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Report

WP 2 in the project: CCM TQP amine 6 – Validation of simulation models

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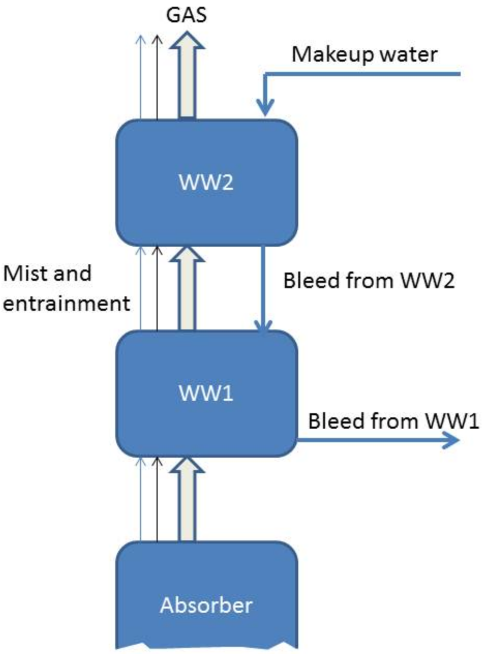

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ABSTRACT

The present report is a result of three different contributions within WP2. The first contribution is about modelling the water-wash unit. Compared to the model used in the first phase of the project the model now includes different temperature levels at different stages and has included a mist stream with the gas phase. The emission tests at Maasvlakte show that mist with high concentrations of MEA is the dominating source of the emission from the absorber column. By using the model to interpret the data from the campaign it is shown that mist particles are saturated with MEA in the absorber section and that the water-wash is only effective for the MEA in gas phase. The second contribution is about validating the gas film resistance used in CO2SIM. The study concludes that this parameter is very sensible in the water-wash section and that resistance was too high in the first CCM study. Also the recycling flow was important. In the third contribution the purpose was to see if the model developed by TNO on Nitrosamines could be confirmed with the experimental data. The conclusion was that more fundamental information is needed in order to improve the model.

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APPENDICES

1 INTRODUCTION

1.1 Background

The CO_2 Capture Mongstad (CCM) project is in an early planning and development phase. The project is, at the moment, organized as a joint project between Gassnova and Statoil. The purpose of the project is to plan and build a large-scale CO_2 capture plant based on amine capture technology.

An amine-based CO_2 capture plant may cause harmful emissions to the atmosphere. Amines and degradation products from reactions in the process and in the atmosphere are of particular concern for the project, but there is limited knowledge about the behaviour of these chemical compounds. Thus, several studies have been initiated by the project to increase this knowledge.

The present project called "Emission reducing technologies, additional work" is a following up project of the work performed by SINTEF in 2010 and documented in the report "Emission Reducing Technologies H&ETQP Amine6" (Kolderup et al., 2010).

The project has been divided into the following 5 work-packages (WP):

- WP1: Quantifying the amine-related gas and liquid phase emissions
- WP2: Validation of simulation model
- WP3: Testing Brownian diffusion demister
- WP4: Identification of other emission reducing technologies
- WP5: HSE

The present report covers the activities in WP2 which makes computer models for emission estimation and validates the model against experimental pilot plant data. These data are obtained and processed as part of the work in WP1 and WP3. The pilot plant used is owned and operated by TNO and it is located at the Maasvlakte coal power plant in Rotterdam. The coal power plant is owned and operated by EON. Prior to the campaign the pilot plant was modified to include a Brownian Demister Unit (BDU).

The experimental part is described in Kolderup et al 2012 and will not be covered in the present report. Only issues that are important for the modelling part will be discussed.

1.2 Structure of report

The report has 3 main contributions, the modelling of water-wash using Matlab (Thor Mejdell, SINTEF), the study of using CO2SIM for water-wash (Geir Haugen and Andrew Tobiesen, SINTEF) and the Matlab model for nitrosamines (P.M. Khakharia, TNO).

2 Matlab model of the water-wash system

2.1 The water-wash system

A water-wash on top of the absorber is the state of the art approach to reduce solvent losses from the leaving gas and keeping the amine emissions to the air as low as possible. In a water-wash section the amine in the gas coming from the absorber is absorbed by the water on the packing material. The water flows from the top of the section and in the bottom it is usually recycled back to the top. A bleed stream is led back to the absorbent liquid system.

The reason for the recycling is that the water balance of the plant does not allow substantial amount of fresh water to be used because any excess water coming into the absorbent must then be removed in the desorber unit by increased reboiler duty which is not energy efficient. In fact, it is very important that the amount of water leaving the absorber wash section with the flue gas is almost equal to the amount of water coming into the absorber with the flue gas. The water balance has only to account for the small amount of water (approx. 1%) leaving with the product CO_2 stream.

Since the packing in the water-wash needs a minimum liquid flow in order to provide wetted surface and good contact between gas and liquid, the water is recycled within the section. The fresh water is there for only a fraction of the total liquid flow. A corresponding bleed stream is taken out from the washing section and led back to the solvent system, keeping the amine loss low. The recycling of liquid in the water-wash also implies that the amine concentrations in the top and the bottom of the section are almost the same. The counter current effect is consequently small and only one single amine/water equilibrium stage is attainable.

Therefore, in order to obtain more stages, several water-wash sections are necessary. In figure 2.1 a two sections water-wash configuration is illustrated. Pure make up water is added to the upper section and a bleed from this section is used as make up in the lower section.

Instead of added make up water one may condense water by cooling down the gas inside the water-wash section. The cooling is provided by heat exchangers in the re-circulation loop (See figure 2.1). Cooling down the gas is generally favourable because the amine solubility in the water increases. However, it may also increase the amount of water and amine on mist particles and thus increase the emissions.

Often a combination of fresh water and condensation is used, and for a certain gas temperature it is the total bleed out of the section that keeps the amine concentration at a low level and keeps the necessary driving forces for amine absorption in the water.

2.2 The gas liquid equilibrium

For low pressure systems the equilibrium vapour pressure of an amine in an aqueous solution is given by the following equation

$$p_{\mathrm{Am}} = \gamma_{\mathrm{Am}} P^{\mathrm{o}}_{\mathrm{Am}} \, x_{\mathrm{Am\_free}} \qquad (2.1)$$

Here $P^{\mathrm{o}}_{\mathrm{Am}}$ is the vapour pressure of pure amine, $x_{\mathrm{Am\_free}}$ the mole fraction of amine in the water in free form, i.e. not reacted with CO_2 or in ionized form, and γ_{Am} is the activity coefficient for the amine in the liquid solution.

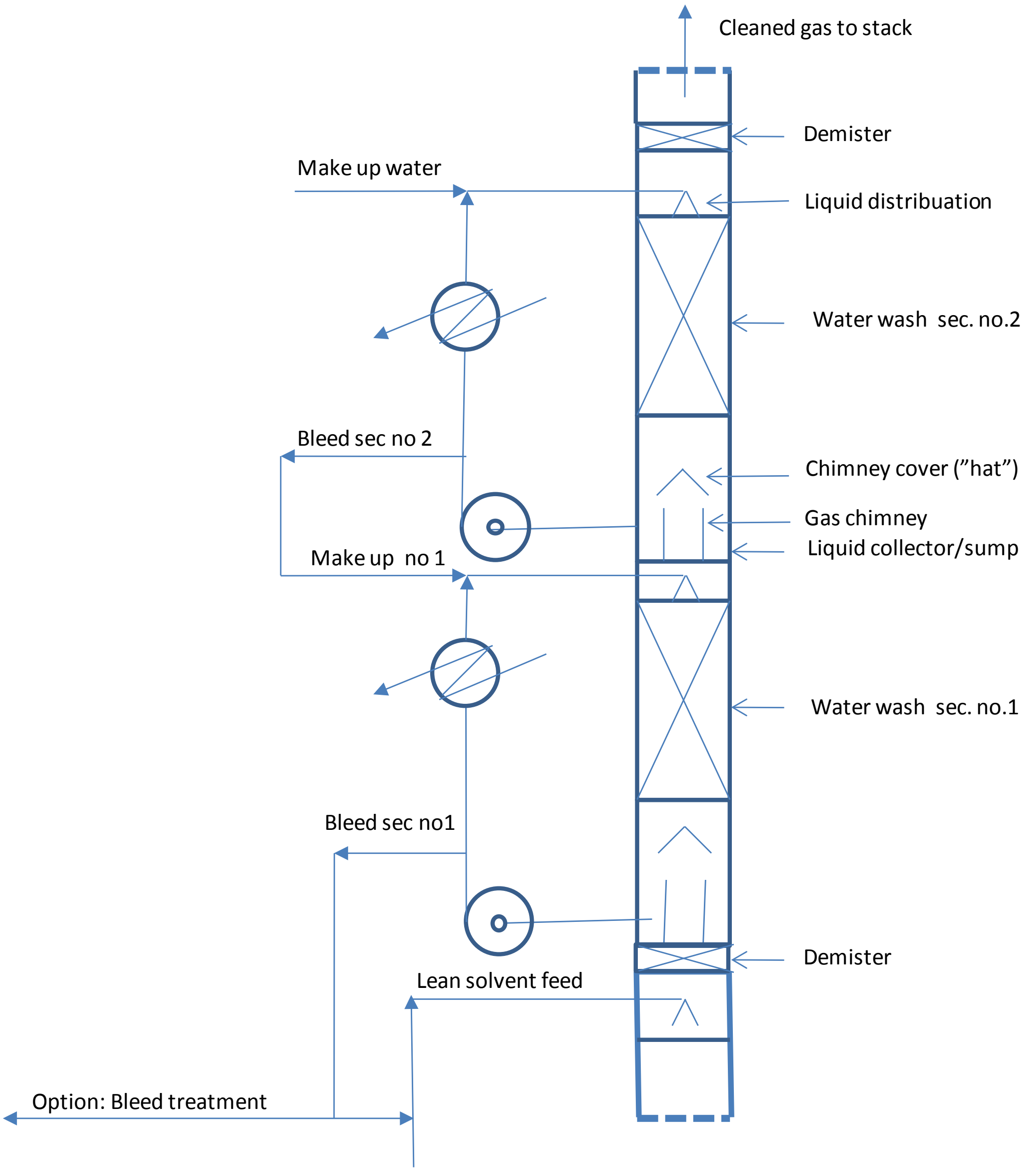


Figure 2.1 Two sections water-wash configuration

The vapour pressure of a pure component is a function of temperature and can be predicted by the following empirical equation:

$$\ln P^{o}_{\mathrm{Am}} = b_1 + b_2 / T + b_3 \ln(T) + b_4 T^{b_5} \qquad (2.2)$$

where P^{o}_{Am} is gas pressure in Pa and T is the temperature in °K.

The activity coefficient γ_{Am} of a component in an aqueous solution depends both on composition and temperature. For a dilute MEA solution, the activity coefficient of MEA is approximately 0.2 at 40 °C and increases to about 0.4 at 100°C. At a constant temperature, higher concentrations of MEA result in higher activity coefficients.

The free MEA is a function of loading. If MEA is the only alkaline compound in the system the reaction with CO_2 will ionize two molecules of MEA:

$$CO_2 + 2MEA = MEAH^+ + MEACOO^- \tag{2.3}$$

Defining the loading α_{MEA} as mole CO_2 reacted with MEA to total amount of MEA, the free MEA may be expressed as

$$x_{MEA\_free} = (1 - 2\alpha_{MEA})x_{MEA} \tag{2.4}$$

where x_{MEA} is the total amount of MEA in the water.

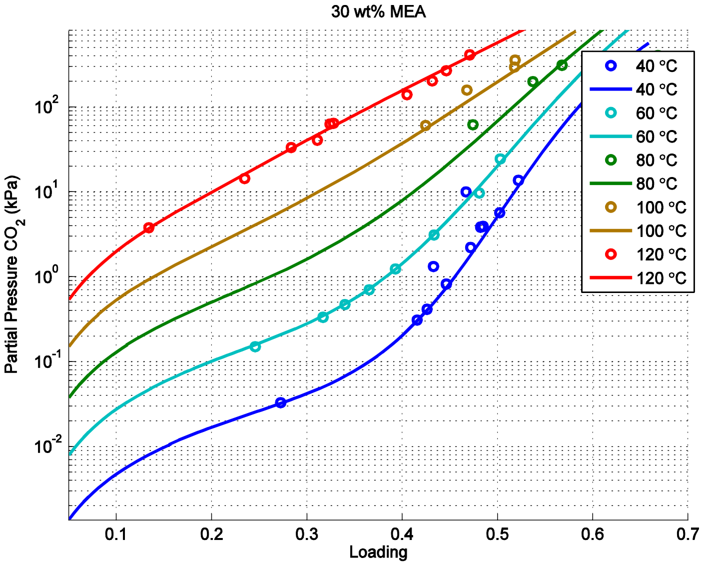


Figure 2.2 Experimental values (circles) compared with the model for various temperatures

The loading α_{MEA} may be fount from experimental equilibrium data relating loading, temperature and partial pressure of CO_2. In Figure 2.2 the partial pressure is shown for different temperatures and loadings for 30 wt% MEA. The data, which is measured in our own lab, has been fitted to a simplified model describing the relationship, i.e.

$$P_{CO_2} = Eq(T, \alpha_{MEA}) \tag{2.4}$$

Knowing the temperature and the partial pressure of CO_2, the loading may be found by iteration. It is important to note that this model obtained at high concentrations of MEA might be somewhat inaccurate applied in water-wash systems with much lower concentrations. The partial pressure of CO_2 in the water-wash section will typically be 0.4 kPa for natural gas exhaust and 1.3 kPa for coal, assuming 90 % CO_2 capture rate.

2.3 Modelling water-wash in Matlab

2.3.1 Model concept

The Matlab model is illustrated in Figure 2.3 for a two stages configuration.

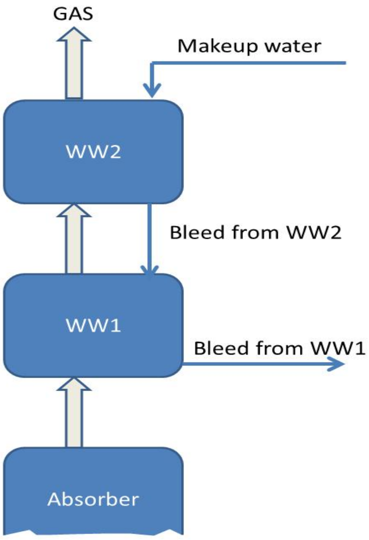


Figure 2.3 Illustration of the model concept.

Due to the high liquid recirculation rates compared to the bleeds the liquid phase is modelled as a continuous stirred tank. The recirculation loops with cooling is a part of the "tank" shown as blue boxes for each stage. On the other hand, the gas phase is modelled as a plug flow through the sections like in a bubble column.

The gas stream and composition from the top of the absorber is input data to the model.

The gas out from the first water-wash stage (WW1) is assumed to be determined by the gas liquid equilibrium (Equation 2.1). However, because the contact time and area between the gas and liquid is limited, the gas leaving the first stage will probably not be completely in equilibrium with the liquid phase. The partial pressure of MEA will then be greater than the equilibrium pressure, and this is modelled with a constant factor f. For a given structured packing section this factor is correlated with the hydrodynamics, i.e. the gas and liquid flows.

The model for the partial pressure of MEA in the gas phase out of a section is then

$$P_{MEA} = f \gamma_{MEA} P_{MEA}^{sat} \left(1 - 2\alpha_{MEA}\right) x_{MEA} \tag{2.5}$$

In the model used in (Kolderup et al, 2010) we used an f-factor of 2.5, but this was based on a very limited amount of experience based on a different plant and solvent.

The Matlab model of the water-wash determines a steady state solution by doing a dynamic simulation of the water-wash. The model starts with pure water in all the water-wash sections and constant liquid flows and a constant gas flow from the CO_2 absorption section. The holdups are artificially and are only used for giving a robust solution. The amines increase in the liquid until steady state where the amount of amine coming into the water-wash system is equal to the amount of amine leaving.

Compared to the model used in Kolderup et al 2010, the model now allows for different temperatures in different sections, but assumes constant temperature within each section. The liquid out of each section will then be the sum of liquid flowing into the section and the amount of condensation. The condensation is based on the difference in saturation temperature of the gas flowing in and out of the section.

2.3.2 Example: 3 stages water-wash unit.

In the following we will demonstrate the model with an example. The temperature in the three sections (section 1 closest to the absorber) is 50, 45 and 40 °C respectively. The amount of make-up water is 4% of the inert flue gas, and the f-factor is set to 2.5. The input gas has an MEA concentration of 330 ppm at 60 °C.

In Figure 2.4 the development of the MEA malefactions are shown from the starting point 1e-10 (pure water) to the end when the steady state has been obtained (2.4e-3, 1.7e-5 and 7e-8). The output gas from each sections contains 0.53, 1.9e-3 and 4e-6 ppm MEA respectively.

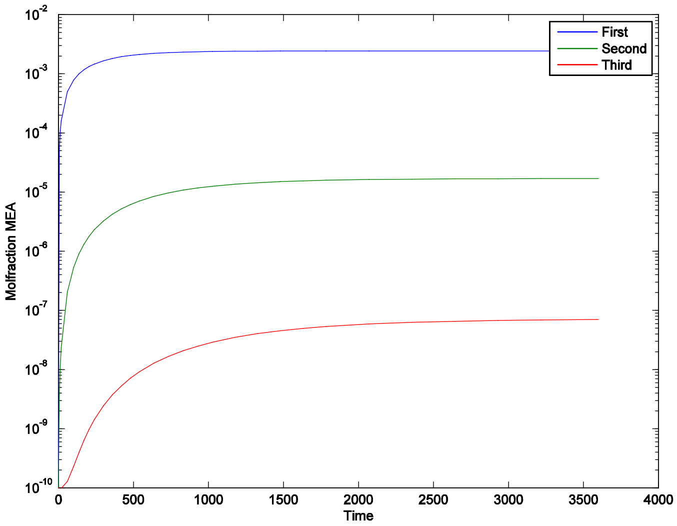


Figure 2.4 Mole fractions of MEA in the liquid.

From the model it should be very simple to reduce the emission to a very low value even though the inlet gas from the absorber contains a substantial amount of MEA.

2.4 Mist and liquid entrainment

Mist is defined as solid and liquid particles less than 10 µm suspended in a gas. The particles are so small that they generally will follow the same flow pattern as the gas. Most of the particles will therefore pass through both the packing sections in the column and the demisters and thus be a direct contribution to the emissions. The mist is usually formed by condensation of water on solids particles (nucleus) in the gas. The solids may have their origin from the power station or the air. Also sulphur acid may origin to mist formation and act as nucleus for condensation (see Kolderup et al, 2012, Table 5-4).

In order to start condensing on small solid particles the gas surrounding the particle must be supersaturated. The smaller particles the higher degree of super saturation is needed. In the absorber locations with super saturation is typically at places with high degree of cooling, like in the top of the absorber where the gas is in contact with a usually cooler lean stream and in the condensing zones in the water-wash section. If intercooling is employed, this will also introduce mist formation.

Liquid entrainment is a result of the forces between the gas flowing upwards and the liquid flowing downwards. The entrained liquid droplets are typically larger than the mist and most of them will be captured by the demisters.

While liquid entrainment has the same composition as the liquid solution itself, mist droplets will only contain substances that is in the surrounding flue gas. Substances in the solvents like ions will not be present in the gas phase and consequently not be in the mist particles.

2.5 Evaluation of the measurements at the Maasvlakte plant.

In this section we will discuss the plant data obtained 4-11 October in Maasvlakte in order to see if there is valuable information that can be used in the Matlab model. Especially, we are looking for data for mist and entrainment, which is very difficult to find in the literature. This work performed in WP1 and WP3 is reported in Kolderup et al 2011.

2.5.1 Test campaign

The main emission results are shown in Table 2.1 and 2.2 taken from Kolderup et al 2012.

Besides the very efficient BDU (Brownian demister unit), one of the most conspicuous results from the Maasvlakte campaign is the very low efficiency of the water-wash. The MEA concentration in the water from the water-wash section is typically around 80 ppm. Compared to other reported results this value is 20-40 times higher. However, the results from the campaign must be evaluated by taking into consideration the special conditions at the pilot plant in Maasvlakte explained in the following.

The pilot plant is treating a flue gas from a coal fired power plant. Compared to a flue gas from natural gas fired power plants like Mongstad this gas has much higher concentrations of CO_2, dust particles and sulphur. The difference in CO_2 concentrations was handled by diluting the flue gas with air. However, the temperature and humidity of the outdoor air was low during the campaign, and since the amount of air to flue gas was about 2:1, this had a large impact on the gas entering the absorber column. A low temperature and humidity in the bottom of the absorber may have an advantageous impact on the CO_2 capture, because the equilibrium conditions then become more favourable. However, it makes it difficult to keep a proper water balance over the plant. This was especially the case at this plant because the only source of fresh water into the water-wash section was condensation. At the top of the absorber one consequently had to cool the gas about 10°C in order to get sufficient fresh water into the wash section. The consequence was that the plant did not keep the water balance, and lost water during the experimental period of time. Long term steady state conditions were then not possible to obtain.

Another unfavourable circumstance was that the water circulation rate in the water-wash was only 20 l/min. With a diameter of 0.65 this gives a specific liquid load of only 3.6 m^3/m^2h. In order to wet the packing properly this should have been around 10 m^3/m^2h. However, this cannot explain the total low efficiency of the water-wash.

The very high level of mist is documented by the catch in the BDU and by particle size distribution measurements. The mist may contain MEA that will not be caught by the water-wash or the demister.

Table 2-1: Gas and aerosol sampling analysis results from the campaign at Maasvlakte. Concentrations of total MEA and liquid aerosols in the gas flow at different sampling points

M = Mol weight MEA	61.08	kg/kmol	ppm = (mg/Nm^3)□V_{NM}/M = (mg/Nm^3(dry)) X(dry)□V_{NM}/M		
V_{NM} = Mol volume	22.414	Nm^3/kmol	X(dry) = Dry gas volume fraction	Mol weight of water 18	
For saturated air at, 30 °C, X(dry) = 0.956				Water cont. 44000 ppm	35,3 g/Nm3

Time of gas sampling by impingers	Date	**2011-10-04**	**2011-10-05**	**2011-10-06**	**2011-10-06**	**2011-10-07**	**2011-10-08**	**2011-10-10**	**2011-10-10**	**2011-10-11**	
	Time Start	10:04	11:27	13:30	19:05	16:52	16:02	12:08	18:04	16:10	
	Stop	13:30	15:12	17:10	21:15	18:46	18:32	16:05	21:05	18:10	
Test number same day		1	1	1	2	1	1	1	2	1	
Average flue gas flow during impinger sampling	Nm^3/h	900	900	920	840	550	850	850	807.5	850	
Temperatures (°C)	Flue gas outlet	32	29	29	32	22	27	33	37	25	
	SP-BDU	35	31	31	31	31	31	35	35	33	**Average**
MEA concentrations (mg/Nm^3 dry gas)	Before WW			**407**	**466**	**213**	**337**	**385**	**460**	**336**	**372**
	After WW									**206**	
	After demister			**241**	**252**	**111**				**272**	**219**
	In BDU	**87**	**129**	**157**	**173**	**86**	**159**	**146**	**177**	**256**	**152**
	Out BDU	**1.18**	**0.97**	**1.15**	**2.10**	**4.37**	**1.27**	**1.89**	**3.95**		**2**
	Condensate collection	**8,4**	**16,6**	**23,9**	**20,9**	**7,9**	**12,7**	**11,3**	**14,8**	**8,8**	**14**
	BDU catch	**58.9**	**112.0**	**134.4**	**245.5**	**34.4**	**147.4**	**140.8**	**188.1**	**161.0**	**136**
Liquid collected in BDU	g/Nm^3 wet	**1.12**	**2.34**	**2.72**	**4.91**	**0.70**	**3.02**	**3.22**	**4.90**	**3.67**	**3.0**
MEA conc. in collected liquid	mmol/l	841	765.5	789	797.5	780	779.5	697.5	613.5	699.5	751
	g/l	51.4	46.8	48.2	48.7	47.6	47.6	42.6	37.5	42.7	46

Table 2-2: Gas and aerosol sampling analysis results from the campaign at Maasvlakte. Concentrations of entrained droplets in the gas flow at different sampling points calculated from tracer experiments.

Time of gas sampling by impingers	Date			**2011-10-08**	**2011-10-10**	**2011-10-10**	**2011-10-11**	**Average**
	Time		Start Stop	16:02 18:32	12:08 16:05	18:04 21:05	16:10 18:10	
Test number same day				1	1	2	1	
Droplet concentration from Li entrainment	mg/Nm3 dry	Before WW	Abs basis	65.0	77.5	91.1	46.2	**69.9**
		After WW	Abs basis				1.9	
		After demister	Abs basis				41.5	
		In BDU	Abs basis	3.2	0.7	1.5	1.3	**1.7**
		Out BDU	Abs basis	3.1	0.6	0.2		**1.3**
Droplet concentration from Rb entrainment	mg/Nm3 dry		WW basis		934.3	1090.2	492.1	**839**
		Before WW	Abs basis		67871.9	4847.2	1069.0	
		After WW	WW basis				54.6	
		After demister	WW basis				0.2	
		In BDU	WW basis			0.4	0.005	
		Out BDU	WW basis			0.1		
Li conc in BDU catch	µg/l			4.8	12.7	18.4	2.8	
Li conc in abs liquid	µg/l			1924	1990	2030	1948	
Entrainment catched by BDU	Liquid entrainment from absorber mg/Nm3 wet			**7.6**	**20.6**	**44.4**	**5.2**	**19.4**
	Rb conc in BDU catch µg/l			0.7	0.9	2.1	1.1	
	Rb conc in WW liquid µg/l			< 0.25	56446	25201	13688	
	Rb conc in abs liquid µg/l			< 0.25	3225	4696	6301	
	Liquid entrainment from WW mg/Nm3 wet				**0.05**	**0.41**	**0.30**	**0.3**
Fog formation catched by BDU g/Nm3 wet				2.971	3.377	4.673	3.721	3.7
Entrainment collected in condensate	Li concentration in condensate µg/l			0.074	0.073	< 0.03	0.14	
	Droplets from absorber mg/Nm3 wet			**0.115**	**0.118**		**0.264**	**0.17**
	Rb concentration in condensate µg/l			< 0.25	0.417	< 0.25	0.4	
	Droplets from WW mg/Nm3 wet				**0.02**		**0.12**	**0.07**

The measurement of tracers shows that entrainment of liquid from the absorber is relatively small, but not insignificant. The Li-tracer measurements show that the amount is about 70 mg/Nm3. With 30% MEA in the liquid this will be about 20 mg MEA /Nm^3, and compared to the total amount of 370 only 5% of the total amount of MEA will enter into the water-wash. In many plants there is a demister before the water-wash making the amount even smaller. Since it is very little found in the BDU catch, this implies that these droplet are quite large and is captured by the water-wash packing and/or the demister above the water-wash.

2.5.2 Liquid analysis

In Table 2.3 the analysis of the MEA concentrations in the water-wash are shown. The results are remarkable constant during the whole campaign. A standard deviation of 11.5% is not large even though the pilot plant was operated quite differently.

Table 2.3 MEA concentrations in the water-wash during the campaign

MEA			
Prøve-ID	**Journal ID**	**MEA**	**Unit**
2011-10-04 LS Test 1 WW	P112452	68.7	mmol/l
2011-10-05 LS Test 1 WW	P112464	74.5	mmol/l
2011-10-06 LS Test 1 WW	P112480	88.3	mmol/l
2011-10-06 LS Test 2 WW tappet 7.10.11	P112496	88.3	mmol/l
2011-10-07 LS Test 1 WW	P112512	82.2	mmol/l
2011-10-08 LS Test 1 WW kl 16:10	P112528	70.7	mmol/l
2011-10-10 LS Test 1 WW sample 1 (Rb) 11:50	P112546	65.7	mmol/l
2011-10-10 LS Test 1 WW sample 2 (Rb) 14:55	P112547	67.9	mmol/l
2011-10-10 LS Test 1 WW sample 3 (Rb) 16:20	P112548	69.9	mmol/l
2011-10-10 LS Test 2 WW	P112567	86.1	mmol/l
2011-10-11 LS Test 1 WW	P112582	83.9	mmol/l
Average		**76.9**	**mmol/l**
Standard deviation		**8.9**	**mmol/l**

In Table 2.4 the concentration of MEA in the collected droplets in the BDU (called BDU catch) is shown. Again the variation during the campaign is quite small with a standard deviation of only 13.9%. It is also remarkable that the concentration in BDU is about 10 times higher compared to the water-wash. It is important to understand why this is the case. Since both mist and water-wash liquid will be able to adsorb the gas phase amine in the water-wash it is interesting to investigate why the mist contains much higher MEA concentrations compared to the water-wash water.

Table 2.4 MEA concentrations in the BDU catch.

MEA			
Prøve-ID	**Journal ID**	**MEA**	**Unit**
2011-10-04 LS Test 1 BDU Catch sample 1	P112447	840.00	mmol/l
2011-10-04 LS Test 1 BDU Catch sample 2	P112448	923.00	mmol/l
2011-10-04 LS Test 1 BDU Catch sample 3	P112449	760.00	mmol/l
2011-10-05 LS Test 1 BDU Catch sample 1	P112459	766.00	mmol/l
2011-10-05 LS Test 1 BDU Catch sample 2	P112460	765.00	mmol/l
2011-10-06 LS Test 1 BDU Catch sample 1	P112475	784.00	mmol/l
2011-10-06 LS Test 1 BDU Catch sample 2	P112476	794.00	mmol/l
2011-10-06 LS Test 2 BDU Catch sample 1	P112491	791.00	mmol/l
2011-10-06 LS Test 2 BDU Catch sample 2	P112492	804.00	mmol/l
2011-10-07 LS Test 1 BDU Catch sample 1	P112507	780.00	mmol/l
2011-10-07 LS Test 1 BDU Catch sample 2	P112508	780.00	mmol/l
2011-10-08 LS Test 1 BDU Catch sample 1	P112523	788.00	mmol/l
2011-10-08 LS Test 1 BDU Catch sample 2	P112524	771.00	mmol/l
2011-10-10 LS Test 1 BDU Catch sample 1	P112541	734.00	mmol/l
2011-10-10 LS Test 1 BDU Catch sample 2	P112542	661.00	mmol/l
2011-10-10 Test 2 BDU Catch sample 1a	P112561	588.00	mmol/l
2011-10-10 LS Test 2 BDU Catch sample 1	P112562	639.00	mmol/l
2011-10-10 LS Test 2 BDU Catch sample 3 100ml 0.1N sulfa	P112564	432.00	mmol/l
2011-10-11 LS Test 1 BDU Catch sample 1	P112577	698.00	mmol/l
2011-10-11 LS Test 1 BDU Catch sample 2	P112578	701.00	mmol/l
Average		**740.0**	**mmol/l**
Standard deviation		**102.8**	**mmol/l**

In Kolderup et al 2012 the mist particle size distribution has been measured. Different techniques have been employed. From the light extinction coefficient the mean Souter diameter during the campaign was 4.3 µm after the water-wash. This implies a total surface of the droplets of about 6-10 m^2/m^3 gas volume. If we base the consideration on the Elpi measurements it will be 10- 20 m^2/m^3. Nevertheless the area is less than 1/10 of the area of the packing material (250 m^2/m^3) if the packing is wetted properly.

This means that the mist cannot compete with the water in the water-wash. The amines must have been absorbed by the mist particles in the absorber column and then rather desorbed in the water-wash. The same conclusion can be drawn from the values in Table 2.5 which shows the amine concentration in the condensate water coming from the pipeline before the BDU. The values are at the same level as the water-wash, meaning that the gas phase concentration of the MEA in the water-wash system is very low compared to the total emission level of MEA.

Table 2.5 MEA concentrations in the BDU catch.

MEA			
Prøve-ID	**Journal ID**	**MEA**	**Unit**
2011-10-04 LS Test 1 Condensate	**P112451**	71.90	**mmol/l**
2011-10-05 LS Test 1 Condensate	**P112463**	106.00	**mmol/l**
2011-10-06 LS Test 1 Condensate	**P112479**	129.00	**mmol/l**
2011-10-06 LS Test 2 Condensate	**P112495**	83.70	**mmol/l**
2011-10-07 LS Test 1 Condensate	**P112511**	47.30	**mmol/l**
2011-10-08 LS Test 1 Condensate	**P112527**	83.00	**mmol/l**
2011-10-10 LS Test 1 Condensate	**P112545**	54.70	**mmol/l**
2011-10-10 LS Test 2 Condensate	**P112566**	49.10	**mmol/l**
2011-10-11 LS Test 1 Condensate	**P112581**	113.00	**mmol/l**
Average		**82.0**	**mmol/l**
Standard deviation		**29.3**	**mmol/l**

2.5.3 Extended emission model

It is clear from the results above that the Matlab model will fail in predicting the emission out of the water-wash since the emissions are dominated by the mist particles. We have therefore tried to include this contribution into the model in some reasonable way. In Figure 2.5 the extended model is shown. In principle both mist and entrainment contribution could have been included, but since the entrainment is very low compared to the mist, only mist is included.

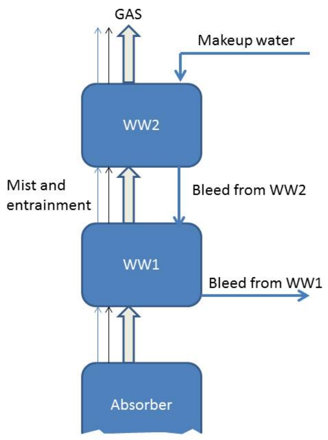


Figure 2.5 Matlab model including droplets in the gas phase

It is not straight forward how to include the mist into the model, and a rigorous way was not possible within the limits of the project. In the present form the amount of mist in the gas is specified together with the outlet concentration of MEA in the mist particles since these two parameters are relatively constant during the campaign.

2.5.4 Using process data for input to the model.

For modelling of emission in the water-wash it is important with accurate data from on-line sensors in the process. A lot of important sensors did not work properly (like flow measurements) and redundancy in the system is not very good. Thus the uncertainties in the data are relatively high.

One of the main parameter in the model is the amount of inert gas through the absorber and water-wash section. While the amount of water and CO_2 in the gas will vary though the column the amount of inert will be constant and thus scale the system in many respects.

There are two locations where the flue gas stream is measured, at the absorber inlet (Tag FT100CF004) and the absorber outlet (FT200CF001). The absorber outlet sensor did not work properly, and then we had to rely on inlet gas measurement. The problem with this location was that the inlet gas was a mixture of two different sources, the flue gas from the pre-scrubber, and the additional air and the specification of these two sources were not clear. In order to calculate the inert gas the amount of water in the inlet gas had to be known.

Since there were no direct measurement of the humidity the following procedure were used for estimation:

It is assumed that the gas from the pre-scrubber is saturated at the liquid temperature into the pre-scrubber (TE100CT002). The humidity of the air is taken from the Royal Netherlands Meteorological Institute. They provide data every hour for the air humidity.

The flow ratio between the two sources was calculated assuming that the amount of CO_2 in the fresh air is insignificant compared to the gas from the pre-scrubber (power plant) and that the concentration of the pre-scrubber gas is 14.45 % on dry basis (value calculated from Table 4-2 in Kolderup et.al. (2012).

Even though the resulting estimation of humidity is not very accurate, the temperature of the gas into the absorber was generally very low, such that the uncertainty should be within 5-10%.

An example of these calculations in Matlab is shown in Appendix 1.

2.6 Results from simulations

In this section we have simulated two runs, the run performed 8th of October and the first run 10th of October. These two runs are evaluated to be the best from an experimental point of view.

The main input to the model is

- amount of inert gas (N2+ O2). This is calculated from the process data as described above.
- percentage of liquid mist relative to the inert gas (estimated from the amount of BDU catch)
- the concentration of MEA in the mist leaving the water-wash section (from Table 2.4)
- Gas temperatures in the top of absorber and in the water-wash.

The results are shown in Table 2.6.

Table 2.6 Simulation of the case 8 and case 10A.

Input variable	Unit	Run 8	Exp.v	Run 10A	Exp.v
Gas stream inert	Nm^3/h	831.5		780	
Molfraction mist	%	0.5		0.5	
MEA in mist out WW	mmol/l	740		740	
Gas temp out of absorber	°C	39.8		46.4	
Tenperature in water wash	°C	26.7		33.2	
Output variable					
Bleed Water out of WW	kmol/h	1.53		2.11	
MEA conc in WW	mmol/l	76.9	70.7	70.1	67.8
Gas phase emmisions	mg/Nm^3	0.03		0.08	
Total emmisions	mg/Nm^3	181.5	159 (167)	179	146 (152)

The amount of bleed water out of the water-wash section is the condensation based on the gas temperatures in and out of the section because no fresh water was supplied. The MEA concentration predicted by the model is very close to the values measured. Also the total emissions are comparable with those measured by the gas sampling before the BDU. The numbers in the brackets are the sum of the BDU catch and the condensate in Table 2.1. Gas phase measurements are always difficult to get completely representative. The liquid concentration measurements are much more reliable, but the amount liquid catch may introduce uncertainty.

This gives a reasonable confidence both for the model and the data measured. An interesting part is that the model predicts very low emission levels of MEA in the gas phase leaving the water-wash. Almost all MEA is within the mist particles. Thus for the gas phase the water-wash is very efficient. In the water-wash section there will be a transport of MEA from the mist droplets to the gas phase and further to the water on the structured packing. A study of these transport mechanisms is necessary in order to build a more predictive model.

2.7 Conclusions

The emission tests at Maasvlakte show that mist with high concentrations of MEA is the dominating source of the emission from the absorber column. Due to the low particle sizes, most of the mist will not be caught by the packing or the demisters, but only by the BDU. The Matlab model, which is based on equilibrium between gas and liquid, had to be modified to cope with this situation.

The two main differences in the present Matlab model compared to the model in Kolderup 2010 are:

1) The temperature may now be specified for each section. This implies also that the bleed stream may differ from one section to another.
2) Inclusion of a mist stream

The simulations showed good accordance with the measured data when specifying amount of mist and MEA concentration in the mist of the water-wash section. The model showed that the gas phase concentration of MEA is very low, and that the MEA in the mist has it origin in the absorber column where the vapour pressure of MEA is substantial higher.

3 Improved performance of the CO2Sim code for water-wash

Although water-wash systems are used for the removal of amine vapour upstream of the absorber packing, there has been little publicly reported modelling work for the purpose of quantitatively determining the performance and to minimize amine losses. Stewart and Lanning (1994) describe 5 categories of amine losses in gas treating units. The method of measuring amine losses was based on an overall mass balance from long term operation of an actual amine plant. They also describe a method based on ideal vapour pressure data using Raoult's law. This approximation may over-or under-estimate the losses. Amine losses can from this method only be roughly estimated and will probably not be accurate at ppm levels. The effect of non-ideal solution thermodynamics as well as effects of CO_2 loading was not considered in any study of the water-wash section.

Another factor, as important as the thermodynamic considerations, is the film resistances to mass transfer, especially the gas film. The correlations used for estimating the mass transfer resistance in the gas film are very important for quantitatively determining amine and water mass transfer and condensation/evaporation. The gas film resistance is less important for estimating CO_2 absorption and desorption since the main resistance is in the liquid film. With the present aim on solvent losses, a new focus on the gas film resistance is therefore necessary.

3.1 Previous work

In a previous report (Kolderup et al 2010) it was indicated that there were significant deviations between expected results compared to modelling results obtained by CO2SIM. The thermodynamic considerations were deemed acceptable (validated e-NRTL model was used) however, the rate at which the driving forces approached equilibrium was found to be slow; indicating that the film model used was inaccurate.

A sensitivity study was therefore performed in order to investigate the effect of the gas film on the amine losses.

3.2 Sensitivity study

A sensitivity study was performed with a water-wash system modelled in CO2SIM for better understanding of the limiting factors in the model. The test water-wash system was based on a simplified 1-stage water-wash of case A1 reported in Kolderup et al., 2010, and a flow diagram of the 1-stage water-wash in CO2SIM is given in Figure 3-1. The case had one water-wash column with 13.2 m diameter and 2 m packing height where a pump recycled 820 tonne/h water cooled to 30 C before entering the top of the column. Six variables/parameters were altered in the sensitivity study. These where the heat transfer and mass transfer coefficient, packing height, recycle rate, water temperature and finally water make-up to the system. In Table 3-1 the test matrix is shown where the cases with low value are designated "low" and vice versa with the high value cases, e.g. the case marked as low for the heat transfer coefficient in Table 3-1 is the base case simulated with 10% of normal heat transfer coefficient relative to base case.

Table 3-1: Test matrix for sensitivity study

	Low	Normal	High
Heat transfer coefficient	10%	100%	1000%
Mass transfer coefficient (gas, Kg)	10%	100%	1000%
Water Temp	20 °C	30 °C	40 °C
Water makeup	0%	2%	10%
Water Flow	50%	100% (820 tonne/hr)	200%
Packing height	50%	100% (2m)	200%

The result from the sensitivity study is shown in Figure 3-2 as a plot of MEA slip (given in PPM) for the different cases. As seen, it was only the water recycle rate that had an impact on the MEA slip among the "manipulated" process variables in the simulations. More cooling or more makeup water had only a minute effect on MEA slip suggesting that the mass transport is not limited by driving forces in the CO2SIM model. The only process variable able to lower the MEA slip was the water recycle rate. The recycle rate used as default in report of (Kolderup et al., 2010) and also as base case in this study, had a liquid load at 6 $m^3/(m^2hr)$ which is quite low for a structured packing. Hence, doubling the recycle rate may be more beneficial due improved wetting of the packing i.e. an increased wetted interfacial area is available for mass transfer and mass flux is proportional to this interfacial area.

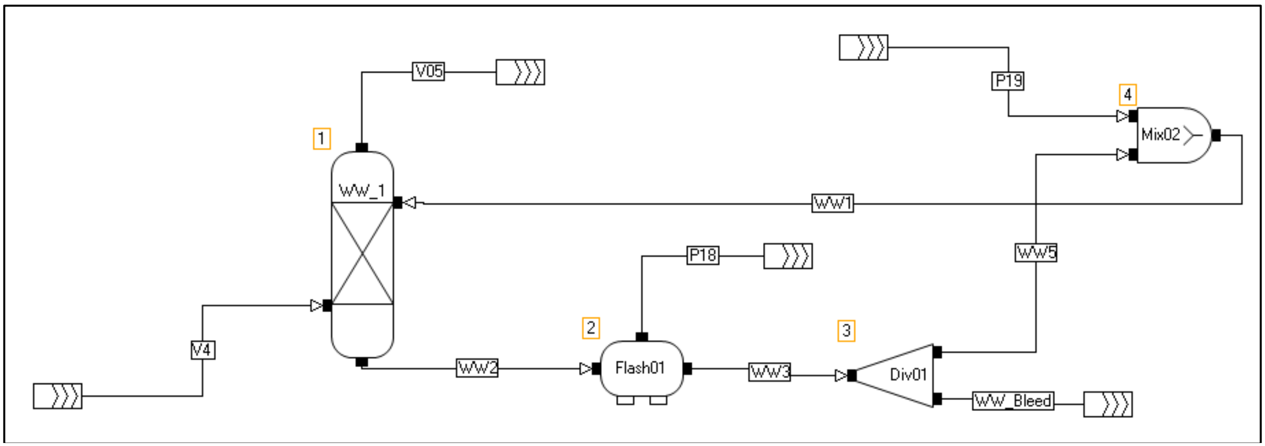


Figure 3-1: Simplified 1-stage water-wash case for sensitivity study (CO2SIM)

Also, the gas mass transfer coefficient and heat transfer coefficient was altered between 10% and 1000% to monitor their influences on MEA slippage. As seen in Figure 3-2, the heat transfer coefficient had only a minute effect on the MEA slip; hence heat transfer is not limiting the MEA mass transfer. The large change in MEA slip with the change in gas side mass transfer coefficient and packing height in Figure 3-2 implies that the MEA slip is limited by the gas mass transfer coefficient. This is further supported in Figure 3-3 where the driving forces are shown to be relative high for the base case. Also, the low sensitivity in water makeup and water cooling suggest that the mass transfer is not limited by the equilibrium relationship, but the resistance (Kg, gas mass transfer coefficient). Increasing the packing area (in Figure 3-2) also had a large effect which is expected when the mass transfer coefficient is the limiting step.

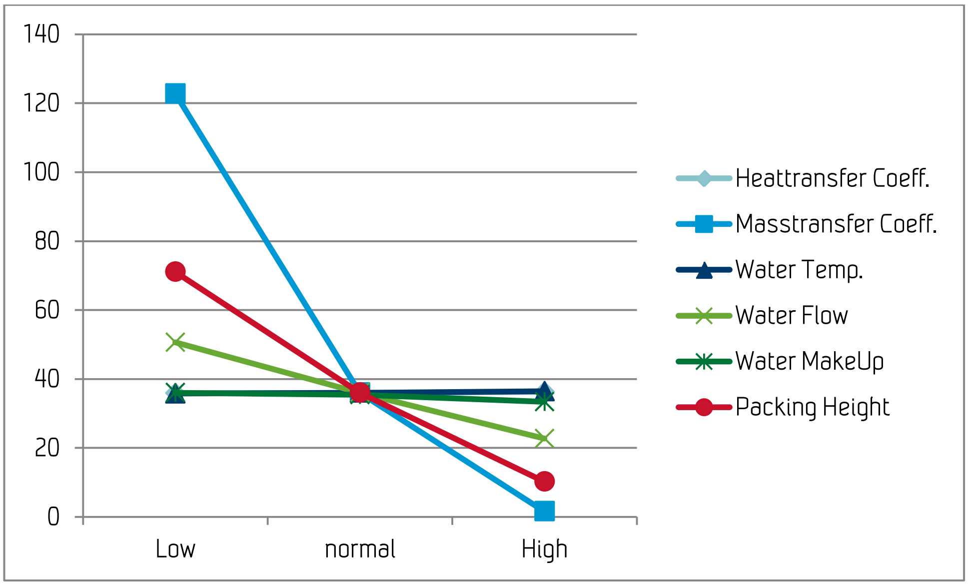
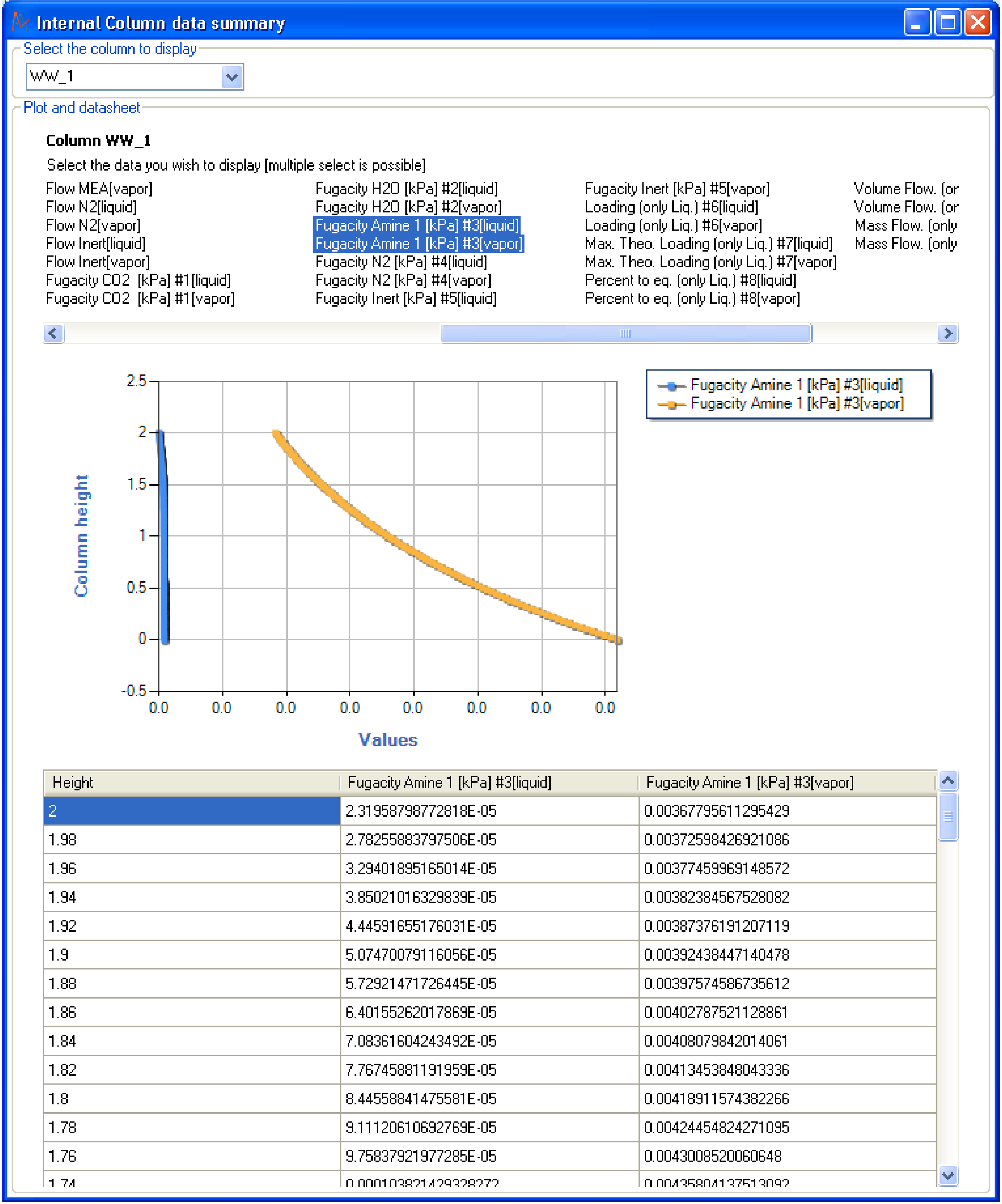


Figure 3-2: MEA slippage in ppm from the sensitivity study

Based on the sensitivity study, one can conclude that the gas mass transfer coefficient was the limited step and improvements in CO2SIM for water-wash should focus on the gas mass transfer, interfacial area and hydraulics correlations for structured packing. However, the liquid load in the water-wash was low in the report by Kolderup et al., 2010 which may explain some part of the high MEA slippage predicted by CO2SIM.



Select the column to display: WW_1

Height	Fugacity Amine 1 [kPa] #3[liquid]	Fugacity Amine 1 [kPa] #3[vapor]
2	2.31958798772818E-05	0.00367795611295429
1.98	2.78255883797506E-05	0.00372598426921086
1.96	3.29401895165014E-05	0.00377459969148572
1.94	3.85021016329839E-05	0.00382384567528082
1.92	4.44591655176031E-05	0.00387376191207119
1.9	5.07470079116056E-05	0.00392438447140478
1.88	5.72921471726445E-05	0.00397574586735612
1.86	6.40155262017869E-05	0.00402787521128861
1.84	7.08361604243492E-05	0.00408079842014061
1.82	7.76745881191959E-05	0.00413453848043336
1.8	8.44558841475581E-05	0.00418911574382266
1.78	9.11120610692769E-05	0.00424454824271095
1.76	9.75837921977285E-05	0.0043008520060648
1.74	0.000103821429328272	0.00435804137513092

Figure 3-3: CO2SIM screenshot of driving forces in water-wash column (base case)

3.3 Mass transfer correlations in CO2SIM

Based on the findings in the sensitivity study above, it was concluded that the gas mass transfer coefficient was the limited step. In
Figure 3-4 show the MEA slippage for the same simulations case in previous section but with different gas mass transfer correlations. As seen in
Figure 3-4, there are large differences in predicted MEA slip for the different models. The model from (Billet 1995) predicts the lowest slip(<2 ppm) while the proprietary default model in CO2SIM predicts the highest slip. The model 2 in CO2SIM is based on (Rocha et al 1996) and predicts almost similar MEA slip. Hence, good models for gas mass transfer resistance is required for accurate prediction of MEA slip. Though, most of the models are empirical and based on dimensional analysis. Also, hydraulic phenomena as entrainment of liquid or mist can play a major role in MEA slip considering the extreme low concentration in the gas.

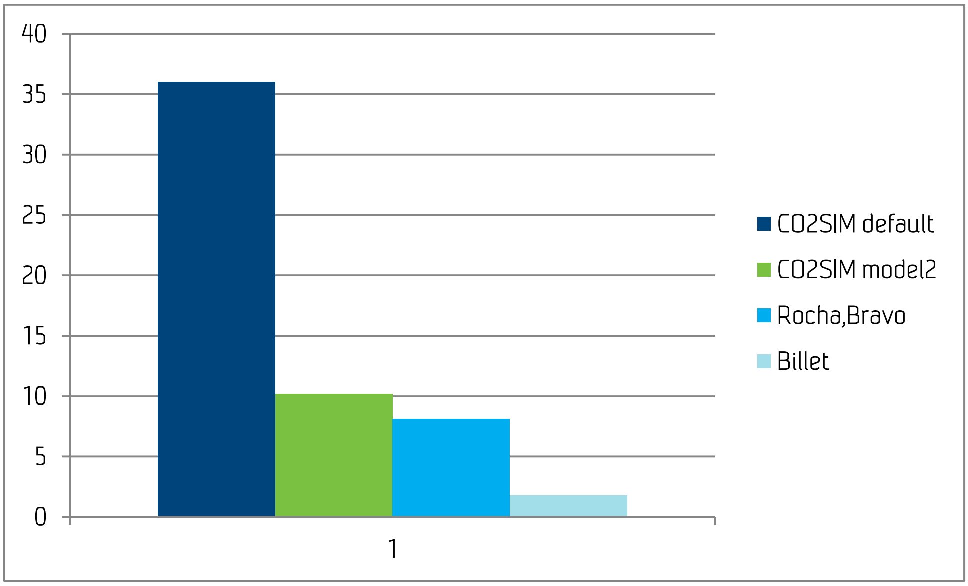


Figure 3-4: MEA slippage in PPM for different mass transfer correlations

3.4 Re-simulation of water-wash case

Kolderup et al., 2010 presented a water-wash case as "Case AA1" (see Figure 3-5) with simulation results. Based on the large differences between the simplified water-wash model and CO2SIM, it was decided to re-simulate the case with improved liquid load (2x) in the water-wash and with the "Rocha,Bravo" sub-model enabled. This also gave an opportunity to recheck the implemented gas film resistance models in CO2SIM. Initially, the liquid load in the water-wash was set equal to the liquid load in the amine scrubber in Kolderup et al., 2010 which in retrospect was too low for the water-wash scrubbers. The liquid load was 6 $m^3/(m^2hr)$ which is also quite low for a structured packing.

Table 3-2: Simulated MEA slippage for Case AA1

	(Kolderup et al., 2010)	This study
Outlet stream	**MEA slippage (ppmv)**	**MEA slippage (ppmv)**
V4	155.5	165
V05	9.5	3.0

V06	0.6	0.05

Hence, doubling the recycle rate may be more beneficial due improved wetting of the packing i.e. an increased wetted interfacial area is available for mass transfer and reduced MEA slippage.

As seen in Table 3-2, the washing efficiency increased significantly with these changes and shows an improvement of 90% regarding MEA slip (last stage) compared to the first simulations. Most of the improvements are related to the higher liquid load though there are many correlated effects as increased cooling and water condensation etc. However, based on the sensitivity analysis in Figure 3-2, insufficient wetting of the packing due low liquid load are the most plausible explanation of the subpar performance of the water-wash system in Kolderup et al., 2010.

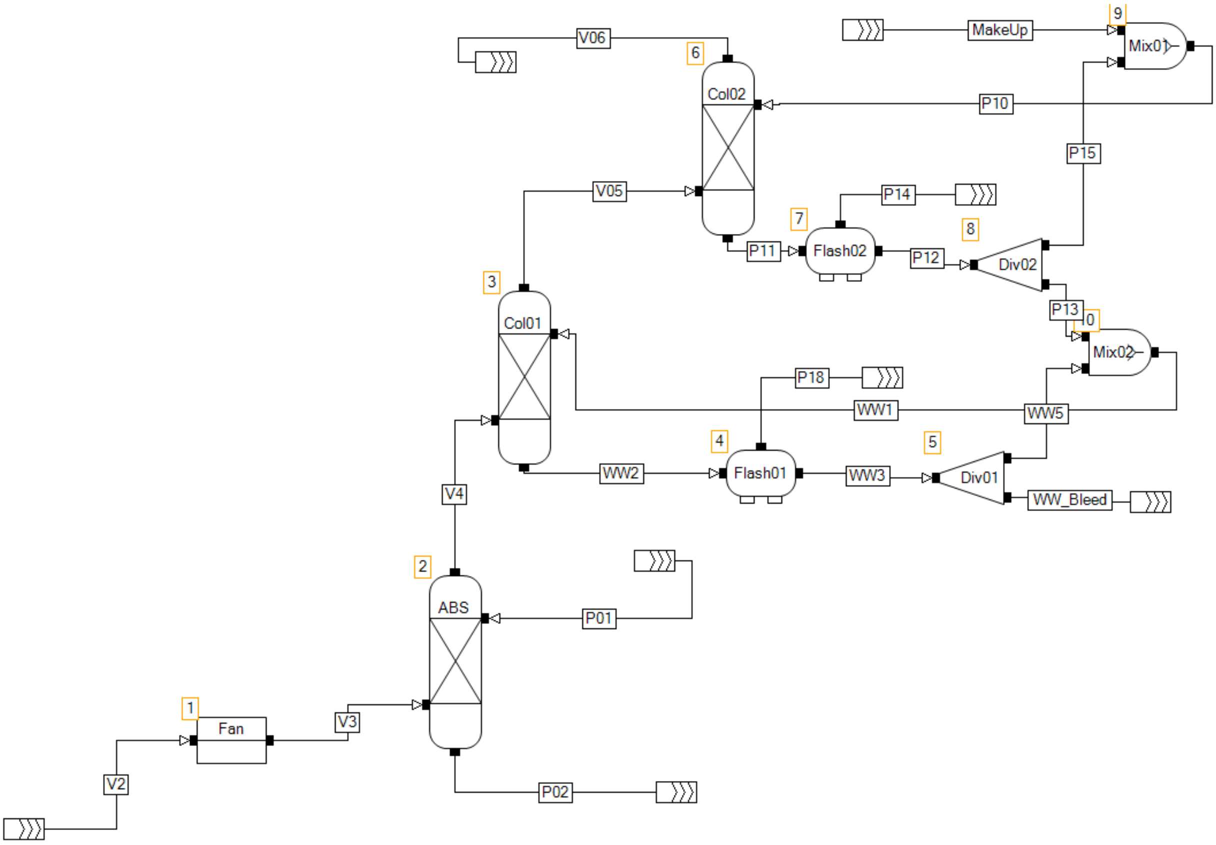


Figure 3-5: CO2SIM flow sheet of case "AA1" from (Kolderup et al., 2010)

3.5 Conclusions simulation:

Compared to experimental indications reported in Kolderup et al., 2010, the major conclusion here is that it is likely that one can design water-wash stages that capture mass transfer of amine to below ppm levels, as these results indicate. This was also indicated in the Matlab model of the water-wash presented in Chapter 2)). Two stages are necessary to ensure low slippage values.

Firstly, the gas film coefficient is important in accurately determining the mass transfer of solvent vapours as well as the importance of operation with regards to sufficient water circulation. Secondly, the other factors tested are less important.

The previous implementation of the gas film resistance correlation was probably erroneous and caused a too slow rate of mass transfer. The CO2SIM simulations reported in Kolderup et al., 2010 therefore include too slow mass transfer and a too high slippage as function of packing height. This was also indicated in the report.

A re-evaluation of the gas film mass transfer coefficient has thus showed a more reliable model compared to experimental data and has increased understanding of the water-wash theoretical considerations.

The simulation results and evaluations show that the gas film model used in CO2SIM in Kolderup 2010 was too slow. The comparative f factor to this model was 14, however, the new gas film model implemented in 2011 gives comparable results to the Matlab model.

4 Modelling of nitrosamines in pilot plant

4.1 Introduction

It has been observed in prior test campaigns at Esbjerg pilot plant as part of CESAR project, that nitrosamines (NA) can be formed in the amine absorption liquid. This is most likely due to reaction of nitrite (resulting from NO_2 absorption) with secondary amines[1] (nitrosation). This is a minor pathway and, therefore, should not consume large amounts of amine or substantially change the amine solution composition. The exact reaction mechanism for the formation of NA is not known at this stage. However, the reaction pathway starts with nitrite present in the absorption liquid.

Due to the fact that nitrosation is only possible for secondary amines, MEA (monoethanolamine), as a pure substance, will not react with nitrite to form NA. However, the MEA used in typical commercial absorption processes and in other test facilities is of technical grade. This means that impurities of secondary amines (e.g. DEA, diethanolamine) can be present. DEA reacts readily with nitrite, forming NAs. Though still subject to research investigation, aldehydes[2] could also catalyse the formation of NAs. In addition, MEA may degrade into secondary amines which can form NAs.

The most relevant degradation product is DEA. Nitrosation of this can lead to N-nitrosodiethanolamine (NDELA). In this case, NAs are second generation degradation products (degradation products of degradation products), thus in small quantities. Next to NDELA, other NA such as nitrosodimethylamine (NDMA) can theoretically occur. NDMA can be formed from the nitrosation of dimethylamine. Dimethylamine (DMA) can be formed as a degradation product. However, in prior pilot plant campaigns the level of DMA emissions were below detection limit (<0.02 mg/Nm^3). It is of importance to note that DMA is a very volatile degradation product. In theory DMA can react with nitrite to from NDMA (nitrosodimethylamine). However, as indicated by the very low emissions of dimethylamine, this component would not be present to a great extent.
It can be concluded that for the presence of NA, NDELA is much more indicative than NDMA.

N-MOR can be formed based on the reaction of nitrite with morpholine (MOR). MOR is a secondary degradation product from MEA. The secondary degradation product MOR originates to a great extent from the degradation products N-(2-hydroxyethyl)-ethylenediamine and diethanol-amine.

4.2 Details of Nitrosamines MATLAB model

The implementation of the model was carried out in Matlab and is based on dynamic mass balances over each part of the CO_2 capture system as shown in Figure 4-1 , absorber, first wash stage, heat exchanger hot and cold sides, stripper and condenser above the stripper.

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[1] The origin of the secondary amines can be that these amines were present as impurities in the starting material or due to degradation of MEA during operation.

[2] Typical degradation product of MEA during operation

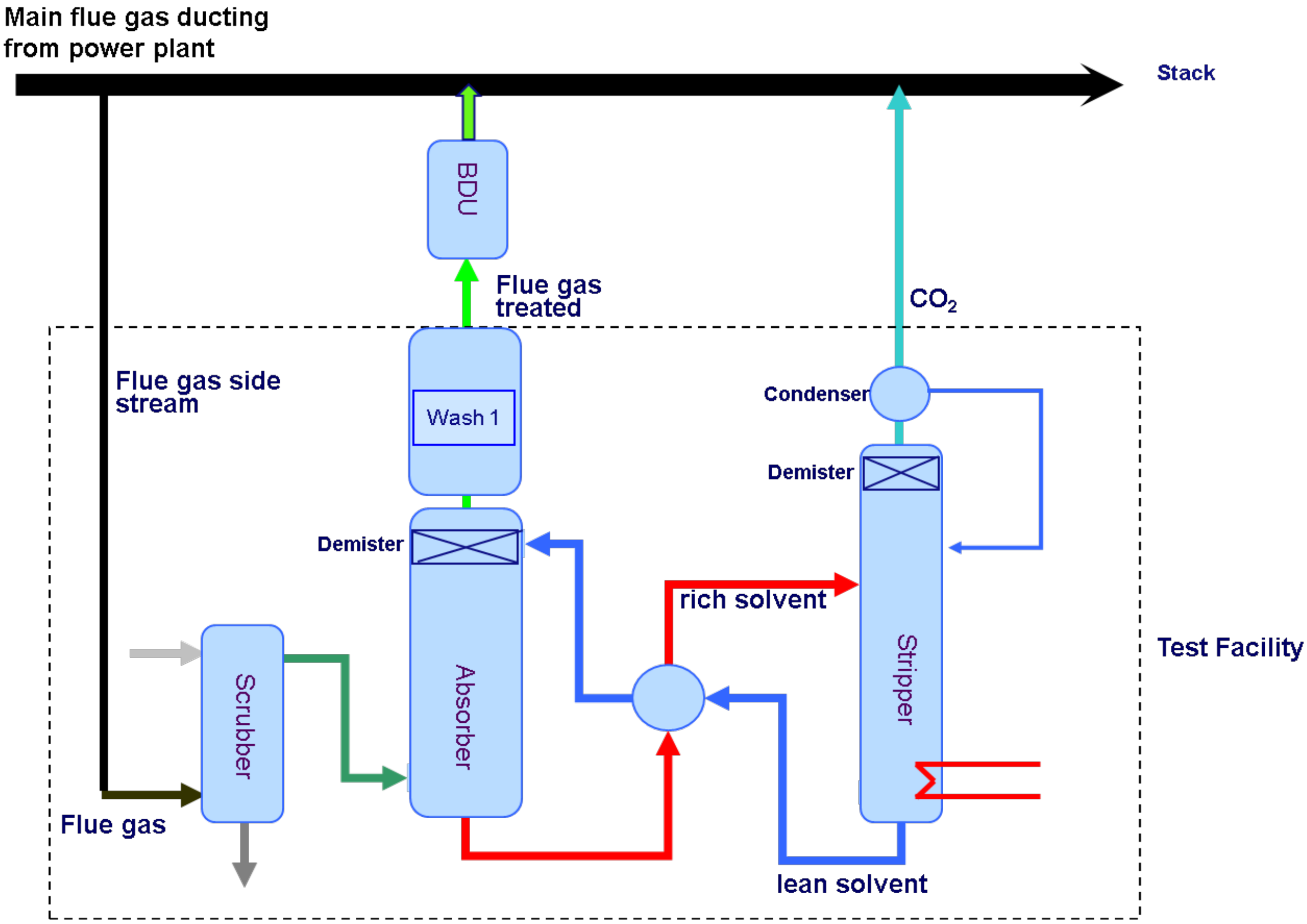

Figure 4-1: Schematic of CO_2 capture plant

Each part of the system is treated as a continuously stirred reactor with chemical reactions and transfer of components between gas and liquid streams. The implementation of the model in MATLAB is as shown in Figure 4-2.The functionality and assumptions of the model are described in the following.

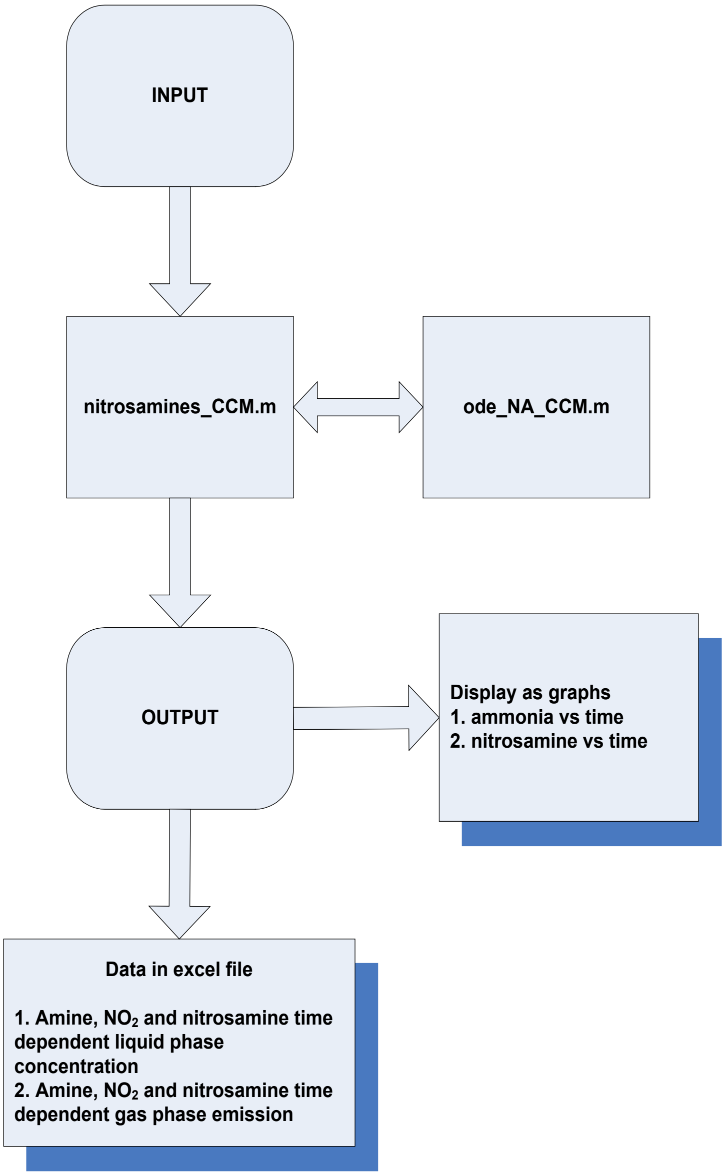

Figure 4-2: Implementation structure of MATLAB files

- **Input:** In the main file nitrosamines_CCM.m, the user should adjust the following parameters:
  - file name for saving results;
  - conditions of inlet gas stream, including NO_2 fraction (mg/Nm^3);
  - absorption and conversion of NO_2 (fractions);
  - formation ratio of nitrosamine in question;
  - solvent conditions(wt % and density);
  - capture level of CO_2 (%).

The parameters for each system part may also be adjusted and should be given in the units specified in the main file.

- **Output:** The data determined by the model are saved in the specified Excel file. These data concern the time-dependent concentrations (mol/L) of the amine, NO_2, and nitrosamines in the liquid phase of each part of the system along with the emissions (mol/s) in the gas phase from both the absorber (treated flue gas) and stripper (captured CO_2). Two figures are created displaying the concentrations versus time of amine and nitrosamines in the first water-wash stage, respectively. The display may be easily changed to any of the saved values.

- **Boundary conditions:** The model is developed to reflect the specific configuration of the CO_2 capture system in Figure 4-1. The operating parameters are flexible and can be varied over a wide range. A summary of the parameters used to generate the results for each day of the campaign shown here are given in Table 4-1.
- **Assumptions:**
  - The fraction of NO_2 that reacts is specified in the main file and forms the nitrosamine completely in the absorber. The model determines the formation of nitrosamines in each part of the capture system, but kinetic data is first required and is not yet available.
  - Each part of the system is well mixed so that the concentrations in the streams leaving the reactors are the same as those in the bulk of the reactor and no spatial gradients are considered.
  - The emissions of the various components are at equilibrium with the liquid streams (wash water or amine solution) and are based on either vapour saturation or solubility (checks for which is the limiting factor are made during the calculations).
  - The change in MEA concentration from the reaction with CO_2 is not yet considered, but is expected to have no effect on the results for the nitrosamines emissions and would only influence the emissions of MEA.

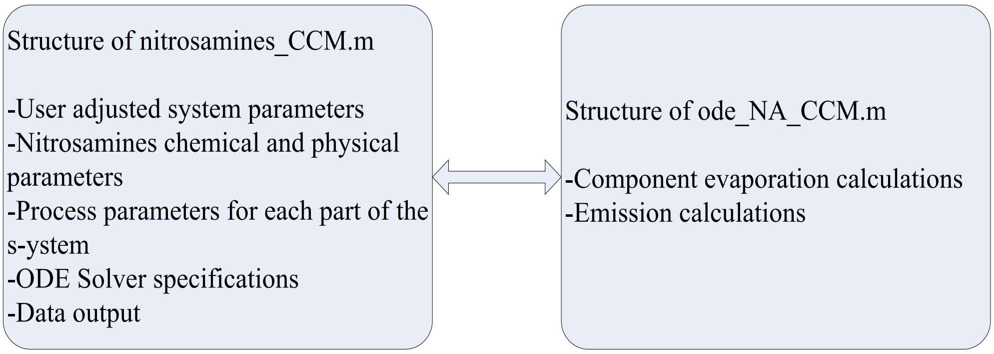

Figure 4-3: Structure of MATLAB files

Table 4-1: Parameters to change in model for each day of the campaign

Flue Gas			Stripper	
Flow rate	*Nm^3/h*		Pressure top	*bar*
Pressure	*bar*		Temperature top	*°C*
Temperature	*°C*			
CO2	*%*			
Absorber			Wash stage	
Pressure top	*bar*		Wash liquid flow rate	*m^3/h*
Temperature top	*°C*		Temperature top	*°C*
Heat Exchanger			Condenser	
Average temperature Hot side	*°C*		Temperature	*°C*
Average temperature Cold side	*°C*			

Use of model: To run the model, the two files must be saved in the same directory, nitrosamines_CCM.m and ode_NA_CCM.m. The input parameters should be adjusted as needed, possibly along with the parameters of each part of the system. These are found in the first two sections of the main file as shown in Figure 4-3.The Matlab files and a memo explaining them are given as appendices.

Current results: The nitrosamines that have been evaluated so far include: N-nitrosodimethylamine (NDMA), N-nitrosodiethanolamine (NDELA) and NMOR (N-nitrosomorpholine). The parameters that are changed with each different species are the energy of solvation and Henry coefficient (Table 4-2).The conversion of the emissions from mg/s to mg/Nm^3 are also given based on the total gas flow of treated flue gas and CO_2. With the current model, the formation of only one nitrosamine species may be considered at a time. Formation of multiple species may be implemented with the appropriate kinetic data.

Table 4-2: Physical parameters for Nitrosamines

Abbreviations	
N-nitrosodimethylamine	NDMA
N-nitrosodiethanolamine	NDELA
N-nitrosomorpholine	NMOR
Molecular weight	(g/mol)
MEA	61,08
NDMA	74,08
NDELA	134,14
NMOR	116,12
Energy of solvation (dG) [1]	(kcal/mol)
MEA	-9,0
NDMA	-2,6
NDELA	-9,0
NMOR	-4,4
Dimensionless Henry Coefficient [2]	
MEA	5,85E-07
NDMA	3,29E-05
NDELA	1,92E-10
NMOR	1,01E-06

[1] Brakstad, O.G. et al., "Evaluation of degradation components," SINTEF Report (2010).

[2] http://toxnet.nlm.nih.gov/index.html

4.3 Approach for comparison of experimental and modelling results

The results from SINTEF measurements for the three Nitrosamines (NDELA, NDMA and NMOR) are presented in Table 4-3. The measurements correspond to liquid phase concentration of each NA in the absorption liquid and wash water. NDELA measurements are not analysed for all the days since the concentration is expected to be more or less constant as compared to other days. The NDMA and NMOR concentration are found to be below the threshold measuring value and thus reported as limiting values.

Table 4-3: SINTEF measurements for liquid phase NA concentration

Date	Sample	NDELA (ng/mL)	NDMA (ng/mL)	NMOR (ng/mL)
4 Oct	Absorption liquid	N.A.	< 100	< 250
	Wash water	2,0	< 10	< 25
5 Oct	Absorption liquid	N.A.	< 100	< 250
	Wash water	1,5	< 10	< 25
6 Oct a	Absorption liquid	N.A.	< 100	< 250
	Wash water	1,2	< 10	< 25
6 Oct b	Absorption liquid	N.A.	< 100	< 250
	Wash water	1,0	< 10	< 25
7 Oct	Absorption liquid	N.A.	< 100	< 250
	Wash water	0,8	< 10	< 25
8 Oct	Absorption liquid	2056,2	< 100	< 250
	Wash water	N.A.	< 10	< 25
10 Oct a	Absorption liquid	2048,0	< 100	< 250
	Wash water	0,4	< 10	< 25
10 Oct b	Absorption liquid	2058,2	< 100	< 250
	Wash water	N.A.	< 10	< 25
11 Oct	Absorption liquid	2034,6	< 100	< 250
	Wash water	N.A.	< 10	< 25

N.A. : Not Analysed

The model can be verified by considering either the concentration in the absorption liquid or wash liquid as a basis to compare it with the experimentally measured value with the other. This way the validity of the model for both the sections of the system can be verified. The three approaches used to compare the SINTEF measurements for NA concentration with the results obtained from the model are explained in the following.

4.3.1 Approach 1

A certain concentration of the absorption liquid is assumed and the corresponding concentration in the wash water is obtained from the model. This value is then compared with the concentration as measured by the liquid sampling measurements. The concentration of each of the NA assumed are given in Table 4-4.

Table 4-4: Assumptions for comparison by approach 1

Nitrosamine	**Concentration in absorption liquid (ng/mL)**
NDELA	2000
NDMA	100
NMOR	250

The assumed values are such that it represents the SINTEF sampling measurements. For NDELA, the measured concentration are in the range of 2000 ng/mL while for NDMA and NMOR the measured concentration was less than the detection limit of 100 and 250 ng/mL, respectively. Thus for NDMA and NMOR limiting cases are assumed.

4.3.2 Approach 2

Another way of comparison of the model and SINTEF measurement is assuming a certain concentration of NA in the wash water and then calculating the corresponding amount of NA in the absorption liquid using the model and compare it with the SINTEF measurements. The assumed concentrations of NA in the wash water based on the SINTEF measurements are given in Table 4-5.

Table 4-5: Assumptions for comparison by approach 2

Nitrosamine	**Concentration in wash water (ng/mL)**
NDELA	Measured value on each day
NDMA	10
NMOR	25

The amount of NDELA assumed was the actual concentration measured in the wash water by SINTEF measurements as shown in Table 4-3. The values assumed for NDMA and NMOR are limiting values as obtained by SINTEF measurements.

4.3.3 Approach 3

The BDU outlet stream can be considered to be a pure vapour phase stream as the BDU is effective in removal of aerosols from the flue gas after the wash section. Since the model does not take into account aerosol formation and entrainment, the BDU outlet stream gas phase NA concentration can be compared with the emissions from the wash section in the model. Based on these gas phase NA concentrations, corresponding NA concentration in the absorption liquid and wash water from the model and experimental results can be compared.

The gas phase concentration of NDELA is not taken into consideration as they are present in significantly small amounts due to their low volatility. The gas phase concentration as measured by SINTEF which are used as assumptions in the model are given in TABLE 4-6 and Table 4-7 for NDMA and NMOR, respectively. Experimental measurements for NA gas phase concentrations are available for the following days of the campaign: 5th October and 10th October Test 2.

Table 4-6: NDMA gas phase measurements at BDU outlet

Emission values assumed	BDU out emission (mol/s)	BDU out emission (µg/Nm3)
5th Oct	9,55E-13	2,80E-04
10th Oct Test 2	1,78E-12	5,81E-04

Table 4-7: NMOR gas phase measurements at BDU outlet

Emission values assumed	BDU out emission (mol/s)	BDU out emission (µg/Nm3)
5th Oct	3,05E-13	1,40E-04
10th Oct Test 2	1,09E-12	5,56E-04

4.4 Results and Discussion

The main results of the Matlab modelling are depicted graphically here and compared with the experimental measurements by SINTEF using different approaches.

4.4.1 Approach 1 comparison

NDELA

NDELA concentration is assumed to be about 2000 ng/mL in the absorption liquid. It can be seen from the SINTEF measurements for liquid phase NA concentration that the concentration of NDELA in the absorption liquid does not change significantly over the entire period of the campaign. The corresponding NDELA concentration in the wash water shows a decreasing trend for the days it was measured.

Figure 4-4 compares the NDELA concentration as predicted by the model with the liquid phase SINTEF measurements. The model under predicts the NDELA concentration in the wash water by about 2 orders of magnitude. This implies that the actual amount of NDELA present in the wash liquid is much higher than the amount predicted by the model. The primary reason for this difference is the under prediction of the vapour pressure by the model. The evaluation of volatility in the model is based on certain assumptions of solvation energy obtained from computational modelling which is applicable only in a certain temperature and pressure range. There are no reported experimental values of NDELA vapour pressure at different temperature in literature. Moreover, the effect of entrainment which is not accounted for in the model can be another cause for the under-prediction.

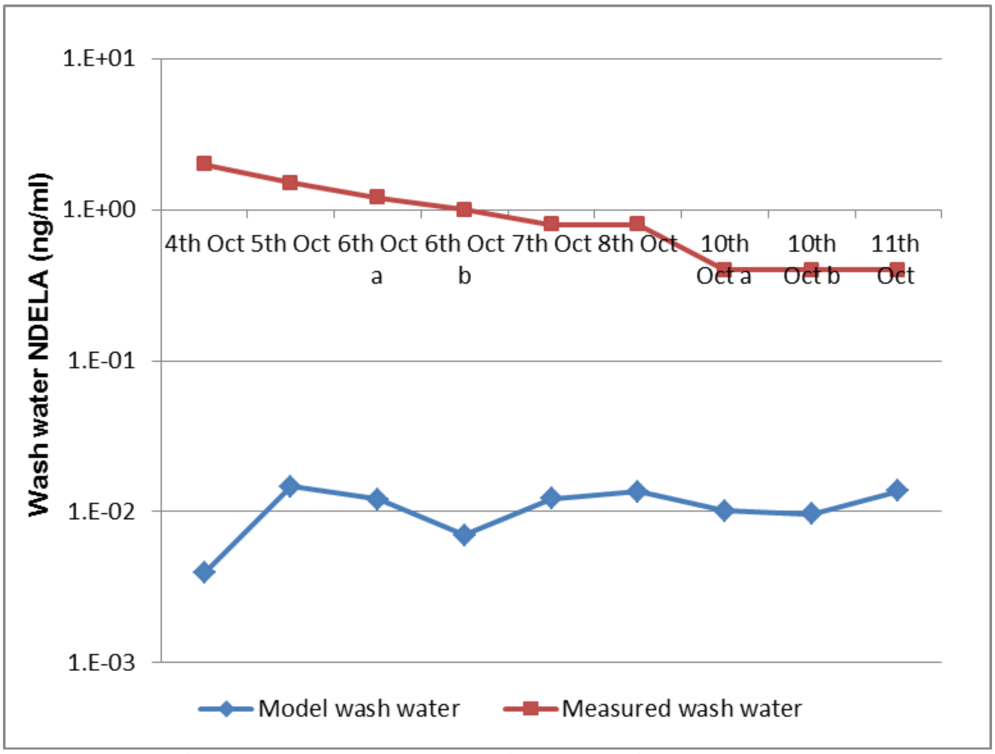

Figure 4-4: Wash water NDELA comparison by approach 1

NDMA

The values reported for NDMA in SINTEF measurements for both absorption liquid and wash water are limiting values indicating the maximum amount of NDMA. Figure 4-5compares the amount of NDMA in wash water with the amount of NDMA in the wash water predicted by the model. The NDMA amount predicted by the model is within an order of magnitude of the actual liquid phase NDMA concentration as measured by SINTEF. The amount predicted is almost always higher than the limiting case. Therefore, it is difficult to judge the accuracy of the model. However, the model indicates the maximum possible NDMA concentration present in the wash water.

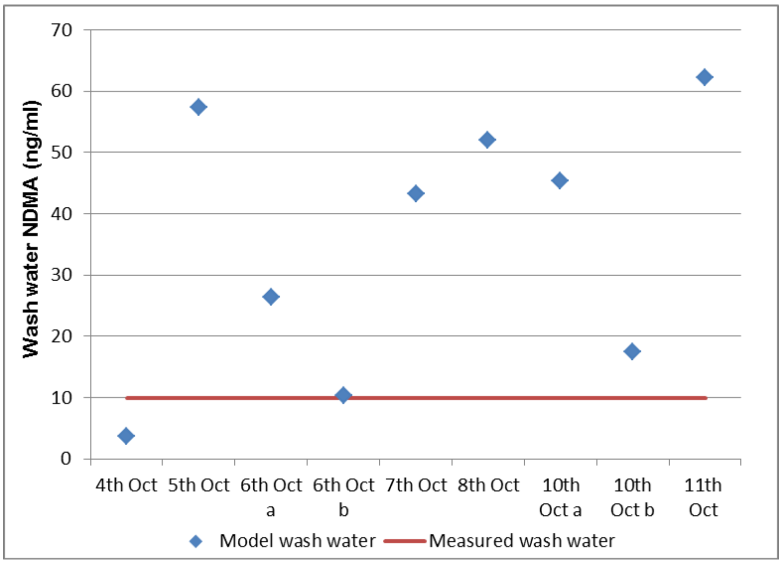

Figure 4-5: Wash water comparison for NDMA by approach 1

NMOR

Similarly, for NMOR values reported by SINTEF measurements for both absorption liquid and wash water are limiting values indicating the maximum amount of NMOR. Figure 4-6 compares the amount of NMOR in wash water with the amount of NMOR in the wash water predicted by the model. The NMOR amount predicted is less than the maximum limit as reported in SINTEF measurements and thus it is difficult to make a quantitative comparison.

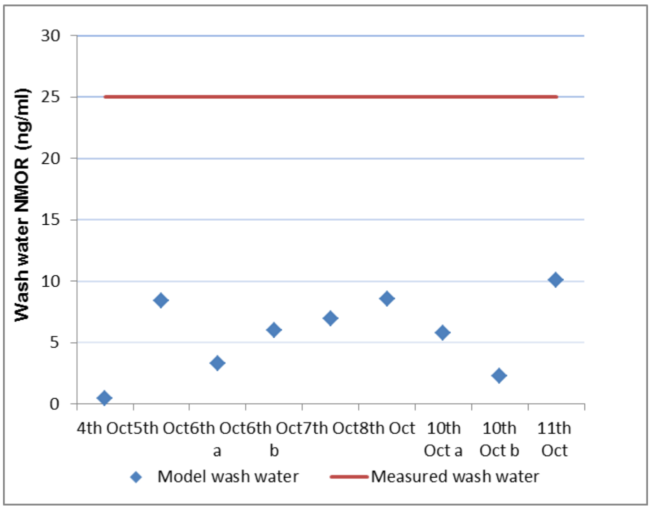

Figure 4-6: Wash water comparison for NMOR by approach 1

4.4.2 Approach 2 comparison

NDELA

Figure 4-7 **Error! Reference source not found.** shows the NDELA amount predicted by the model as compared to the SINTEF measurements. The NDELA amount predicted by the model is about 2 orders of magnitude higher than the measured value. These results are expected as it is opposite to the scenario in approach 1. Thus, for the same amount of NDELA to be present in the wash water the amount of NDELA that needs to be present in the absorption liquid is much higher than the experimental values due to the under prediction of the vapour pressure. Moreover, the model does not take into account carry-over of liquid from the absorber and the entrainment effects in the washing section.

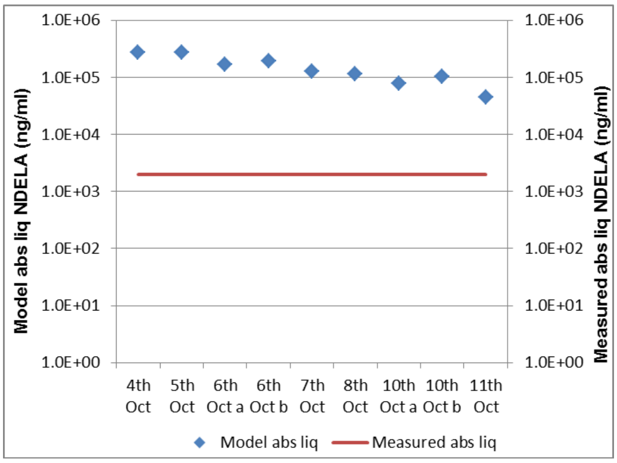

Figure 4-7: Absorption liquid comparison for NDELA by approach 2

NDMA

Figure 4-8 shows the amount of NDMA in the absorption liquid as predicted by the model and the maximum limit from SINTEF measurements. The amount of NDMA predicted is much lower than the maximum limit but within an order of magnitude. This is expected based on the results of comparison by approach 1. Thus, the model can predict the NDMA values in the absorption liquid within an order of magnitude accuracy but the exact values cannot be ascertained owing to the lack of experimental values in this range.

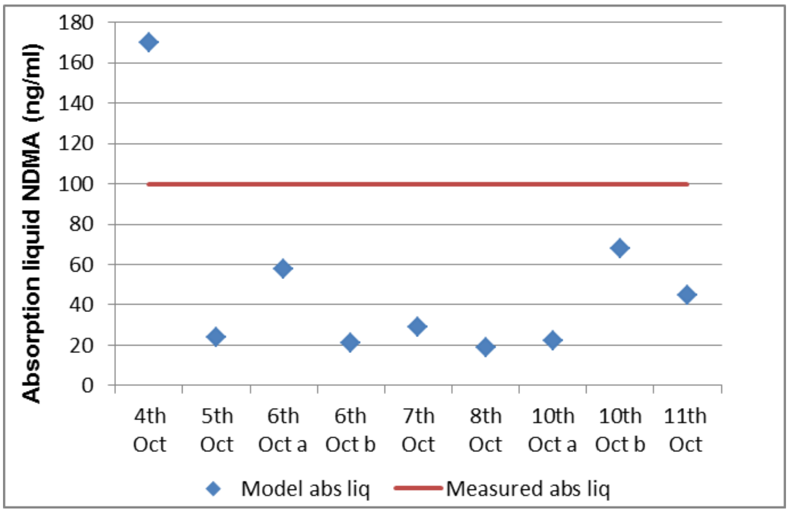

Figure 4-8: Absorption liquid comparison for NDMA by approach 2

NMOR

The amount of NMOR predicted in the absorption liquid is compared with the maximum limit from SINTEF measurements is shown in Figure 4-9. The amount of NMOR predicted is much higher than the maximum limit from experimental measurements, sometimes even an order of magnitude higher. These results from the model are not as expected since in approach 1 comparison the predictions were within an order of magnitude of the SINTEF measurements.

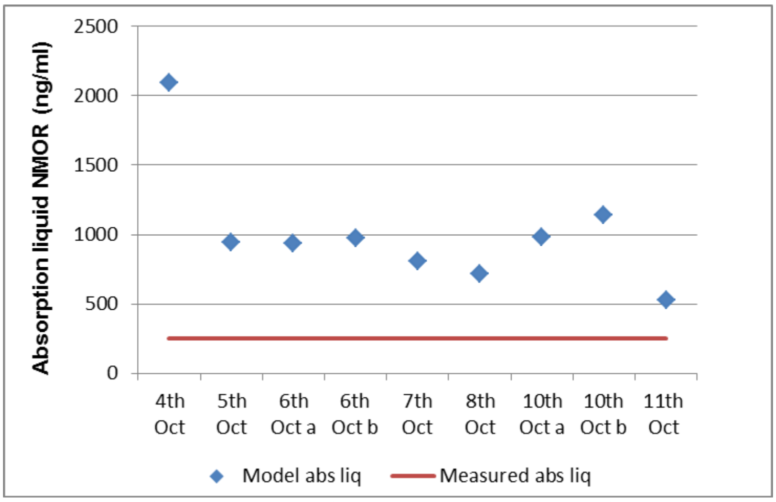

Figure 4-9: Absorption liquid comparison for NMOR by approach 2

4.4.3 Approach 3 comparison

NDMA

The results of modelling are compared with the experimental results from SINTEF for NDMA in Table 4-8. The amount of NDMA predicted by the model to give the same gas phase concentration at the BDU outlet is much lower than the limits for experimental measurement.

As a limiting case is assumed for NDMA concentration, the extent of deviation of the model as compared to the experimental measurements cannot be accounted for.

Table 4-8: NDMA liquid phase comparison based on gas phase measurements

	Absorption liquid		Wash water	
	Model (ng/mL)	**Experimental (ng/mL)**	**Model (ng/mL)**	**Experimental (ng/mL)**
5th Oct	1,67E-02	<100	8,75E-03	<10
10th Oct Test 2	3,27E-02	<100	1,67E-02	<10

NMOR

The results of modelling are compared with the experimental results from SINTEF for NMOR in Table 4-9. The NMOR concentration in the absorption liquid and the wash water as predicted by the model based on gas phase measurements is in agreement with the limiting values for the experimental measurements. However, quantitative comparison cannot be done as the exact values for NMOR are not available.

Table 4-9: NMOR liquid phase comparison based on gas phase measurements

	Absorption liquid		Wash water	
	Model (ng/mL)	**Experimental (ng/mL)**	**Model (ng/mL)**	**Experimental (ng/mL)**
5th Oct	88,39	<250	0,16	<25
10th Oct Test 2	160,50	<250	0,54	<25

4.5 Conclusions and recommendations

4.5.1 NDELA

- The model under-predicts the amount of NDELA present in the wash water while over predicts the amount present in the absorption liquid when compared to SINTEF NA measurements
- The model needs to be refined to include experimental volatility measurements at different temperatures for NDELA
- The carryover of liquid in the absorber and the entrainment effect in the wash section cannot be accounted for in the model

4.5.2 NDMA

- The model is indicative in predicting the maximum possible NDMA concentration present in the wash water
- The predicted liquid phase concentrations (absorption liquid and wash water) are in agreement with the limiting cases, but quantitative evaluation of the deviation cannot be done.

4.5.3 NMOR

- The model predicts the amount of NMOR present in wash water within an order of magnitude accuracy for limiting case as presented in SINTEF measurements
- The amount of NMOR predicted in the absorption liquid is much higher than expected and the cause for this needs to be investigated
- The predicted liquid phase concentrations (absorption liquid and wash water) are in agreement with the limiting cases, but quantitative evaluation of the deviation cannot be done.

The most important recommendation for future work is obtaining volatility data for all the NAs. Accurate volatility measurements based on experiments at different temperatures needs to be incorporated to refine the model. Moreover, detailed information on entrainment factor and/or aerosol formation needs to be obtained to compare the experimental results.

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Appendix A: Example of pre-processing calculations (Matlab)

```
Run='2011-10-04';
load(Run) % Process Data from the process control system in time series
DAT=s;
load Fysdata % various kind of physical data for the case of 30 wt% MEA
tid=t+2/24;
Tid=(t-floor(t(1)))*24+2; % Compensate for differences in time
t0i=finx(tidconv('10:04'),tid);
tfi=finx(tidconv('13:30'),tid); % index for average data

% Meteorological data
Patm=mean(xlsread('Weather in Sept-Oct.xls','Sheet4','o839:o842'))*10; %Pa
Tair=mean(xlsread('Weather in Sept-Oct.xls','Sheet4','j839:j842')/10)+273.15; %K


% Estimation of absorber inlet conditions (for estimating Vinert (kmol/s))

% Air
P_h2o=psat(Tair,s.kvap(1,:));
yair_h2o=P_h2o/Patm;

% Gas from pre-scrubber
Tsc=mean(TE1CT2(t0i:tfi))+273.15;% Temp for liquid scrubber. TE1ECT2 is a tag name for a temperature
ysc_h2o=steamsat(Tsc)/Patm;
ysc_co2=0.1445*(1-ysc_h2o); %wet  basis, assuming 14.45 is the dry value.

%Inlet absorber conditions
Vabs=mean(FT1CF4(t0i:tfi))* 1.2393e-005; %kmol/s converted from Nm3/h
yabs_co2=mean(QE2CQ7(t0i:tfi))/100; % wet CO2 molfraction
Pabs=mean(PT1CP3(t0i:tfi))*1e5+Patm; %Pa


Vsc=Vabs*yabs_co2/ysc_co2; %Total flow from scrubber
Vair=Vabs-Vsc;           %Total air flow
Vabs_h2o=Vsc*ysc_h2o+Vair*yair_h2o; %Water flow into absorber kmol/s
Vabs_co2=yabs_co2*(Vabs-Vabs_h2o);
Vinert=Vabs-Vabs_co2-Vabs_h2o;

NT=1;  % Number of water-wash sections

Dabs=0.65; %Diameter absorber (m)  %
%Vinert= 0.00998083827706137; % (from Vinertcalc) (N2+O2+Ar) flue gas stream (kmol/s)
T0=mean(TE2CT1(t0i:tfi))+273.15; % Gas temperature (K) out of absorber and into first section
Tw=mean(TE2CT6(t0i:tfi))+273.15; % Temperatures (K) in each section. Section 1 is closest to the
absorber.
Pww=mean(PT2CP1(t0i:tfi))*1e5+Patm; % Pressure (Pa) in the water-wash sections, assumes the same in
all sections
MupWf=0.0;    % Makeup water, in fraction of inert gas (kmol/kmol)
y_co2=0.004; %molfracion of CO2 (dry basis) in the gas coming from the absorber
y_mea=336*22.414/61.08*1e-6*0.347;% molfraction of MEA (dry basis) in the incoming gas
```

Appendix B: Nitrosamine model

```
%15 July 2011

%Written by Erin Kimball

%Nitrosamines model
%System:
%Absorber (A)
%Wash stage (W1)
%Heat exchanger, hot and cold streams (HXH, HXC)
%Stripper (S)
%Condenser

%Script calculates the dynamic build-up of nitrosamines in each part of the
%system (tubing not considered)

%Calls ode_NA_CCM

global Fl Fgout cNO2in capNO2 absorption  capCO2 uv_on deg
global Tgin Pgin Fgin mgin xCO2in FginSTP
global HNA mwNA dGNA HMEA rhoAm
global TA THxc THxh TS TC  PS PA
global VA VHxc VHxh VS
global FlW1 VW1 TW1
global emitAMEA emitW1MEA emitANA emitW1NA
global emitSMEA emitCMEA emitSNA emitCNA
global FevapW1H2O FcondH2O

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Parameters to be adjusted by user

%File name for saving results
filename = 'NA_CCM_modeling_04 10 2011.xls'

%Option for UV degradation in condensate stream from wash stage to absorber
uv_on = 0; %0 = off, 1 = on
deg = 0.25; %fraction of NA that is degraded by UV

%Case scenario parameters
xNO2in = 1; %mg/m3; inlet fraction of NO2
absorption = 1; %absorbption fraction of NO2 into amine solution
conversion = 0.5; %conversion precent of NO2 to NA
formation_ratio = 0.01; %ratio of formation of NA relative to max formation

%Nitrosamine to be evaluated
%1 = NDMA; 2 = NDELA; 3 = NMOR
NA_select = 3;

%Feed conditions
R = 0.083145; %L-bar/mol-K
mgin = 0.266 ; %kg/s; inlet gas flow rate by mass; based on density=1.2 kg/m3
Tgin = 25.32+273.15; %K; inlet gas temperature
Pgin = 1.04; %bar; inlet gas pressure
FginSTP = 748.51*1000/3600; % l/s %Fgin/(1.01325/273.15)/(Tgin/Pgin); %L/s; inlet gas flow rate
converted to STP
Fgin = (FginSTP*Tgin*1.01325)/(273.15*Pgin); %L/s; inlet gas flow rate at actual conditions;

MWNO2 = 46; %g/mol
cNO2in = xNO2in/1000/MWNO2/1000; %mol/L; inlet NO2 concentration

xCO2in = 0.0445; %fraction of CO2 in flue gas, by volume
cCO2in = xCO2in*Pgin/(R*Tgin); %mol/L; inlet CO2 concentration

%System specifications
capNO2 = absorption*conversion*formation_ratio;
capCO2 = 0.9607; %fraction of CO2 captured
Fgout = FginSTP*(1-xCO2in*capCO2); %flue gas leaving absorber

Fl = 6.2*1000/3600; %L/s; liquid flow
```

```
rhoAm = 0.967; %kg/L; density of 30 wt% MEA
mwAm = 61.08E-3; %kg/mol, MW of MEA
cAm = rhoAm*0.30/mwAm; %mol/L; concentration of amine in 30 wt% solution

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Nitrosamines chemical and physical parameters based on selected NA above.
%Parameters to be set:
%   NA_name: name of NA for saving data (NMOR NDELA NDMA)
%   HNA: dim'less Henry's law constant (c_gas/c_liquid) (1.01e-6 1.92e-10 3.29e-05)
%   mwNA: kg/mol, MW of nitrosamine (116.12e-3 134.14e-3 74.08e-3)
%   dGNA: J/mol, solvation energy of NA (1 kcal = 4184 J) (-4.4 -9.0 -2.6)

if NA_select == 1
    NA_name = 'NDMA';
    HNA = 3.29e-05;
    mwNA = 74.08e-3;
    dGNA = -2.6*4184;
    tf = 3e7;
elseif NA_select == 2
    NA_name = 'NDELA';
    HNA = 1.92e-10;
    mwNA = 134.14e-3;
    dGNA = -9.0*4184;
    tf = 3e5;
elseif NA_select == 3
    NA_name = 'NMOR';
    HNA = 1.01e-6;
    mwNA = 116.12e-3;
    dGNA = -4.4*4184;
    tf = 3e10;
else
    error('ErrorTests:convertTest', strcat('Only 3 NAs currently supported. \n ', ...
          'NA_select must be equal to either 1 (NDMA), 2 (NDELA), or 3 (NMOR)'));
end


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Parameters for each part of the system

%Absorber
TA = 40.17+273.15; %K; temperature in the absorber
PA = 1.01; %bar; pressure in the absorber (top)
VA = (pi*0.325^2*15.5)*1000; %L; absorber volume <-- based on (0.65m D x 15.5m H)
kA = 0;%.001; %L/mol-s; formation rate constant in the absorber

%Heat exchanger, cold stream
THxc = (314.22+376.93)/2; %K; average temperature
VHxc = 34.5; %L; heat ex. cold stream holdup  <-- update when necessary
kHxc = 0;%.0001; %L2/mol-s; formation rate constant in the cold stream

%Heat exchanger, hot stream
THxh = (387.1+323.79)/2; %K; average temperature
VHxh = 34.5; %L; heat ex. hot stream holdup   <-- update when necessary
kHxh = 0;%.0005; %L/mol-s; formation rate constant in the hot stream

%Stripper
TS = 100.21+273.15; %K; temperature in the stripper; top temp expected
PS = 2.11; %bar; pressure at the stripper outlet
VS = (pi*0.225^2*10)*1000; %L; stripper volume <-- based on (0.45m D x 10m H)
kS = 0;%.0004; %L/mol-s; formation rate constant in the stripper

%Wash 1 (above absorber)
FlW1 = 1.2*1000/3600; %L/s
VW1 = (pi*0.325^2*4)*1000; %L; wash section volume <-- based on (0.65m D x 4 H)
TW1 = 28.4+273.15; %K, outlet temperature
HMEA = 5.85e-7; %dim'less Henry's law constant for MEA in water (c_gas/c_liq)

%Condenser (above stripper)
TC = 19.37+273.15; %K, outlet temperature
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Solver

%Time specification
to = 0;
tf = 3e7; %seconds
nt = 500; %number of time points

tout=linspace(to,tf,nt);

%Initial conditions
num_part = 6 + 4; %6 system components + 4 emissions streams
num_comp = 3;     %3 components reacting: MEA, NO2, NA
u0 = zeros(num_part*num_comp, 1);

u0(3*0+1) = cAm*VA;
u0(3*1+1) = cAm*VHxc;
u0(3*2+1) = cAm*VS;
u0(3*3+1) = cAm*VHxh;

%Mass matrix to specify mixed DAE system
M = eye(num_part*num_comp,num_part*num_comp);
for i = 5:num_part-1
M(3*i+1,3*i+1) = 0;
M(3*i+3,3*i+3) = 0;
end

%ODE integration
reltol=1.0e-08; abstol=1.0e-08;
%outputsel = [3,6,9,12,15];
options=odeset('RelTol',reltol,'AbsTol',abstol,'Mass',M);%,...
               %'OutputFcn',@odeplot,'OutputSel',outputsel);

[t,u]=ode15s(@ode_NA_CCM,tout,u0,options);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Data output

V = [VA, VHxc, VS, VHxh, VW1, FcondH2O];

uAm = zeros(nt,num_part);
uNO2 = zeros(nt,num_part);
uNA = zeros(nt,num_part);

%Save concentrations in system components
for i = 0:5
    uAm(:,i+1) = u(:,3*i+1)/V(i+1);
    uNO2(:,i+1) = u(:,3*i+2)/V(i+1);
    uNA(:,i+1) = u(:,3*i+3)/V(i+1);
end

%Save emissions in gas streams
for i = 6:num_part-1
    uAm(:,i+1) = u(:,3*i+1);
    uNO2(:,i+1) = u(:,3*i+2);
    uNA(:,i+1) = u(:,3*i+3);
end

emissions = {'Emissions from gas outlets (mol/s)','','';
             '', 'MEA', 'NA';
             'Absorber', emitAMEA, emitANA;
             'Wash 1', emitW1MEA, emitW1NA;
             'Stripper', emitSMEA, emitSNA;
             'Condenser', emitCMEA, emitCNA};

condensed = {'Flow rates of condensed water streams (L/s)','';
             'From Wash 1 back to absorber', FevapW1H2O;
             'From Condenser back to Stripper', FcondH2O};

figure;
```

```
plot(t,uAm(:,5))
colormap(jet)
title('Amine in first wash section');
xlabel('Time (s)')
ylabel('Concentration (mol/L)')
legend('Amine, W1');

figure;
plot(t,uNA(:,5))
colormap(jet)
title('Nitrosamine in first wash section');
xlabel('Time (s)')
ylabel('Concentration (mol/L)')
legend('NA, W1');

%Save to file

columns = {'Time(s)', 'Absorber','HeatEx Cold','Stripper','HeatEx Hot',...
           'Wash 1', 'Condenser','From Absorber','From Stripper',...
           'From Wash 1','From Condenser' };
%{
header = cat(1,{'','MEA Concentration (mol/L)','','','','','',...
                'MEA emissions (mol/s)','','',''},columns);
sheet = strcat('MEA_',num2str(xNO2in),'mg');
xlswrite(filename, header, sheet, 'A1');
xlswrite(filename, t, sheet, 'A3');
xlswrite(filename,uAm, sheet, 'B3');

header = cat(1,{'','NO2 Concentration (mol/L)','','','','',''...
                'NO2 emissions (mol/s)','','',''},columns);
sheet = strcat('NO2_',num2str(xNO2in),'mg');
xlswrite(filename, header, sheet, 'A1');
xlswrite(filename, t, sheet, 'A3');
xlswrite(filename,uNO2, sheet, 'B3');
%}
header = cat(1,{'','Nitrosamine Concentration (mol/L)','','','','',''...
                'NA emissions (mol/s)','','',''},columns);
sheet = strcat(NA_name,'_',num2str(xNO2in),'mg');
xlswrite(filename, header, sheet, 'A1');
xlswrite(filename, t, sheet, 'A3');
xlswrite(filename,uNA, sheet, 'B3');

xlswrite(filename, emissions, 'Emissions', 'A3');
xlswrite(filename, condensed, 'Emissions', 'A11');
%}


%Written by Erin Kimball

%ODE equations to solve for build-up of nitrosamines
%Called by nitrosamines_CCM.m

function ut = ode_NA_CCM(t,u)

global Fl Fgout cNO2in capNO2 absorption  capCO2 uv_on deg
global Tgin Pgin Fgin mgin xCO2in
global HNA mwNA dGNA HMEA rhoAm
global TA TS TC  PS PA
global VA VHxc VHxh VS
global VW1 TW1
global emitAMEA emitW1MEA emitANA emitW1NA
global emitSMEA emitCMEA emitSNA emitCNA
global FevapW1H2O FcondH2O FCO2out

%{
Variable definitions
t = time
u = mol
ut = derivative wrt time
%}

%{
```

```
Indexing, u(3*i+j)
i = part of system -->
    0: Absorber
    1: Heat exchanger, cold side
    2: Stripper
    3: Heat exchanger, hot side
    4: 1st Wash section (above Absorber)
    5: Condenser (above Stripper)

j = component -->
    1: Amine
    2: NO2
    3: Nitrosamine
%}

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Component evaporation calculations

mwAm = 61.08E-3; %kg/mol, MW of MEA
mwH2O = 18e-3; %kg/mol, MW of water
mwNO2 = (14+2*16)*1e-3; %kg/mol, MW of NO2

dGMEA = -9.6*4148; %J/mol, solvation energy of MEA
R = 0.083145; %L-bar/mol-K

FCO2in = xCO2in*capCO2*Fgin; %L/s
mCO2out = FCO2in/R/Tgin*Pgin*0.044; %kg/s; CO2 flow rate out of stripper
mgout = mgin - mCO2out; %kg/s; flue gas mass flow rate out of the absorber

%Absorber
molTotA = (u(3*0+1)+u(3*0+2)+u(3*0+3))+55.56*VA; %mol, total mol
mTotA = (u(3*0+1)*mwAm + u(3*0+2)*mwNO2 + u(3*0+3)*mwNA + 38.89*VA*mwH2O)/molTotA;
        %kg/mol, total mass of 1 mol solution
PvapANA = R*TA*rhoAm * u(3*0+3)/molTotA/mTotA * exp(dGNA/(R*100*TA));
PvapAMEA = R*TA*rhoAm * u(3*0+1)/molTotA/mTotA * exp(dGMEA/(R*100*TA));
PvapNO2 = 0; %bar; vapor pressure of NO2 at 40 C

PvapAH2O = exp(77.3450 + 0.0057*TA - 7235/TA)/TA^8.2 * 1e-5; %bar
xAH2O = (286.9/461.5)*PvapAH2O/(PA-PvapAH2O); %kg H2O/kg gas; factor is gas constant ratio Air/H2O
evapAH2O = xAH2O*mgout/0.018; %mol/s; water evaporated from absorber
rhoAH2O = 0.0022*PvapAH2O*1e5/TA/1000; %kg/L; water vapor density
FevapAH2O = evapAH2O/54.378; %L/s; water evaporated from liquid
FAout = 1/(PA*10^5/(286.9*TA)*(1+xAH2O)/(1+xAH2O*461.5/286.9))*(mgout+xAH2O*mgout)*1000;
        %L/s; gas leaving the absorber

%Stripper
molTotS = (u(3*2+1)+u(3*2+2)+u(3*2+3))+55.56*VS; %mol, total mol
mTotS = (u(3*2+1)*mwAm + u(3*2+2)*mwNO2 + u(3*2+3)*mwNA + 38.89*VS*mwH2O)/molTotS;
        %kg/mol, total mass of 1 mol solution
PvapSNA = R*TS*rhoAm * u(3*2+3)/molTotS/mTotS * exp(dGNA/(R*100*TS));
PvapSMEA = R*TS*rhoAm * u(3*2+1)/molTotS/mTotS * exp(dGMEA/(R*100*TS));

PvapSH2O = exp(77.3450 + 0.0057*TS - 7235/TS)/TS^8.2 * 1e-5; %bar;
xH2O = (188.9/461.5)*PvapSH2O/(PS-PvapSH2O); %kg H2O/kg CO2; factor is gas constant ratio CO2/H2O
evapSH2O = xH2O*mCO2out/0.018; %mol/s water

FSout = 1/(PS*10^5/(188.9*TS)*(1+xH2O)/(1+xH2O*461.5/188.9))*(mCO2out+xH2O*mCO2out)*1000;
        %L/s; gas leaving the stripper
FCO2out = mCO2out/0.044/PS*TS*R; %L/s
FevapSH2O = evapSH2O/54.378; %L/s; water evaporated from liquid

%1st Wash section
molTotW1 = (u(3*4+1)+u(3*4+2)+u(3*4+3))+55.56*VW1; %mol, total mol
mTotW1 = (u(3*4+1)*mwAm + u(3*4+2)*mwNO2 + u(3*4+3)*mwNA + 38.89*VW1*mwH2O)/molTotW1;
         %kg/mol, total mass of 1 mol solution
PvapW1NA = R*TW1*rhoAm * u(3*4+3)/molTotW1/mTotW1 * exp(dGNA/(R*100*TW1));
PvapW1MEA = R*TW1*rhoAm * u(3*4+1)/molTotW1/mTotW1 * exp(dGMEA/(R*100*TW1));

PvapW1H2O = exp(77.3450 + 0.0057*TW1 - 7235/TW1)/TW1^8.2 * 1e-5; %bar
xW1H2O = (286.9/461.5)*PvapW1H2O/(PA-PvapW1H2O); %kg H2O/kg CO2; factor is gas constant ratio
CO2/H2O
```

```
evapW1H2O = xW1H2O*mgout/0.018; %mol/s; water evaporated from 1st wash section
FevapW1H2O = (evapAH2O-evapW1H2O)/54.378; %L/s; water back to the absorber
FW1out = 1/(PA*10^5/(286.9*TW1)*(1+xW1H2O)/(1+xW1H2O*461.5/286.9))*(mgout+xW1H2O*mgout)*1000; %L/s

%Condenser
PvapCH2O = exp(77.3450 + 0.0057*TC - 7235/TC)/TC^8.2 * 1e-5; %bar
xCH2O = (188.9/461.5)*PvapCH2O/(PS-PvapCH2O); %kg H2O/kg CO2; factor is gas constant ratio CO2/H2O
FCout = 1/(PS*10^5/(188.9*TC)*(1+xCH2O)/(1+xCH2O*461.5/188.9))*(mCO2out+xCH2O*mCO2out)*1000; %L/s
evapCH2O = xCH2O*mCO2out/0.018; %mol/s water
FcondH2O = (evapSH2O-evapCH2O)/54.378; %L/s; water condensed from CO2
FCO2outSTP = mCO2out/0.044/1.01325*273.15*R; %L/s; flow rate of CO2 at STP

molTotC = (u(3*5+1)+u(3*5+2)+u(3*5+3))+(evapSH2O-evapCH2O); %mol/s, total mol/s
mTotC = (u(3*5+1)*mwAm + u(3*5+2)*mwNO2 + u(3*5+3)*mwNA + ...
        (evapSH2O-evapCH2O)*mwH2O)/molTotC; %kg/mol, total mass of 1 mol solution
PvapCNA = R*TC*rhoAm * u(3*5+3)/molTotC/mTotC * exp(dGNA/(R*100*TC));
PvapCMEA = R*TC*rhoAm * u(3*5+1)/molTotC/mTotC * exp(dGMEA/(R*100*TC));


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Calculations of all emissions

%Absorber
if (PvapAMEA/(R*TA) > HMEA*u(3*0+1)/VA)
    emitAMEA = HMEA*u(3*0+1)/VA*FAout;
else emitAMEA = PvapAMEA/(R*TA)*FAout; end

if (PvapANA/(R*TA) > HNA*u(3*0+3)/VA)
    emitANA = HNA*u(3*0+3)/VA*FAout;
else emitANA = PvapANA/(R*TA)*FAout; end

%Stripper
if (PvapSMEA/(R*TS) > HMEA*u(3*2+1)/VS)
    emitSMEA = HMEA*u(3*2+1)/VS*FSout;
else emitSMEA = PvapSMEA/(R*TS)*FSout; end

if (PvapSNA/(R*TS) > HNA*u(3*2+3)/VS)
    emitSNA = HNA*u(3*2+3)/VS*FSout;
else emitSNA = PvapSNA/(R*TS)*FSout; end

%1st Wash section
if (PvapW1MEA/(R*TW1) > HMEA*u(3*4+1)/VW1)
    emitW1MEA = HMEA*u(3*4+1)/VW1*FW1out;
else emitW1MEA = PvapW1MEA/(R*TW1)*FW1out; end

if (PvapW1NA/(R*TW1) > HNA*u(3*4+3)/VW1)
    emitW1NA = HNA*u(3*4+3)/VW1*FW1out;
else emitW1NA = PvapW1NA/(R*TW1)*FW1out; end

%Condenser
if (PvapCMEA/(R*TC) > HMEA*u(3*5+1)/FcondH2O)
    emitCMEA = HMEA/FcondH2O*u(3*5+1)*FCout;
else emitCMEA = PvapCMEA/(R*TC)*FCout; end

if (PvapCNA/(R*TC) > HNA*u(3*5+3)/FcondH2O)
    emitCNA = HNA*u(3*5+3)/FcondH2O*FCout;
else emitCNA = PvapCNA/(R*TC)*FCout; end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Solvent loop

%Absorber
ut(3*0+1) = 0; % <-- assuming makeup keeps concentration of MEA constant
            %Fl/VHxh*u(3*3+1) - Fl/VA*u(3*0+1) - 0.5*Fgout*cNO2in*capNO2 ...
            %- emitAMEA + FevapW1H2O/VW1*u(3*4+1) + (emitW1MEA+emitCMEA);
ut(3*0+2) = Fl/VHxh*u(3*3+2) - Fl/VA*u(3*0+2) + Fgin*cNO2in*absorption - ...
            Fgin*cNO2in*capNO2 - PvapNO2/(R*TA)*Fgout;
if uv_on
ut(3*0+3) = Fl/VHxh*u(3*3+3) - Fl/VA*u(3*0+3)+ Fgin*cNO2in*capNO2 ...
            - emitANA + FevapW1H2O/VW1*u(3*4+3)*(1-deg);
```

```
else
ut(3*0+3) = Fl/VHxh*u(3*3+3) - Fl/VA*u(3*0+3)+ Fgin*cNO2in*capNO2 ...
            - emitANA + FevapW1H2O/VW1*u(3*4+3);
end

%Heat Exchanger, Cold
ut(3*1+1) = Fl/VA*u(3*0+1) - Fl/VHxc*u(3*1+1);
ut(3*1+2) = Fl/VA*u(3*0+2) - Fl/VHxc*u(3*1+2);
ut(3*1+3) = Fl/VA*u(3*0+3) - Fl/VHxc*u(3*1+3);

%Stripper
ut(3*2+1) = 0; % <-- assuming makeup keeps concentration of MEA constant
            %Fl/VHxc*u(3*1+1) - Fl/VS*u(3*2+1) - emitSMEA + FcondH2O/VC*u(3*7+1);
ut(3*2+2) = Fl/VHxc*u(3*1+2) - Fl/VS*u(3*2+2);
ut(3*2+3) = Fl/VHxc*u(3*1+3) - Fl/VS*u(3*2+3) - emitSNA + u(3*5+3);

%Heat Exchanger, Hot
ut(3*3+1) = Fl/VS*u(3*2+1) - Fl/VHxh*u(3*3+1);
ut(3*3+2) = Fl/VS*u(3*2+2) - Fl/VHxh*u(3*3+2);
ut(3*3+3) = Fl/VS*u(3*2+3) - Fl/VHxh*u(3*3+3);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Wash sections/condenser

%1st Wash section
ut(3*4+1) = -FevapW1H2O/VW1*u(3*4+1) + emitAMEA - emitW1MEA;
ut(3*4+2) = 0;
ut(3*4+3) = emitANA - emitW1NA - FevapW1H2O/VW1*u(3*4+3);

%Condenser
ut(3*5+1) = emitSMEA - emitCMEA - u(3*5+1);
ut(3*5+2) = 0;
ut(3*5+3) = emitSNA - emitCNA - u(3*5+3);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%Save calculated emissions in solution vector

ut(3*6+1) = emitAMEA - u(3*6+1);  %absorber MEA emissions
ut(3*6+2) = 0;                    %possibility to calculate NO2 emissions
ut(3*6+3) = emitANA - u(3*6+3);   %absorber NA emissions

ut(3*7+1) = emitSMEA - u(3*7+1);  %stripper MEA emissions
ut(3*7+2) = 0;                    %possibility to calculate NO2 emissions
ut(3*7+3) = emitSNA - u(3*7+3);   %stripper NA emissions

ut(3*8+1) = emitW1MEA - u(3*8+1); %wash 1 MEA emissions
ut(3*8+2) = 0;                    %possibility to calculate NO2 emissions
ut(3*8+3) = emitW1NA - u(3*8+3);  %wash1 NA emissions

ut(3*9+1) = emitCMEA - u(3*9+1);  %condenser MEA emissions
ut(3*9+2) = 0;                    %possibility to calculate NO2 emissions
ut(3*9+3) = emitCNA - u(3*9+3);   %condenser NA emissions

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

ut = ut';
```

Appendix C: Nitrosamine modelling - memo