on the liquid side for all transferring components; CO2, water and MEA.   Where Dx indicates liquid phase diffusivity of transferring component. kgx is the gas phase mass transfer coefficient and Px and Px\* are the partial pressures of transferring component in the gas phase and at the interface respectively.  The boundary conditions for all ions in the solution are;   * At dimensionless radius =1, heat is transferred both as sensible heat and latent heat. MEA and water are assumed to condense, or evaporate and the heat associated with these processes is assumed released at the interface. CO2 may also carry latent heat as the interface and gas temperatures are normally not the same.     Here k and R are liquid phase thermal conductivity and droplet radius, while h, Ti and Tg denote gas side heat transfer coefficient, temperature at interface and temperature of gas. | 8 |

### Growth of Droplet

The effect of coalescence or breakup of droplets is not considered in this model so the growth of the single aerosol droplet will become quite simple. The rate of change in volume with respect to time is;

|  |  |
| --- | --- |
|  | 9 |

|  |  |
| --- | --- |
|  | 10 |

Where Ntotal represents the total mass flux of transferring components, e.g. amine, CO2 and water. R and represent varying droplet radius and density.

## Modelling Case

As described earlier, Monoethanolamine (MEA, 30 wt% aqueous solution) can be considered as a base amine for CO2 capture by absorption for state of the art PCCC (Abu-Zahra et al., 2007; Ahn et al., 2013; Puxty et al., 2009) and is used as example amine in this work.

### Reaction Mechanism and Kinetics

The following reactions may occur when CO2 absorbs and reacts within an aerosol droplet containing aqueous MEA solution.

Ionization of water

2H2O ⇌ H3O+ + OH-

Hydrolysis of dissolved CO2

CO2 + 2H2O ⇌ HCO3- + H3O+

Dissociation of carbonate ion

HCO3-+ H2O ⇌ CO3 2- + H3O+

Amine Protonation

MEA + H3O+ ⇌ MEAH+ + H2O

Carbamate formation

MEA + H2O + CO2 ⇌ MEACOO- + H3O+

The reaction kinetics for CO2 and aqueous MEA solution can be based on two mechanisms namely the zwitterion mechanism introduced by Danckwerts (Danckwerts, 1979)and the termolecular mechanism introduced by Crooks and Donnellan (Crooks and Donnellan, 1989). In the termolecular or direct mechanism amine reacts with one molecule of a base and one molecule of CO2 at the same time (Crooks and Donnellan, 1989; da Silva and Svendsen, 2007) and is used in this work.

The concentration based rate equation for MEA and CO2 can be written as:

|  |  |
| --- | --- |
|  | 11 |

The kinetic constants are stated with Arrhenius type temperature dependency and the equilibrium reaction constant is expressed in terms of activities as below;

|  |  |
| --- | --- |
|  | 12 |

|  |  |
| --- | --- |
|  | 13 |

|  |  |
| --- | --- |
|  | 14 |

### Kelvin effect

The Kelvin effect is also introduced in this work to understand the change in [vapour pressure](https://en.wikipedia.org/wiki/Vapour_pressure) due to a curved liquid-vapour interface.

The Kelvin equation can be written as (Thomson, 1872);

|  |  |
| --- | --- |
|  | 15 |
|  |  |

Where {\displaystyle p}Px is the actual component vapour pressure, Pxs{\displaystyle p\_{0}} is the [saturation vapour pressure](https://en.wikipedia.org/wiki/Saturated_vapour_pressure),  {\displaystyle \gamma } is the [surface tension](https://en.wikipedia.org/wiki/Surface_tension), {\displaystyle V\_{\text{m}}} V is the [molar volume](https://en.wikipedia.org/wiki/Molar_volume) of the liquid droplet, Rg{\displaystyle R} is the [universal gas constant](https://en.wikipedia.org/wiki/Universal_gas_constant), R{\displaystyle r} is the radius of the droplet, and T{\displaystyle T} is [temperature](https://en.wikipedia.org/wiki/Temperature).

## Solution Methodology

The whole system comprises a set of partial differential equations that needs to be solved by a suitable numerical method. In order to solve these PDE’s a discretized model is created in Matlab. There are three main classes of discretization schemes 1) Finite difference 2) Finite volume 3) Weighted Residual Methods. The areas of application for these techniques have traditionally been different (Hoff and Svendsen, 2014) (Hirsch, 1988). Finite difference methods are used for simple geometry problems formulated in Cartesian co-ordinates, finite volume methods are usually accepted in computational fluid dynamics, whereas weighted residual methods like collocation and spectral methods are well suited for structure problem analysis. This Matlab model is based on a subclass of weighted residuals for boundary value problems named, the orthogonal collocation method.

In one dimensional problem the solution relies on only one position as the radial direction in this work. The unknown exact solution is expanded in a series of known functions, {yi(r)} which are chosen to satisfy as many conditions of the problem as is feasible. The series of these functions is named the trial function.

The unknown coefficents in the series are to be determined in such a way that the differential equation is satisfied in some ‘best’ way. In the collocation method the differential equation is required to be zero at set grid points, named as collocation points. The trial function is substituted into differential equations, resulting in residuals. The residuals will be zero throughout the space for an exact solution (Finlayson, 1974).

The model predicts the droplet size, the droplet internal variable profiles and the mass transfer fluxes as function of position in the absorber, and thus also at the outlet condition.

# Data input

The model description is provided in the previous section. Input data required and characteristics of the absorption column are presented in Table 1.

Table 1: Design parameters for the absorption system selected for this work (Aspen Plus, 2015)

|  |  |
| --- | --- |
| Amine solution (mol/L) | 0.0001M or 5M MEA |
| Temp of liquid at inlet (K) | 314.15 |
| Temp of flue gas at inlet (K) | 313.15 |
| Column height (m) | 15 |
| Packing material | MellaPak 250Y |
| Column Pressure (kPa) | 101.8 |

Literature sources with kinetic data used in this model is tabulated in Table 2.

Table 2: Kinetic data

|  |  |
| --- | --- |
|  | (Luo et al., 2015 2015) |
|  | (Luo et al., 2015) |

The diffusivity of the gases like CO2 and N2O in water or infinite dilute solution can be estimated by the correlation proposed by (Littel et al., 1992)and(Versteeg and Van Swaaij, 1988)*.* The Stokes-Einstein correlation was proposed for the diffusivity of CO2 and alkanolamine in aqueous solutions. Diffusivity data included in this model are presented below in Table 3.

Table 3: Diffusivity data

|  |  |
| --- | --- |
| C = conc. of amine ( mol m-3 ) | (Snijder et al., 1993) |
|  | (Versteeg and Van Swaaij, 1988) |
|  | (Versteeg and Van Swaaij, 1988) |

|  |  |
| --- | --- |
|  | (Geankoplis, 2003) |
|  | (Yuge, 1960) |

Table 4: Mass and Heat transfer coefficients data

# Results and Discussions

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig2.tifAs basis for the droplet behaviour, the absorber column gas phase composition and temperature profiles are needed. For this purpose an ASPEN simulation was performed using ELECNRTL Rate Based MEA model (Aspen Plus, 2015). The flue gas and liquid side temperature and composition changes with respect to position throughout the absorber are shown in Figure 2.

Figure 2: Gas and liquid phase composition and temperature profiles in column

In the droplet model it is considered that the droplet follows the gas phase from bottom to top of the column with a velocity relative to the gas phase given by the droplet terminal velocity. This velocity is very small for typical aerosol droplets. The different cases are modelled as presented in Table 5, by varying droplet size and the initial composition of the droplet to understand the behaviour of droplet inside the column. The model predicts how the varying gas phase and the initial droplet composition and size affect the internal variable profiles and size change of the droplet as a function of position in the column.

Table 5: Modelled Cases

|  |  |
| --- | --- |
| Case 1(validation case) | Droplet, initial radius 0.15μ, containing 0.0001M MEA travelling from bottom to top of column, turning some variables off and on |
| Case 2 | Droplet, initial radius 0.15μ, containing 0.0001M MEA travelling from bottom to top of column (0-15 m) |
| Case 3 | Droplet, initial radius 1.5μ, containing 0.0001M MEA travelling from bottom to top of column (0-15 m) |
| Case 4 | Droplet, initial radius 0.15μ, containing 5M MEA travelling from bottom to top of column (0-15 m) |
| Case 5 | Droplet, initial radius 1.5μ, containing 5M MEA travelling from bottom to top of column (0-15 m) |
| Case 6 | Effect of Kelvin on Case 2 |

In all these six cases that are generated the main focus is on characterisation of the aerosol droplet entering in the system in terms of internal variable profiles, effect of mass transfer and heat transfer on aerosol droplet from surroundings and how the size change of the droplet is affected.

Case 1 is generated for validation purposes in which the legitimacy of the model will be discussed by turning off and on some variables to discuss the effects.

In case 2 to 5 the effect of heat and mass transfer of all transferring components and the full reaction scheme are implemented and also the Kelvin effect is taken into account. In case 6 the Kelvin effect is turned off to see how this affects the results.

## Model validation

No data have been found in the literature that could serve as comparison so the model is validated with cases where functions are turned off and on.

Figure 3: Temperature profiles without heat transfer (Case 1)

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig3.tif

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig4.tif

Figure 4: Droplet size development with and without heat transfer (Case 1)

In Case 1 a droplet with radius 0.15 µ composed of 0.0001M MEA enters the absorber with the same temperature as the inlet gas. Water is the only transferring component and there is no mass transfer of CO2 and MEA and no reaction between CO2 and MEA. As the droplet enters the absorber, the gas composition and temperature are determined by the Aspen simulation as shown in Figure 2. Since the droplet is small, changes take place very rapidly and to show the initial changes with good resolution. Figure 3 and Figure 4 are only integrated over the first 0.2 mm. In Figure 3 the radial coordinate is normalized to the variable droplet radius and this is done in all other figures. It should be noted that these results are for an idealized plug flow model and will not be fully representative for a real absorber where a certain degree of axial mixing will affect the bottom gas phase conditions and make changes even more abrupt than visualized by the model. The results in Figure 3 and Figure 4 are only used to support the validation of the model. Figure 3 shows that because of evaporation of water from the droplet surface, the temperature falls very rapidly. In Figure 3 sensible heat transfer was turned off so no heat was received from the surrounding gas to compensate for heat loss due to evaporation. Turning on sensible heat transfer gave a very similar profile but the droplet temperature levelled out at a higher level and when integrated further into the column (not shown), it would start increasing. The temperature increase was marginal, about 0.1 oC, but still very important. It should be noted that the internal temperature profiles are flat apart from at the very initial stages where a small drop in temperature toward the interface is seen. The effect on size is, however, significant as heat transfer, maintaining a slightly higher interface temperature will lead to more evaporation and a more significant reduction in size, as seen in Figure 4. Both these effects are physically reasonable. When integrating further into the absorber, without heat transfer the particle size remains practically unaltered. This is also reasonable as evaporation or condensation both will affect the temperature, counteracting any change. With sensible heat transfer the particle almost vanishes, evaporates, after only a few centimetres; which is also what is expected. Simulations with a 1.5µ radius droplet gave similar results, but the particle lasted about 30 cm before nearly evaporating.

In order to support the validation further, mass transfer of CO2 and MEA were turned on along with reaction between CO2 and MEA in this case. MEA concentration profiles are plotted in Figure 5 indicating radial profiles as a function of position. The initial droplet consists of 0.0001M MEA with radius 0.15µ entering the absorber at the same temperature as the inlet gas. To show the initial stages the integration is limited to 0.02mm into the column. Profiles start to build up as water evaporates and MEA and CO2 transfer into the droplet. The processes are fast and there is a rapid increase in MEA concentration and radial gradients can be seen from the interface towards the centre of the droplet. Similarly the CO2 concentration profiles are plotted in Figure 6. It is seen that the transport of CO2 is even faster. At the bottom of the absorber the CO2 partial pressure is at its highest thereby giving high driving forces. The liquid phase diffusivity is sufficient to give rapid penetration into the centre of the droplet but weak radial gradients are seen even with a 0.15µ droplet size.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig5.tif

Figure 5: MEA concentration profile (Case 1)

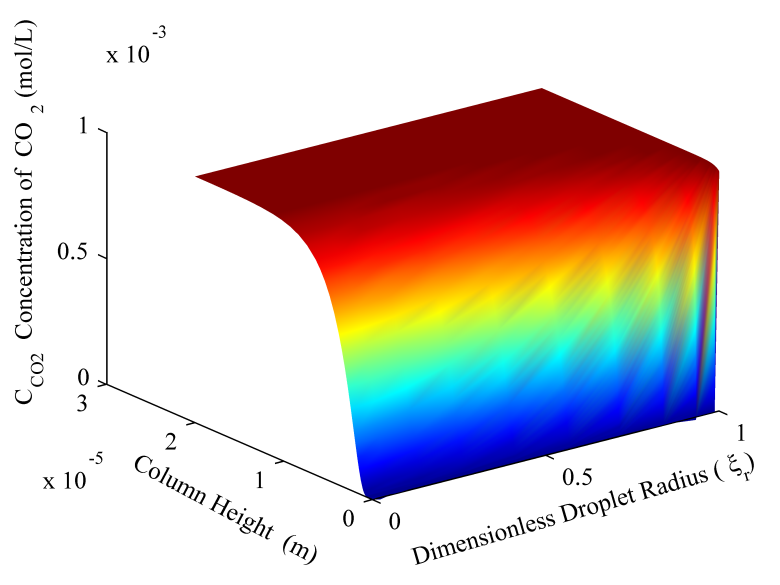


Figure 6: CO2 concentration profile (Case 1)

Water concentration profiles are plotted in Figure 7 and indicate a reduction in concentration with the passage of time because of evaporation. A sharp decrease is observed at the interface when CO2 starts to build up and react with MEA at the interface.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig7.tif

Figure 7: Water concentration profile (Case 1)

## Internal Concentration Profiles

In case 2 an initial aerosol droplet with radius 0.15µ containing 0.0001M MEA is exposed to an atmosphere with changing gas phase composition and temperature as shown in Figure 2.

Predicted MEA concentration profiles are shown in Figure 8. Figure 8a shows that initially, during the first 6 cm of the absorber, the MEA concentration increases rapidly, as also indicated by Case 1. After a few cm the free MEA concentration decreases as CO2 diffuses in and reacts with MEA. Further into the absorber the free MEA concentration rises gradually up to about 2.5 mol/L at the outlet. This is caused by the increasing MEA partial pressure in the absorber gas phase and the outlet free MEA concentration is very close to the inlet lean amine free MEA concentration. A small bulge in the middle section is caused by the combination of the absorber MEA partial pressure and temperature profiles.

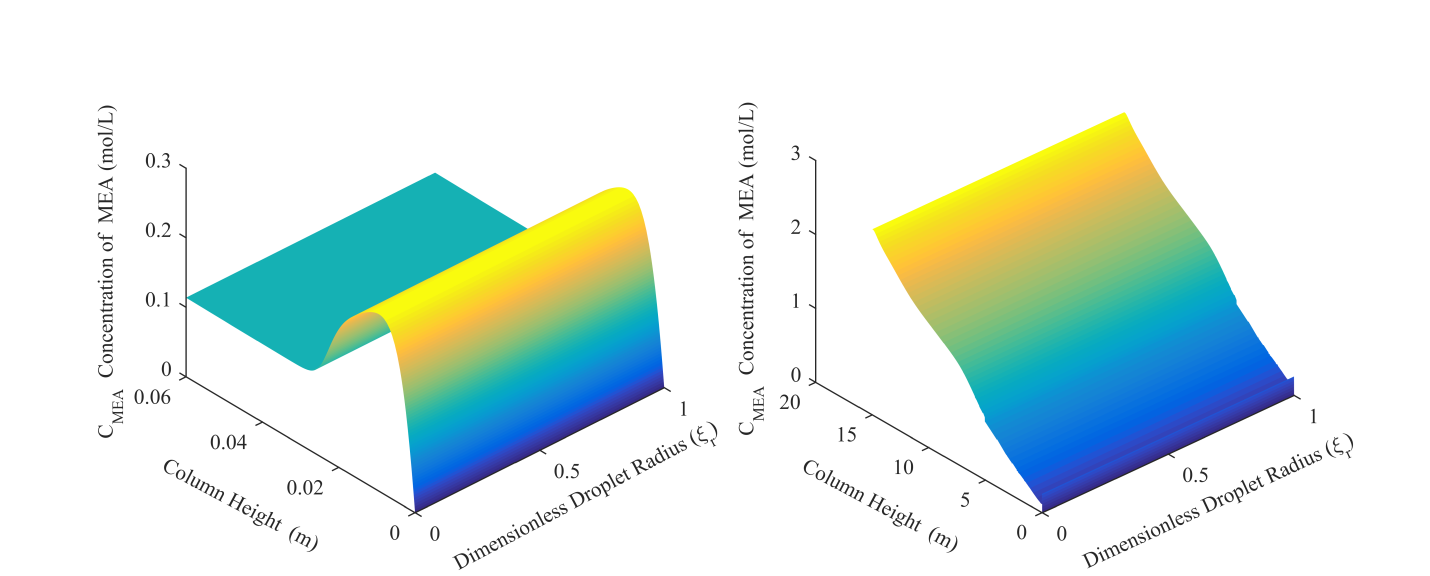


Figure 8: (a) Initial MEA concentration profile (Case 2), (b) MEA concentration profile whole column (Case 2)

The CO2 concentration profiles are shown in Figure 9. The CO2 concentration builds up very rapidly at the absorber bottom, as also indicated in Figure 6. However, rapidly it starts reacting with MEA and the concentration is reduced. As the free MEA concentration and temperature increase upwards in the absorber, and the CO2 partial pressure decreases, the concentration of free CO2 also decreases. The variations in the rate of decrease are caused by combined effects of temperature, free MEA and CO2 partial pressure levels. Toward the column top the CO2 concentration becomes very low. This is a cause of the high free MEA concentration and the low CO2 partial pressure toward the absorber top.

Figure 9: (a) Initial CO2 concentration profile (Case 2), (b) CO2 concentration profile whole column (Case 2)

Figure 10 shows the carbamate concentration profiles. Basically these support the findings from the CO2 and free MEA concentration profiles. As the CO2 and MEA concentrations build up, carbamate starts forming and as MEA and CO2 peak, so does the rate of carbamate formation. It levels off at about 1.5 mol/L, goes up and down as the CO2 and MEA concentrations and the temperature (see Figure 11) vary when moving up in to the absorber.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig10.tif

Figure 10: (a) Initial Carbamate concentration profile (Case 2), (b) Carbamate concentration profile whole column (Case 2)

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig11.tif

Figure 11: Droplet temperature profiles; (a) Case 2, (b) Case 3

In Figure 11 are shown the temperature profiles for Case 2 and Case 3. After the initial rapid temperature drop caused by water evaporation, as shown in Figure 3, the temperature is seen to steadily go up and in practice almost follow the gas phase temperature profile. This is true for all cases.

In conclusion from Case 1 and 2 it is seen that with a 0.15µ droplet the changes are very rapid and after very initial radial gradients in component concentrations, the radial profiles become flat. In addition the concentration levels relatively rapidly become very close to the bulk liquid levels at the same point in the absorber as presented in Figure 2.

It is also seen that the behaviour is complex in the sense that e.g. the carbamate concentration, being a result of temperature and CO2 and free MEA concentrations, does not increase monotonously, but fluctuates as one moves up the absorber.

Case 3 is analogous to that of case 2 except that the initial droplet radius was set to 1.5µ.

The results are shown in Figure 12 and Figure 13.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig12.tif

Figure 12: (a) Initial MEA concentration profile (Case 3), (b) Initial CO2 concentration profile (Case 3), (c) Initial Carbamate concentration profile

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig13.tifFrom Figure 13 we see that the profiles for the full length of the absorber are close to the same as for the 0.15µ droplet. Thus, also for a larger droplet, the concentration levels become close to the levels in the bulk liquid. However, as seen from Figure 12, the changes at the bottom of the absorber are much slower, in fact approximately 10 times slower. This is reasonable as the diameter in Case 3 was 10 times larger, and the diffusional processes have 10 times longer to go.

Figure 13: (a) MEA concentration profile whole column (Case 3), (b) CO2 concentration profile whole column (Case 3), (c) Carbamate concentration profile whole column

In Case 4 the initial MEA concentration was set to 5M MEA. Other conditions were kept

unchanged. The droplet with size 0.15μ containing 5M MEA solution is travelling along the gas phase in absorption column and the internal variable profiles are given in Figure 14.

Figure 14 illustrates that MEA concentration decreases rapidly from the inlet 5 mol/L to a bottom level of about 0.1 mol/L after 5-6 cm. Then it gradually starts increasing again and at the top reaches about 2.5 mol/L. This value is very close to the value reached at the top for case 2 when the initial MEA concentration was 0.0001 mol/L. This supports the earlier findings that the droplet concentrations will reach values close to the bulk liquid values, and this is the case regardless of the initial MEA concentration.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig14.tif

Figure 14: (a) Initial MEA concentration profile (Case 4), (b) MEA concentration profile whole column (Case 4)

The CO2 concentration profiles inside the droplet are shown in Figure 15. Comparing Figure 15b with Figure 9b shows that the conclusion drawn above regarding reaching a concentration level close to the bulk liquid, also holds for CO2. However, comparing Figure 15a and Figure 9a shows that with low initial MEA concentration, the CO2 levels reach initially much higher values than with 5 mol/L initially. This is reasonable because of reaction with the already present MEA.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig15.tif

Figure 15: (a) Initial CO2 concentration profile (Case 4), (b) CO2 concentration profile whole column (Case 4)

The development in carbamate the concentration profile for Case 4 is shown in Figure 16 and can be compared with Figure 10. For the initial phase, the absorber bottom up to 6 cm from the gas inlet, it can be seen that carbamate starts building up immediately with 5 mol/L initial MEA concentration. As soon as CO2 diffuses into the droplet it reacts with MEA. This is in line with the lower CO2 concentrations seen initially in Figure 15a compared to Figure 9a. The final level for carbamate given in Figure 16b is similar to the one shown in Figure 10b and indicates that the initial droplet MEA concentration does not influence the final value in a column of industrial size with droplet retention time about 7.5sM:\Model_MEA_1_journal_algebricversion\journal1figures\fig16.tifec.

Figure 16: (a) Initial Carbamate concentration profile (Case 4), (b) Carbamate concentration profile whole column (Case 4)

Case 5 is similar to Case 4 except the droplet radius is increased to 1.5μ and MEA and carbamate concentration profiles are shown in Figure 17. The final values for free MEA and carbamate are similar to the ones found for the 0.15μ droplet and show that even for this droplet size a retention time of 7.5sec is sufficient to reach close to bulk phase concentration levels.

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig17.tif

Figure 17: (a) MEA concentration profile whole column (Case 5), (b) Carbamate concentration profile whole column (Case 5)

However, as shown in Figure 18, the CO2 profiles are affected by the droplet size. Significant radial gradients are seen initially and concentration gradients close to the gas/liquid interface are seen to prevail all through the absorber.



Figure 18: (a) Initial CO2 concentration profile (Case 5), (b) CO2 concentration profile whole column (Case 5)

## Droplet Size Change

In Figure 19 is shown the droplet size changes taking place in Case 2 and 3 with initial radii 0.15µ and 1.5µ respectively. The results are in reasonable agreement with conclusions from Fulk (Fulk and Rochelle, 2013). In both cases the size decreases initially because of water evaporation and for the smallest droplet radius values reach below 0.04µ before starting to increase again. The increase is caused by increased MEA concentration, reaction with CO2 and subsequent transport of water into the droplet. In both cases water transport out of the droplet takes place at the very top of the absorber because of reduction in temperature and gas phase water and MEA partial pressure.

At the absorber exit the 0.15µ droplet has grown to 2.2µ in radius whereas the initially 1.5µ droplet has grown to about 3.6µ in radius. It is thus clear that the relative growth rate of the small particle is much faster than that of the large particle. This of great practical importance when assessing a possible removal of particle of different initial size after passage through an absorber.



Figure 19: Droplet radius development; (a) Case 2, (b) Case 3

In Figure 20 the same two initial droplet sizes were used but with initial MEA concentration 5mol/L. It is seen, when comparing with Figure 19, that the initial drop in droplet size is not so pronounced. The 0.15µ droplet shrinks to about 0.1µ whereas the 1.5µ droplet hardly shrinks at all. This is because of the reduced evaporation of water caused by the higher initial MEA concentration resulting in reduced water vapour pressure initially. The final droplet sizes are about 2.4µ and 4.5µ respectively and shows that high initial MEA concentration does have an effect but that this effect is not very strong.



Figure 20: Droplet radius development; (a) Case 4, (b) Case 5

## Kelvin Effect on Droplet Size

In all the proceeding cases, Case 1-5, the Kelvin effect was taken into account. Case 6 is a repetition of Case 2 where the Kelvin effect was turned off. Figure 21 shows a comparison between Cases 2 and 6 and also an enlarged picture of the initial size changes. It can be seen that even for an initial droplet size of 0.15µ, the Kelvin effect is relatively weak. The evaporation of water is somewhat stronger when including the Kelvin effect, as expected, but the final radius is only 10% smaller. For the 1.5µ initial droplet size the effect is negligible (not shown). These findings are in line with the conclusions of Imle (Imle et al., 2014).

M:\Model_MEA_1_journal_algebricversion\journal1figures\fig21.tif

Figure 21: Droplet growth with and without kelvin effect (Case 2 and 6)

Conclusively the profiles of all these transferring components and droplet radii in both the cases indicate that model is working reasonably well.

## The Need for a 2D Model

All results in this work are based on a 2D model where inner radial concentration and temperature profiles in the droplets are resolved. As discussed in section 4.2, temperature profiles were found to be flat for all cases studied, also for the initial section of the absorber. In the case of concentration profiles the situation is more complex. For small droplets, in this case 0.15µ in radius, the concentration profiles are for all practical purposes flat except for the very initial part of the absorber, as shown in Figures 8-10. For the larger droplet, here 1.5µ in radius, significant gradients are found as shown in Figure 22 giving the CO2 concentration gradients 1.5m into the absorber for Case 3 and Case 5. In Case 3 the gradients are weak but will still influence both the internal external mass transfer. For Case 5, with initially 5 mol/L of MEA in the droplet, the gradients are strong. This shows that in cases where the inlet droplets contain a reactant which reacts rapidly with CO2, in this case MEA, but other examples could be SO3 or H2SO4 and then there is absolutely a need for a 2D model to capture the mass transfer processes correctly.



Figure 22: CO2 Concentration profiles; (a) Case 3, (b) Case 5

## Heat and Mass Transfer to Droplet

The gas side heat and mass transfer correlations used are given in Table 4 and simple Sh and Nu-number correlations involving the droplet Reynolds number are used. The correlation for mass transfer is strictly for forced convection but as the terminal velocity of the droplets is very low the Re-dependent parts of the correlations become insignificant and one is left with Sh = Nu = 2. This corresponds to a stagnant gas surrounding the droplet. These values are uncertain but lead to gas side mass and heat transfer resistances that are low but still significant. Unfortunately, no good correlations were found for so small droplets under nearly stagnant conditions.

## Comparison with experimental investigations

Although no experimental investigations are available specifically for the droplet internal characterization provided by the model in this work, still work has been done in several test campaigns on mist and aerosol formation where droplet growth in the presence of added nuclei has been studied together with particle number concentrations, and size distributions. One of these experimental investigations (Mertens et al., 2014) reports that aerosol droplets grow in size as they travel through the absorber but no size measurement is reported. This is line with the findings of the current paper and the reason being take-up of MEA and water inside the aerosol droplet is also corroborated.

Mertens et al. (2014) also report that MEA emissions of 3500 mg/Nm3 were measured by FTIR at the absorber outlet and seemed to continue increasing in the absence of water wash or any demisting equipment in mini absorber used with height 3.5m. H2SO4 containing particles were used and they state that the measurements were uncertain. We cannot compare directly with our results. However, considering Case 2, in which a pure water droplet is travelling through the absorber having an initial radius of 0.15 micron, our results, when extended to 106 droplets per cm3, predict around 7000 mg/m3 of MEA at the absorber outlet. It should be kept in mind that the conditions in the current work are not the same as in (Mertens et al., 2014) as the current column height is 15 meters while (Mertens et al., 2014) used a column height of 3.5 meters.

Submicron (<1 µm) particulate matter or H2SO4 aerosols may act as nuclei for the formation of amine aerosols. (Khakharia et al., 2013) expressed that particles in the form of soot (106 droplets per cm3) can cause 200 mg Nm3 of MEA emissions, while H2SO4 aerosols with a particle number concentration in the order of 108 per cm3 can lead to MEA emissions in the range of 600–1100 mg Nm3.

# Conclusions and Future Work

Aerosol based emissions of solvents from PCCC plants need to be understood in detail from both an experimental and modelling approach.

A 2D model has been developed to enable prediction of internal component concentration profiles, size changes and mass and heat transfer to micron scale aerosol droplets passing through an industrial size absorber column. Case studies were performed with two droplet sizes, 0.15µ and 1.5µ initial radius, and with initial MEA concentrations 0.0001 and 5M.

The droplet was found to undergo complicated changes governed by the combined heat and mass transfer into the droplet, the chemical reactions with CO2 and the changing absorber gas phase conditions encountered by the droplet.

Initially the droplet experienced rapid cooling caused by water evaporation but during most of the passage the temperature was governed by rapid sensible heat transfer between gas and droplet and the resulting temperature profiles were similar for all cases tested.

It was found that for both droplet sizes and initial MEA concentrations, the final droplet compositions were close to the same and also close to the composition of the absorber bulk liquid phase at the absorber top. This was the result of a transient approach taking place during the passage through the absorber and caused by the relatively long retention time, 7.5 sec. in the absorber.

For most cases the droplet size was found to decrease in the lower part of the absorber, reach a stable size, and then gradually increase on size. The initial size influenced the final size significantly, as expected, but also the small droplet grew to more than 2.2µ radius as compared to about 4.5µ for the large droplets. The initial MEA concentration did not affect the final size dramatically, only about 10%.

Apart from in the entry zone to the absorber and for the case of a 1.5µ particle with 5M MEA as initial concentration, the internal concentration profiles were found to be relatively flat. Thus, a 1D model may suffice in many cases. However, with fast reacting systems, e.g. MEA or SO3/H2SO4 containing droplets, a 2D model seems necessary to catch the rapid changes taking place.

The Kelvin effect on component partial pressure was found to have effect for the 0.15µ droplet but the effect was not strong.

Due to the lack of studies for small particles, improved mass and heat transfer correlations for micron and submicron droplets should be developed.

The present work cannot be directly compared to existing experimental studies from pilot plants. However, a qualitative comparison indicates that our model gives results in reasonable agreement with the experimental studies. Future work on the model is directed towards implementing possible depletion of components in the gas phase, to study the effect of water wash and sulphuric acid containing aerosols. Also the effect of gas phase CO2 concentration will be studied.

# Acknowledgement

The financial support of, The faculty of Natural Sciences and Technology

Norwegian University of Science and Technology (NTNU), Trondheim, Norway is significantly acknowledged.

# Appendix

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Notation | | | | |
|  |  | **Constants** |  | |
|  |  |  |  | |
| aMEA | Activity coefficient of MEA | KMEA | Kinetic rate constant of MEA (m6 kmol-2 sec-2) |
| aCO2 | Activity coefficient of CO2 | KH2O | Kinetic rate constant of water (m6 kmol-2 sec-2) |
| aMEAH+ | Activity coefficient of MEAH+ | Rg | Gas constant (m3 pa-1 mol-1 K-1) |
| aMEACOO- | Activity coefficient of MEACOO- |  |  |
| Cx | Concentration of any component (mol L-1) | **Greek letters** |  | |
| Cp | Heat capacity (kj kg-1K-1) |  |  | |
| Dx | Diffusivity of any component (m2 sec-1) | 𝝆x | Density of any component (kg m-3) | |
| EMEA | Activation energy of MEA | µ | Viscosity (kg m-1 sec-1) | |
| EH2O | Activation energy of water | Φv | Viscous dissipation function | |
| h | Heat transfer coefficient (kW m-2 K-1) | ξ | Dimensionless droplet radius | |
| kg | Over all mass transfer coefficient (kmol m-2 sec-1 kPa-1) | θ | Polar angle | |
| Nx | Flux of any component (kmol m-2 sec-1) |  | Azimuthal angle | |
| P | Partial pressure (kPa) |  |  | |
| R | Droplet radius (m) | **Indices** |  | |
| rx | Rate of reaction (kmol m-3 sec-1) |  |  | |
| S | Degree of saturation | MEA | Monoethanol amine | |
| t | Time (sec) | MEACOO- | Carbamate | |
| T | Temperature (K) | MEAH+ | Protonated MEA | |
| us | Superficial velocity (m sec-1) |  |  | |
| v | Velocity (m sec-1) |  |  | |

# References

Abu-Zahra, 2009. Carbon dioxide capture from flue gas: development and evaluation of existing and novel process concepts (PhD Thesis). Technical University of Delft, The Netherlands.

Abu-Zahra, M.R.M., Schneiders, L.H.J., Niederer, J.P.M., Feron, P.H.M., Versteeg, G.F., 2007. CO2 capture from power plants: Part I. A parametric study of the technical performance based on monoethanolamine. Int. J. Greenh. Gas Control, 8th International Conference on Greenhouse Gas Control TechnologiesGHGT-8 1, 37–46. doi:10.1016/S1750-5836(06)00007-7

Ahn, H., Luberti, M., Liu, Z., Brandani, S., 2013. Process configuration studies of the amine capture process for coal-fired power plants. Int. J. Greenh. Gas Control 16, 29–40. doi:10.1016/j.ijggc.2013.03.002

Aspen Plus, 2015. ELECNRTL Rate Based Monoethanol amine Model. Aspen Plus.

Bird, R.B., Stewart, W.E., Lightfoot, E.N., 2002. Transport Phenomena, 2nd Edition. ed. John Wilwy & Sons, Inc.

Crooks, J.E., Donnellan, J.P., 1989. Kinetics and mechanism of the reaction between carbon dioxide and amines in aqueous solution. J. Chem. Soc. Perkin Trans. 2 331–333.

da Silva, E.F., Svendsen, H.F., 2007. Computational chemistry study of reactions, equilibrium and kinetics of chemical CO2 absorption. Int. J. Greenh. Gas Control 1, 151–157. doi:10.1016/S1750-5836(07)00022-9

Danckwerts, P.V., 1979. The reaction of CO 2 with ethanolamines. Chem. Eng. Sci. 34, 443–446.

Ehrig, R., Ofenloch, O., Schaber, K., Deuflhard, P., 2002. Modelling and simulation of aerosol formation by heterogeneous nucleation in gas–liquid contact devices. Chem. Eng. Sci. 57, 1151–1163. doi:10.1016/S0009-2509(02)00015-5

Finlayson, B.A., 1974. Orthogonal collocation in chemical engineering. Marcel Dekker Inc.

Fulk, S.M., Rochelle, G.T., 2013. Modeling Aerosols in Amine-based CO2 Capture. Energy Procedia, GHGT-11 Proceedings of the 11th International Conference on Greenhouse Gas Control Technologies, 18-22 November 2012, Kyoto, Japan 37, 1706–1719. doi:10.1016/j.egypro.2013.06.046

Geankoplis, C.J., 2003. Transport Processes and Separation Process Principles, 4 edition. ed. Prentice Hall, Upper Saddle River, NJ.

Gretscher, H., Schaber, K., 1999. Determination of active condensation nuclei for the aerosol formation in absorption and condensation processes. J. Aerosol Sci. 30, S29–S30.

Hirsch, C., 1988. Numerical Computation of Internal and External Flows, Volume 1: Fundamentals of Numerical Discretization. Wiley & Sons, Inc.

Hoff, K.A., Juliussen, O., Falk-Pedersen, O., Svendsen, H.F., 2004. Modeling and Experimental Study of Carbon Dioxide Absorption in Aqueous Alkanolamine Solutions Using a Membrane Contactor. Ind. Eng. Chem. Res. 43, 4908–4921. doi:10.1021/ie034325a

Hoff, K.A., Poplsteinova, J., Jakobsen, H.A., Falk-Pedersen, O., Juliussen, O., Svendsen, H.F., 2002. Modeling of Membrane Reactor. Int. J. Chem. React. Eng. 1. doi:10.2202/1542-6580.1011

Hoff, K.A., Svendsen, H.F., 2014. Membrane contactors for CO2 absorption – Application, modeling and mass transfer effects. Chem. Eng. Sci. 116, 331–341. doi:10.1016/j.ces.2014.05.001

IEAGHG, 2010. Environmental Impacts of Amine Emissions During Post Combustion Capture Workshop.

Imle, M., von Harbou, E., Brachert, L., Schaber, K., Hasse, H., 2014. Predicting supersaturation by rate-based simulations of reactive absorption. Chem. Eng. Sci. 118, 41–49. doi:10.1016/j.ces.2014.07.031

Khakharia, P., Brachert, L., Mertens, J., Anderlohr, C., Huizinga, A., Fernandez, E.S., Schallert, B., Schaber, K., Vlugt, T.J.H., Goetheer, E., 2015. Understanding aerosol based emissions in a Post Combustion CO2 Capture process: Parameter testing and mechanisms. Int. J. Greenh. Gas Control 34, 63–74. doi:10.1016/j.ijggc.2015.01.001

Khakharia, P., Brachert, L., Mertens, J., Huizinga, A., Schallert, B., Schaber, K., Vlugt, T.J.H., Goetheer, E., 2013. Investigation of aerosol based emission of MEA due to sulphuric acid aerosol and soot in a Post Combustion CO2 Capture process. Int. J. Greenh. Gas Control 19, 138–144. doi:10.1016/j.ijggc.2013.08.014

Littel, R.J., Versteeg, G.F., Van Swaaij, W.P., 1992. Solubility and diffusivity data for the absorption of carbonyl sulfide, carbon dioxide, and nitrous oxide in amine solutions. J. Chem. Eng. Data 37, 49–55.

Luo, X., Hartono, A., Hussain, S., F. Svendsen, H., 2015. Mass transfer and kinetics of carbon dioxide absorption into loaded aqueous monoethanolamine solutions. Chem. Eng. Sci. 123, 57–69. doi:10.1016/j.ces.2014.10.013

MacDowell, N., Florin, N., Buchard, A., Hallett, J., Galindo, A., Jackson, G., Adjiman, C.S., Williams, C.K., Shah, N., Fennell, P., 2010. An overview of CO2 capture technologies. Energy Environ. Sci. 3, 1645. doi:10.1039/c004106h

Mertens, J., Brachert, L., Desagher, D., Thielens, M.L., Khakharia, P., Goetheer, E., Schaber, K., 2014. ELPI+ measurements of aerosol growth in an amine absorption column. Int. J. Greenh. Gas Control 23, 44–50. doi:10.1016/j.ijggc.2014.02.002

Mertens, J., Knudsen, J., Thielens, M.-L., Andersen, J., 2012. On-line monitoring and controlling emissions in amine post combustion carbon capture: A field test. Int. J. Greenh. Gas Control 6, 2–11. doi:10.1016/j.ijggc.2011.11.015

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G.A., Stoffregen, T., Richter, T., 2015. The wet electrostatic precipitator as a cause of mist formation—Results from the amine-based post-combustion capture pilot plant at Niederaussem. Int. J. Greenh. Gas Control 41, 229–238. doi:10.1016/j.ijggc.2015.07.010

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G.A., Stoffregen, T., Rösler, F., 2014. Demonstrating Emission Reduction – Results from the Post-combustion Capture Pilot Plant at Niederaussem. Energy Procedia, 12th International Conference on Greenhouse Gas Control Technologies, GHGT-12 63, 902–910. doi:10.1016/j.egypro.2014.11.100

Neiburger, M., 1968. Theory of Fog Condensation. A. G. Amelin. Translated from the second Russian edition (Moscow, 1966, B. V. Deryagin, Ed.) by Z. Lerman. Israel Program for Scientific Translations. Jerusalem; Davey, New York, 1967. xii + 236 pp., illus. $14. Science 160, 61–61. doi:10.1126/science.160.3823.61

Nguyen, T., Hilliard, M., Rochelle, G.T., 2010. Amine volatility in CO2 capture. Int. J. Greenh. Gas Control 4, 707–715. doi:10.1016/j.ijggc.2010.06.003

Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns, R., Maeder, M., Attalla, M., 2009. Carbon dioxide postcombustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. Environ. Sci. Technol. 43, 6427–6433.

Rochelle, G.T., 2009. Amine Scrubbing for CO2 Capture. Science 325, 1652–1654. doi:10.1126/science.1176731

Sanchez-Fernandez, E., Mercader, F. de M., Misiak, K., van der Ham, L., Linders, M., Goetheer, E., 2013. New Process Concepts for CO2 Capture based on Precipitating Amino Acids. Energy Procedia 37, 1160–1171. doi:10.1016/j.egypro.2013.05.213

Schaber, K., Körber, J., Ofenloch, O., Ehrig, R., Deuflhard, P., 2002. Aerosol formation in gas–liquid contact devices—nucleation, growth and particle dynamics. Chem. Eng. Sci. 57, 4345–4356.

Snijder, E.D., te Riele, M.J., Versteeg, G.F., Van Swaaij, W.P.M., 1993. Diffusion coefficients of several aqueous alkanolamine solutions. J. Chem. Eng. Data 38, 475–480.

Thomson, W., 1872. 4. On the Equilibrium of Vapour at a Curved Surface of Liquid. Proc. R. Soc. Edinb. 7, 63–68. doi:10.1017/S0370164600041729

Versteeg, G.F., Van Swaaij, W., 1988. Solubility and diffusivity of acid gases (carbon dioxide, nitrous oxide) in aqueous alkanolamine solutions. J. Chem. Eng. Data 33, 29–34.

Wall, T.F., 2007. Combustion processes for carbon capture. Proc. Combust. Inst. 31, 31–47. doi:10.1016/j.proci.2006.08.123

Yuge, T., 1960. Experiments on Heat Transfer From Spheres Including Combined Natural and Forced Convection. J. Heat Transf. 82(3), 214–220. doi:10.1115/1.3679912