In collaboration with Climax Molybdenum b.v.

Ammonia recovery from calciner off-gas

The effect of reclaiming ammonia by direct injection into the plant system

by

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This thesis is confidential and cannot be made public

Abstract

Ammonia (NH_3) has been recognized as an effective leaching agent in hydro-metallurgical processes for the recovery of metals[1]. These processes result in ammonia-metal crystals, whereby in the last step, water and ammonia are removed from the crystals by a calcination process. In the past, the vaporized ammonia is considered a waste stream. However, regulations in the last few decades make it impossible for companies to dispose large amounts of ammonia into the air[2][3]. Therefore, expensive installations, like catalytic oxidizers (CATOX) or membrane separators, need to be installed for ammonia reduction in the effluent gas stream.

Climax Molybdenum b.v. installation in the Botlek Rotterdam produces pure molybdenum oxide according to the process described above. With the production, molybdenum oxide is leached in an ammonia solution to remove all contaminants, then crystallized and calcined. For the calcination process, the crystals are heated by a gas burner to vaporize the ammonia and water. The off-gas contains air, NH_3, CO_2, dust particles, and water vapor. The objective is to recycle the ammonia from the off-gasses of the calciner. Reclaiming the ammonia from the off-gas stream could reduce the costs up to €2000 per day. In this thesis, insights are gathered related to the chemical and physical reactions that occur when off-gasses of the calciner enter the process. Additionally, both the beneficial effects and potential complications of reclaiming ammonia from the off-gas are explained.

This research is conducted by making mass balances on three different options for off-gas handling. These options include absorption into the leaching fluid (ARS:Ammonia Reduction System), absorption by water through a scrubbing system (AER:Ammonia Emission Reduction), and absorption by water through a scrubbing system with additional carbon dioxide removal with sodium hydroxide (AER+NaOH). In order to understand what happens when inorganic carbon (IC) comes into the system, experiments are conducted on both the leaching procedure of molybdenum and the stripping and condensing process of ammonia.

Results show that inorganic carbon reaches its solubility in the leaching fluid at 2.12 mol/kg. Also, no effect on the solubility of ammonium molybdate was found, and no additional precipitation occurs on metals like zinc, calcium, magnesium, and iron. In the leaching fluid, the solubility of ammonium bicarbonate (NH_4HCO_3) is reached at 183 grams per liter.

Additionally, the influence of inorganic carbon on the stripping process showed that the strip rate of ammonia was reduced by 1.4. Also, could be concluded that stripping of ammonia was done efficiently at 80 degrees until the total ammonia nitrogen (TAN) mole concentration equals the total inorganic carbon (TIC) mole concentration. As a result, additional water treatment is needed for the discharge water to ensure the amount of ammonia does not exceed 25kg per day. Both ARS and AER-system have 1.34 and 1.65 tonnes of ammonia in the discharge water per day, respectively. Furthermore, another complication found was scaling. Scaling happens in both ARS and AER-system in the form of ammonium bicarbonate. In contrast, AER+NaOH system does not have the complication of scaling or ammonia in the discharge water, but the pH of the solution needs to be neutralized before discharge. Moreover, higher pH in the recycling water of the scrubber causes lower absorption efficiency of ammonia.

ARS, AER, and AER+NaOH-system have an ammonia recovery of 1.73(41%w), 1.38(33%w), and 3.08(73%w) tonnes per day, respectively. Here the number between the brackets indicates the weight percentage of the overall ammonia usage per day. For the ARS and AER-system, this means a cost-saving of €1.160,- and €920,- per day, respectively. The AER+NaOH-system has a direct cost of €10.130,- per day, due to the expensive sodium hydroxide. The cost of sodium hydroxide as a water treatment agent is higher than the cost savings of ammonia recovery from the off-gasses of the calciner. Therefore can be concluded that, ammonia recovery from off-gasses has large potential, but other methods are needed to treat ammonia in the discharge water to make it economically feasible. Further research can elaborate on alternatives for ammonia treatment in discharge water. Examples include the use of lime (CaO)[4], increasing the stripping temperature[5], and leaching in sulfuric acid (H_2SO_4)[6]. However, this does not solve the scaling problem in the process. Therefore, further research should shine a light on the reduction of carbon dioxide that enters the chemical plant system. Examples proposed in this research, include condensing ammonia from the calciner off-gas stream. Multiple studies [7][8] show that, the condensing recovery is more effective for ammonia than carbon dioxide. Furthermore, this research also gives an economically feasible example of using an alternative calcination process without natural gas.

Preface

This thesis is the final step in completing my master in the European Mining, Minerals and Environmental Programme. This study has been completed in collaboration with Climax Molybdenum b.v. and the Delft University of Technology.

For the topic of my thesis, I would like to thank Dravin Mahes, Irene Morittu, and Dirkjan Kooijman for providing me the opportunity at Climax Molybdenum b.v. to work on this innovative and exciting project. I would like to graciously thank my supervisor from Climax, Dirkjan Kooijman, for his supervision during the past nine months. He was always able to make time for me when I had difficulties with my thesis. The support provided by Dirkjan and by other employees of Climax Molybdenum b.v., has allowed me to thrive throughout my thesis, providing me with the guidance and resources I required. A special thanks to Kees Groenendijk and other technicians for their time, space, and assistance in the lab.

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This thesis was completed with resources from both Climax Molybdenum b.v., the Delft University of Technology, and combined knowledge of Dirkjan, Peter, Mike, Maarten along with others. However, a special thank you have to go to my family and friends, who supported me throughout my thesis and I hope they are proud of what I am achieving.

At last, I would like to add weight to the gratitude to those who I already mentioned. This thesis had barely begun before lockdown in the Netherlands and the rest of the world because of the COVID-19 pandemic of 2020. Therefore, measures hindered the production of this thesis at some time. However, the persistence of those mentioned in this acknowledgment made it able to work towards the completion of this thesis despite this unique situation.

Wout Lohle
Delft, November 2020

Contents

List of Figures

List of Tables

List of Abbreviations

NECD	National Emission Ceilings Directive
EEA	European Environment Agency
LRTAP	Long-Range Transboundary Air Pollution
PMO	Pure Molybdenum Oxide
ADM	Ammonium Dimolybdate
CATOX	Catalytic Oxidation
ARS	Ammonia Reduction System
AER	Ammonia Emission Reduction
E32	condenser
S40	filter press
d3A	drying tower
d3B	calciner
CS7	scrubber system
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
TIC	Total Inorganic Carbon
TAN	Total ammonia nitrogen
ppm	parts per million
AAS	Atomic Absorption Spectroscopy
SRM	Standard Reference Material
ICP	Inductively Coupled Plasma
NDIR	Non-Dispersive Infrared Sensor
IC	Inorganic Carbon

1 Introduction

1.1 General introduction

Ammonia has been recognized as an effective leaching agent in hydro-metallurgical processes for the recovery of metals[1]. The selectivity of ammonia for specific metals, makes it a very useful substance in the metal industry. After selection of the specific metal, ammonia is separated from the bounded metal. An easy and widely used application of separation, is vaporizing ammonia and water by a calcination process, whereby the metals remain as solids.

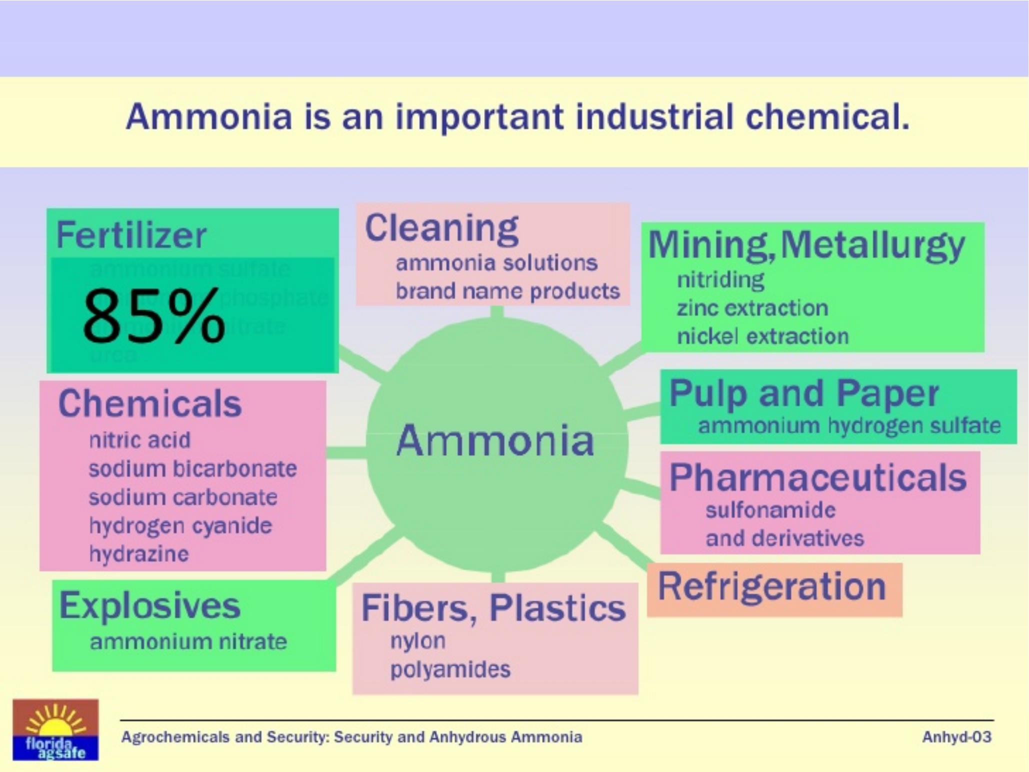
The vaporized ammonia can either be re-used in the process of metal recovery or it can go into the effluent stream of off-gasses into the air. In many cases companies choose for the second option, because of the expensive installations for ammonia re-winning and uncertainties related to the effluent off-gas stream on the processes of metal recovery. Regulations on ammonia emissions developed in the last few decades[2][3], moved industries to install expensive installations for the reduction of ammonia emissions. These costly installations make it worth looking at the possibility of recovering ammonia from the off-gas air.

Ammonia production

Majority of ammonia is made by the Haber-Bosch process. The Haber-Bosch process is an industrial process that produces ammonia (NH_3) from hydrogen (H_2) and nitrogen (N_2). Since its development at the beginning of the 20th century, the Haber-Bosch process has evolved into a technology that now consumes over 1%-2% of the world's energy sources in the production of nearly 150 million tonnes of NH_3 worldwide per year. Majority of this NH_3 is produced by this energy intensive process, requiring high temperatures($\pm 500\,^\circ C$) and pressures($\pm 20\,MPa$)[13][14].

Ammonia application

Ammonia has a wide range of applications in various industries. In Figure 1.1 the application of ammonia is shown in for these different industries[9].



Ammonia is an important industrial chemical.

Ammonia

Fertilizer
85%
ammonium sulfate
phosphate
itrate
urea

Cleaning
ammonia solutions
brand name products

Mining, Metallurgy
nitriding
zinc extraction
nickel extraction

Chemicals
nitric acid
sodium bicarbonate
sodium carbonate
hydrogen cyanide
hydrazine

Pulp and Paper
ammonium hydrogen sulfate

Pharmaceuticals
sulfonamide
and derivatives

Refrigeration

Explosives
ammonium nitrate

Fibers, Plastics
nylon
polyamides

florida agsafe

Agrochemicals and Security: Security and Anhydrous Ammonia

Anhyd-03

Figure 1.1: Application of ammonia in various industries[9].

The major part of the use of ammonia is in the agricultural sector (85%), where it is used as a fertilizer. Furthermore, ammonia and ammonium salts have been recognized as effective leaching agents in hydrometallurgical processes due to low toxicity and costs, easy recovery and high selective recovery of metals, such as copper, zinc and molybdenum oxide.[1].

Ammonia is also described in various methods for innovative carbon dioxide capture processes in order to limit the emissions of greenhouse gas from large carbon dioxide point sources such as power plants[15][16][17].

Ammonia emission

Ammonia emission is recognized by the European Environment Agency (EEA) and Dutch authorities as an air pollutant. Ammonia emissions can lead to disturbances in the function and structure of ecosystems. Atmospheric deposition of nitrogen compounds has impact on the pH levels of soils and waters, it contributes to a depletion of the buffering capacity and causes excessive demand on buffering rates. Consequences of the changing pH levels are the release of toxic metals and leaching of nutrients from soils, causing damage to flora and fauna. Atmospheric deposition of nitrogen compounds can also lead to an oversupply of nutrient nitrogen in terrestrial and water ecosystems, this phenomena is also known as eutrophication [18].

Emissions of NH_3 are covered by the EU National Emission Ceilings Directive (NECD) and the Gothenburg protocol under the United Nations Convention on Long-Range Transboundary Air Pollution (LRTAP) [2]. This states that the ammonia emission ceiling for the Netherlands is 122 kilotonnes in 2020. This ceiling is planned to get lower every decade. The magnitude of critical load exceedance for ammonia emissions is expressed in equivalents per hectare per year[3].

In order to meet the stringent ammonia ceiling, companies need to invest in expensive installations for ammonia reduction in the off-gasses. Examples of these installations are membrane separation, absorption units and catalytic oxidizers. For companies these installations are mostly not beneficial for the cash flow but are an obligation for permitting and approval of operation. Unless the ammonia can be re-used into the process.

1.2 Problem description

Climax Molybdenum b.v. installation in the Botlek Rotterdam produces technical molybdenum oxide, Pure Molybdenum Oxide (PMO) and Ammonium Dimolybdate (ADM). With the production of PMO, a mixture of molybdenum in ammonia solution is crystallized and calcined. For the calcination process, the crystals are heated by a gas burner to vaporize the ammonia and water. The off-gas contains air, NH_3, CO_2, dust particles and water vapor. In Figure 1.2 a schematic overview is given of the calciner (d3B).

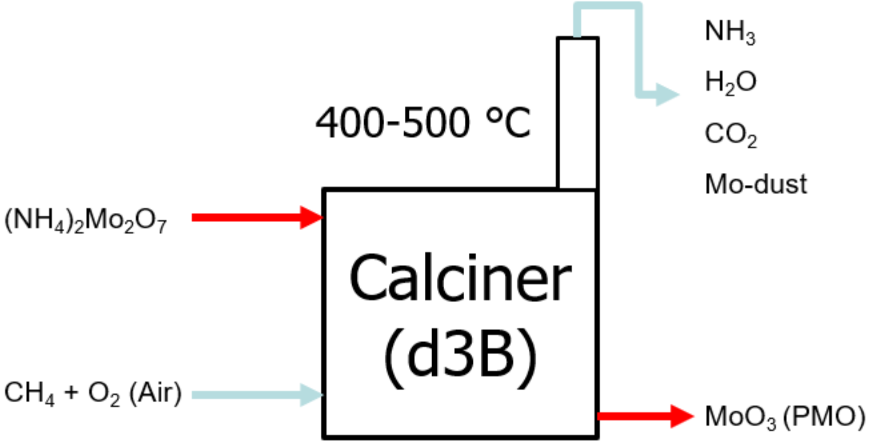


Figure 1.2: Schematic overview of the d3B-calciner, with incoming and effluent streams

In the current situation the gas flows through a filter (for dust collection) and then to the Catalytic Oxidation (CATOX)-unit. Here, the off-gasses are neutralized by combusting NH_3 to N_2 and H_2O. This method is costly, but also necessary to meet the nitrogen emissions requirements. Next to the high operational and maintenance costs there are other drawbacks: there is no ammonia recovery and the CATOX is very sensitive for damage by dust particles in the off-gas. Because ammonia is also used in the production of PMO, it would be beneficial to reuse the ammonia that goes to the CATOX and win it back for the production. Climax Molybdenum b.v. already developed a technique of injecting the off-gasses into the solution stream of the plant. By re-using the ammonia in the off-gasses, it would reduce the ammonia consumption by 70%. This results in an annual cost reduction of 720 thousand euro. In addition to that, it is possible to replace the CATOX-unit totally or partly, saving up to 500 thousand euro per year.

Sending the off-gas back in the system will cause CO_2 to be absorbed into the solution. Various studies emphasize the likelihood of using NH_3 as an absorbent for carbon dioxide because of its high absorption load, low regeneration energy requirement, low corrosiveness, low cost and high removal efficiency[15][16][17]. In other words, carbon dioxide is very soluble in an ammonia solution. When carbon dioxide is let into the system of the chemical plant, it is unclear where carbon dioxide leaves the system. Moreover, there is no knowledge yet what kind of influence this has on the processes of the plant.

1.3 Scope, research questions and methodology

1.3.1 Scope

The objective of this project is to re-use the ammonia in the off-gas air of the d3B-calciner. As a result, less ammonia is needed at the inlet stream of the process, that could maybe reduce the costs by €2.000 per day.

The scope of this research includes three different technical setups to reuse the ammonia from the d3B-calciner by injection into the current system.

1. In this option, the off-gasses are injected into the batch tank. Hereby, ammonia from the off-gas is absorbed by batch fluid. This is called an Ammonia Reduction System (ARS) and is illustrated in Figure 1.3.
2. In this option, the off-gasses are injected into the scrubber system. Hereby, ammonia from the off-gas is absorbed by cold water. This is called an Ammonia Emission Reduction (AER)-system and is illustrated in Figure 1.4.
3. In this option, the off-gasses are injected into the scrubber system and sodium hydroxide is added just before stripping at high temperature. This is called AER+NaOH-system and is illustrated in Figure 1.5.

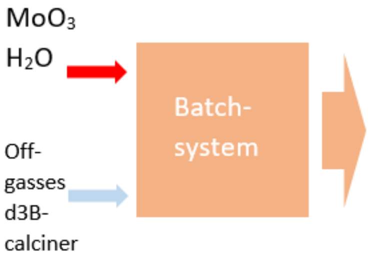


Figure 1.3: Schematic overview of ARS

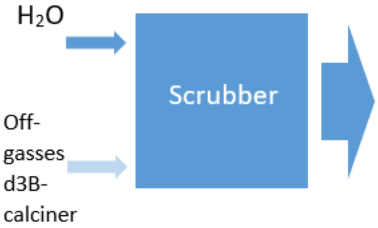


Figure 1.4: Schematic overview of AER

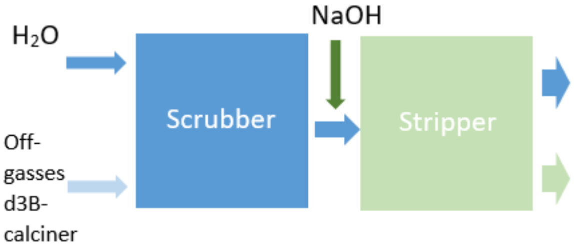


Figure 1.5: Schematic overview of AER+NaOH

Additionally, the research is scoped by only considering ammonia, water, molybdenum, carbon dioxide, and sodium hydroxide for the input and output streams of the system. To compare the three technical setups, the following aspects will be considered: The changes of the current equipment of the chemical plant, the financial benefit of the ammonia reclamation, the reduction of metal content in the product, and the potential complications in the system due to the recovery of ammonia from the off-gasses.

Due to time limitations, the following aspects will not be included in the scope: A financial analysis on the equipment, other ammonia treatment procedures then sodium hydroxide, and optimization of the absorption temperature and volume flow handling of the off-gasses.

1.3.2 Research questions

The main research question for this thesis includes: *What is the effect of reclaiming ammonia from the calciner by direct injection into the processing plant?*

In order to answer the main research question, the following two sub-questions and sub-sub-questions are considered:

1. *What is the influence of carbon dioxide on the processes in the batch tank?*
    (a) Will ammonium molybdate precipitate when carbon dioxide is added to the solution?
    (b) Will the injection of carbon dioxide have a positive influence on metal precipitation?
    (c) When do inorganic carbons reach their solubility in the batch tank?
    (d) What is the ratio $[HCO_3^-]$ - $[CO_3^{2-}]$ in the batch solution?
2. *What is the influence of carbon dioxide on both the process of stripping ammonia at 80 degree Celsius and condensing ammonia to 20 degree Celsius?*
    (a) What is the difference in stripping rates?
    (b) Will all ammonia evaporate out of the solution?
    (c) What is the ratio CO_2-H_2O-NH_3 in gas phase?
    (d) What is the ratio CO_2-H_2O-NH_3 in liquid phase after condensing?

1.3.3 Methodology

In order to give an answer to the research question, several steps are required. The description of these steps are as follows:

- A literature study will be performed on the absorption chemistry of carbon dioxide in ammonia solutions.
- An analysis of the current molybdenum production process will be undertaken.
- A mass balance of the current system is calculated in Microsoft Excel as a reference to the alternation of the processes due to off-gas handling.
- Assumptions are made for each processing step in the current system, based on literature study on the absorption chemistry of carbon dioxide in ammonia solution.
- Mass balances are made for three possible scenarios for off-gas handling of the d3B-calciner.
- The previously made assumptions are validated in two experimental procedures.
- Apply the results of the experiments into the mass balance for the three different options for off-gas handling of the d3B-calciner.
- Analyse and compare the three different options for off-gas handling.
- Conclude and recommend, propose a plan of action for moving forward.

Report structure
In Section 2.1 is elaborated on the current system of the chemical plant and the amount of off-gasses that the calciner produce per day. Thereafter, Section 2.2 involves the description of the absorption

chemistry of carbon dioxide in ammonia solution. The influence of carbon dioxide on the different processing equipment of the chemical plan will also be included in this section.

In Chapter 3, the assumptions that are made in the previous chapter are validated by means of an experimental procedure. Two different experiments are conducted to gather insights related to the physical and chemical reactions that occur in both the batch and the stripper-condenser process.

The results of these experiments are included in Chapter 4 and Chapter 5. Afterwards, these results are used to create mass balances related to the three different options for off-gas handling. This can be found in Chapter 6. At the end of the chapter, these three systems are compared with each other. In Chapter 7 an answer is given to the main research question of this study. At last, Chapter 8 is used to provide recommendations and a path forward for further research.

2 Theoretical background

In this chapter, the current system of the chemical plant is explained. This is done by explaining the chemical reactions and thermodynamic laws concerning the specific processes. Furthermore, it is shown why carbon dioxide is extremely soluble in ammonia solution and therefore, it can affect the process in the chemical plant by causing precipitation of ammonium bicarbonate salts.

2.1 Current chemical plant system

First, molybdenum oxide (MoO_3) is leached in hot water to remove the impurities that dissolve in water. In the flow diagram described in Figure 2.1, it can be seen that the solids continue to the "Batch process" in which the Molybdenum oxides are dissolved in diluted ammonia (NH_4OH). Ammonium-molybdate is formed according to Equation 2.1. The temperature of the operation is monitored and maintained at 60 degree Celsius. Also, the pH of the operation is maintained at around 10.5.

$$2\,\mathrm{NH_4OH\,(aq) + MoO_3(s) \longrightarrow (NH_4)_2MoO_4(aq) + H_2O\,(l)} \tag{2.1}$$

Molybdenum and copper make ammonia-ammonium bonds. All other metals do not go into the solution. To remove copper from the solution, hydrogensulfide (H_2S) is added to precipitate the copper molecules, as described in Equation 2.2.

$$\mathrm{Cu(NH_3)_4{}^{2+}(aq) + H_2S\,(aq) \longrightarrow 2\,NH_4{}^{+}(aq) + 2\,NH_3(aq) + CuS\,(s)} \tag{2.2}$$

Afterwards, solids are removed by a filter press (S40), and the solution with the ammoniummolybdate go to the crystallizer, see Figure 2.1. In the crystallizer, the solution is heated and stirred. Due to this process, ammonia and water vapor leave the solution and ADM crystals are formed, as described in Equation 2.3.

$$2\,\mathrm{(NH_4)_2MoO_4(aq) \longrightarrow (NH_4)_2Mo_2O_7(s) + 2\,NH_3(g) + H_2O\,(g)} \tag{2.3}$$

The crystals are centrifuged and led to the drying tower (d3A) and the calciner (d3B). In the d3A, the material is heated to remove the remaining water and ammonia. Afterwards, the material is send to the stockpile of ADM concentrate. In the d3B, the ADM crystals are heated with a gas burner to 400-500 degree Celsius. ADM crystals decompose to molybdenum oxide, ammonia and water, equation (2.4).

$$\mathrm{(NH_4)_2Mo_2O_7(s) \longrightarrow 2\,MoO_3(s) + 2\,NH_3(g) + H_2O\,(g)} \tag{2.4}$$

Two streams leave the d3B. The first stream including of the off-gasses are guided to the Catalytic Oxidizer, such that the ammonia decomposes into N_2 and H_2O. The second stream includes the solid stream of molybdenum oxide, which is stockpiled in bags for shipment.

The vapor from the crystallizer, containing ammonia and water, go to the condenser (E32), in which the gas is cooled to 18 degree Celsius. The liquid either goes back to the "batch process" or to the re-boiler (stripper). In the stripper, the solutions from the condenser and the scrubber are combined and heated to 80 degree Celsius. Ammonia and water evaporate out of the solution and go back to the condenser. Most of the water goes to an overflow tank and disappears out of the system.

Throughout the whole plant, off-gas is caught by suction pipes from different tanks. This 'air' is led to the scrubber system (CS7). The scrubber system is absorbing ammonia from the air using cold water. A mass balance of the whole system is given in Figure 2.1.

The mass balance has three input streams and four outlet streams. The inlet and outlet streams are illustrated in Table 2.1.

Table 2.1: Inlet and outlet streams of water, ammonia, molybdenum in tonnes/day

	Inlet	S40	Vent.Air	Briquette	Vb(bleed)	d3A	d3B
H_2O	0	24	0	-1.58	-19.29	-0.75	-2.38
NH_3	3.56	0	0.65	-0.15	0	-0.98	-3.08
Mo	22.93	0	0	-0.25	0	-5.44	-17.24

The inlet streams are at the 'Inlet','S40' and 'Ventilation Air'. The outlet streams are at the 'Briquette', 'Vb(bleed)', 'd3A' and 'd3B'. In total, 24 tonnes of water is entering the plant at the S40, where the filters are washed. 4.21 tonnes of ammonia is going into the chemical plant at the inlet and the ventilation system of the plant. Then, 22.93 tonnes of Molybdenum is put in the batch system as Molybdenum oxide.

The sum of outlet streams should equal the total inlet streams. Most of the water is leaving the system at the Vb(bleed). A minor part of the water is leaving the system at the d3A and d3B, where it is also partly captured by the ADM crystals. Most of the ammonia is leaving the system at the d3B and d3A: 0.98 and 3.08 tonnes per day respectively. A small part is going to the briquette. The major part of ammonia is leaving the plant at the d3B (73%). Since molybdenum is the product of the chemical plant, almosta all molybdenum(99%) will leave the system at the d3A or d3B.

2.1.1 Off-gas d3B-calciner

In the drying process, a gas burner uses methane and oxygen from the air to increase the temperature to 450 degrees Celsius. The reaction for methane with air is given in Equation 2.5. For every tonnes methane, 17.13 tonnes air is needed, see Table 2.2.

$$\mathrm{CH_4 + 2\,(O_2 + 3.76\,N_2) \longrightarrow CO_2 + 2\,H_2O + 7.52\,N_2} \tag{2.5}$$

Table 2.2: Flow of methane and air towards the d3B

	m3/day	tonnes/day
Methane	2640	1.73
Air	22945	29.67

The amount of material that goes into gas phase from the d3B is shown in Table 2.3. Thereby, taking in consideration the amount of ammonia and water that vaporize from the ADM crystals, as shown in Equation 2.4.

Table 2.3: Off-gas from d3B

	tonnes/day
H2O	6.27
NH3	3.08
CO2	4.75

The total effluent air of the d3B is 10 000 m^3 per hour at 450 degree Celsius. The density of air at this temperature is 0.5 g/L[19]. This means that alongside the products of the reactions inside the calciner, also many additional air is used during combustion. The total effluent air flow is given in Table 2.4.

Table 2.4: Effluent airflow from the d3B

	m3/day	tonnes/day	℃
Air mixture	240 000	120	450

The extra airflow is needed to transport all ammonia and water from the ADM crystals. Also, a lot of air is used to be sure the combustion is a complete reaction, and no carbon mono-oxide is created.

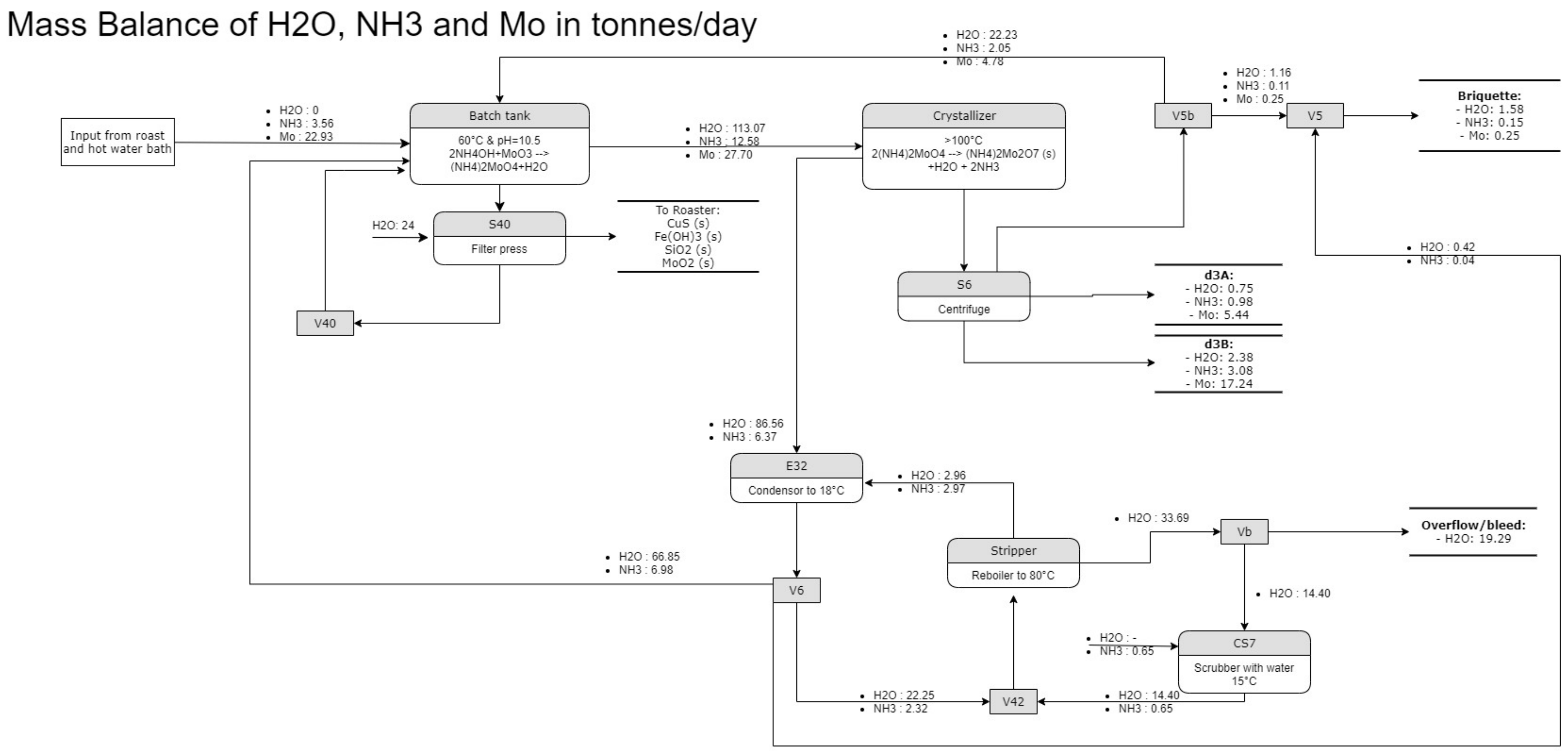


Figure 2.1: Mass balance of the current system

2.2 Carbon dioxide in ammonia solution

As already described in the introduction in Chapter 1, off-gasses from d3B do not only contain water and ammonia but also carbon dioxide. This chapter elaborates on what happens when CO_2 comes in contact with a solution of water and ammonia. Also, is explained why carbon dioxide is extremely soluble in ammonia solution. Afterwards, Section 2.3 describes the implementation of the obtained insights from this section in the different processing steps of the chemical plant. This is done to get a complete overview of the uncertainties and assumptions at the different processing steps.

2.2.1 Absorption chemistry

The CO_2 absorption process using aqueous ammonia solution depends on the temperature, ion concentration and pH value of the solution. All three variables have influence on the equilibrium constant of the reaction. The chemical reactions of a CO_2-NH_3-H_2O system are given in Equation (2.6-2.12)[20][21][22].

$$\mathrm{H_2O\,(l)} \longleftrightarrow \mathrm{H^+\,(aq)} + \mathrm{OH^-\,(aq)} \tag{2.6}$$

$$\mathrm{CO_2\,(aq)} + \mathrm{H_2O\,(l)} \longleftrightarrow \mathrm{HCO_3{}^-\,(aq)} + \mathrm{H^+\,(aq)} \tag{2.7}$$

$$\mathrm{HCO_3{}^-\,(aq)} \longleftrightarrow \mathrm{CO_3{}^{2-}\,(aq)} + \mathrm{H^+\,(aq)} \tag{2.8}$$

$$\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} \longleftrightarrow \mathrm{NH_4{}^+\,(aq)} + \mathrm{OH^-\,(aq)} \tag{2.9}$$

$$\mathrm{NH_3\,(aq)} + \mathrm{HCO_3{}^-\,(l)} \longleftrightarrow \mathrm{NH_2COO^-\,(aq)} + \mathrm{H_2O\,(aq)} \tag{2.10}$$

$$\mathrm{CO_2\,(aq)} + \mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} \longleftrightarrow \mathrm{NH_4HCO_3\,(aq)} \tag{2.11}$$

$$\mathrm{NH_4HCO_3\,(aq)} + \mathrm{NH_3\,(aq)} \longleftrightarrow \mathrm{(NH_4)_2CO_3\,(aq)} \tag{2.12}$$

Carbon dioxide is absorbed into the ammonia solution, including three different occurrences; ammonium carbamate (2.10), ammonium bicarbonate (2.11) and ammonium carbonate (2.12). Higher pH values accelerate the production of free ammonia, shifting the equilibrium towards the left in Equation 2.9. Due to the higher pH and increased concentration of aqueous ammonia, more carbon dioxide is absorbed, as described in Equation 2.11 [17]. In the next section, the equilibrium constant of carbon dioxide in aqueous solution is described, including the influence of the pH.

2.2.2 Depending pH and ammonia-concentration

As already described, the pH has a large influence on the chemical composition of carbonate or bicarbonates. The equilibrium constant for the carbonate concentration is given in Table 2.5 [23].

Table 2.5: Solution reaction of carbonates

Solution reaction	Equilibrium constant
$H_2CO_3 = HCO_3{}^- + H^+$	$K_{1a} = 4.47 \cdot 10^{-7}$
$HCO_3{}^- = CO_3{}^{2-} + H^+$	$K_{2a} = 4.68 \cdot 10^{-11}$

The following expressions are used to calculate the mole fraction of carbonate in the solution. First, Equation 2.13 is used to calculate the mole fraction of $CO_3{}^{2-}$ in the solution. Secondly, Equation 2.14 is used to calculate the mole fraction of $HCO_3{}^-$ in the solution. Finally, Equation 2.15 to calculate the mole fraction of H_2CO_3 in the solution [23]. The subscript T and aq represent the total and species concentration in solution, respectively.

$$[CO_3{}^{2-}]_{aq}/[CO_3{}^{2-}]_T = K_{1a}\cdot K_{2a}/([H^+]^2 + K_{1a}\cdot[H^+] + K_{1a}\cdot K_{2a}) \tag{2.13}$$

$$[HCO_3{}^-]_{aq}/[CO_3{}^{2-}]_T = K_{1a}\cdot[H^+]/([H^+]^2 + K_{1a}\cdot[H^+] + K_{1a}\cdot K_{2a}) \tag{2.14}$$

$$[H_2CO_3]_{aq}/[CO_3{}^{2-}]_T = [H^+]^2/([H^+]^2 + K_{1a}\cdot[H^+] + K_{1a}\cdot K_{2a}) \tag{2.15}$$

In Figure 2.2 the calculated distribution of ammonium carbonates as a function of pH is given.

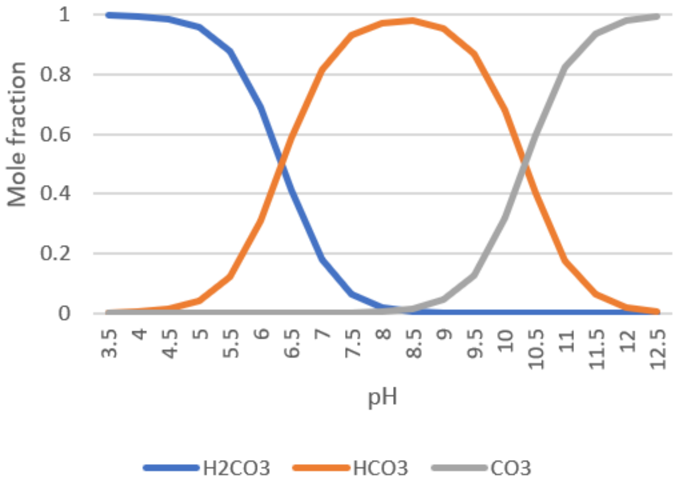


Figure 2.2: Calculated distribution of total inorganic carbon as a function of pH at a temperature of 15℃.

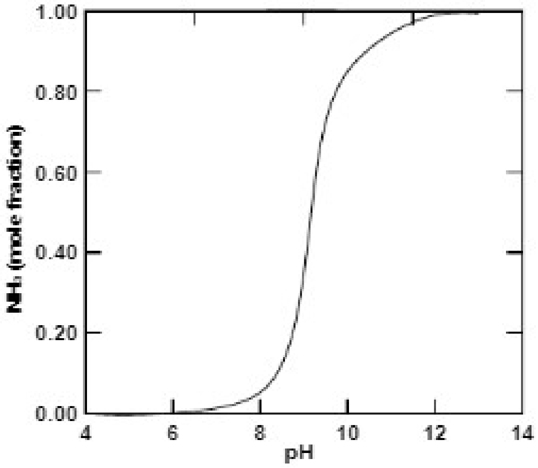


Figure 2.3: Dissociation of NH_3 varies with pH at 8 degree Celsius[10].

As can be seen in Figure 2.2, the solution with pH < 6.5 contains mainly carbonic acid, H_2CO_3. When the pH is between 6.5-10, the predominant species is $HCO_3{}^-$, with a minimal amount of $CO_3{}^{2-}$ and H_2CO_3. Then, when the pH > 10, the solution contains mainly $CO_3{}^{2-}$. The relation of this equilibrium of the carbonate solution is given in Equation 2.16, 2.17 and 2.18.

$$H_2CO_3(aq) + H_2O\,(l) \longleftrightarrow H_3O^+(aq) + HCO_3{}^-(aq) \tag{2.16}$$

$$HCO_3{}^-(aq) + OH^-(aq) \longleftrightarrow CO_3{}^{2-}(aq) + H_2O\,(l) \tag{2.17}$$

$$HCO_3{}^-(aq) + H_2O\,(aq) \longleftrightarrow CO_2\cdot H_2O\,(aq) + OH^-(aq) \tag{2.18}$$

At higher pH, more OH^- molecules are present in the solution and more carbon dioxide is absorbed by aqueous ammonia. In Figure 2.3, the relation between pH and the NH_3 concentration is given in mole fraction[10] at 8 degree Celsius. When pH is increasing, the mole fraction of NH_3 also increases. The absorption of ammonia in water can be described by the following Equations 2.6 and 2.9. In these equations can be seen that a higher pH shifts the balance towards ammonia instead of ammonium in the solution [24].

2.2.3 Solubility of ammonium carbonates

The absorption of carbon dioxide into an aqueous ammonia solution can result in the production of solid carbonate salts. The concentration of ammonium ions, temperature and pH of the solution influence the type of carbonate salts that will be produced. Formation of crystals in the process could cause scales on the walls or plugging of the pipes. The solubility of $(NH_4)_2CO_3$ in water is 1000 grams/liter at 15 degrees Celsius[25].

$$2\,NH_4{}^+(aq) + CO_3{}^{2-}(aq) \longleftrightarrow (NH_4)_2CO_3\,(s) \tag{2.19}$$

The solubility of NH_4HCO_3 in water is 217grams/Liter at a temperature of 15 degree Celsius.

$$\mathrm{NH_4}^+(\mathrm{aq}) + \mathrm{HCO_3}^-(\mathrm{aq}) \longleftrightarrow \mathrm{NH_4HCO_3}\,(\mathrm{s}) \tag{2.20}$$

The precipitation reaction is dependent on the operation conditions; pH, CO_2-concentration, NH_3-concentration and temperature are leading. By increasing temperature of water, the solubility increase. However, the ammonium carbonates will decompose (dec) at a certain point. Table 2.6 describes the solubility of ammonium carbonates and ammonium bicarbonates for different temperatures in water [26].

Table 2.6: Solubility in water in grams/100mL water, at atmospheric pressure and different temperatures.

Substance	Formula	0 ℃	15 ℃	30 ℃	60 ℃	90 ℃
Ammonium bicarbonate	NH_4HCO_3	11.9	21.7	28.4	59.2	dec
Ammonium carbonate	$(NH_4)_2CO_3$	55.8	100		dec	

The solubility of ammonium carbonate and ammonium bicarbonate in aqueous solution are needed to reveal the mass balances at which precipitation occurs.

2.3 Mass balance options with off-gas d3B

In Section 2.1, it is shown that the off-gasses of the d3B-calciner contain 4.75 tonnes of CO_2 and 3.08 tonnes of NH_3 per day. The previous section shows that carbon dioxide is extremely soluble in ammonia solution and therefore, forms carbonate, bicarbonate and carbamate bonds with ammonium ions. This section describes what happens with the inorganic carbon in the process and where the material enter and leave the system. The chemical plant is divided in three sections, which are Batch, Crystallizer and Scrubber-Stripper system. Per section is described what assumptions are made for the mass balance of the ARS, AER and AER+NaOH system. These mass balances can be seen in Appendix A.1, A.2 and A.3. To simplify the mass balances, the total inorganic carbon in the system can be classified as either ${CO_3}^{2-}$ or ${HCO_3}^-$. The fraction of CO_2 in the solution is considered to be very small in this pH range, see Figure 2.2.

2.3.1 Batch-system

As already described in Section 2.1, the operation conditions in the Batch include a pH 10.5 and a temperature of 60 degrees Celsius. According to Figure 2.2, the carbonates will be dominantly in the form of ${CO_3}^{2-}$. Each mole carbonate correspond to two ammonium ions. Which is different to ${HCO_3}^-$, where only one ammonium ion is bound to. In Section 2.2.3, it can be seen that NH_4HCO_3 has a much lower solubility than $(NH_4)_2CO_3$. Therefore, NH_4HCO_3 reaches solubility in the batch, as shown in the mass balance models in Appendix A. An overview of the batch system is given in Figure 2.4.

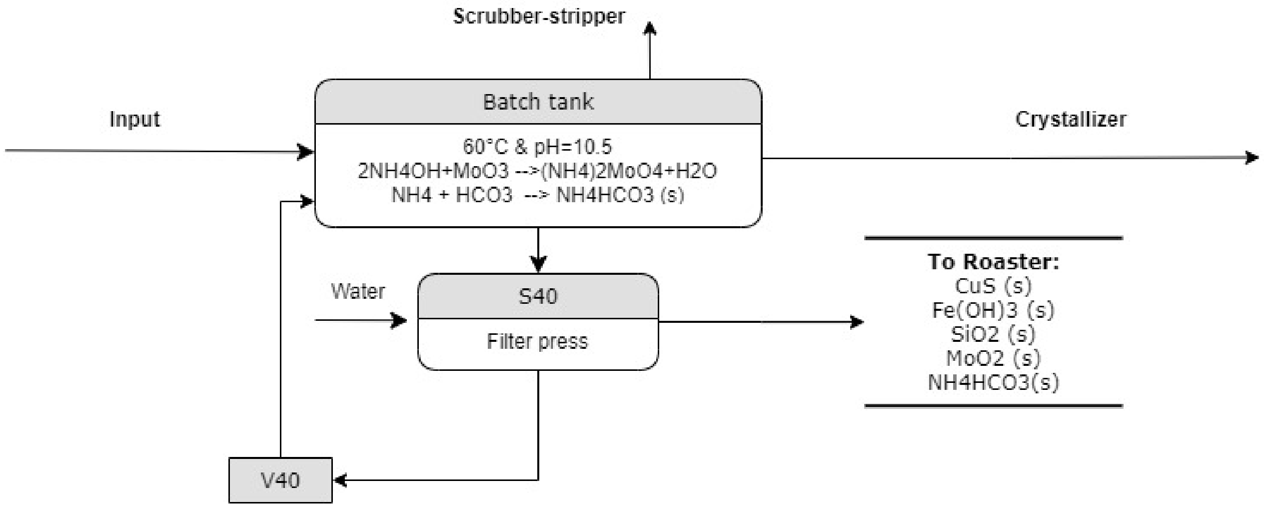


Figure 2.4: Overview input and output streams in the batch process

Figure 2.4 shows that once inorganic carbons are in the system, there are three options: they precipitate as carbonates, stay in the solution or are caught in the exhaust air to the scrubber. This is explained further in Section 2.3.3.
After leaching that took place in the batch tank, the solution is filtered, and the solids are brought to the roaster. The carbonate precipitates can be in the form of metal carbonates as well as ammonium carbonates. Carbonate precipitate leave the system permanently after filtering. The main reactions in the batch tank are given down here. Table 2.7 gives an overview of the solubility of metal carbonates in water at 25 degree Celsius.

$$\mathrm{NH_4{}^+(aq) + OH^-(aq) + MoO_3(s) \longleftrightarrow (NH_4)_2MoO_4(aq) + H_2O\,(l)} \tag{2.21}$$

$$\mathrm{Cu(NH_3)_4(aq) + H_2S\,(aq) \longleftrightarrow 2\,NH_4{}^+(aq) + 2\,NH_3(aq) + CuS\,(s)} \tag{2.22}$$

$$\mathrm{Fe^{3+}(aq) + 3\,NH_4{}^+(aq) + 3\,OH^-(aq) \longleftrightarrow Fe(OH)_3(s) + 3\,NH_4{}^+(aq)} \tag{2.23}$$

Table 2.7: Solubility of metals and metal carbonates in water at 25 degree Celsius

Solubility at 25 degree	Solubility (mg/L)
CuS[27]	0.33
$Fe(OH)_3$[28]	0.214
$Fe(OH)_2$[28]	0.18
$Mg(OH)_2$ [29]	9.80
$FeCO_3$[30]	6.7
$MgCO_3$[29]	106
$CaCO_3$ [30]	13
$MnCO_3$ [30]	$4.7E^{-3}$

The metals in basic conditions have a very low solubility product; it is lower than the solubility product of metal carbonates. Therefore, carbonates will probably not precipitate with other metals in the solution. As described before, the solubility of ammonium carbonates is much higher than the solubility of ammonium bicarbonate. An overview of the possible chemical reactions is given in Figure 2.5.

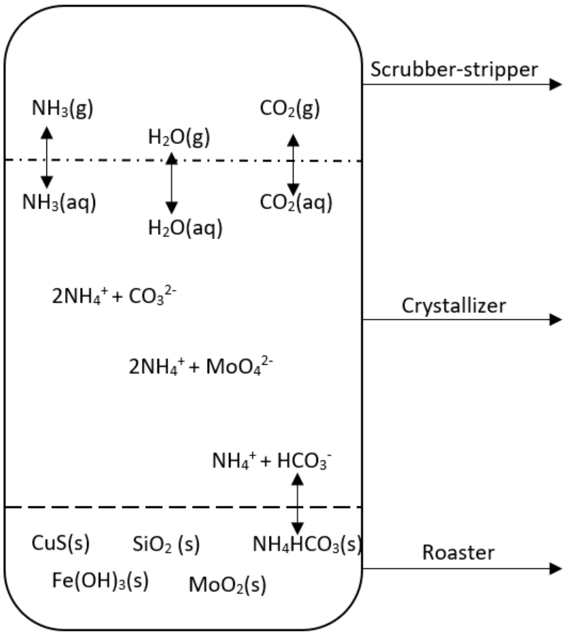


Figure 2.5: Chemical composition inside the the batch tank, operation temperature 60 degree Celsius and pH 10.5

In the batch, inorganic carbon can leave the chemical plant system, but only first if the carbonates reach solubility. For the models, described in Appendix A, it is assumed that the solubility of NH_4HCO_3 is the same as in water at this temperature;592g/l.

2.3.2 Crystallizer-system

The crystallizer has one input, coming from the batch. In the crystallizer, the temperature is increased to over 100℃. The crystallizer has two output streams: One at which, water, ammonia and carbon dioxide evaporate out of the solution. Secondly, solid ammonium dimolybdate crystals precipitate to the bottom. This is a continues process and requires a constant feed from the batch. The crystals at the bottom of the crystallizer are stripped from the fluid by a centrifuge and send to the d3A or d3B. Fluids from the centrifuge are partly used to make briquettes. The rest is send back to the batch. An overview of this scheme is given in Figure 2.6.

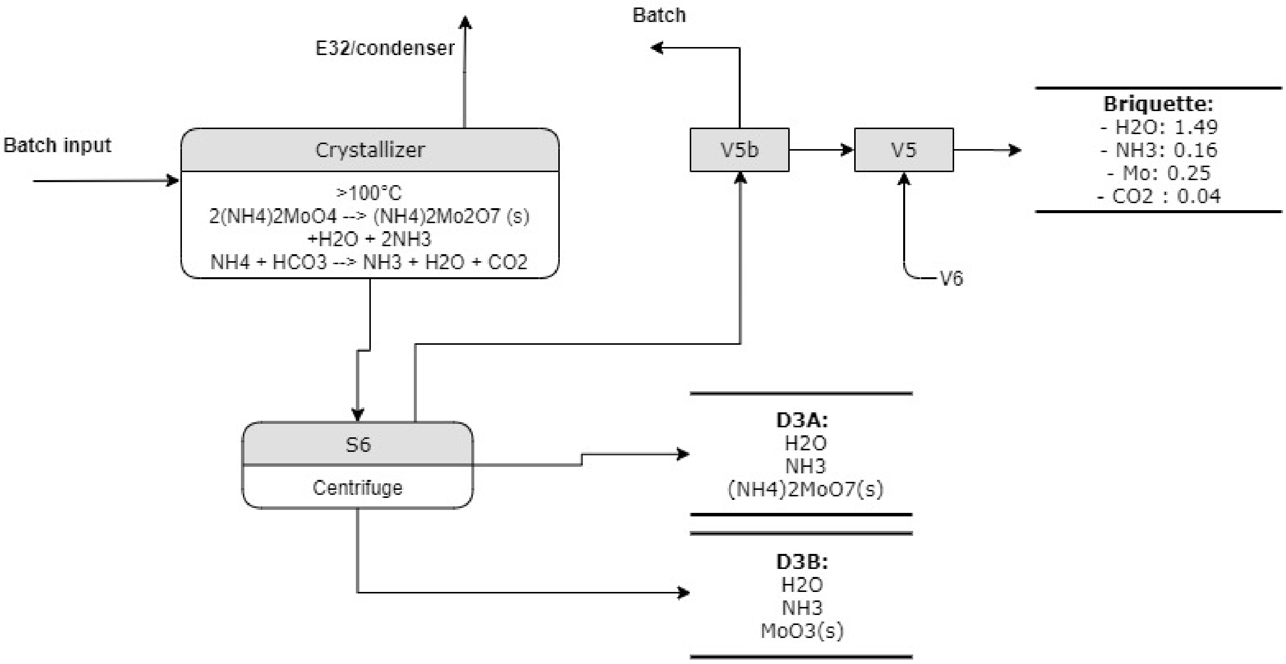


Figure 2.6: Overview processes in the crystallizer system

Both ammonium carbonate or ammonium bicarbonate salts decompose at high temperatures, 60 and 90 degree Celsius respectively. Therefore, if the carbonates do not leave the fluid in the crystallizer, they decompose in the d3A or d3B. Evaporated air from the crystallizer will go towards the condenser. Related to the mass balance, it is assumed that all the carbonates decompose in the crystallizer. The major stream of water, ammonia and carbon dioxide evaporates towards the condenser. This assumption is made based on the decomposition table in Section 2.2.3.

A schematic overview of the processes inside the crystallizer is shown in Figure 2.7.

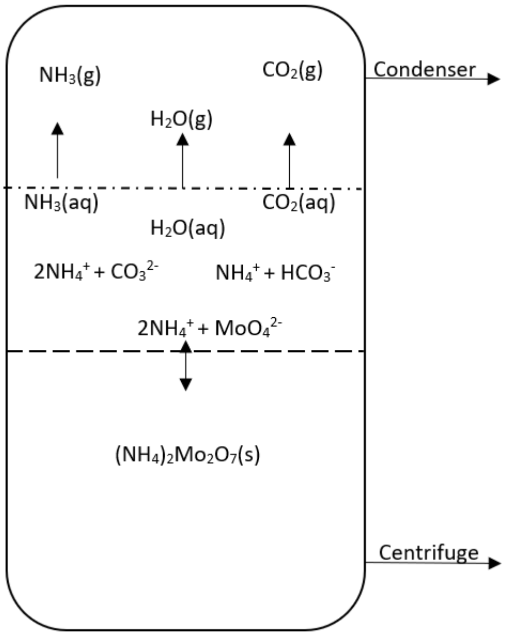


Figure 2.7: Schematic overview of processes in the crystallizer

2.3.3 Scrubber-stripper-system

By looking at Figure 2.8, it can be seen that the scrubber-stripper and condenser system have two input streams: one at the condenser (E32), where gasses from the crystallizer enter, and a second input stream at the scrubber (CS7), where air caught in the ventilation system from the whole chemical plant enters. The output streams are at the overflow from the Vb, from V6 towards the Batch and scrubbed effluent gas at the scrubber.

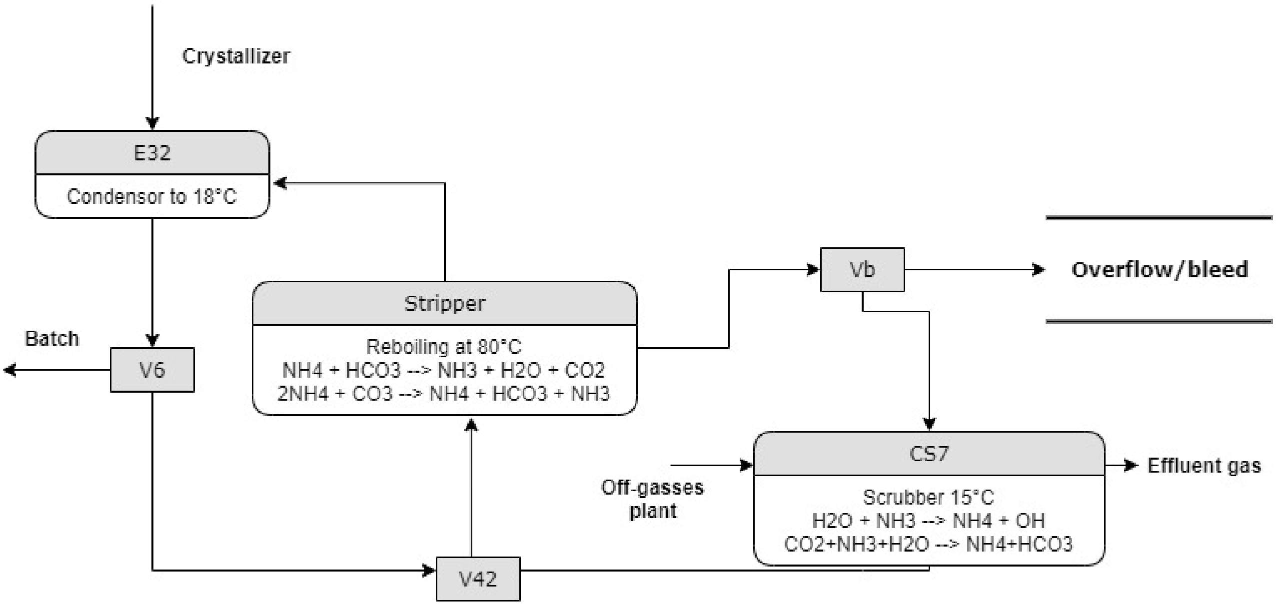


Figure 2.8: Overview in and output streams scrubber-stripper system

The following paragraphs elaborate on the movement of carbon dioxide, ammonia and water inside the three main equipment of this system; the scrubber (CS7), the stripper and the condenser (E32).

Absorption tower (scrubber)
The absorption tower (scrubber) of the chemical plant is a spray tower. Ammonia is absorbed by water droplets. A gas stream containing both CO_2 and NH_3 enables the solvation of carbon dioxide into water. In this solution, both ammonium bicarbonates and ammonium carbonates are formed.

Air from the ventilation system of the chemical plant is guided through the scrubber. Water from the Vb is used to "wash" the air from its ammonia. Washed air leaves the plant system in the effluent air stream from the scrubber. The solution with dissolved ammonia goes towards V42, shown in Figure 2.8.

The absorption of NH_3 in water can be described by Henry's law, which states that the amount of gas that is dissolved in a liquid is directly proportional to the partial pressure of that gas around the liquid, at constant temperature. The mathematical formula for Henry's law is given by the following equation.

$$\mathrm{P} = \mathrm{k_H} \cdot \mathrm{C} \tag{2.24}$$

In the equation, P represents the partial pressure of the gas in the atmosphere, C represents the concentration of the dissolved gas and k_H is the Henry's law constant of the gas. Important aspects that influence Henry's law constant are pressure, temperature, composition of the solvent and composition of the gas [31]. In Figure 2.9, Henry's law approximation of ammonia and water is given at 15 degree Celsius. In this model, the real approximation, calculated by Dirkjan Kooijman, is given as well.

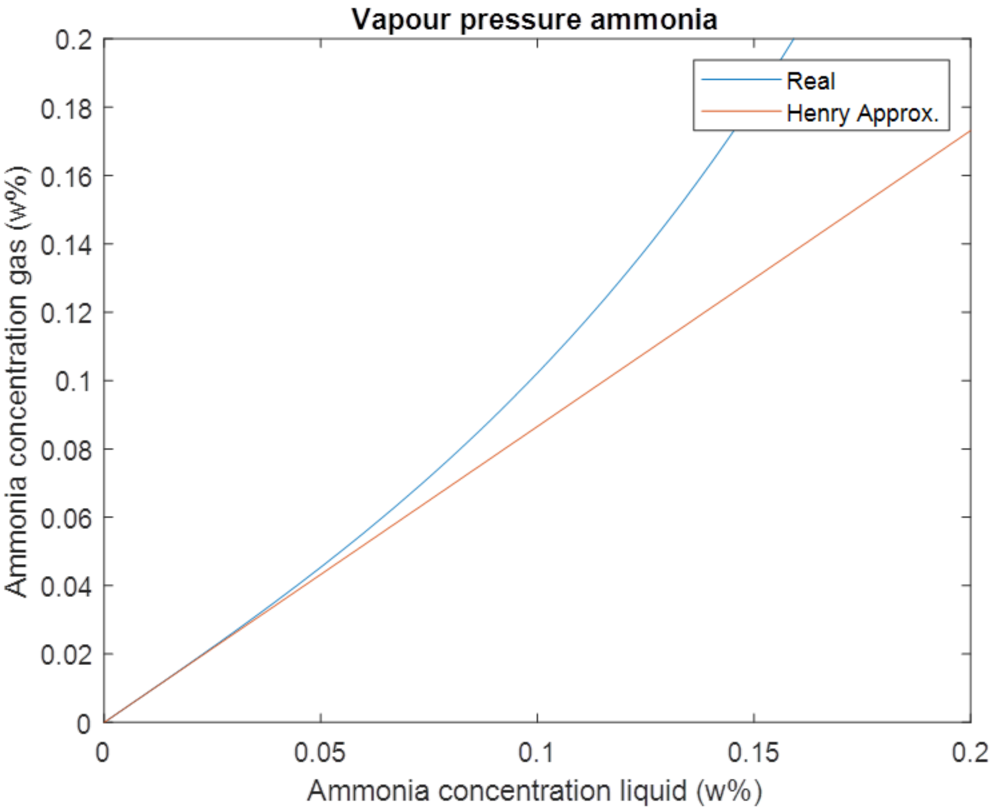


Figure 2.9: Vapour pressure ammonia and Henry's law approximation at 15 degree Celsius[11].

Figure 2.9 shows that if the ammonia concentration of the gas is 0.05%w, the ammonia concentration in the absorbent fluid is also 0.05%w, according to Henry's law. The minimal amount of water that is needed for complete absorption of ammonia in a scrubber system can be calculated for this temperature.

The amount of CO_2 that can dissolve in the solution also depends on Henry's law constant and the pH of the solution. Henry's law constant of CO_2 decreases at increasing temperature and ionic strength of the solution. The absorbed carbon dioxide can dissociate to form bicarbonate and carbonate ions, as described before in Section 2.2.1. Higher pH values result in a more effective absorption of carbon dioxide [17]. Ammonia on the other hand, has a more efficient absorption at lower pH.

In the scrubber system, the temperature of the absorption is 15℃. A cooling system is needed to keep the temperature low, such that all ammonia can be absorbed by water droplets. Low temperature stimulates the absorption of ammonia[31]. With addition of carbon dioxide in the air an endothermic reaction occurs during absorption by aqueous ammonia [16]. Cooling will probably not be necessary anymore.

Based on findings from literature related to the absorption of CO_2 by ammonia and water in a spray tower, the following assumptions are made [32] [33]:

- The amount of absorbent liquid is equivalent to the amount that is needed to absorb all NH_3 from the air. Therefore, in any scenario, the minimal amount of water is used to scrub all ammonia from the air.
- Absorbent concentration of NH_3 in liquid is equivalent to %Wt of NH_3 in air. This principle is based on Henry's law, which is explained in Figure 2.9.

- Absorbent concentration of CO_2 is equivalent to the concentration of NH_3 in the absorbent liquid in mole ratio 1:1. In experiments conducted by Zhuang et al.[32] and Ma et al.[33],the high absorption load of carbon dioxide by ammonia is emphasized. This absorption load is based on the weight percentage of ammonia compared to carbon dioxide. The molar mass of ammonia is 2.5 times smaller than the molar mass of carbon dioxide. The leanest load of absorption ammonia and carbon dioxide is at a mole ratio of 1:1.

Due to the increasing ammonia concentration in the AER-system, the amount of water needed to scrub all the ammonia from the off-gas will be 120 tonnes/day.

Desorption tower (stripper)
The desorption tower (stripper) is used in this process to strip ammonia from the solution using heating. The ammonia water mixture is explained according to the thermodynamic state of vapor-liquid equilibrium. An accurate prediction of the vapor-liquid equilibrium is of importance for the calculation and modelling of the desorber. An exact determination of the composition at given temperature and pressure is essential. Figure 2.10 shows the bubble and dew lines for an ammonia-water mixture at different temperatures at 1 atmosphere. The model is created by Dirkjan Kooijman and based on Xu-Goswami's[7] equilibrium of state.

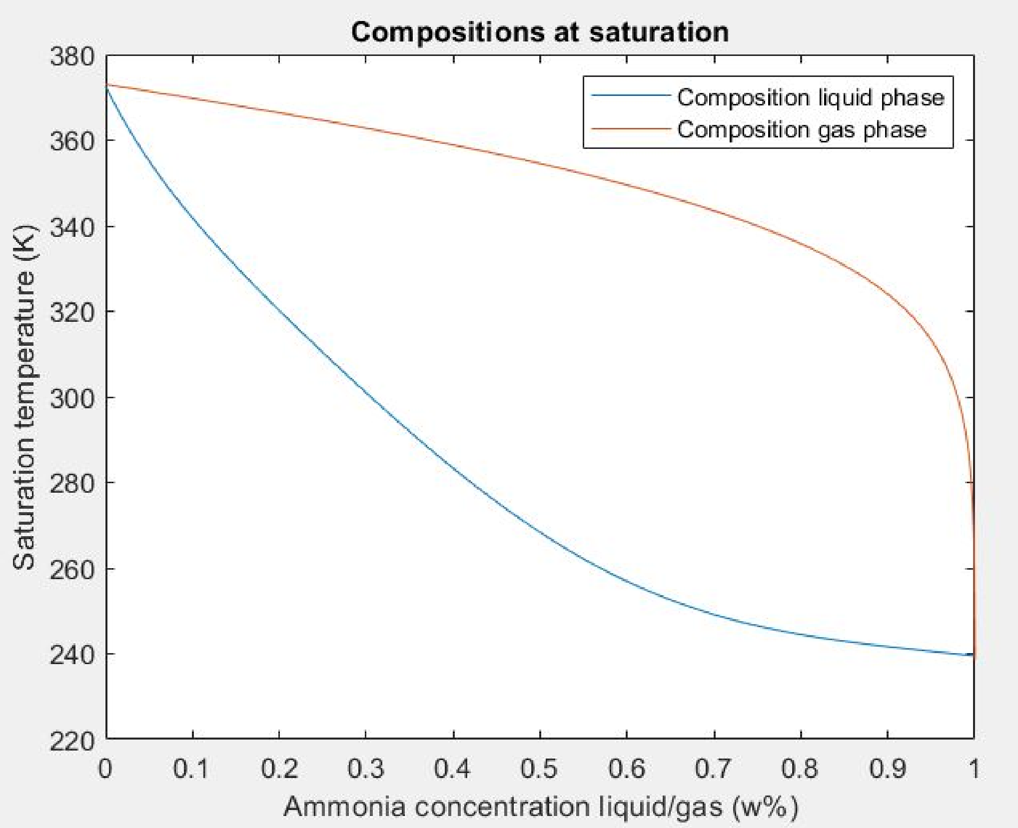


Figure 2.10: Ammonia water equilibrium at saturation for gas and liquid phase at 1 atm.[12].

The re-boiler operates at a temperature of 80 degree Celsius, which corresponds to an ammonia:water mixture in the gas phase of 55:45 %w. The gas is transported to the condenser in which it condensates to a temperature of 18 degree Celsius.

Carbon dioxide in the solution will lead to a more difficult stripping mechanism[34]. Not only CO_2 brings an extra dimension in the model, also the concentrations of inorganic carbon and ammonia have influence on this balance. To be able to give an estimation of what happens in the stripper during the process with additional carbon dioxide, experimental procedure must be done to find the NH_3:H_2O:CO_2-balance for this specific case.

The expected reactions of an NH_3:H_2O:CO_2-system are given in Equation 2.25-2.29[21].

$$\mathrm{NH_4{}^+(aq) + HCO_3{}^-(aq) \longleftrightarrow NH_3\,(g) + H_2O\ (g) + CO_2(g)} \tag{2.25}$$

$$\mathrm{2\,NH_4{}^+(aq) + CO_3{}^{2-}(aq) \longleftrightarrow 2\,NH_3\,(g) + H_2O\ (g) + CO_2(g)} \tag{2.26}$$

$$\mathrm{NH_3\,(aq) \longleftrightarrow NH_3\,(g)} \tag{2.27}$$

$$\mathrm{H_2O\ (l) \longleftrightarrow H_2O\ (g)} \tag{2.28}$$

$$\mathrm{CO_2\,(aq) \longleftrightarrow CO_2\,(g)} \tag{2.29}$$

For the three mass balances, described in Appendix A, it is assumed that all dissolved inorganic carbon and ammonia is decomposed to carbon dioxide and ammonia in gaseous state.

In the AER+NaOH model, described in Appendix A.3, sodium hydroxide is added to the solution, just before stripping. Sodium hydroxide is an easy and quick method to increase the pH of the solution. If the pH of the solution is high, the equilibrium shifts to the free ammonia gas[35]. As shown in Equation 2.9, the equilibrium shifts to the left. Increasing the sodium ion concentration in the solution causes the inorganic carbon to react towards sodium carbonate, described by the following reaction:

$$\mathrm{Na^+(aq) + OH^-(aq) + NH_4{}^+(aq) + HCO_3{}^-(aq) \longleftrightarrow NaHCO_3(aq) + NH_3(g) + H_2O\,(l)} \tag{2.30}$$

$$\mathrm{2\,Na^+(aq) + 2\,OH^-(aq) + HCO_3{}^-(aq) \longleftrightarrow Na_2CO_3(aq) + H_2O\,(l) + OH^-(aq)} \tag{2.31}$$

Sodium hydroxide reacts with carbonate in a ratio 2:1. Whereby, sodium carbonate is formed which is dissolved in the solution. Ammonium ions in the solution transform into ammonia, which evaporates in the stripper and leaves the solution.

Condenser
The condenser has two injection streams of gasses: one from the stripper and one from the crystallizer. Both gas streams are cooled to 18℃, hereby the gas condensates to liquid. The remaining gasses are caught in this system by suction pipes and transported to the scrubber. As illustrated in Figure 2.10, the ammonia:water concentration in the effluent solution stream is at maximum 35:65 %w. Figure 2.1 shows the ammonia:water relation of the current system is 9:90 %w. This condition changes when there is an ammonia:water:carbon dioxide system.

For the models in Appendix A, it is assumed that all carbon dioxide will condensate.

2.4 Mass balance options

By going through the different processes of the chemical plant in Section 2.3 and implementing the knowledge gained from Section 2.2.1 (Absorption chemistry), three different mass balances are made in Figure A.1, A.2 and A.3 of Appendix A.

The three options are developed under the following assumptions;

- All off-gasses from the d3B-calciner are absorbed into the processes of the chemical plant, independent of the injection point.
- NH_4HCO_3 has the same solubility in the batch as in water at a temperature of 60℃; 592g/l
- In the crystallizer, all inorganic carbon is decomposed to carbon dioxide
- In the condenser all carbon dioxide is dissolved back into the solution formed

- In the stripper, all dissolved inorganic carbon and ammonia are decomposed in carbon dioxide and gaseous ammonia.
- Sodium hydroxide reacts with carbonate in a ratio 2:1, Na_2CO_3 will be formed and dissolved in the solution. Ammonium in the solution will be transform into ammonia and evaporate out of the solution when it is stripped.

In the next chapter, the methodology of the experiments is explained to validate the assumptions made in this chapter.

3 Materials and methods

In Chapter 2 assumptions are listed to create a first indication of the mass balances. These assumptions are made mostly for the processes in the batch and at the stripper-condenser. In this chapter, two different experiments are described that are conducted to validate these assumptions. First, the batch experiment is described, in which the influence of inorganic carbon on the leaching processes is analyzed. Secondly, the stripper-condenser experiment will be described, in which the influence of inorganic carbon on the stripping and condensing ratio of an ammonia, water and carbon dioxide system is analyzed.

3.1 I-Batch experiment

In the first experiment, a solution was used that represents the mixture in the batch. In this experiment, the goal is to answer the question; *What is the influence of inorganic carbon on the processes in the batch tank?*. There is focused on finding the solubility of inorganic carbon in the batch solution under the same conditions as the current system. When the solubility is reached, what is the influence on the solubility of ammonium molybdate and on the concentration of contaminating metals in the solution. Also, it must be able to analyse which form of inorganic carbon is dominant in the solution.

3.1.1 Material and equipment

Table 3.1 shows the materials and tools used for the setup and sampling procedure of the experiment. The first column gives the materials used, the second column gives the different sizes.

Table 3.1: List of materials

Material	Size
Beaker	2000mL
Graduated cylinder	1000mL, 25mL
Volumetric flask	250mL, 100mL
Stir bar	-
Heating element IKA C-MAG HS7	-
pipette VWR-High Performance	5mL, 1mL, 200uL
Sampling bottles	250mL, 100mL

Batch setup
A sample of 1 liters solution was tapped from the batch tank, right before transportation to the crystallizer. This solution was placed on a hot plate in a ventilation cabinet in the lab. The solution was stirred and regulated at a temperature of 60 degree Celsius. Figure 3.1 shows a schematic overview and Figure 3.2 shows a picture of the setup. In Appendix B.1 a picture of the setup is given with the used materials.

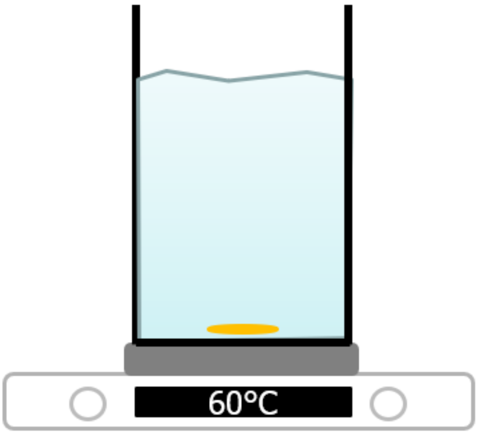


Figure 3.1: Schematic overview setup for batch experiment

Figure 3.2: Setup for batch experiment

Analytic material and equipment

The measured parameters and equipment used for data collection and laboratory analysis are reported below.

- Molybdenum concentration was measured by Analytik Jena's Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Plasma Quant MS. The measuring range of molybdenum in the ICP-MS is between 0-100ug/L. The measuring method can be found in Appendix B.2.
- Total ammonia nitrogen (TAN) concentration in the solution was measured using the Macherey-nagel nanocolor ammonium 200 tube tests. The solution needs to be diluted to the right range of 40-160 mg/L. The measuring method can be found in Appendix B.3.
- Total Inorganic Carbon (TIC) concentration was measured by a Shimadzu TOC-Vcph analyzer. The measuring range of inorganic carbon in the TOC-analyzer is between 0-500 parts per million (ppm) (mg/kg). The measuring method can be found in Appendix B.5.
- Mass-measurement was done by using a Kern PCB 6000-1 digital precision balance. This balance was used to determine the amount of $(NH_4)_2CO_3$-powder added to the solution, but also to distinguish the specific weight of the batch solution, before and after the test. For the specific weight, the solution was placed on the balance in a 1000mL graduated cylinder. The specific weight was used for the interpretation of the molybdenum concentration of the batch solution.
- pH was measured by Macherey-Nagel pH-fix 1-14 strips. They are needed to verify that the pH stays the same during the experiment.
- Temperature was measured by IKA C-MAG HS7. This equipment controls the temperature of the solution at 60 degree Celsius.
- Free NH_3 concentration was measured by a Mettler Toledo EasyPlus Titration. It provided the NH_3 concentration in grams per liter (g/L). The measuring method can be found in Appendix B.6.
- Metal concentrations in the solution were measured by Atomic Absorption Spectroscopy (AAS). The iCE 3500 AAS measured the metal concentration of potassium, copper, magnesium, zinc, iron, calcium and sodium in ppm (mg/kg).

3.1.2 Experimental procedure

Solution from a finished batch was taken after filtration and just before it was transported to the crystallizer. Ammonium carbonate powder ($(NH_4)_2CO_3$) was added to the solution until precipitation. When precipitation was formed, the solution was filtered over 0.45um. The specific weight, free-NH_3 concentration, temperature, pH, TIC and TAN of the solution were measured. Also, samples were taken before and after precipitation to measure the molybdenum concentration and metal concentration. Since the solution was kept at a constant temperature and stirred continuously, it was possible that ammonia evaporated out of the solution. As a result, the pH of the solution dropped and thus, was measured frequently. When the pH dropped, 30%w NH_3 solution was added to the solution.

Sampling was done with a VWR-High Performance pipette. Dilution was done in a volumetric flask or a graduated cylinder. As dilution fluid, demineralized water was used. The dilution procedure is given in Appendix B.7. The specific weight of the total solution before and after the test was measured by a graduated cylinder. Table 3.2 shows which samples are taken and what measurements are performed on those samples.

Table 3.2: Samples taken from solution

	Quantity	Elements measured
Before addition of $(NH_4)_2CO_3$	25mL	Mo, TAN, TIC, NH_3, AAS
2-6x during addition of $(NH_4)_2CO_3$	1mL	TAN, TIC
After precipitation and filtering	25mL	Mo, TAN, TIC, NH_3, AAS

For the 25mL samples, a graduated cylinder was used, and for the 1mL sample a pipette was used.

3.2 II-Stripper-condenser experiment

In the second experiment, the influence of inorganic carbon on the process of stripping ammonia in aqueous solution at 80 degree Celsius and condensing to 20 degree Celsius was examined. There was focused on the difference in stripping rates of ammonia. Also, was measured until what extend ammonia evaporated out of the solution. Furthermore, was looked at the gas-liquid equilibrium of $NH_3-H_2O-CO_2$ for specific starting concentrations of TAN and TIC.

A solution was made with the same ammonia concentration that would be transported to the stripper of the chemical plant. This NH_3 concentration is 4.2 g/L. Ammonium carbonate powder was added until the TIC concentration meets the TIC concentration of the absorbed carbon dioxide from the off-gasses of the d3B. This is 0.65 g/L taking into account the additional scrubbing water for the ammonia absorption in the chemical plant. The calculation for the TIC and TAN concentrations are given in Appendix B.8.

3.2.1 Materials and equipment

For the stripper-condenser setup the following materials were used, see Table 3.3. Also, a list of consumables and chemicals are given in Table 3.4.

Table 3.3: List of materials

Material	
Beaker	3 000mL
Volumetric flask	100mL, 250mL
Stir bar	-
Heating element VELP ANEX DIGITAL	-
pipette VWR-High Performance	1mL, 200uL
Thermometer	-
Sampling bottles	60 mL
Nylon tube 5mm inner diameter	6meter length
VAClean Vacuum Pump Unit	1.7m^3/h
Bucket	50 L

Table 3.4: List of consumables and chemicals used in the experiment

Consumables	Quantity
$(NH_4)_2CO_3$-powder	500gr
30%w NH_3	2 500mL
Demineralized water	20 000mL
Ice cubes	6 000mL

Stripper-condenser setup

A beaker with diluted ammonia and inorganic carbon solution was put on a heating element. The solution was stirred and regulated at a temperature of 80 degree Celsius. Evaporation from the solution was caught and condensed to 20 degree Celsius. The condensed solution was dropped in a bottle. Figure 3.3 shows a schematic overview of the setup and Figure 3.4 gives a picture of the setup. Also, a picture of the setup with the additional materials used, can be found in Appendix B.1.

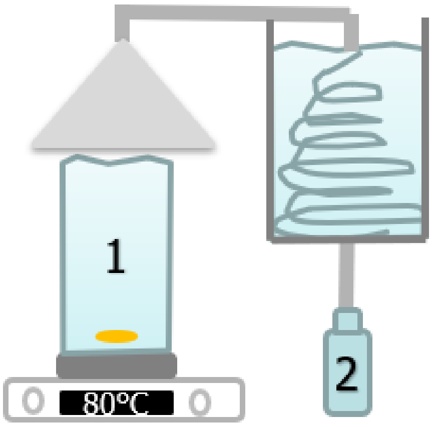


Figure 3.3: Schematic overview setup for stripper-condenser experiment

Figure 3.4: Setup for stripper-condenser experiment

Analytic material and equipment

Below, the variables that were measured during the experiment are listed together with the equipment that was used.

- TAN concentration was measured by Hach cuvette test LCK 303 NH4-N with a DR3900 benchtop spectrophotometer. The solution was diluted to the right total ammonia nitrogen range of 2-47mg/L. Also, dilution was needed to ensure the ${CO_3}^{2-}$ concentration did not exceed the interference levels of 50 mg/L . The measuring method can be found in Appendix B.4.
- TIC concentration was measured by a Shimadzu TOC-Vcph analyzer. All inorganic carbon was diluted to measure between a range of 0-500 ppm (mg/kg). The measuring method can be found in B.5.
- Mass-measurement was done by using a Kern PCB 6000-1 digital precision balance. This balance was used to determine both the amount of $(NH_4)_2CO_3$-powder added to the solution and to measure the weight of the solution before and after the test to see for evaporation.
- pH was measured by Macherey-Nagel pH-fix 7-14 strips. They were needed to see what happens with the pH during the experiment.
- Temperature was measured by VELP ANEX DIGITAL combined measuring machine and heater element. This equipment regulated the solution at a constant temperature of 60 degree Celsius.

3.2.2 Experimental procedure

2000 grams water was heated in a 3000ml beaker until 80 degree Celsius. Ammonia 30%w solution was added until the TAN concentration was around 4.2 mol/L. $(NH_4)_2CO_3$-powder was added to the solution until the concentration of TIC was 0.65 mol/L. This procedure was repeated for 1.5 times the TIC concentration and for a solution without addition of $(NH_4)_2CO_3$-powder as reference experiment, see Table 3.5. The calculation for making the ammonia mixture of 4.2 mol/L is explained in Appendix B.9.

Table 3.5: Aimed total inorganic carbon concentration and total ammonia nitrogen concentration of experiment 1, 2 and 3

Experiment	TIC (mol/L)	TAN (mol/L)
1	0.9	4.2
2	0.65	4.2
3	0	4.2

The solution was kept on the hot plate at a temperature of 80 degrees Celsius. In the first 30 minutes samples were taken every 7.5 minutes. After that every 45 minutes a sample was taken.

The vapor mixture that evaporated from the solution was guided through an ice-cooled tube such that it condensed into a bottle. Samples were taken from this condense, three in the first hour and two in the last two hours in equal time-intervals. The total duration of the experiment was 3 hours and 30 minutes.

The solution of the condense was cooled to 20 degrees Celsius. Therefore, the length, airflow and thickness of the tube was determined for the right design. Also, the temperature of the cooling water needed to be controlled. Therefore, it was necessary to add ice cubes to the water during the experiment. The calculations for the tube design of the condenser are given in Appendix B.10.

Sampling was done with a VWR-High Performance pipette. Dilution was done in a volumetric flask. As dilution fluid demineralized water was used. The dilution procedure is given in Appendix B.7. Table 3.6 indicates which samples are taken and what measurements are performed on those samples.

Table 3.6: Samples taken from solution

	Bottle 1	Bottle 2	Elements measured
Before addition of $(NH_4)_2CO_3$	2mL	-	TIC, TAN
5-8x during stripping/condensing	2mL	2mL	TIC, TAN

TIC and TAN were measured during the experiment. The TAN value before addition of $(NH_4)_2CO_3$ provides the free ammonia concentration of the solution. Since there was no condense at the beginning of the experiment, no samples could be taken from bottle 2. After 10 minutes, it was assumed that around 40mL water was evaporated and partly condensed into the bottle. An indication of the amount of evaporated water during the experiment at different time intervals can be found in Appendix B.11. After the experiment was finished, the samples were taken directly to the TOC-analyzer and the DR3600 for TIC and TAN measurement.

4 Results and discussion batch experiment

In this chapter the results and discussion of experiment I are given, where the influence of inorganic carbon is explained on the processes in the batch system. In the following sections is shown that TIC has no effect on the solubility of ammonium molybdate, and that the solubility of TIC in the batch solution is on average 2.12 mol/L. Also, is shown that carbonates have no positive influence on metal precipitation and that TIC is dominated in the form of bicarbonate.

4.1 Molybdenum analysis

Ammonium molybdate is the main product in the batch reaction. In this section the influence of TIC on the molybdenum concentration is explained in the batch. Molybdenum concentration in the solution of the batch is quickly measured by the specific weight of the solution. Figure 4.1 shows the molybdenum concentration of the batch against the specific weight of the solution.

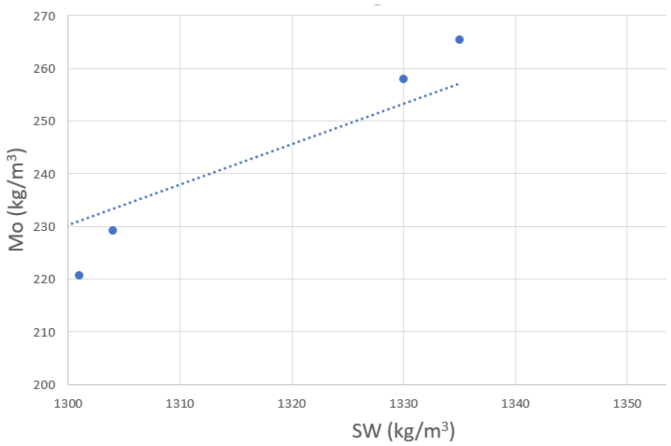


Figure 4.1: Molybdenum concentration of batch solutions against specific weight of the solution at 60℃

When the molybdenum concentration of the solution increases, the specific weight of the solution also increases. The dotted line is a linear fit through the origin and the points in the graph. The origin of this line is located at 980 and 0 kg/m^3, which is the specific weight of water at 60℃ when no molybdenum is present in water.

The influence of TIC on the solubility of molybdenum in the batch is given in Table 4.1. Where molybdenum concentrations were measured of the solution before and after the solution showed precipitation and was filtered over 0.45um.

Table 4.1: Influence of TIC on solubility of molybdenum

Experiment	Mo (g/L)
1.before	265.5
1.after	262.9
2.before	257.9
2.after	258.0

By looking at the results, molybdenum precipitation can be excluded from the possibilities. The small differences in molybdenum concentration can be explained by error during dilution of the monsters, Appendix B.7. The Standard Reference Material (SRM), which ICP-MS uses for the exact measurement of the molybdenum concentration is given in Appendix C.1.

4.2 Solubility TIC

The TIC concentration at which precipitation occurs in the batch is plotted in Table 4.2. The solution compositions in the batch are different in; the specific weight, ammonia concentration and molybdenum concentration. This is because one cannot exactly predict the composition of the added metals. The TAN is the total amount of ammonia nitrogen that is present in the form of NH_3 and NH_4^+. TIC is the total amount of inorganic carbon that is present in the solution, this can be in the form of CO_2, HCO_3^-, and CO_3^{2-}.

Table 4.2: Experiment 1 and 2 until solubility of finished batch solution at 60 ℃

Experiment	TIC (mol/kg)	Spec. W (kg/m^3)	pH	NH_3 (g/L)	Mo (g/L)	TAN (mol/kg)
1	2.02	1304	10	17.6	233	6.81
2	2.22	1323	10	22.27	248	7.58

Experiment 1 and 2 give TIC concentrations when precipitation is reached of 2.02 and 2.22 mol/kg respectively. The small difference can be explained by the difference in NH_3 concentration during the experiment. Figure 4.2 shows how the TIC concentration is plotted against the total added carbon during the experiment. At the dashed line, the solubility of TIC is reached.

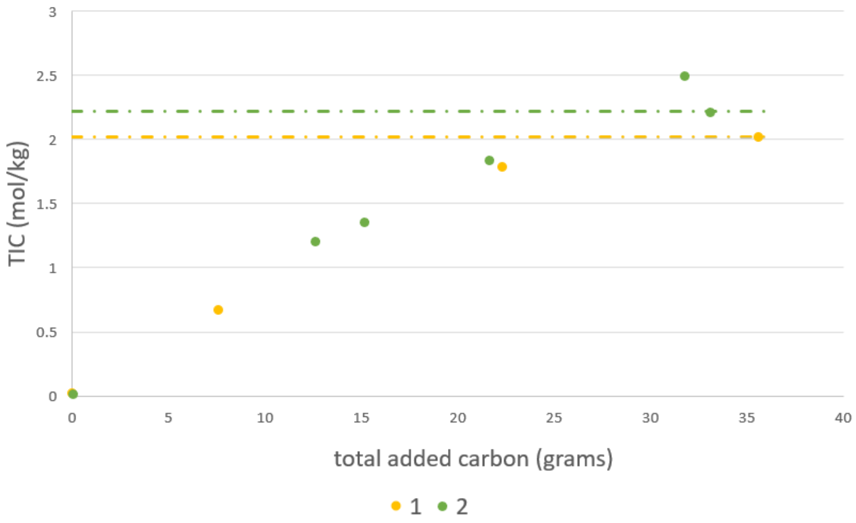


Figure 4.2: Solubility of TIC in batch solution for experiment 1 and 2

In both, experiment 1 and 2, TIC is increasing linear towards its solubility. At the solubility, the maximal TIC concentration is reached in the solution under these conditions, table 4.2. Experiment 2 in figure 4.2 has one point above the solubility line. This sample is taken of the monster without filtration of the solution over 0.45um.

4.3 Metal-carbonate precipitation

Due to the presence of other metals in the batch, carbonates can react with these metals in the solution. In this section is elaborated on the influence of inorganic carbon on the precipitation of other metals. Only then can be concluded that the precipitation consists only of ammonium carbonate or ammonium bicarbonate. Figure 4.3 shows the concentration of metals before and after addition of ammonium carbonate until precipitation.

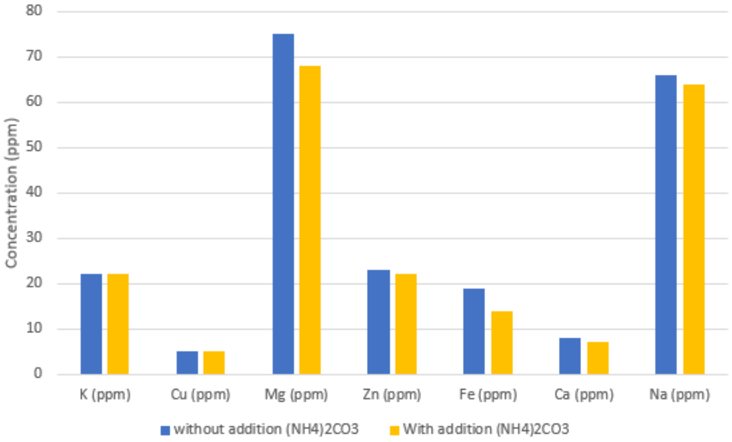


Figure 4.3: Metals present in the batch with and without addition of carbonates

As can be seen, no big differences in metal contents are present. In this thesis is elaborated on only the positive effect of carbon dioxide on metals. The negative effect; increment of metal solubility due to carbon dioxide, is not elaborated on in this thesis. For more information see Appendix C.2.

4.4 Ratio between bicarbonate and carbonate

In the previous sections of this chapter, it is excluded that the precipitation in the fluid is different from a combination of ammonium and a carbonate. In this section is shown in what fraction TIC is present in the solution of the batch during precipitation. Also, there is elaborated on why the precipitation is ammonium bicarbonate and what the solubility product of ammonium bicarbonate is in the batch solution.

4.4.1 Material balances

In the aqueous phase of the solution, material balances may be written; Equation 4.1, 4.2 and 4.3. These material balances are written in moles per liter. In Equation 4.2 it is important to mention that the concentration of total ammonia nitrogen is all the free ammonia plus two ammonium ions that are bound to molybdate plus one ammonium ion that is bound to bicarbonate and two ammonium ions that are bound to carbonate.

Total inorganic carbon balance:

$$[\mathrm{TIC}] = [\mathrm{CO_2}] + [\mathrm{HCO_3}^-] + [\mathrm{CO_3}^{2-}] \approx [\mathrm{HCO_3}^-] + [\mathrm{CO_3}^{2-}] \tag{4.1}$$

Total ammonia nitrogen balance:

$$[TAN] = [\mathrm{NH_3}] + [\mathrm{NH_4}^+] = [\mathrm{NH_3}] + 2\,[\mathrm{MoO_4}^{2-}] + [\mathrm{TIC}] = [\mathrm{NH_3}] + 2\,[\mathrm{MoO_4}^{2-}] + [\mathrm{HCO_3}^-] + 2\,[\mathrm{CO_3}^{2-}] \tag{4.2}$$

Ion balance of the main components in the batch is as follows:

$$[\mathrm{NH_4}^+] + [\mathrm{H_3O}^+] = 2\,[\mathrm{MoO_4}^{2-}] + [\mathrm{HCO_3}^-] + 2\,[\mathrm{CO_3}^{2-}] + [\mathrm{OH}-] \tag{4.3}$$

Considering the high concentration of ammonium, molybdate and carbonate ions, the hydroxonium and hydroxyl ions may be neglected. The fraction of carbon dioxide inside the batch solution is very small, that is why this concentration can be neglected from this balance. The total ammonia nitrogen that is present is dependent on the free ammonia and the ammonia ions that are bound to molybdate and TIC ions.

4.4.2 Mass fraction TIC

In section 2.2, is explained that the ammonium:carbonate mole ratio for ammonium carbonate is 2:1, and for ammonium:bicarbonate, 1:1. The ammonium molecules are calculated that bind to TIC in Equation 4.4.

$$[\mathrm{TAN}] - 2\,[\mathrm{MoO_4}^{2-}] - [\mathrm{NH_3}] = [TAN]_{bindedtoTIC} = [HCO3^-] + 2[CO3^{2-}] \tag{4.4}$$

Table 4.3 shows the concentrations of molybdenum, ammonia, TAN and TIC for experiment 1 and 2.

Table 4.3: Concentration molybdenum, ammonia, TAN and TIC in mol/kg

Experiment	Mo (mol/kg)	NH_3 (mol/kg)	TAN (mol/kg)	TIC (mol/kg)
1	1.90	0.79	6.91	2.02
2	1.99	0.99	7.57	2.22

TIC in the solution must equal the sum of carbonates and bicarbonates,

$$[TIC] = [\mathrm{CO_3}^{2-}] + [\mathrm{HCO_3}^-] \tag{4.5}$$

To satisfy both Equations 4.4 and 4.5, first a guess is made of the fraction of carbonates in the solution. After that multiple iterations are performed to find the fraction of CO_3^{2-}. The sum of both fractions CO_3^{2-} and HCO_3^- must be equal to 1. In Table 4.4 and 4.5 the fractions are shown of two batch experiments.

Table 4.4: Division of mole fraction TIC for experiment 1 in mol/kg

	CO_3^{2-}	HCO_3^-	total
Frac	0.14	0.86	1

Table 4.5: Division of mole fraction TIC for experiment 2 in mol/kg

	CO_3^{2-}	HCO_3^-	total
Frac	0.17	0.83	1

As can be seen the fraction of carbonates are 14 and 17%, for experiment 1 and 2 respectively. The difference in these concentrations are also likely due to the difference in the batch solutions. Although it gives a good indication of the mole fraction of TIC in the solution under these conditions in the batch.

The fraction of bicarbonates in the solution is much bigger, 86 and 83% for experiment 1 and 2 respectively. Also from section 2.2.3, is seen that the solubility product of ammonium bicarbonate in water is much lower than ammonium carbonate. It can then be concluded from these two findings that it is most likely the precipitation is caused by ammonium bicarbonate.

4.4.3 Solubility product of ammonium bicarbonate

The solubility of ammonium bicarbonate in these batch solutions are calculated by taking the fraction of bicarbonates times the TIC and the mole mass of the molecule as given in Equation 4.6.

$$S = [TIC] * frac * \mathrm{M_{NH4HCO3}} \tag{4.6}$$

Where S is the solubility in g/kg, TIC given in mol/kg, frac. is the fraction of TIC that is ammonium bicarbonate given in Table 4.4 and 4.5, and $\mathrm{M_{NH4HCO3}}$ is the mole mass of ammonium bicarbonate in g/mol. From here the solubility product of ammonium bicarbonate can be calculated. The results are shown in Table 4.6.

Table 4.6: Results of solubility of ammonium bicarbonate for two experiments and in water at 60℃

	Solubility (g/L)
exp 1	176
exp 2	190
water	592

There is a very large difference between the solubility product of ammonium bicarbonate in the batch and in water conditions[36]. In batch conditions ammonium bicarbonate precipitates much faster as can be seen from Table 4.6.

4.5 Implementation mass balance

The findings of this section are used to illustrate what happens to the mass balance when carbon dioxide is injected in the batch system. In Section 4.1 is shown that no influence on the molybdenum production is recorded with the addition of carbonates in the system. Also, can be excluded that carbonates cause extra precipitation of metal-carbonates in Section 4.3. In Section 4.2 is shown that the solubility of TIC in the batch solution is 2.12 mol/kg. In Section 4.4 is shown that the ratio CO_3^{2-}:HCO_3^- is 0.14:0.86 and 0.17:0.83, respectively for experiments 1 and 2.

For the implementation in the mass balance, in the batch a ratio of 0.16:0.84 will be taken for CO_3^{2-}:HCO_3^-. Also precipitation occurs when the NH_4HCO_3 concentration reaches above 183 g/L. These numbers are an average of the results conducted by the experiments. The TIC ratio and bicarbonate concentration at precipitation are used in the mass balance. Instead of the earlier assumption of ammonium bicarbonate precipitation at a concentration of 592 g/L.

5 Results and discussion of stripping-condensing experiment

The main purpose of this experiment is; describe what happens in the stripper-condensing system of the plant with addition of inorganic carbons in the solution. In the first section, the stripping results are described. Here is shown that TIC has influence on both the stripping rate and the stripping efficiency of ammonia from the solution. The second section shows that in the condensing system a large part of the CO_2 is not condensed back into the liquid solution and causes an extra output of CO_2. These results are implemented in the mass balances for the three different off-gas handling options.

5.1 Stripping experiment

In this section is shown that the influence of inorganic carbon on the stripping rate is 1.4. Also, is shown that the stripping efficiency is reduced to the ammonium bicarbonate concentration.

5.1.1 Stripping rate of ammonia

Figure 5.1 shows the total ammonia nitrogen of the solution over time. The solution with- and without additional carbonates are compared. In Table 5.1 the concentration of total inorganic carbon, free ammonia and total ammonia nitrogen are given. Where TIC is the variable.

Table 5.1: Total inorganic carbon and total ammonia nitrogen of experiment 1, 2 and 3

Experiment	TIC (mol/L)	NH_3 (mol/L)	TAN (mol/L)
1	0.82	4.2	5.04
2	0.61	3.64	4.34
3	0	4.43	4.43

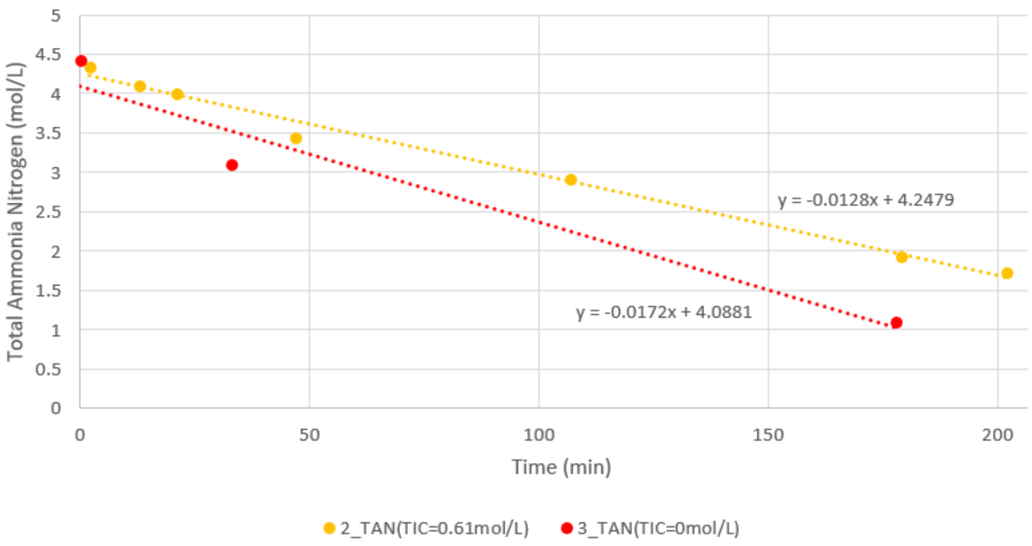


Figure 5.1: Total ammonium nitrogen over time at 80 degree Celsius

Figure 5.1 shows that the speed of evaporation of ammonia without addition of inorganic carbon is 1.4 times faster. The graph is simplified by making a linear approximation of the points to be able to compare the two different experiments.

5.1.2 Carbon dependency of stripping

The stripping rate of inorganic carbon is less efficient than the stripping rate of ammonia in the same solution. The amount of TIC in the solution is given over time in Figure 5.2.

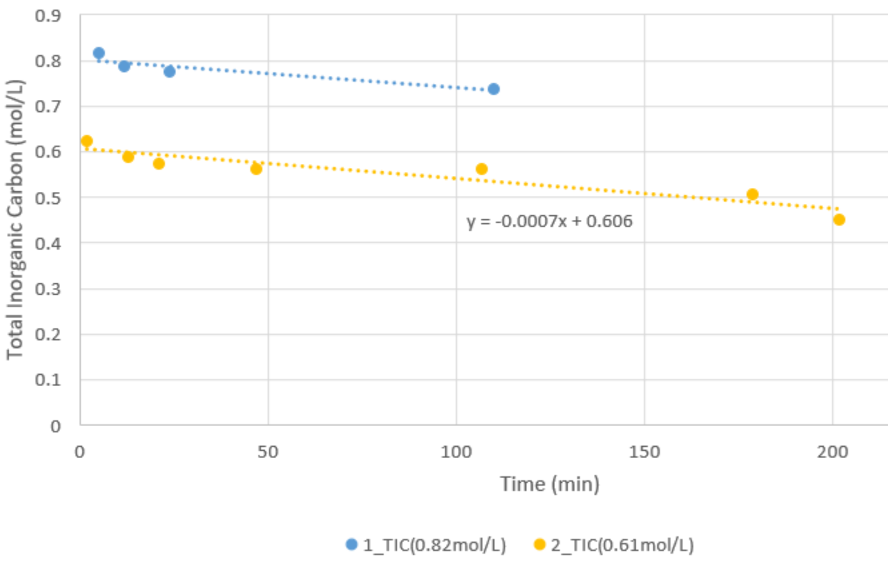


Figure 5.2: Total inorganic carbon over time at 80 degree Celsius

Figure 5.2 shows that the stripping rate of total inorganic carbon is independent from the starting concentration. To distinguish to what extent stripping is efficient, the following formula's are used below. The formula's are linear approximations from graphs in Figure 5.1 and Figure 5.2. The two approximations intersect with each other where the molar concentration of TAN is the same as TIC.

It is chosen to stop at this point. Free ammonia has evaporated, and the ammonium ions are bound to the bicarbonates in the solution.

$$-0.0128x + N_{TAN} = -0.0007x + N_{TIC} \tag{5.1}$$

$$X_{inters} = (N_{TIC} - N_{TAN}) / -0.0121 \tag{5.2}$$

$$Y = -0.0007X_{inters} + N_{TIC} \tag{5.3}$$

Where X_{inters} is the value at which point the two formulas intersect. N_{TIC} is the starting molarity of total inorganic carbon in the solution, N_{TAN} is the starting molarity of total ammonia nitrogen in the solution and Y the molarity where TIC=TAN. The TAN mole concentration decreases until it has the same mole concentration as TIC, whereby it reaches equilibrium forming ammonium bicarbonate. This process is described in Darde et. al. [20] and Milella [22] where the decreasing ammonia concentration causes the equilibrium to move towards ammonium bicarbonate instead of ammonium carbonate. The starting concentration of TIC is important, because it describes towards which extend it is worth to strip the ammonia out of the solution. The size of the re-boiler is dependent on the starting concentrations of ammonia and TIC in the solution.

5.1.3 Evaporation ratio and implementation into mass balance

During stripping three elements evaporate from the solution, as already described in Section 2.3.3, these are CO_2, NH_3 and H_2O. The evaporation ratio is given in Table 5.2.

Table 5.2: Evaporation ratio NH_3-CO_2-H_2O of experiment 1, 2 and 3 in %w

Experiment	TIC (g/L)	NH_3 (frac)	H_2O (frac)	CO_2 (frac)
1	9.8	0.50	0.27	0.23
2	7.5	0.41	0.48	0.11
3	0.1	0.59	0.41	-

The sum of all fractions is one. Stripping ammonia without any additional carbonates results in a ratio NH_3:H_2O of 59:41 %w. This is almost in line with the Tillner-Roth's[34] equilibrium of state model for the dew and bubble point of an ammonia-water mixture described in Section 2.3.3.

Table 5.2 shows the results of the stripping experiments, where the evaporation ratio of ammonia, water and carbon dioxide are calculated under different concentrations of inorganic carbon. For the implementation into the mass balance, an average of the evaporation ratio of test one and two is given and divided over test three. The result is the influence of inorganic carbon on the stripping efficiency of ammonia, water and carbon dioxide. This was -23% for ammonia and -9% for water. An average is calculated of how much the ratio of CO_2 is during stripping, which is +17%. For the calculations see Appendix D.1.

In the mass balance of the current system the ammonia:water ratio in gas phase is 0.55:0.45 %w. This ratio is multiplied by the influence on the stripping efficiency by inorganic carbon of ammonia and water. The results are given in Table 5.3.

Table 5.3: Evaporation ratio in mass balance NH_3-CO_2-H_2O in %w

	NH_3	H_2O	CO_2
Current operation (frac)	0.55	0.45	-
Influenced by carbon (%)	-23%	-9%	-
Influenced by carbon operation (frac)	0.42	0.41	0.17

Evaporation ratio of 0.42, 0.41 and 0.17 respectively for NH_3, H_2O and CO_2 are used in the mass balance. This is different from the previous mass balance where is assumed that all ammonia and carbon dioxide would evaporate in the stripper.

5.2 Condensing

In this section is shown that condensing carbon dioxide is less efficient than ammonia. This means an outlet of carbon dioxide can be created. Furthermore, in this section is shown; the composition of condensed solution, the influence of carbon dioxide on the ammonia:water ratio, and how these findings are implemented in the mass balance. The condensed solution has a fluctuating temperature between 19-25 degree Celsius and a pH of 11-11.5.

5.2.1 Ratio of condensed solution

In the condense, the following ratio of TAN, water and TIC are found, Table 5.4.

Table 5.4: Ratio TAN-H_2O-TIC of condensed gas in %w

	TAN(frac)	H_2O(frac)	TIC(frac)
1	0.18	0.78	0.03
2	0.31	0.60	0.09

The TAN:H_2O:TIC ratio in the solution is 0.18:0.78:0.03 respectively for experiment 1, and 0.31:0.60:0.09 for experiment 2. Comparing this to the thermodynamic law of condensing a ammonia-water mixture to 20 degrees Celsius gives a maximum of 35:65%w, as already described in Section 2.3.3. Table 5.4 shows that the total ammonia nitrogen fraction is lower in the NH_3:H_2O:CO_2 mixture.

5.2.2 Outlet of carbon dioxide in condenser

The amount of carbon dioxide that goes into solution is much smaller than the ratio of ammonia. One of the reasons is because the evaporation rate of carbon dioxide is much lower. In this section is shown that the relative condensing ratio of carbon dioxide is lower in reference to ammonia. This indication can be used to see if at the condensing activity an outlet can be created for CO_2. Table 5.5 shows the condensed NH_3 and CO_2 in weight percentage from the total evaporated ammonia and carbon dioxide.

The condensed %w is made by calculating the fraction of condensed material against the total evaporated material per time step. The calculations are explained in Appendix D.2.

Table 5.5: The weight percent of condensed CO_2 and NH_3 form evaporated total

	Condensed %w
1_{TAN}	21
1_{TIC}	12
2_{TAN}	45
2_{TIC}	34

Table 5.5 shows that from the total evaporated TAN in experiment 1, only 21%w is condensed and from the total evaporated TIC in experiment 1, only 12%w is condensed. Ammonia is condensed in the first experiment 1.9 times more efficient than carbon dioxide. In experiment 2 this is 1.3 times

more efficient. This shows that it is possible to create an outlet at the condenser for CO_2 towards the scrubber.

5.3 Implementation into mass balance

In this section is shown that the stripping rate of ammonia is reduced by 1.4, due to the addition of inorganic carbon. Also is shown that the concentration of inorganic carbon has influence on the stripping efficiency. Stripping is done until the TAN mole concentration meets the TIC mole concentration. Moreover, the evaporation ratio is reduced from 55:45 %w in an NH_3-H_2O system to 42:41:0.17 in an NH_3-H_2O-CO_2 system.

The condenser is designed to condense all ammonia from gas to liquid phase. In the previous section is shown that the efficiency of carbon dioxide condensing is 1.3-1.9 times smaller.
The ratio of NH_3-H_2O-CO_2 implemented in the mass balance is 0.31:0.60:0.09, respectively. This means that the maximum ratio of carbon dioxide and ammonia in the condensed fluid is 9%w and 31%w, respectively.

6 Results mass balances

In this chapter the results of the experiments shown in Chapter 4 and Chapter 5 are used to make three different mass balances. The mass balances are based on the three different off-gas handling options listed below:

1. Off-gas inlet in the batch process, ARS
2. Off-gas inlet in the scrubber-stripper, AER
3. Off-gas inlet in the scrubber-stripper with NaOH addition in stripper, AER + NaOH

These three mass balances give an overview of the inlet and outlet streams of water, ammonia, molybdenum and carbon dioxide. Also, the potential complications, equipment change and cost analysis per model are given. In the last section of this chapter the results of all three mass balances are compared in an overview. Also, it is explained the influence this has on the use of the CATOX.

6.1 Off-gas inlet in the batch process, ARS

The results of the ARS are illustrated in Figure 6.3. The off-gasses of the d3B-calciner are injected at the batch system. Table 6.1 shows the amount of water, ammonia, molybdenum and carbon dioxide that enter and leave the chemical plant in tonnes per day.

Table 6.1: Results inlet and outlet streams of water, ammonia, molybdenum and carbon dioxide in tonnes/day of the ARS-system

	Inlet	Off-gas d3B	S40	CS7	S40	d3A&d3B	Briquette	Vb(bleed)	CS7
H_2O	0	3.89	24	0	0	-0.75	-1.49	-25.66	0
NH_3	1.83	0	0	0.65	0	-0.97	-0.16	-1.34	0
Mo	22.93	0	0	0	0	-22.68	-0.25	0	0
CO_2	0	4.75	0	0	0	0	-0.04	-3.47	-1.25

It can be seen that 3.89 and 4.75 tonnes of water and carbon dioxide enters the chemical plant extra due to the combustion of natural gas, respectively. On the other hand, only 1.83 tonnes of ammonia enters the chemical plant at the inlet in reference to 3.56 tonnes of ammonia without reclamation of the off-gasses from the d3B-calciner. This means a saving of 1.73 tonnes of ammonia per day, which is 41% of the total inlet of ammonia in the current system.

Most of entered water leaves the system at the Vb(bleed). A small part is going to the briquette and is present in the ADM crystals which is a product at the d3A. Ammonia has an effluent stream at the Vb(bleed), this is the result of what is seen in Section 5.1.2. Where was shown that ammonia is present in this effluent stream because it is bound to carbon dioxide in the form of ammonium bicarbonate. This is also a large outlet of carbon dioxide in the process. Another outlet of carbon dioxide is at the scrubber. A large portion of carbon dioxide enters the scrubber from the condenser, which causes an oversupply of carbon dioxide which the fluid cannot absorb.

6.1.1 Reference to model under first assumptions

In comparison to the earlier model of the ARS shown in Appendix A.1, carbon dioxide is leaving the system at the Vb(bleed) and at the scrubbed gas instead of leaving the system at precipitation in the batch at S40.

The ammonia reduction of the new mass balance is 1.73 tonnes of ammonia per day, which is more in reference to the old model of 1.29 tonnes of ammonia per day. The difference is caused by a different outlet stream of carbon dioxide at the scrubber. At the scrubber the carbon dioxide that leaves the system is not taking ammonia molecules with them, which is the case at the Vb(bleed) and was the case at the S40 in the old model.

6.1.2 Potential complications and solutions

The complications that are found are scaling at the scrubber-stripper system, and ammonia in the overflow water at the Vb. The size of the complication is given in this section and suggestions are done to solve them. In the appendices, two other complications are described that were found in literature but couldn't be validated in this report: One in the scrubbing system due to ammonium bicarbonate, Appendix E.1.1, and the second concerning sublimation reaction during condensing, Appendix E.1.2.

Scaling
Section 2.2.3 shows the solubility of ammonium bicarbonate at different temperatures in water. The solubility of ammonium bicarbonate in water at 15 degree Celsius, is 217grams per liter. In the mass balance of Figure 6.3 is searched for the ammonium bicarbonate concentration. If the solubility is reached, it will precipitate and causing scaling in tanks and pipes. At two points in the mass balance the solubility of ammonium bicarbonate is reached for the temperature of 15 degree Celsius. These points are illustrated in Figure 6.1 in red.

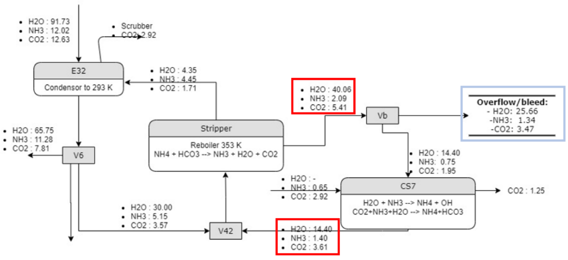


Figure 6.1: Complications in the scrubber-stripper system, scaling (red) and ammonia in overflow water (blue).

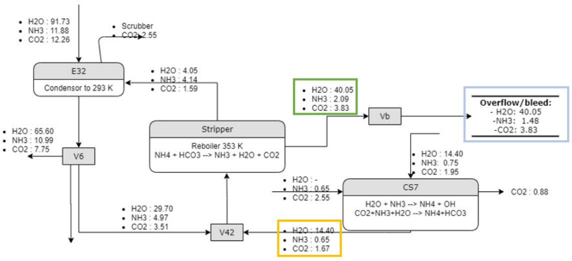


Figure 6.2: Complications in the scrubber-stripper system, where scaling solved by new inlet water.

Figure 6.1 emphasizes the scrubber-stripper system of the total mass balance of the chemical plant. The columns where the concentration of ammonium bicarbonate is above 217 grams per liter are emphasized in red. This complication could be solved by not re-using water from the Vb tank. This means that a new water inlet is created at the CS7, illustrated in Figure 6.2. The ammonium bicarbonate concentration is now below the solubility at 15 degree Celsius. Table 6.2 gives an overview of the ammonium bicarbonate concentrations at the emphasized points in Figure 6.1 and Figure 6.2.

Table 6.2: Ammonium bicarbonate concentration at critical points in the mass balance in gram/L for the ARS-system

	Stripper->Vb (g/l)	CS7->V42 (g/l)
ARS normal	243	450
ARS new water CS7	172	210

A full mass balance model of Figure 6.2, where new water enters the plant at CS7, is given in Appendix E.1.

Ammonia bleed
At the overflow of the Vb-tank, water is disposed out of the system. In this water ammonium bicarbonate is still present. It is not allowed to dispose large amounts of ammonia into surface water, so additional water treatment is needed.

The amount of ammonia in the overflow waters is 1.34 tonnes/day. Water treatment is needed to get rid of the ammonia. 6.3 tonnes of sodium hydroxide is needed, for calculation see Section 2.4.

Equipment change
For the application of the ARS, changes have to be made to the current system to be able to work with the amount of off-gasses. Table 6.3 gives an overview of what equipment should be changed in order to run the ARS.

Table 6.3: Change of equipment for ARS

	Current system (tonnes/day)	ARS (tonnes/day)	Increment
Stripper	2.97	4.45	2.1
Condenser	9.34	16.48	1.8

The stripper needs to be able to strip 1.5 times more ammonia in the ARS than the current system, also is the strip rate reduced 1.4 by addition of carbonates in the solution, Section 5.1. To process the amount of ammonia in the ARS with the same rate as the current system, the capacity of the machine needs to increase 2.1 times.
The condenser needs to increase 1.8 times to be able to condense the increment of ammonia that is passing in the condenser with the ARS system.

6.1.3 Cost analysis

A cost estimation is given for the ARS system in Table 6.4. In this system is taken into account the amount of sodium hydroxide that is needed for the treatment of ammonia in the overflow water.

Table 6.4: Cost analysis for ammonia recovery and use of sodium hydroxide for the ARS-system

	€per day
Ammonia recovery	1.160,-
Sodium hydroxide + ammonia recovery	-8.910,- 900,-
Total sum of cost	-6.850,-

At Climax Molybdenum the price for ammonia is €0,67 per kg 100%w. For saving 1.73 tonnes of ammonia, the savings per day come to €1.160,-. This means that it would save €406.000,- per year, considering 350 days of work.

To be able to get the installation to work, several machinery need to be installed or increased. At the Vb overflow, is looked at the possibility to use sodium hydroxide. However, at Climax Molybdenum the price for 17%w NaOH is €0,24 per kg. This would mean with a consumption of 6.3 tonnes of NaOH 100%w, the price becomes €8.910,- per day. It is not profitable using NaOH as water treatment agent.

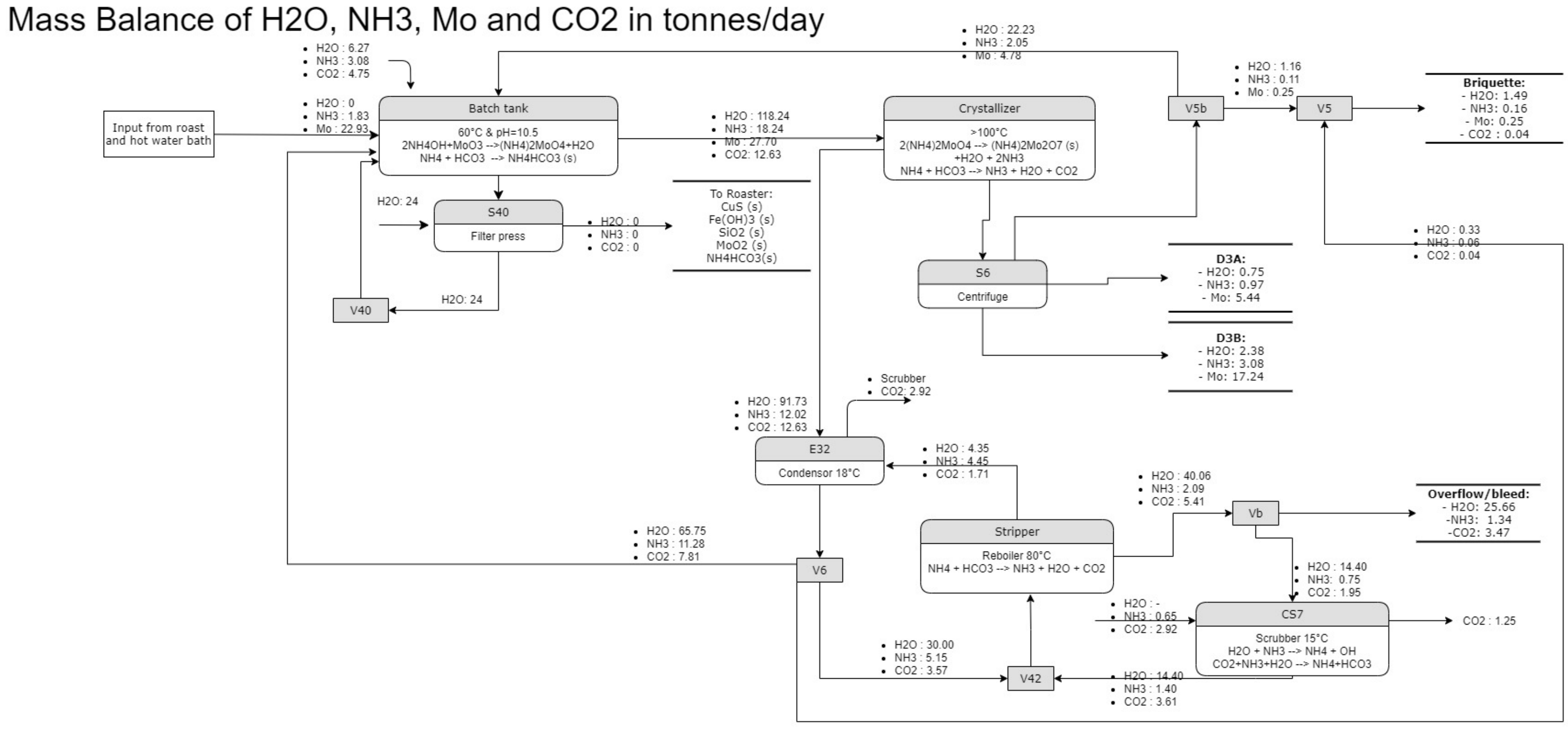


Figure 6.3: Mass balance of the ARS system

6.2 Off-gas inlet in the scrubber-stripper, AER

The results of the AER system are illustrated in Figure 6.5. The off-gasses of the d3B-calciner are injected at the scrubber (CS7). Table 6.5 shows the amount of water, ammonia, molybdenum and carbon dioxide that enters and leaves the chemical plant in the AER-system.

Table 6.5: Results inlet and outlet streams of water, ammonia, molybdenum and carbon dioxide in tonnes/day of the AER-system

	Inlet	S40	CS7	S40	d3A&d3B	Briquette	Vb(bleed)	CS7
H_2O	0	24	3.89	0	-0.75	-1.76	-25.38	0
NH_3	2.19	0	0.65	0	-0.97	-0.21	-1.65	0
Mo	22.93	0	0	0	-22.68	-0.25	0	0
CO_2	0	0	4.75	0	0	-0.05	-4.70	0

From the table above, can be seen that 3.89 and 4.75 tonnes of water and carbon dioxide enters the chemical plant extra at the scrubber, respectively. At the inlet, 2.19 tonnes of ammonia enters the chemical plant instead of 3.56 from the current plant system. This is a saving of 1.38 tonnes of ammonia per day, which is 33% of the total inlet of ammonia in the current system.

Table 6.5 also shows the effluent streams of water, ammonia, molybdenum and carbon dioxide of the AER-system. Most of the water leaves the system at the Vb(bleed), a small part is going to the briquette and is present in the ADM crystals, which is a product of the d3A. Ammonia has an effluent stream at the Vb(bleed). Therefore, ammonia is bound to carbon dioxide in the form of ammonium bicarbonate. Carbon dioxide leaves the system mostly at the Vb(bleed) and a small portion to the briquette.

6.2.1 Reference to model under first assumptions

In comparison to the earlier model shown in Appendix A.2, carbon dioxide is leaving the system at the Vb(bleed) instead of leaving the system as precipitation in the batch at S40.

The ammonia reduction of the new balance is 1.38 tonnes/day in reference to the old model of 1.27 tonnes/day. These two results have only slight difference because the principle of the output is the same. In both S40 and Vb(bleed) ammonia leaves the system bound to bicarbonate molecules. The slight difference is that in the S40 of the old model the ammonium bicarbonate leaves the system as precipitate and in the Vb(bleed) ammonium bicarbonate leaves the system as dissolved fluid.

6.2.2 Potential complications and solutions

The complications that are found are scaling in the scrubber-stripper system and ammonia in the effluent water stream.

Scaling
In Section 2.2.3, the solubility of ammonium bicarbonate is given at different temperatures in water. The solubility for ammonium bicarbonate in water at 15 degree Celsius, is 217 grams per liter. In the mass balance of Figure 6.5, is looked if the ammonium bicarbonate concentration reaches this solubility. Again, at two points in the mass balance the solubility of ammonium bicarbonate is reached at the temperature of 15 degree Celsius. These points are illustrated in Figure 6.4 in red.

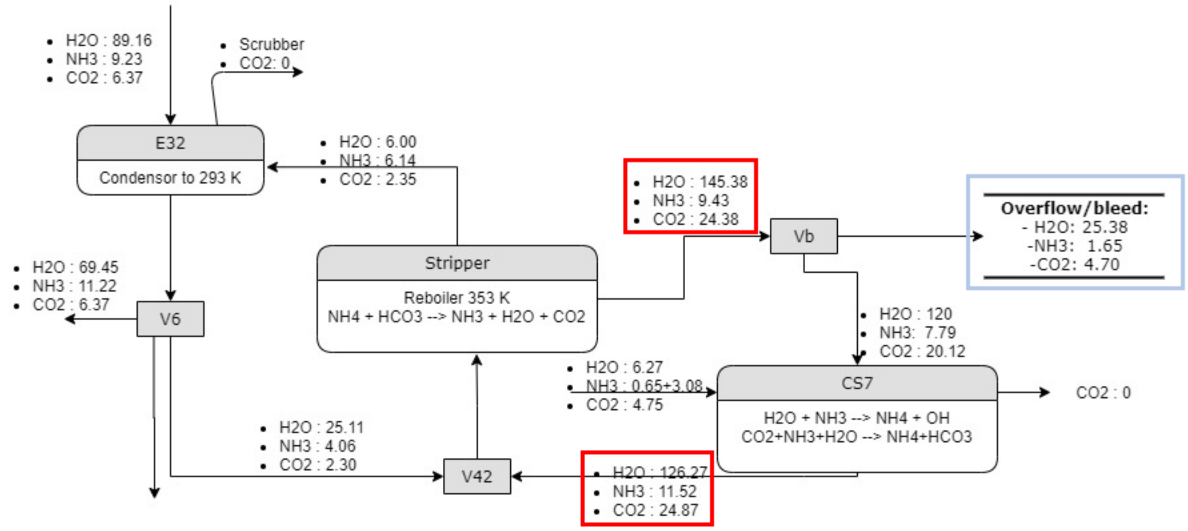


Figure 6.4: Complications in the scrubber-stripper system, scaling (red) and ammonia in overflow water (blue) for the AER-system

Figure 6.4 emphasizes on the scrubber-stripper system of the full mass balance of the AER-system. Table 6.6 shows the ammonium bicarbonate concentrations for the red marked points in Figure 6.4. In this model it is difficult to create an extra inlet of water at the scrubber(CS7), like done in Section 6.1, because an inlet of 120 tonnes of water per day is considered too much. Also, a water treatment of 145 tonnes of water per day is needed. This amount of water is also considered as too much.

Table 6.6: Ammonium bicarbonate concentration at critical points in the mass balance in gram/L for the AER-system

	Stripper->Vb (g/l)	CS7->V42 (g/l)
AER	302	354

Ammonia bleed

At the overflow of the Vb-tank, water is disposed out of the system. In this water, ammonium bicarbonate is present. It is not allowed to dispose large amounts of ammonia into surface water, additional treatment is needed.

The amount of ammonia in the overflow waters is 1.65 tonnes/day. Water treatment is needed to get rid of the ammonia. 8.5 tonnes of sodium hydroxide is needed, for calculation see Section 2.4.

Equipment change

For the application of the AER-system, changes have to be made to the current system to be able to let the mass balance work. Table 6.7 gives an overview of what equipment should be changed in order to run the AER-system.

Table 6.7: Change of equipment for AER-system

	Current system (tonnes/day)	AER (tonnes/day)	Increment
Stripper	2.97	6.14	2.8
Condenser	9.34	15.37	1.6
Scrubber	0.65	3.73	5.8

The stripper needs to be able to strip 2 times more ammonia in the AER-system then the current

system, also is the strip rate reduced by 1.4 due to the addition of carbonates in the solution, see Section 5. To process the ammonia that goes through the stripper in the AER-system, the stripper needs to increase by capacity of 2.8.
The condenser needs to increase 1.6 times to be able to condense all the ammonia that passes through. The scrubber needs to increase by a magnitude of 5.8. This is needed because of the increasing amount of ammonia that goes through the process. Instead of 14.4 tonnes water that flows through the process in the current system, the amount of water needs to be scaled up to 120 tonnes per day.

6.2.3 Cost analysis

A cost estimation for the AER-system is given in Table 6.8. In this table the amount of money that is saved due to the recovery of ammonia is shown and also a cost estimation for the treatment of the overflow water with sodium hydroxide. With this treatment the rest of the ammonia is recovered.

Table 6.8: Cost analysis for ammonia recovery and use of sodium hydroxide in the AER-system

	€/ day
Ammonia recovery	920,-
Sodium hydroxide + ammonia recovery	-12.060,- 1.110,-
Total sum of cost	-10.030,-

At Climax Molybdenum the price for ammonia is €0,67 per kg 100%w. For saving 1.38 tonnes of ammonia, the savings per day are €920,-. This means that it would save €324.000 per year, considering 350 days of work.

At the Vb overflow, is looked at the possibility to use sodium hydroxide. Sodium hydroxide is €0.24 per kg 17%w. This would mean with a consumption of 8.5 tonnes of NaOH 100%w the costs are €-12.060,- per day.

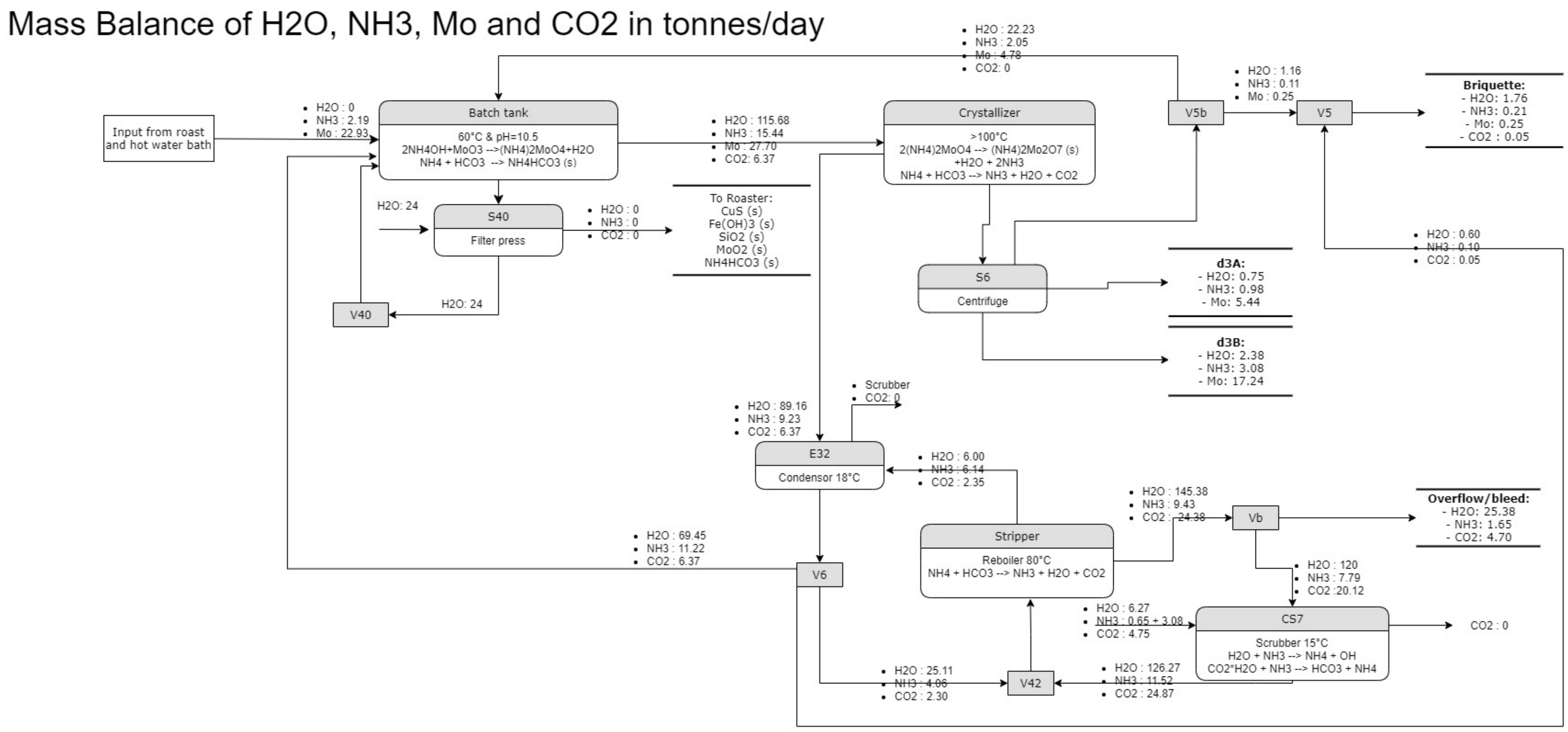


Figure 6.5: Mass balance of the AER system

6.3 Off-gas inlet in the scrubber-stripper with NaOH addition in the stripper, AER + NaOH

The results of the AER+NaOH system are illustrated in Figure 6.7. The off-gasses of the d3B-calciner are injected at the scrubber (CS7). Just before the fluid enters the stripper, NaOH is added to the solution. The carbonate binds to the sodium and leaves the system at the Vb(bleed). Ammonium ions move its equilibrium towards ammonia with increasing pH as already seen in Figure 2.3. Table 6.9 shows the amount of water, ammonia, molybdenum, carbon dioxide and sodium that enters and leaves the chemical plant in the AER+NaOH-system.

Table 6.9: Results inlet and outlet streams of water, ammonia, molybdenum, carbon dioxide and sodium in tonnes/day of the AER+NaOH-system

	Inlet	**S40**	**CS7**	**Stripper**	**S40**	**d3A&d3B**	**Briquette**	**Vb(bleed)**	**CS7**
H_2O	0	24	3.89	0	0	-0.75	-1.58	-25.58	0
NH_3	0.49	0	0.65	0	0	-0.98	-0.15	0	0
Mo	22.93	0	0	0	0	-22.68	-0.25	0	0
CO_2	0	0	4.75	0	0	0	0	-4.75	0
Na	0	0	0	4.96	0	0	0	-4.96	0

From the off-gasses 3.89 tonnes of water and 4.75 tonnes of carbon dioxide enters the plant extra at the scrubber. At the stripper 4.96 tonnes of sodium, in the form of NaOH enters the plant system. Which makes it equivalent to 8.64 tonnes of sodium hydroxide that enters per day. Due to the recycling of ammonia, only 0.49 tonnes is needed at the inlet. This comes to a saving of 3.08 tonnes of ammonia per day, which is 73% of the total inlet of ammonia in the current system.

Table 6.9 also shows the effluent streams of water, ammonia, molybdenum, carbon dioxide and sodium of the AER+NaOH-system. Most of the water leaves the system at the Vb(bleed). Ammonia has an effluent stream only to the briquette and in the product of the d3A. Carbon dioxide leaves the system at the Vb(bleed), because all carbonates in the Vb are neutralized by sodium hydroxide. That is why in the Vb(bleed), all the sodium is leaving the system as well.

6.3.1 Reference to model under first assumptions

There is no difference with the earlier model shown in Appendix A.3. This because there is no additional finding done on the ability of stripping ammonia from a solution of $NH_3-H_2O-CO_2$ with addition of sodium hydroxide. The same assumptions are valid in this model based on literature findings in Section 2.4.

6.3.2 Potential complications

The potential complications that occur when operating this model are found in the solution towards the Vb. Solution with a high pH leaves the system in the Vb(bleed) and scrubbing is then done with high pH water.

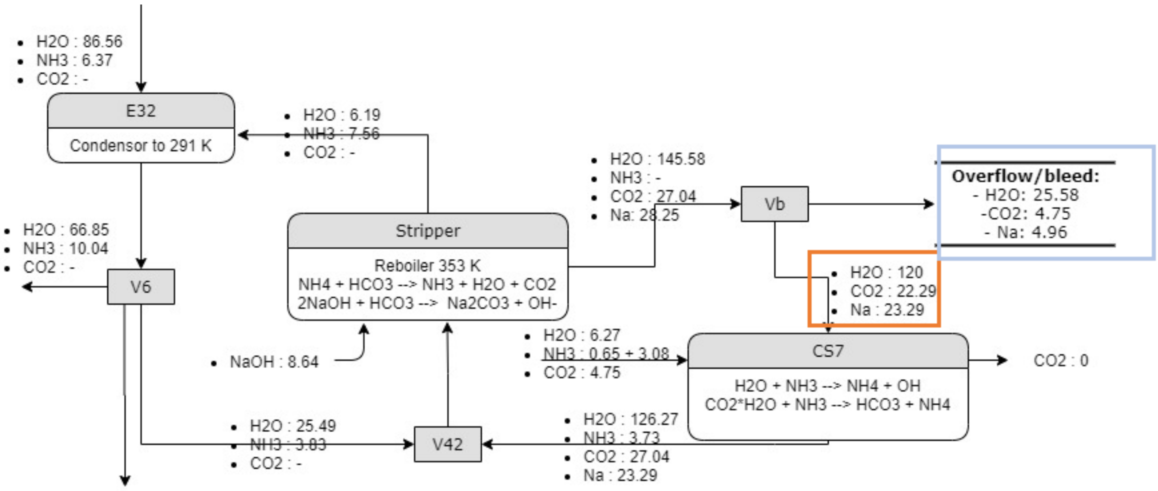


Figure 6.6: Potential complications in the scrubber-stripper system; sodium hydroxide in scrubbing water(red) and overflow water (blue) for the AER+NaOH-system

Figure 6.6 focuses on the scrubber-stripper system of the full mass balance of the AER+NaOH-system. The red and blue marked points are the points in the mass balance where potential complications can occur.
The overflow water at the Vb contains no ammonia anymore, but this water is probably in a high pH range. The water needs to be neutralized, before it can completely leave the system.

Equipment change

Table 6.10 gives an overview of what equipment should be changed in order to run this model.

Table 6.10: Change of equipment for AER+NaOH-system

	Current system (tonnes/day)	AER+NaOH (tonnes/day)	Increment
Stripper	2.97	7.56	2.6
Condenser	9.34	13.93	1.5
Scrubber	0.65	3.73	5.8

The stripper needs to be able to strip 2.6 times more ammonia in the AER+NaOH-system than the current system. There are carbonates in this system but assumed is, that they won't interfere with the ammonia molecules due to the addition of NaOH. That is why the 1.4 strip rate reduction is not applicable here. Literature emphasizes on even an acceleration of the stripping process due to sodium hydroxide[10][24].
The condenser needs to increase by 1.5 times the current size to be able to condense all the ammonia. The scrubber is increased by a magnitude of 5.8. The increasing amount of ammonia from the off-gas causes an increment in the amount of cold water to strip all the ammonia from the air. The scrubbing water that comes from the Vb can have a high pH value. Due to the high pH value, it is uncertain if all ammonia is absorbed by the water droplets, described in Section 2.3.3.

6.3.3 Cost analysis

Table 6.11: Cost analysis for ammonia recovery and use of sodium hydroxide in the AER+NaOH-system

	€/ day
Ammonia recovery	2.060,-
Sodium hydroxide	-12.190,-
Total sum of cost	-10.130,-

At Climax Molybdenum the price for ammonia is €0,67 per kg 100%w. For saving 3.08 tonnes of ammonia, this saves €2.060,- per day. On yearly base, this would save €722.000,-, considering 350 days of operation per year.

The price for sodium hydroxide that is paid at Climax is €0,24 per kg 0.17%w. This means, for a consumption of 8.64 tonnes of 100%w NaOH, the costs are €12.190,- per day.

Considering the high cost of NaOH, it is not profitable.

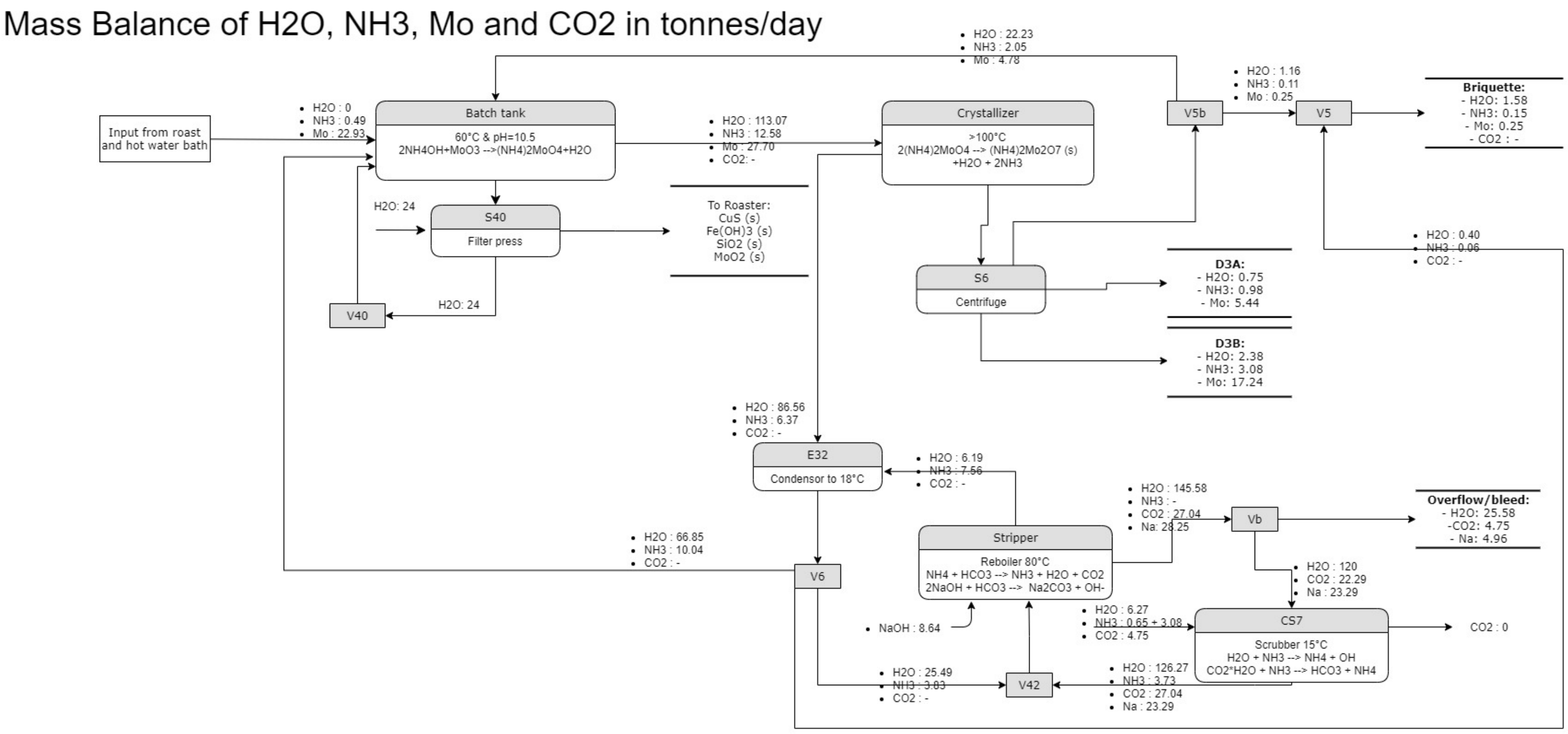


Figure 6.7: Mass balance of the AER+NaOH system

6.4 Comparison of the three models

In the previous sections of this chapter the three mass balances were elaborated on, their inlet and outlet streams, potential complications and ammonia recovery individually. In this section the three models are compared with each other to get an overview of the benefits and complications per model. An overview is given in Table 6.12.

Table 6.12: Current system compared by ammonia usage in tonnes/day with the ARS, AER and AER+NaOH model.

	Current (tonnes/day)	ARS (tonnes/day)	AER (tonnes/day)	AER+NaOH (tonnes/day)
Stripper	2.97	4.45	6.04	7.56
Condenser	9.34	16.48	15.37	13.93
Scrubber	0.65	0.65	3.73	3.73
Water treatment at Vb(bleed)	No	H_2O: 25.65 NH_3: 1.34 CO_2: 3.47	H_2O: 25.38 NH_3: 1.65 CO_2: 3.70	H_2O: 25.58 NH_3: - CO_2: 4.75
Scaling pipes	No	Yes/No	Yes	No
Ammonia recovery	0	1.73 (41%)	1.38 (33%)	3.08 (73%)

The stripper and condenser need to increase in size in order to be able to strip and condense the amount of ammonia. The scrubber system needs to be changed in the case of the AER and AER+NaOH system. With the ARS, the same scrubber can be used.

All three systems have their complications; in the ARS and AER-system, ammonia is present in the overflow water that leaves the system. The maximum amount of TAN in the discharge water is 25kg per day, with an average of 15kg over 10 days. Furthermore, scaling in pipes and processes are present in the ARS and AER-system. For the AER+NaOH system no scaling or ammonia are present in the discharge stream, but there is the possible complication for high pH water in the scrubbing water and in the overflow.

The ammonia recovery of the AER+NaOH-system is most efficient. It reduces the ammonia consumption by 73%. After that, it is the ARS-system, 41%, and at last place the AER, 33%. The cost analysis for the recovery of ammonia and using NaOH as water treatment agent is given in Table 6.13.

Table 6.13: Cost and benifit for the ARS, AER and AER+NaOH model in €/day.

	Current (€/day)	ARS(€/day)	AER(€/day)	AER+NaOH (€/day)
Ammonia recovery	-	1.160,-	920,-	2.060,-
NaOH for treatment Re-win ammonia	-	-8.910,- 900,	-12.060,- 1.110,-	-12.190,-
Total	0	-6.850,-	-10.030,-	-10.130,-

The benefit for the recovery of ammonia is highest for the AER+NaOH-system, although for the use of NaOH, they have also the highest total costs. The ARS-system has the best total outlook, still there is a cost of €6.850,- per day if NaOH is used in the discharge water treatment.

NaOH is in the ARS and AER-system too expensive to use as water treatment agent for this amount of TAN and TIC.

6.4.1 CATOX-unit

What is not taken in account in this thesis, is the cost reduction for partly replacing the CATOX-unit. Due to the recovery of the ammonia out of the off-gas of the d3B, only the off-gas of the d3A is led to the CATOX. Therefore an ammonia reduction of 75% is expected. Furthermore, this also reduces the airflow, because the d3A is heated to only 100 degrees Celsius which needs substantial less air. With a smaller airflow, the dustflow is also reduced, as a result the filters have less complications and less downtime.

On the other hand, the temperature for the catalytic oxidation process is 350 degree Celsius. This temperature was reached by little extra energy effort with both the air streams of the d3A and d3B. By taking only the air stream of the d3A, the temperature needs to be increased by at least 250 degree Celsius. This causes a lot of extra energy consumption.

Taking these two measurements into account, it was difficult to estimate the price reduction for the catalytic oxidation process.

7 Conclusion

The main goal of this work was to create an insight into the effect of reclaiming ammonia from the off-gasses of the d3B-calciner into the chemical plant system. Three different mass balances were created, where the off-gasses are injected into the chemical plant system. The mass balances that were created are ARS, AER and AER+NaOH system. With the ARS the off-gasses are injected into the batch solution of ammonium molybdate. The AER-system absorbs the off-gasses into an ammonia scrubbing system by water. AER+NaOH absorbs the off-gasses into an ammonia scrubbing system by water, with removal of carbon dioxide by addition of sodium hydroxide before stripping.
In order to obtain valuable information on the processes during operation, two different experiments were conducted. These experiments were specially designed to get insight into the influence of carbon dioxide on the processes in the batch tank and the stripper-condenser. These findings were implemented in the mass balances of the three different options for the chemical plant. The main conclusions drawn from the obtained experimental results are reported in this chapter.

Influence of carbon dioxide on the processes in the batch
Results of the first experiment showed that inorganic carbon has no influence on the solubility of ammonium molybdate in the batch tank. Also, no additional precipitations was found of metals like calcium, magnesium, zinc and iron in the form of metal carbonates due to the addition of inorganic carbon. Therefore, can be concluded that carbon dioxide has no negative influence on the processes of leaching molybdenum in ammonia solution.

The solubility of inorganic carbon in the the batch is reached with a TIC concentration of 2.12 mol/kg. From the results could be calculated that 84 %w of the TIC is in the form of ammonium bicarbonate. This means that most of the inorganic carbon in the batch is bound to only one ammonium ion. Therefore, less ammonia is needed to leach molybdenum at the right pH then if it was bound to carbonate. From here is concluded that the precipitation of TIC is in the form of ammonium bicarbonate, which has a solubility of 183 grams per liter in the batch solution.

Influence of carbon dioxide on the processes of stripping and condensing
Results of the second experiment showed that the strip rate of ammonia is reduced by 1.4 due to the addition of inorganic carbon in the stripping process. Furthermore, it is shown that stripping ammonia can be done efficiently until the total ammonia nitrogen mole concentration equals the total inorganic carbon mole concentration. This means that additional water treatment is needed for the overflow water that comes from the stripper, because not all ammonia is stripped from the solution.

The results of the stripping-condensing test show the following ratios of $NH_3-H_2O-CO_2$ are used for the mass balances created in this thesis:

- In the stripper; 0.42:0.42:0.17 in gas phase at 80 degree Celsius, respectively.
- In the condenser; at max 0.31:0.60:0.09 in liquid phase at 20 degree Celsius, respectively.

Inorganic carbon decreases the ratio of ammonia in gas phase at 80 degree Celsius compared to the same test without inorganic carbon in the solution. Furthermore, can be concluded that it is possible to create an extra outlet of carbon dioxide in the condenser if the carbon concentration in the gas exceeds the 9%w.

Mass balance
The findings of these two experiments were implemented in the mass balances, thus answering the main research question: *What is the effect of reclaiming ammonia from the calciner by direct injection into the chemical plant system?* This question focuses on how much ammonia is recovered and gives an insight on the potential complications.

Table 7.1: Current system compared by ammonia usage in tonnes/day with the ARS, AER and AER+NaOH model.

	Current (tonnes/day)	ARS (tonnes/day)	AER (tonnes/day)	AER+NaOH (tonnes/day)
Ammonia recovery	0	1.73 (41%)	1.38 (33%)	3.08 (73%)
Water treatment at Vb(bleed)	No	H_2O: 25.65 NH_3: 1.34 CO_2: 3.47	H_2O: 25.38 NH_3: 1.65 CO_2: 3.70	H_2O: 25.58 NH_3: - CO_2: 4.75
Scaling pipes	No	Yes/No	Yes	No

In terms of ammonia recovery per day, most ammonia is reclaimed in the AER+NaOH-system. Here, all the ammonia from the off-gas of the d3B-calciner is re-used. After that comes the ARS system, where 1.73 tonnes of ammonia is recovered and at last the AER-system, where 1.38 tonnes of ammonia is recovered.

The major complications that occur in the ARS and AER-systems are scaling and ammonia in the discharge water of the scrubber-stripper system. Scaling happens in both cases at the stripper to the Vb and from the scrubber to the V42. Scaling is a problem for the continuous operation of the plant because it decreases the lifetime of equipment and transport pipes. Also, it increases the downtime of the chemical plant due to cleaning and replacement.
In both the discharge water of the ARS and AER-systems is ammonia present. However, it is not allowed to have high concentrations of ammonia in the discharge water. The maximum amount of TAN in the discharge water is 25kg per day, with an average of 15kg over 10 days. A water treatment installation is needed to treat the overflow water of the chemical plant.
AER+NaOH has no scaling and no ammonia in the effluent streams of water, although the solution in the Vb has a high pH. Absorption of ammonia is less efficient with higher pH values in the scrubber also the overflow water needs to be neutralized before discharge.

The results of the cost analysis show that recovering ammonia from the off-gasses of the d3B have a cost reduction for the use of ammonia. Although NaOH-treatment for the ammonia in the overflow water is too expensive.

- The ARS-system saves €1.160,- per day with re-winning ammonia from the off-gasses of the d3B-calciner. It needs €8.900,- for the treatment of ammonia in the Vb(bleed) water with NaOH.
- The AER-system saves €920,- per day with re-winning ammonia from the off-gasses of the d3B-calciner. It needs €12.000,- for the treatment of ammonia in the Vb(bleed) water with NaOH
- The AER+NaOH-system cost €10.130,- per day for the recovery of ammonia

Other methods are needed to treat ammonia in the overflow water from the scrubber-stripper system for solutions in the ARS- and AER-system, otherwise it is economically not feasible. The AER+NaOH-system has higher accompanying cost with the treatment with NaOH in the stripper compared to the recovery of ammonia from the off-gasses.

This cost analysis is without taking into account the effect of reclaiming the off-gasses on the costs of the CATOX-unit. It is difficult to estimate the cost reduction of the CATOX, because by reclaiming all off-gasses from the d3B-calciner results in ammonia reduction of 75% towards the CATOX-unit. On the other hand, more energy is needed to heat the lower temperature ammonia gas from the d3A towards the CATOX-unit.

8 Recommendations and validation

The mass balances of the three different options in this report, present the possibility of re-using ammonia from the off-gasses of the d3B-calciner into the chemical plant system. The results in this research provide that there are several improvements ideas. The most relevant recommendations are collected in this chapter. The focus of the improvements and further studies are on ammonia treatment in the discharge water, scaling in the model, and reducing inlet of carbon dioxide into the chemical plant system.

Ammonia in discharge water
In both ARS and AER-system the discharge water, Vb(bleed), contains ammonia. The opportunity to treat ammonium bicarbonate in the overflow solution with NaOH is analyzed. The costs for using NaOH do not yield against the ammonia recovery from the off-gasses of the d3B-calciner. That is why alternative solutions should be analyzed in a further research. In Kinidi et al.[37] is described about various other methods for the treatment of ammonia in aqueous solutions. The methods that are most applicable for high concentrations of ammonium bicarbonate in discharge water are the following:

1. Use of lime (CaO) prior to ammonia stripping[4]: It causes pH to increase and TIC precipitates (to $CaCO_3$). Lime has a price on Alibaba[38] of $130-180 per ton.
2. Stripper with high temperature (95℃): In Kim et al.[39] is described that ammonium bicarbonate evaporation at a temperature of 95 degree Celsius reduces the NH_4HCO_3 concentration to ppm level. If thereafter condensing is used, then only a part of the CO_2 goes into solution.
3. Treatment with H_2SO_4 for $(NH_4)_2SO_4$-fertilizer production. Decreasing the pH evaporates TIC from the solution and ammonium sulphate will be produced[6]. Ammonium sulphate is sold for $139 per ton[40].

Lime is a common reagent in water treatment plants for ammonia recovery. The downside is precipitation and scaling that occurs in several processes. Increasing the stripping temperature can also be used directly after the first stripper. With increasing stripping temperature the ammonia-water balance in gas phase will shift towards a larger amount of water.
For the third point, sulfuric acid is produced by Climax Molybdenum in an earlier process. This has no additional costs. Only further research have to be done for an ammonium sulphate plant installation.

Reduction carbon dioxide recovery due to condensing
In this research is assumed that all carbon dioxide from the d3B-calciner is absorbed into the chemical plant system. Section 5.2.2 shows that the condensing process, with temperature drop from 80 to 20 degree Celsius will be more effective for NH_3 recovery than CO_2. Also, Figure 2.10 shows that the dew point fraction of ammonia in an ammonia-water balance is higher with even lower temperatures[8][7].

Condensing on the other hand is an energy consuming and expensive process, especially if the temperature difference is large. The condenser needs to cool large volumes of gas from 450 degree

Celsius to temperatures around 20 degrees or lower. Whereby most of the ammonia will go into solution. Afterwards, these cooled gasses go to a scrubber to wash the remaining ammonia. Due to the low ammonia content, less carbon dioxide will be absorbed by the cold water in the scrubber. If less carbon dioxide is absorbed into the chemical plant system, the mass balance can be revised on the new implementations and input values.

Alternative for calcination process
The ADM crystals are heated by a natural gas burner to vaporize the water and ammonia. In this process methane is used as heat source and a lot of carbon dioxide is produced, as described in Section 2.1. It could be beneficial to look at an alternative for the natural gas burner, where no carbon dioxide is produced in the product of the calciner.
Alternatives can be in the form of direct heating, whereby the combustion products are in contact with the material being processed. Or indirect heating, where the products are not in contact. Down here a quick cost analysis is made for the combustion of hydrogen vs methane for a financial feasibility:

The energy density of hydrogen is 120MJ/kg. This is much higher than coal (±30 MJ/kg) or natural gas (±55 MJ/kg). The price of hydrogen is €1.5 /kg [41].

$$2\,\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O} \tag{8.1}$$

In the calciner 1.73 tonnes of methane is burned per day. Which means 0.79 tonnes of hydrogen is needed per day, taking into account the different energy density.

In Table 8.1 the costs of combustion with natural gas is elaborated against the same combustion with hydrogen.

Table 8.1: Methane combustion vs. hydrogen combustion

	€/MWh	MJ/kg	tonnes/day	MJ/day	MWh	€/dag
Natural gas	20	55	1.73	95.000	26	530,-
Hydrogen	45	120	0.79	95.000	26	1190,-

In the end the natural gas combustion is twice as cheap as the hydrogen combustion. But the products of hydrogen combustion contain only water, Equation 8.1. Which means that no complications will be present concerning inorganic carbons in the processes of the chemical plant. Assuming a fully recovery of ammonia from the off-gasses, saving 3.08 tonnes of ammonia per day. Table 8.2 shows the comparison of the ARS-system with natural gas combustion, and the hydrogen combustion system.

Table 8.2: Natural gas-system against hydrogen combustion

	Combustion cost (€/day)	NH_3-recovery(€/day)	Total profit (€/day)
Natural gas-system	-530,-	1.160,-	630,-
Hydrogen-system	-1.190,-	2.060,-	870,-

The last column of Table 8.2 shows the profit of the hydrogen system to be €250,-/day higher for the hydrogen combustion system due to the fully recovery of the ammonia.

This is a rough estimation of course, and not going into the physical and chemical possibility of hydrogen combustion for the calcination process of ADM, but it shows that it is worth looking at the possibility of changing the combustion in the d3B-calciner.

Validation of data

In a similar molybdenum processing plant in Fort Madison (USA), ammonia is already recovered by ARS. The operations differ a little bit from the proposed ARS in this report, but it is possible to ask if they found the same complications in the processes and how they solved this.
Also, this plant could have valuable information on the temperature difference and volume flow of the off-gas handling that was outside the scope of this research.
Based on literature study the assumption is that all carbon dioxide is absorbed by the batch solution in the ARS. Also this assumption can be validated in the similar molybdenum processing plant in Fort Madison.

At last, lab scale experiments have differences from plant scale operations. The experiments conducted in the lab are batch based and give a visualization on the processes in the chemical plant. It would be good to build a prototype of the operations in the chemical plant, where can be tested in a continues process on the validations of the findings in this report.

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A Mass balances under assumptions

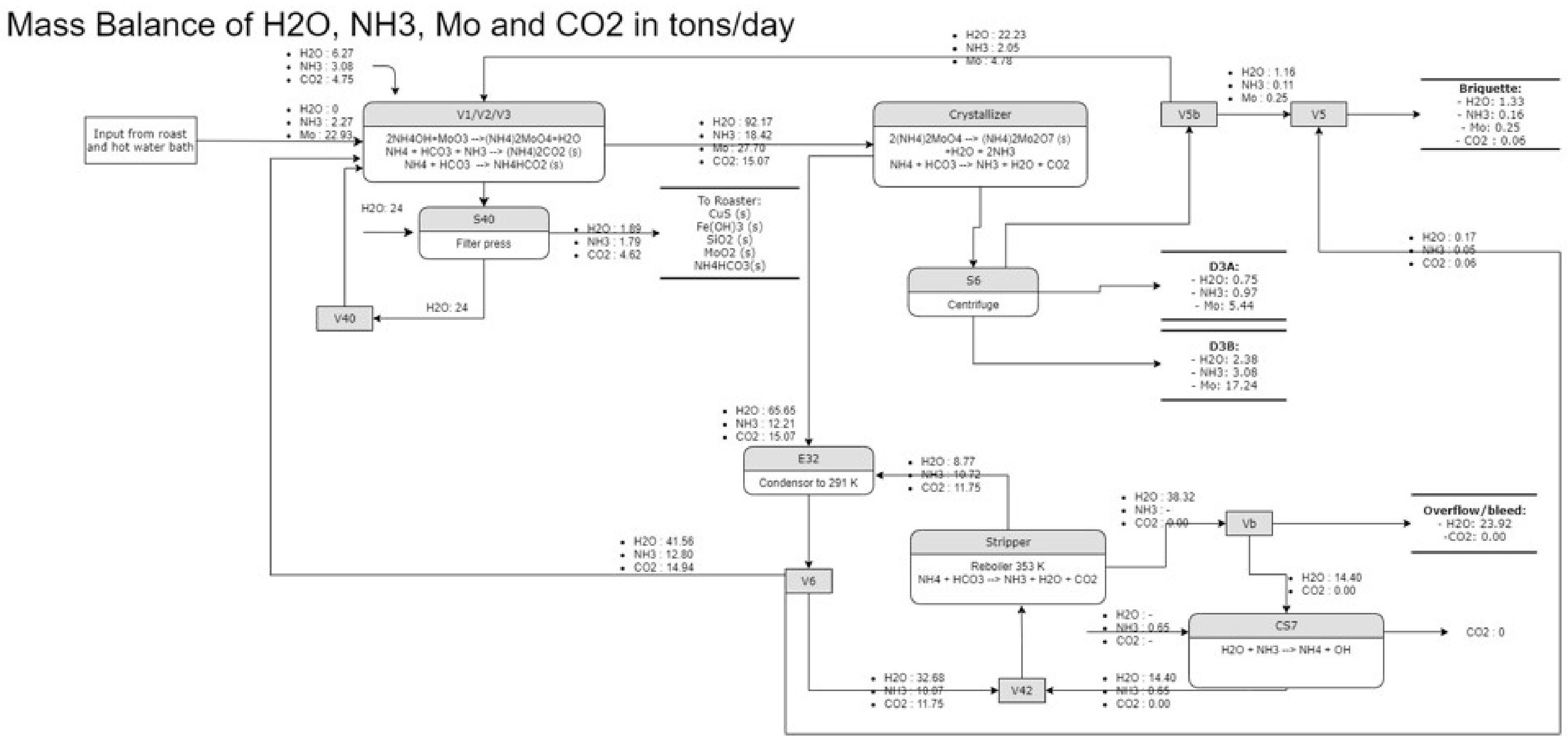


Figure A.1: ARS under first assumptions

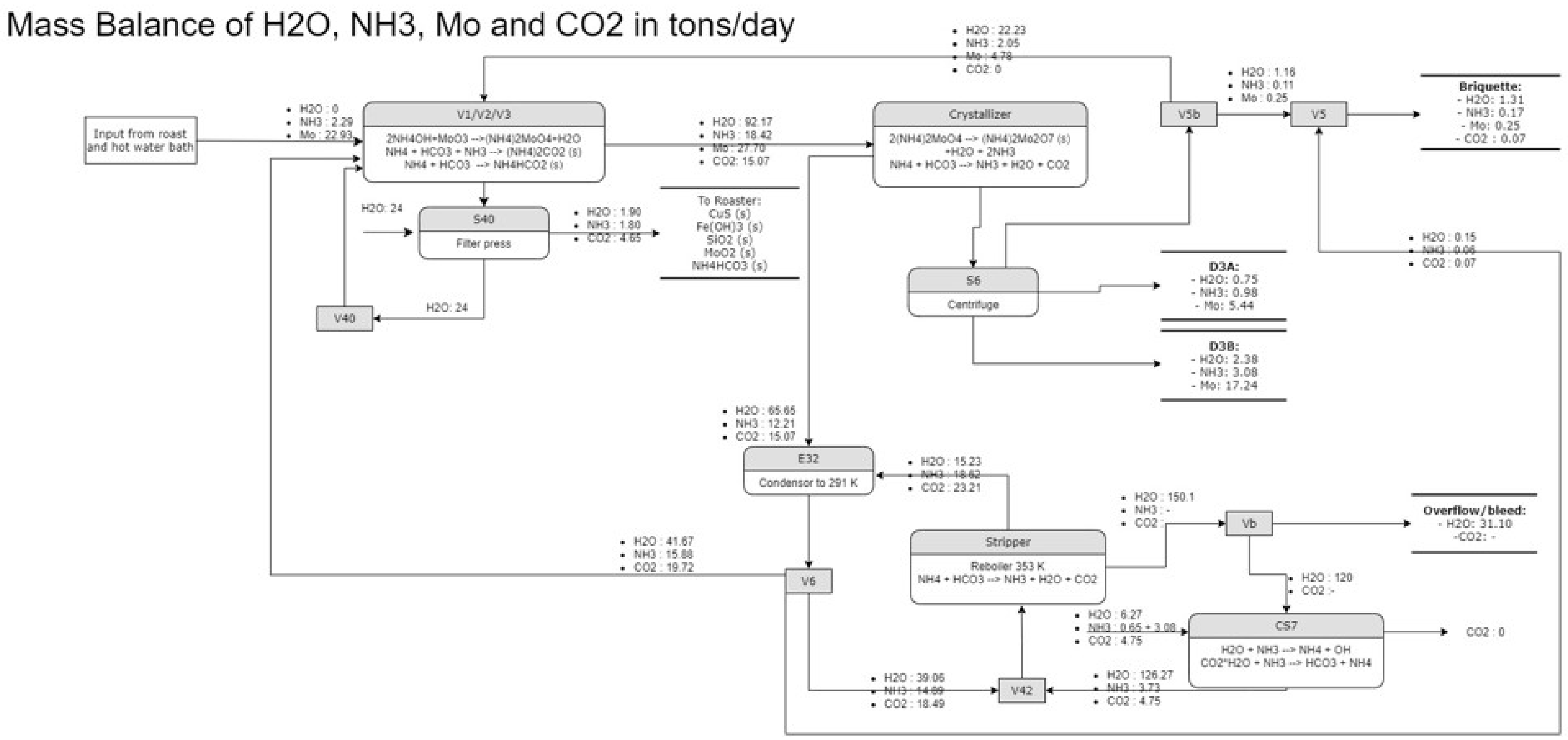


Figure A.2: AER under first assumptions

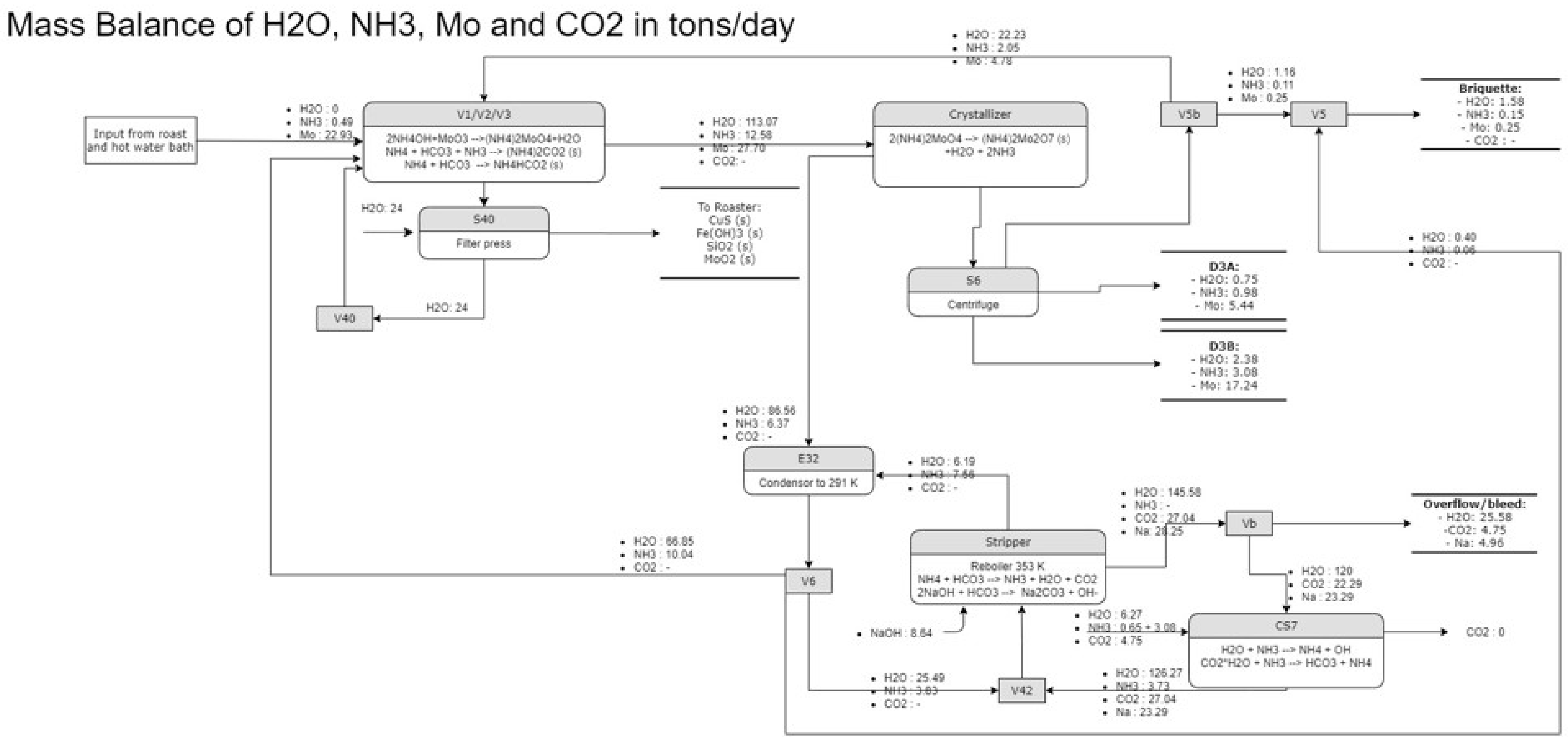


Figure A.3: AER-NaOH under first assumptions

B Measuring methods

B.1 Setup experiments I and II

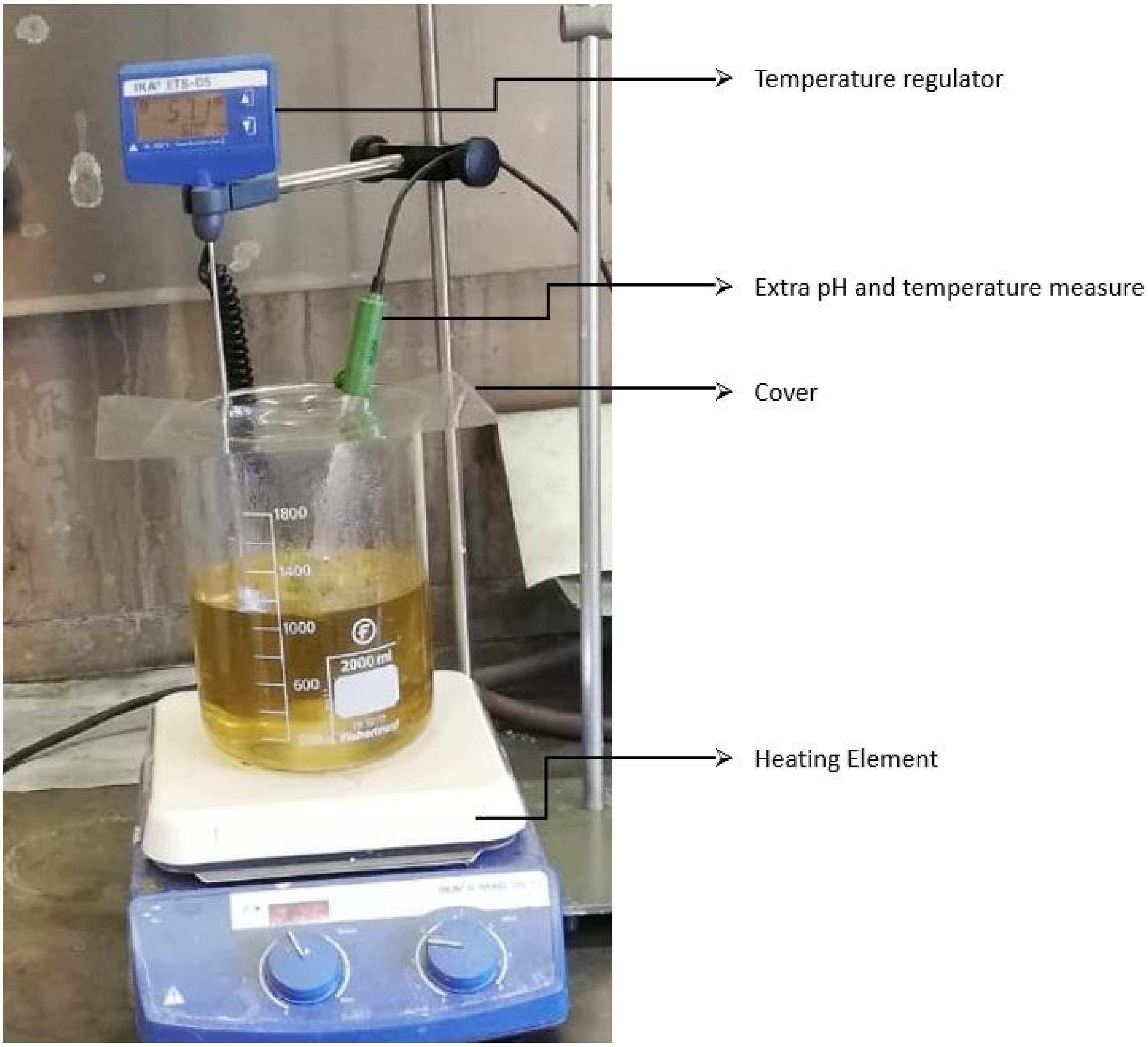


Figure B.1: Setup of batch experiment with used material and equipment

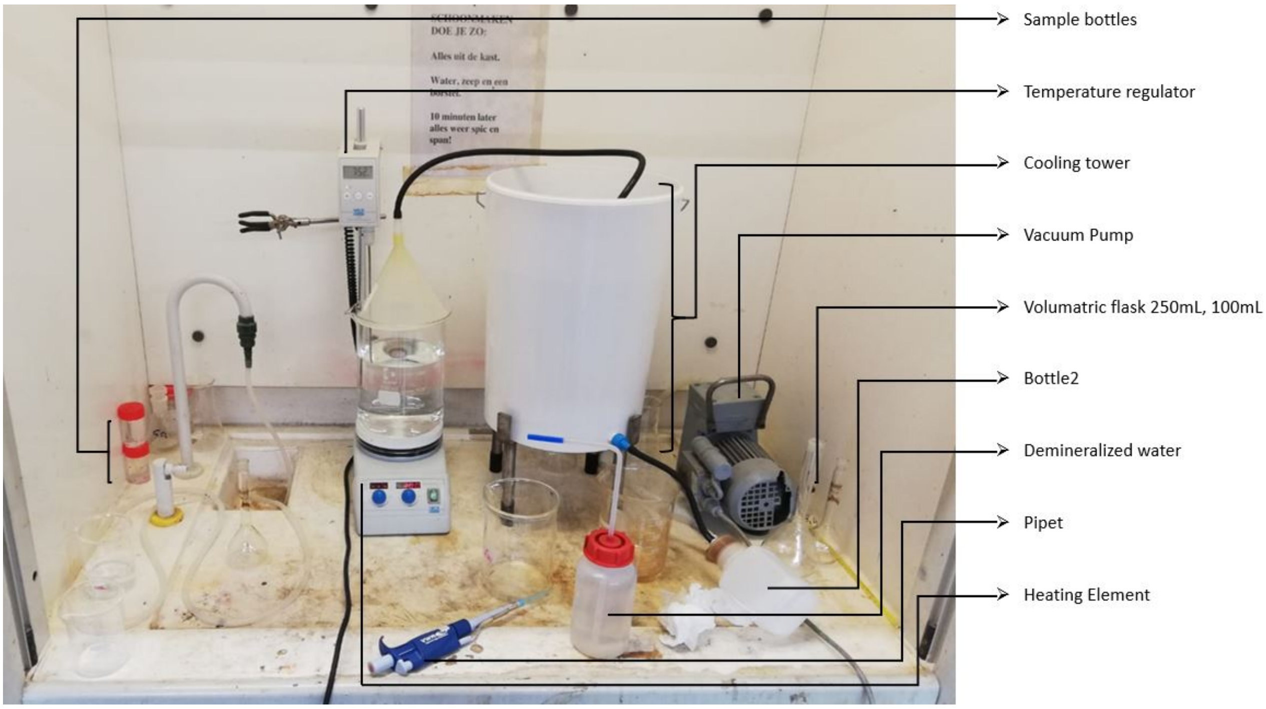
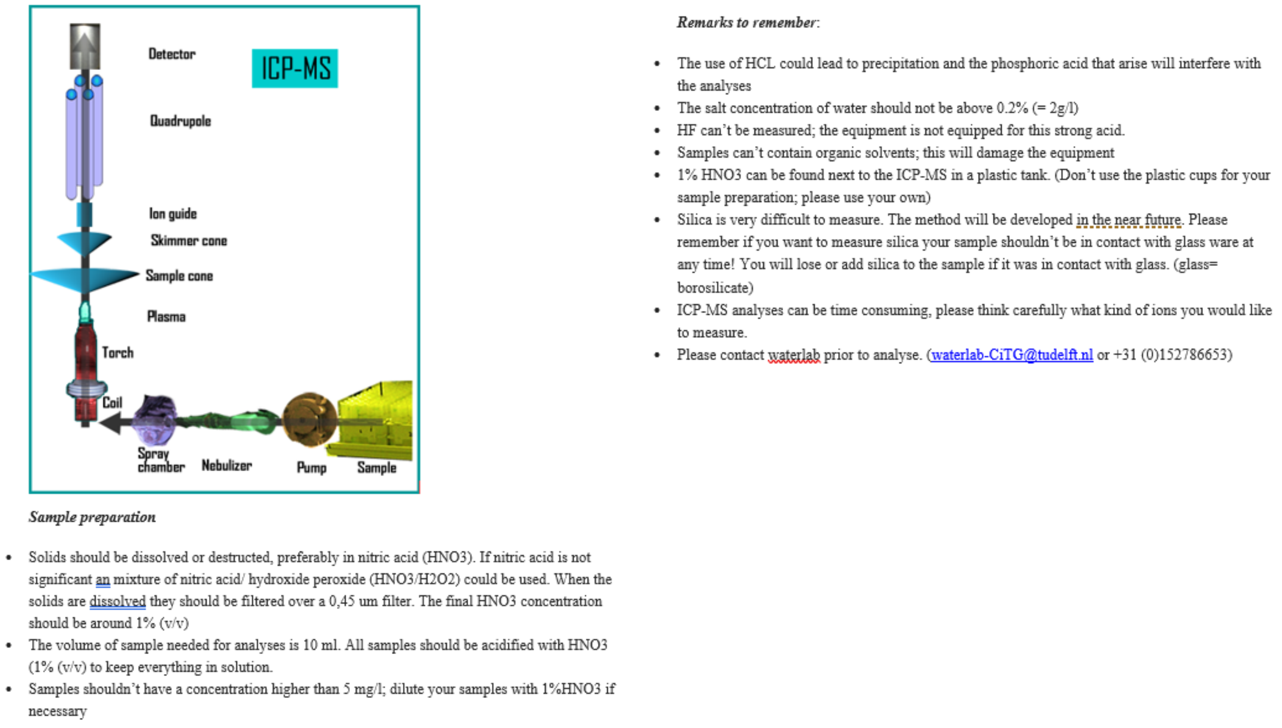


Figure B.2: Setup of stripper-condenser experiment with used material and equipment

B.2 ICP-MS working procedure

Inductively Coupled Plasma (ICP) makes use of a standard high-temperature ion source to make a plasma where all bonds of the molecules are broken. The data acquired from a plasma ion source corresponds to the total content of an element in the sample. The ions from the ICP are aimed on a measuring vision of a mass spectrometer[42]. The following working procedure is used for the ICP-MS molybdenum measurement:



Sample preparation

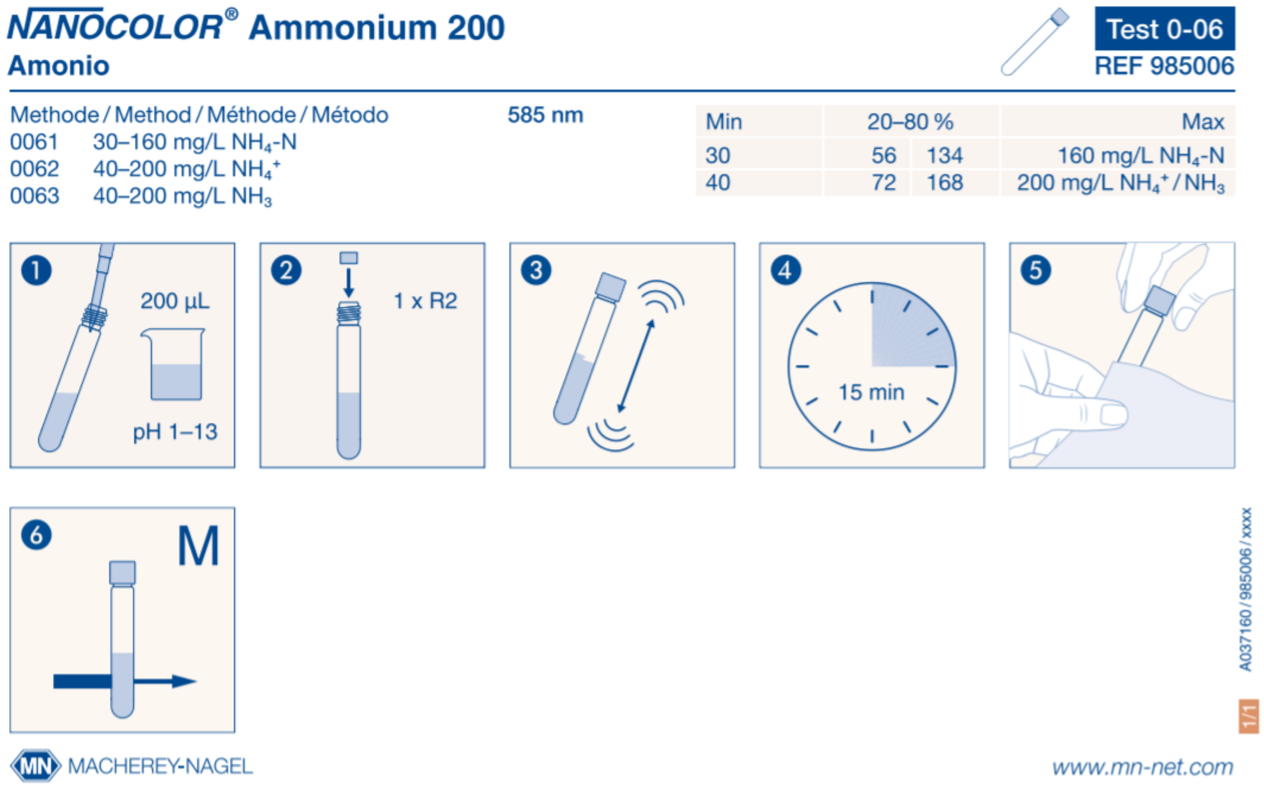
- Solids should be dissolved or destructed, preferably in nitric acid (HNO3). If nitric acid is not significant an mixture of nitric acid/ hydroxide peroxide (HNO3/H2O2) could be used. When the solids are dissolved they should be filtered over a 0,45 um filter. The final HNO3 concentration should be around 1% (v/v)
- The volume of sample needed for analyses is 10 ml. All samples should be acidified with HNO3 (1% (v/v) to keep everything in solution.
- Samples shouldn't have a concentration higher than 5 mg/l; dilute your samples with 1%HNO3 if necessary

Remarks to remember:

- The use of HCL could lead to precipitation and the phosphoric acid that arise will interfere with the analyses
- The salt concentration of water should not be above 0.2% (= 2g/l)
- HF can't be measured; the equipment is not equipped for this strong acid.
- Samples can't contain organic solvents; this will damage the equipment
- 1% HNO3 can be found next to the ICP-MS in a plastic tank. (Don't use the plastic cups for your sample preparation; please use your own)
- Silica is very difficult to measure. The method will be developed in the near future. Please remember if you want to measure silica your sample shouldn't be in contact with glass ware at any time! You will lose or add silica to the sample if it was in contact with glass. (glass= borosilicate)
- ICP-MS analyses can be time consuming, please think carefully what kind of ions you would like to measure.
- Please contact waterlab prior to analyse. (waterlab-CiTG@tudelft.nl or +31 (0)152786653)

B.3 Macherey-Nagel TAN Measurement

The measurement is done by photometric determination of a blue indophenol dye based on a reaction with hypochlorite and salicylate at a pH of 12.6 in the presence of sodium nitroprusside [43]. TAN measures all the nitrogen in the solution in the form of ammonia and ammonium. The following working procedure is used for the measurement:



NANOCOLOR® Ammonium 200
Amonio

Test 0-06
REF 985006

Methode / Method / Méthode / Método		585 nm
0061	30–160 mg/L NH_4-N	
0062	40–200 mg/L NH_4^+	
0063	40–200 mg/L NH_3	

Min	20–80 %		Max
30	56	134	160 mg/L NH_4-N
40	72	168	200 mg/L NH_4^+ / NH_3

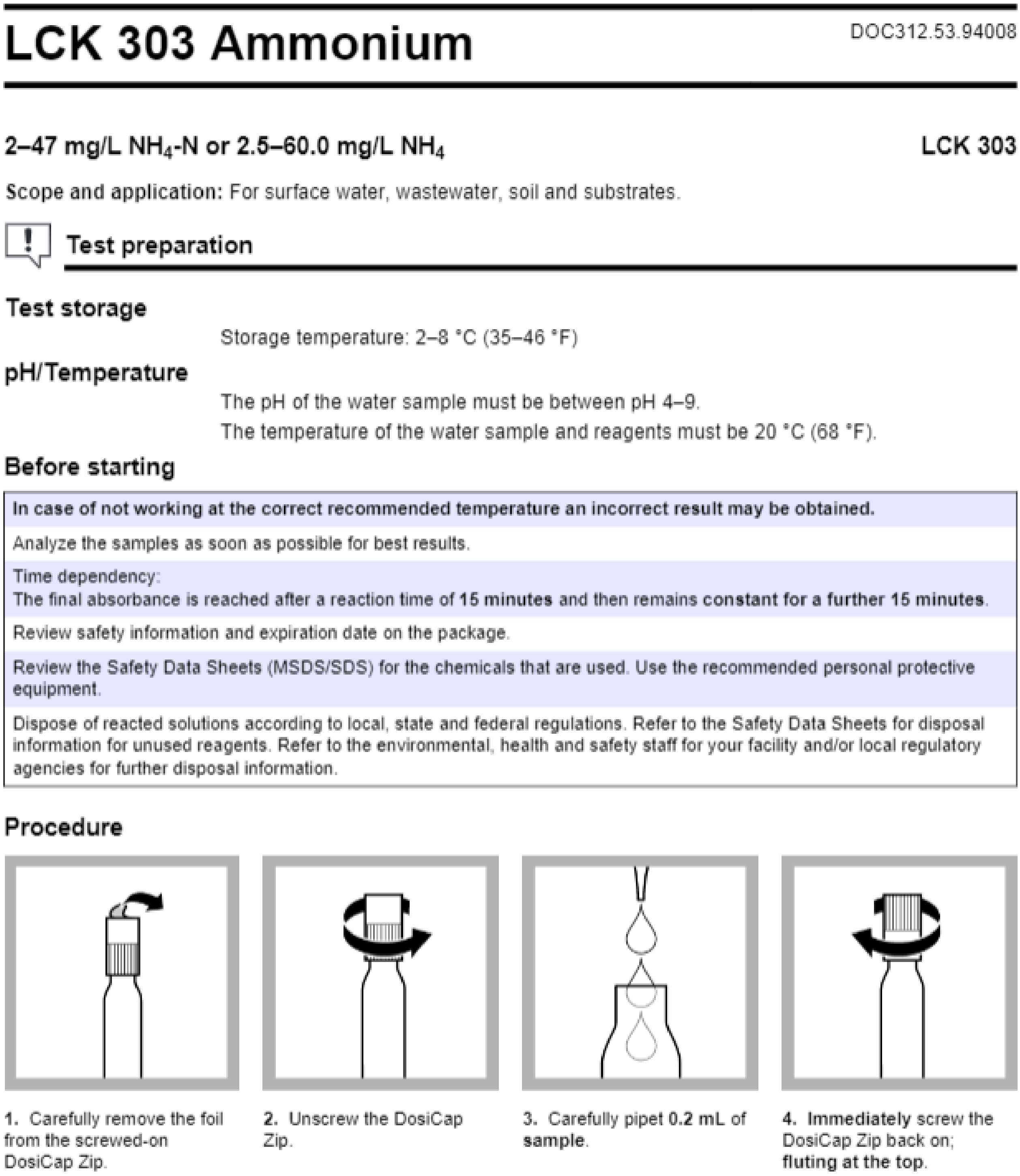
❶ 200 µL pH 1–13
② 1 x R2
③
④ 15 min
⑤
⑥ M

A037160 / 985006 / xxxx
1/1

MACHEREY-NAGEL
www.mn-net.com

B.4 Hach Lange TAN Measurement

The ammonium ions react at a pH of 12.6 with hypochlorite ions and salicylate ions in the presence of sodium nitroprusside as a catalyst to form indophenol blue [44]. The following working procedure is used for the measurement:



LCK 303 Ammonium

DOC312.53.94008

2–47 mg/L NH_4-N or 2.5–60.0 mg/L NH_4 **LCK 303**

Scope and application: For surface water, wastewater, soil and substrates.

Test preparation

Test storage

Storage temperature: 2–8 °C (35–46 °F)

pH/Temperature

The pH of the water sample must be between pH 4–9.

The temperature of the water sample and reagents must be 20 °C (68 °F).

Before starting

In case of not working at the correct recommended temperature an incorrect result may be obtained.

Analyze the samples as soon as possible for best results.

Time dependency:
The final absorbance is reached after a reaction time of **15 minutes** and then remains **constant for a further 15 minutes**.

Review safety information and expiration date on the package.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Procedure

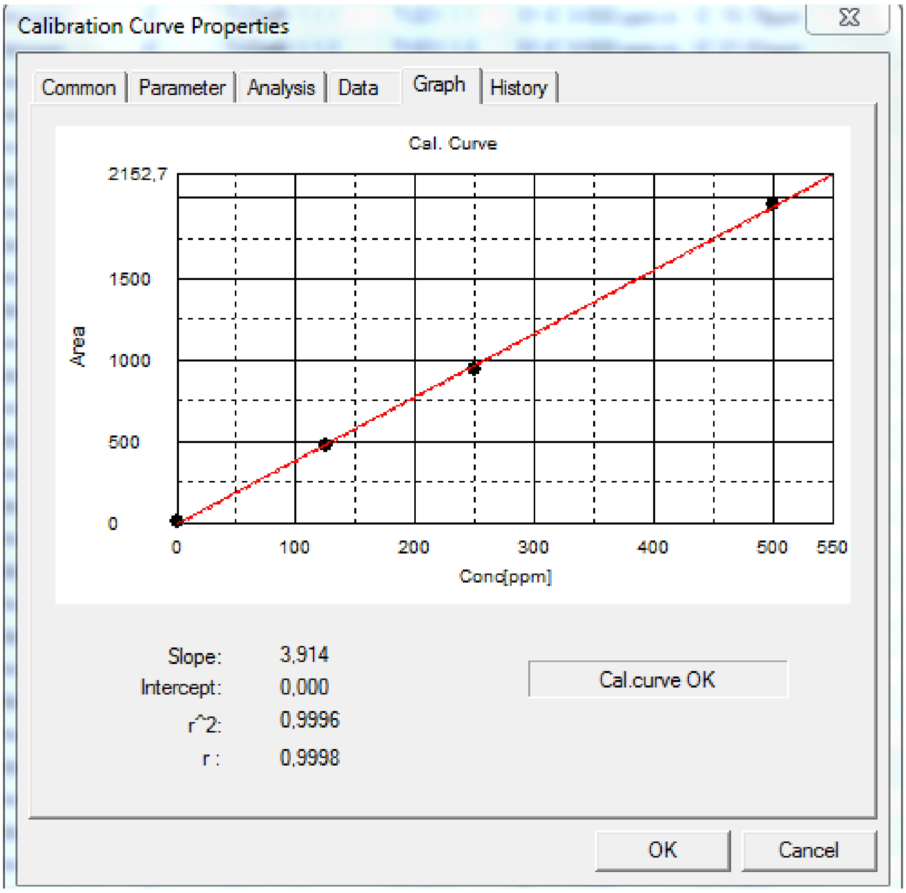
1. Carefully remove the foil from the screwed-on DosiCap Zip.
2. Unscrew the DosiCap Zip.
3. Carefully pipet **0.2 mL** of **sample**.
4. **Immediately** screw the DosiCap Zip back on; **fluting at the top**.

B.5 TIC Measurement

The solution to be measured is injected in a vessel which is filled with phosphoric acid H_3PO_4-25%w to convert all the Inorganic Carbon (IC) to CO_2. Sparging the sample in the vessel with carrier gas removes the CO_2 originating from the IC content and the dissolved CO_2 and will be determined by the Non-Dispersive Infrared Sensor (NDIR)-detector[45].

B.5.1 Calibration TIC

For IC-stock solution is needed, sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$). The 1000 mgC/l stock solution is made according the following procedure: Dissolve 4,412 g Na_2CO_3 and 3,497 g $NaHCO_3$ in 500 ml H_2O filled in a 1000 ml volumetric flask and make up to volume with pure water. This solution is stable for about 2 weeks stored tightly at room temperature. IC Standard solution absorb atmospheric CO_2 and undergoes concentration changes. A calibration curve is produced which looks as follows:



Slope: 3,914
Intercept: 0,000
r^2: 0,9996
r : 0,9998

B.6 Free ammonia measurement

This autosampler dilutes the solution with 0.1 M H_2SO_4. During the dilution the electrochemical potential is measured of the solution in eV. The machine calculates the amount of 0.1 M H_2SO_4 needed before all the free ammonia is converted to ammonium.

B.7 Dilution

B.7.1 Batch experiment

The dilution procedure for the elements in the batch experiment is given in the table below:

Table B.1: Dilution procedure for measurement

Measurement	Dilution	Step 1	Step 2	Step 3
Mo	5 000 000	25mL to 225mL	40uL to 39960uL	20uL to 9980uL
TIC	100	1mL to 99mL	-	-
TAN	1000	1mL to 9mL	1mL to 99mL	-
K, Cu, Mg, Zn, Fe, Ca, Na	100	1mL to 99mL	-	-
Free-NH_3	1mL to 40mL	-	-	-

The samples are taken directly for measurement or stored for measuring later that week. In the table above step 1 is taken directly during the experiment. Step 2 or later, are conducted just before the to be measured element is put into the measuring machine.

B.7.2 Stripper-condenser experiment

The sampling procedure for the elements in the stripper-condenser experiment is given in the table below.

Table B.2: Dilution procedure for measurement

Measurement	Dilution	Step 1	Step 2
TIC	250	1mL to 249mL	-
TAN	2500	1mL to 99mL	4mL to 96mL

All dilution steps are taken directly after each other. After the experiment has finished, the samples are taken directly to the TOC-analyzer and the DR3600 for TIC and TAN measurement.

B.8 0.6 mol/L TIC concentration solution

The calculation to get an approximation of the TIC concentration of 0.6 mol/L is shown in Equation B.1.

$$\mathrm{M_{CO2}/M_{total}/u_{CO2}} \tag{B.1}$$

Where M_{CO2} is the mass (kg) of carbon dioxide entering the stripper in one day. M_{total} is the total mass (kg) of the fluid that is passing through the stripper in one day and u_{CO2} is the molar mass of carbon dioxide (g/mol). The density of water is around 1kg/m^3, this means that the total mass can be assumed as total volume. The following values are used; M_{CO2} = 4.75, M_{total} = 127+39 = 166, which is the volume that enters the V42 in the AER-system, and u_{CO2}=44.

B.9 Ammonia 4.2-4.4 mol/L solution

For the experiment at the stripper-condenser a base solution of 4.2-4.4 mol/L needs to be created.

	%w	g/L	mol/L
NH_3-concentration1	30	266.07	15.62
NH_3-concentration2	8	71.54	4.2

To get NH_3-concentration2, the solution needs to be diluted 3.72 times. To make a 2 liter solution in the experiment, the following formula is applied;

$$\mathrm{V_{H2O}} + \mathrm{V_{NH3(30\%)}} = \mathrm{V_{NH3(8\%)}} \tag{B.2}$$

Volume water: V_{H2O} = 2.72*(2/3.72) Liter
Volume ammonia(30%): $V_{NH3(30\%)}$ = 1*(2/3.72) Liter

B.10 Tube design condenser

The airflow through the condenser is managed by a vacuum pump attached to the condenser. The retention time of air inside the tube is important for the cooling capacity of the condenser. Therefore, the velocity is managed of the vacuum pump. The pump has a capacity to create a volume flow of 1.7 m^3/h. The tube has a length of 5.7 meters and an inner diameter of 5 millimeters. According to formula B.3 and B.4, the velocity and retention time of air in the pipe is calculated.

$$velocity = Volumeflow/(\pi * (0.5 \cdot \mathrm{Diameter\,tube})^2) \tag{B.3}$$

$$Time = lengthtube/velocity \tag{B.4}$$

To increase the retention time, the volume flow of the air through the pipe is decreased. This is done by creating an extra suction pipe with a smaller length. Therefore, the velocity and volume flow of air through the condenser pipe is decreased. The length of the second pipe is dependent on the time the air needs to stay in the condenser tube. The formula looks as follows:

$$\mathrm{v_{total}} = \mathrm{V}_{p1}/\mathrm{A} + \mathrm{V}_{p2}/\mathrm{A} = \mathrm{v}_{p1} + \mathrm{v}_{p2} \tag{B.5}$$

The total velocity (v_{total}) is the speed the air can travel through both sections of the pipe is dependent on the volume flow of air traveling through both tubes. In this model, both tubes have the same inner diameter, that is why surface A is the same. V_{p1} is the velocity of the condenser tube and V_{p2} is the velocity of the second tube to decrease the velocity in the condenser tube. The length of the second tube is calculated as follows;

$$\mathrm{L}_{p2} = \mathrm{v}_{p2}/\mathrm{v_{total}} * \mathrm{L_{total}} \tag{B.6}$$

Where L_{p2} is the length of the second tube to assure that the velocity of the condenser tube is small enough so that air has time to condense. The outcome of the calculation of the velocities and length tube pipes are given in the table below.

	velocity	Length(m)	time(sec)
Tube-condenser	1.3	5.7	4.3
Tube section2	22.7	0.3	0.015

B.11 Validation of evaporated water

In stripper-condenser experiment water evaporates during heating towards 80 degree Celsius. To get an indication about the amount, so that this water can be added again in the solution so the right dilution levels are maintained for ammonia, the following calculation is made;

$$\mathrm{G}_s = \Theta\mathrm{A}(\mathrm{x}_s\text{-x})/_{3600} \tag{B.7}$$

Where G_s is the amount of evaporated water per second (kg/s), A is the water surface area (m^2), x_s is the maximum humidity ratio of saturated air at the same temperature as the water surface (kg/kg). In the equation x is the humidity ratio of air in kg water per kg dry air. Θ is the evaporation coefficient in (kg/m^2s) determined by 25+19v. Where v is the velocity of air above the water surface (m/s) [46].

	60℃	80℃
Gh(kg/h)	0.05	0.230
Θ(kg/ $m^2 h^{-1}$)	25.00	25.29
v(m/s)	0	0.015
A(m^2)	0.0133	0.0177
xs(kg/kg)[47]	0.152	0.543
x(kg/kg)[48]	0.016	0.022

Gh is the amount of evaporated water per hour, this is 50mL for 60℃ and 230mL for 80℃. The evaporation rate is very dependent on temperature as you can see.

C Results batch experiment

C.1 Molybdenum measurement

Results of Molybdenum measurement done by ICP-MS. In the table blow, the results of the Molybdenum measurement are shown with the SRM used in the ICP-MS. [49].

Sample label	Mo98[H2] (ppb)	Mo98[nG] (ppb)	Mo98[He] (ppb)
$Mo_{1\,before}$	52.6125	53.4689	53.1025
$Mo_{1\,after}$	54.2611	51.2558	52.5802
$Mo_{2before}$	53.6654	52.4196	51.5775
Mo_{2after}	51.2315	51.4139	51.5912
$Mo_{3before}$	65.29	63.27	59.49
Mo_{3after}	47.27	46.24	44.13

C.2 Filtered batch solution in stead of unfiltered batch solution

In experiment 1, a just finished batch solution after filtration of the contaminants like metals is used. This is done because in a solution it is possible to visualize the precipitation when ammonium carbonate is added. In an unfiltered batch solution this was not possible due to the insoluble metals. In this research is emphasized on the positive effect of ammonium carbonate on metal precipitation. There was no sign of metal precipitation in the solution due to addition of ammonium carbonate. The metal content in the tested solution was already in ppm concentration. Inorganic carbon could have other effects on the solubility of metals.

D Results scrubber-stripper experiment

D.1 Influence of inorganic carbon on the stripping efficiency

Equation D.1, D.2 and D.3 show the calculation for the influence of inorganic carbon on the stripping efficiency of NH_3, H_2O and CO_2.

$$\mathrm{Z} = \sum_{\mathrm{i}=1}^{\mathrm{N}} (\mathrm{Z}_i - \mathrm{Z}_0)/(\mathrm{Z}_0) \tag{D.1}$$

$$\mathrm{W} = \sum_{\mathrm{i}=1}^{\mathrm{N}} (\mathrm{W}_i - \mathrm{W}_0)/(\mathrm{W}_0) \tag{D.2}$$

$$\mathrm{V} = \sum_{\mathrm{i}=1}^{\mathrm{N}} \mathrm{V}_i \tag{D.3}$$

Where Z_i, W_i and V_i are the fractions NH_3, H_2O and CO_2 evaporated respectively of the i^{th} experiment. Z_0 and W_0 are the fractions NH_3 and H_2O evaporation respectively where no carbonates are added to the experiment. Z, W and V are the average fraction of NH_3, H_2O and CO_2 in gas phase at the process of stripping ammonia at 80 degree Celsius.

D.2 Outlet of carbon dioxide

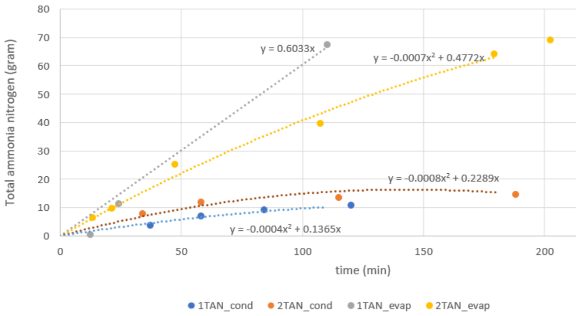


Figure D.1: Total ammonia nitrogen against time cumulative for the total evaporated and total condensed ammonia from the stripper-condenser experiment

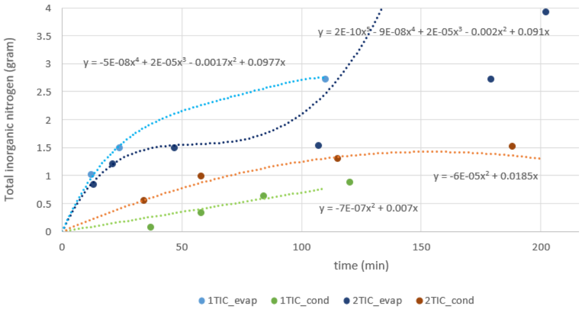


Figure D.2: Total inorganic carbon against cumulative time for the total evaporated and total condensed carbon dioxide from the stripper-condenser experiment

As can be seen in the two figures above is that not all evaporated ammonia and carbon dioxide is going into solution again with condensing. From these figures the ratio evaporated against condensed material can be calculated. The approximation of the exact values are closest in the time area between 15 and 40 minutes. Before and after that the deviation is too large. This ratio is given in the table below.

Table D.1: Condensation of CO_2 and NH_3

	Condensed %w
1_{TAN}	21
1_{TIC}	12
2_{TAN}	45
2_{TIC}	34

The table above gives the percentage of evaporated TAN or TIC that is condensed into solution. As can be seen from the table, condensing carbon dioxide goes less efficient than ammonia. The difference can be 1.3 to 1.9 times.

E Results mass balances

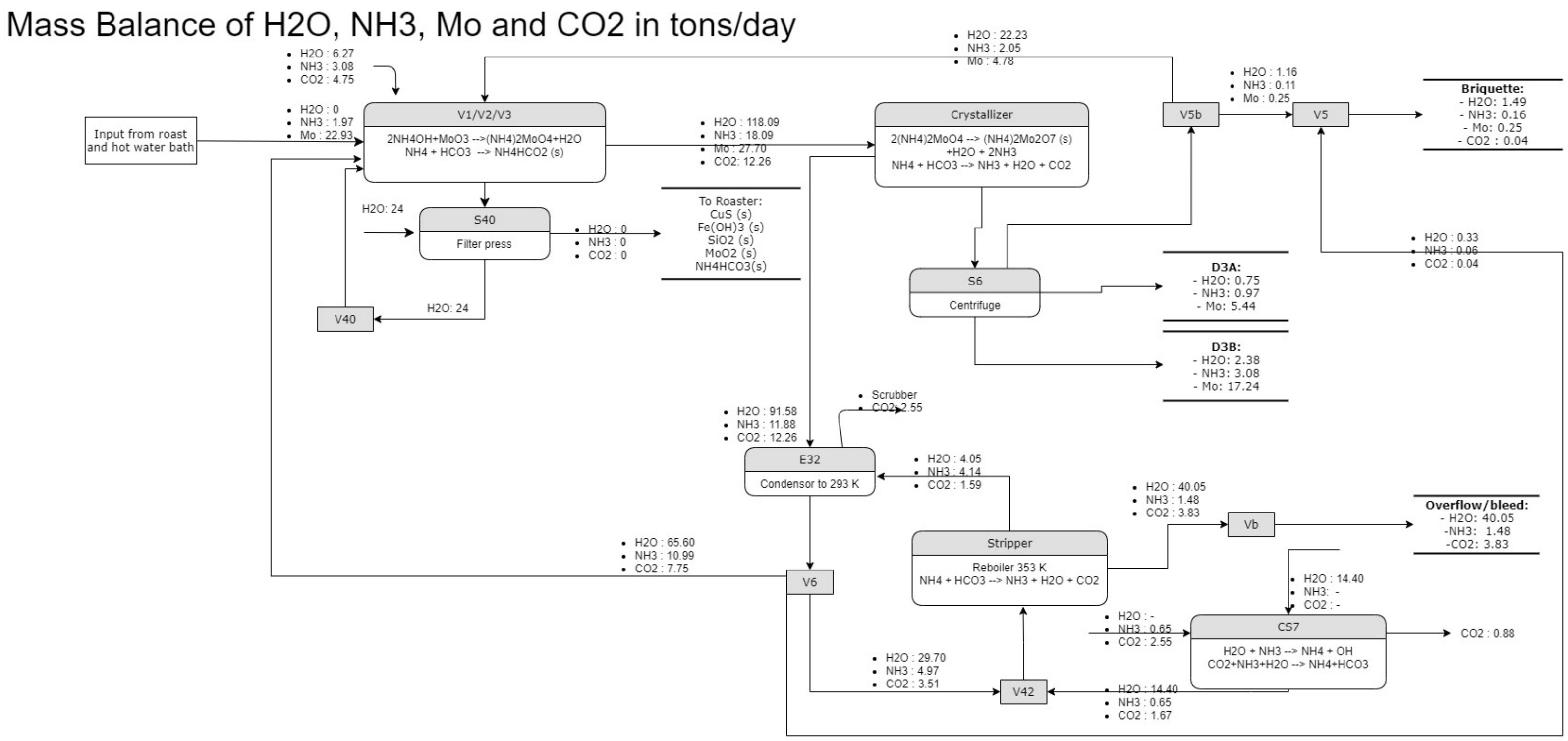


Figure E.1: ARS with new water at the scrubber

E.1 Complications described in literature

E.1.1 Absorption ammonia in diluted ammonium bicarbonate solution in the scrubber

In the scrubber the absorption of ammonia is based on Henry's law constant described in Section 2.3.3, where stated that the amount of gas that is dissolved in a liquid is directly proportional to the partial pressure of that gas around the liquid when the temperature is kept constant. In the case of ammonia at 15 degree Celsius, the concentration of water that is needed, is equivalent to the concentration of ammonia in the gas in %w. In this thesis is assumed that the absorption of ammonia and carbon dioxide by water from the Vb is as efficient as the absorption of ammonia and carbon dioxide with undiluted water. This assumption is not validated in this research. Literature describes that the amounts of ammonia and carbon dioxide gases absorbed by ammonium bicarbonate solutions were above 50% of that by water[5]. This means that in the worst case scenario the scrubbing water content must be doubled.

E.1.2 Sublimation of ammonium bicarbonate in condensing system

In the condenser, gas is cooled from either 100 or 80 degree Celsius to 20 degree Celsius. In this process water, carbon dioxide and ammonia go completely or partially into liquid solution. In Kim et al.[5], an issue rose with transport of a $NH_3 - H_2O - CO_2$ gas mixtures. The temperature difference in the transportation pipes caused a sublimation reaction of ammonia and carbon dioxide due to the below reverse reaction at low temperature, Equation E.1.

$$NH_3(g) + CO_2(g) + H_2O(g) \longrightarrow NH_4HCO_3(s) \tag{E.1}$$

The experiment by Kim et al. were conducted with lower temperatures, around 60 degree Celsius. With these lower temperatures less water evaporate. In this research is assumed that due to the higher evaporation temperatures the amount of water causes the potential sublimate to go into liquid solution.