

# Operating procedures and evaluation of a carbon capture pilot plant

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## Abstract

The rise in global emissions of carbon dioxide and the need for new technologies to combat climate change has prompted extensive research into carbon capture methods. This master thesis focuses on a novel carbon capture absorption technology, developed at Lund University, that utilizes the amine 2-amino-2-methyl-1-propanol (AMP) in the organic solvent dimethyl sulfoxide (DMSO) to capture CO<sub>2</sub>. A characteristic of this system is that when AMP in the AMP/DMSO system reacts with CO<sub>2</sub>, a carbamate that precipitates is produced, and a two-phase system is formed. Previous research has shown that during the regeneration of the absorbent the carbamate is dissolved, CO<sub>2</sub> is separated and the regenerated AMP/DMSO solution is precipitate-free. Encouraged by promising results, a pilot plant to assess this technology on a larger scale has been built.

The primary objectives of this master thesis were to try and achieve operational functionality of the pilot plant, develop sampling methods to measure emissions of AMP, DMSO and the nitrosamine N-dimethylnitrosamine (NDMA) and to investigate the regeneration conditions (e.g., temperature, time) for the AMP/DMSO system.

During the course of this work, continuous operation of the pilot plant could not be achieved due to low temperatures that caused the AMP/DMSO system to freeze and due to issues with regeneration that left precipitate in the solution, which resulted in clogging. Despite difficulties caused by persistent clogging, noteworthy findings were obtained. Contrary to previous research, it was discovered that precipitate remained present in the AMP/DMSO solution even after undergoing regeneration. Additionally, the results in this master thesis showed that the structure of the precipitate might be influenced by the presence of water in the solution. Regeneration experiments conducted at the regeneration conditions employed at the pilot plant, 80°C and – 10 mbarg, indicated that the conditions should be sufficient for regenerating the AMP/DMSO system to the equilibrium curve of the solubility of CO<sub>2</sub> in AMP/DMSO.

Emissions of AMP, DMSO and NDMA demonstrated lower levels than the initial estimation based on the temperature and vapor pressure of the pure components. However, these results are not representative for continuous operation of the pilot plant since only intermittent operation could be achieved due to the clogging issues.

Regarding the future for the pilot plant project, the persistence of precipitate in the solution after the regeneration step and the potential impact of water on the precipitates structure are subjects of interest for further research. Additionally, addressing the clogging challenges at the pilot plant remain crucial for future research.



## Populärvetenskaplig sammanfattning

I takt med att vi blir fler människor på jorden så förbrukar och förbränner vi också mer fossila bränslen, vilket har lett till en drastisk ökning av koldioxid ( $\text{CO}_2$ ) i vår atmosfär. En ökning som leder till att jordens medeltemperatur ökar vilket kan komma att ha ödesdigra konsekvenser för klimatet, jordens ekosystem och i slutändan människors liv. Ny teknik behövs för att kunna bekämpa och motverka klimatförändringarna och den globalt växande uppmärksamheten för klimatkrisens har föranlett omfattande forskning om metoder och tekniker för att minska våra utsläpp.

Detta examensarbete fokuserar på en ny teknik som har potentialen att kunna fånga in och separera koldioxid som släpps ut av energisektorn. För att fånga in koldioxiden så utnyttjas ett fenomen som kallas absorption, vilket är egenskapen hos ett ämne att ta upp andra ämnen, och att vissa aminer har förmågan att reagera med koldioxid. Detta öppnar upp möjligheten till att kunna fånga in, separera och sedermera avskilja  $\text{CO}_2$  från industrins rökgaser (avgaser) för att sedan lagra den i en permanent förvaring.

Tekniken är utvecklad av forskare vid Lunds universitet och består av en absorbent i form av aminen 2-amino-2-metyl-1-propanol (AMP), löst i det organiska lösningsmedlet dimetylsulfoxid (DMSO). En egenskap hos detta system är att när AMP i AMP/DMSO-systemet reagerar med  $\text{CO}_2$  bildas det ett fast ämne, en karbamat, som faller ut och kristalliserar i lösningen och bildar ett tvåfasssystem, bestående av en fast fas, karbamaten, och en vätskefas (lösningen). Lovande resultat i labbskala har lett till att en pilotanläggning byggts för att utvärdera denna teknik i större skala.

De primära målen för detta examensarbete har varit att få pilotanläggningen i drift, utveckla provtagningsmetoder för att mäta utsläpp av AMP, DMSO och nitrosaminen N-dimethylnitrosamine (NDMA) samt att undersöka olika driftförhållanden (t.ex. temperatur, uppehållstid) för AMP/DMSO-systemet.

Arbetet med att få pilotanläggningen i drift har präglats av problem med igensättning av utrustning och orsaken har varit tvåfaldiga. Dels har låga temperaturer bidragit till att lösningen stelnat och rören och utrustningen har satts igen, dels har den fasta fasen i AMP/DMSO-lösningen, fällningen, fastnat och orsakat igensättningar. Men även om det inte har varit möjligt att hålla pilotanläggningen i kontinuerlig drift, har arbetet ändå resulterat i värdefulla resultat.

I motsats till tidigare forskning upptäcktes det att fällningen som bildas när AMP reagerar med  $\text{CO}_2$  inte försvinner efter att AMP/DMSO lösningen har regenererats. Dessutom visade detta arbete att fällningens struktur påverkas och förändras i närvaro av vatten. Resultat från regenereringsexperiment i labbskala indikerade att de förhållanden som används vid pilotanläggningen,  $80^\circ\text{C}$  och  $-10$  mbarg, borde vara tillräckliga för att regenerera AMP/DMSO lösningen till jämviktspunkten.

Halterna av AMP, DMSO och NDMA visade sig vara lägre än de nivåer som ursprungligen förväntades enligt förstudien av pilotanläggningen innan den byggdes. Dessa resultat är dock inte representativa, eftersom kontinuerlig drift av pilotanläggningen inte kunde uppnås.

Med avseende för framtida forskning så är det av intresse att undersöka varför fällningen finns kvar i lösningen efter regenereringssteget samt undersöka vattens potentiella påverkan på

fällningsstrukturen. Dessutom är det av största intresse att ta itu med igensättningsutmaningarna vid pilotanläggningen så att vidare forskning kan fortskrida.



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## Nomenclature

AMP	2-amino-2-methyl-1-propanol
CapEx	Capital expenditure
CCS	Carbon Capture and Storage
CO	Carbon monoxide
DEA	Diethanolamine
DMSO	Dimethyl sulfoxide
H <sub>2</sub>	Hydrogen gas
Ln/min	Liter normal per minute
Load ( $\alpha$ )	$\frac{mol_{CO_2}}{mol_{AMP}}$
LOQ	Limit of quantification
MEA	Ethanolamine
MFC	Mass flow controller
NDMA	N-Nitrosodimethylamine
OpEx	Operating expenditure
ST1	Stripper tank 1
ST2	Stripper tank 2
VEAB	Växjö Energi AB
Wt-%	Weight percentage



# 1. Introduction

In 2017, Sweden adopted a new climate policy framework that stated that Sweden should have net zero emissions of greenhouse gases to the atmosphere by 2045 and negative emissions thereafter. The framework also states that to reach the goal, the capture and storage of carbon dioxide from fossil and organic origins can be implemented where other reasonable alternatives are missing [1]. Sectors that can be regarded to lack reasonable alternatives are socially critical operations such as the production of electricity and district heating, coming from e.g., cogeneration plants. To target these emissions, other solutions such as the capture and storage of carbon dioxide must be implemented.

According to EU:s climate policy, carbon capture and storage (CCS) is an important part in the joint effort to reduce global greenhouse gas emissions [2]. Carbon capture presents itself as one of the most viable solutions to target the emissions of e.g., cogeneration plants besides replacing fossil fuels with biofuels and/or waste incineration as a source of energy. Emissions of greenhouse gases from electricity production and district heating in 2021 represented 8% of Sweden's total emissions (4 million tonnes of carbon dioxide equivalents), which is a sizable amount [3]. If confidence in CCS technologies and large-scale proof of concepts start to emerge, CCS could also in extension be implemented to reduce the emissions from the industrial sector of Sweden. A sector which is responsible for a third of Sweden's total greenhouse gases emissions (16 million tonnes of carbon dioxide equivalents)[4].

Even though several organizations and agencies state that implementation of CCS technologies are needed to be able to reach the climate goals in time, the incentives for implementing CCS technology are low. Both the capital expenditure (CapEx) and operational expenditure (OpEx) are too high and for CCS technology to become a reality on a larger scale the costs, especially the OpEx, must be reduced [5].

The absorption technology that is used in this report has been researched extensively by a research group at Lund University who has shown that with this new CCS technology, much lower temperatures (70 – 90°C) can be used to regenerate the solvent [6, 7]. This is in contrast with traditional technologies that require higher temperatures (>120°C) to regenerate the solvent. The lower operational temperatures of this technology mean that residual heat from other processes could be used to regenerate the solvent, making it a promising candidate for CCS-implementation in the energy and industrial sector. This has the potential to significantly reduce the energy needs and operational expenses, making the technology more viable.

The cost of regenerating the solvent is often the major obstacle in creating a viable CCS technology but with the use of residual heat, the OpEx could significantly be reduced, and the incentives improved. Although, there would still be need for infrastructure to handle and store all the captured CO<sub>2</sub>, and a national or EU directive regarding the transport and storage of CO<sub>2</sub> would instill the confidence in CCS technologies that is needed for it to be implemented on a large scale.

## 2. Background

Carbon capture and storage (CCS) refers to a set of technologies that can separate a relatively pure stream of carbon dioxide from industrial or energy-related sources, compress it and transport it to a long-term storage location [8]. If the carbon source is biomass, such as wood, long-term storage of captured carbon dioxide effectively removes carbon dioxide from the carbon cycle and reduces the amount of carbon dioxide in the atmosphere. If the carbon source is fossil fuel on the other hand, long-term storage will only remove the carbon emissions but not lower the atmospheric concentration of carbon dioxide.

Carbon dioxide is formed during combustion when carbon from hydrocarbon fuels (i.e wood, coal, natural gas and oil) reacts with oxygen from the air. Depending on the type of combustion process there are three types of CO<sub>2</sub>-capture technologies that can be utilized: pre-combustion, oxyfuel combustion and post-combustion.

### 2.1 Types of CO<sub>2</sub>-capture systems

In pre-combustion, carbon dioxide is separated before the combustion during pretreatment of the fuel, typically coal. The process involves a gasification process which produces a synthetic gas consisting mainly of CO and H<sub>2</sub>. The synthetic gas will then go through a water gas shift reaction to form CO<sub>2</sub> and more H<sub>2</sub>, producing a H<sub>2</sub>/CO<sub>2</sub> gas containing 15 – 50 % CO<sub>2</sub> [9]. The CO<sub>2</sub> can be captured and separated from the synthetic gas, creating a H<sub>2</sub> rich fuel. Alternatively, the synthetic gas can be burned producing a CO<sub>2</sub>-rich stream that can then be captured. [10]

In oxyfuel combustion, pure oxygen is used instead of air during the combustion which reduces the amount of nitrogen (originally coming from air) in the flue gas [11]. The major composition of the flue gas is CO<sub>2</sub>, water, particulates and SO<sub>2</sub>. The two former components can be separated with conventional technologies and the remaining gas contains 80 – 98% CO<sub>2</sub>. [10]

In post-combustion the carbon dioxide is separated from the flue gases after combustion, using different separation methods. This is the technology that the pilot plant in this work uses and one of the advantages with post-combustion CO<sub>2</sub>-capture systems is that they can be retrofitted to existing processes, without needing any modifications to the existing process itself. [12]

### 2.2 CO<sub>2</sub> separation technologies

There are several different available technologies for separating CO<sub>2</sub> that can be used to isolate CO<sub>2</sub> from fuel/flue gases to create a stream of highly concentrated CO<sub>2</sub> that can be compressed and transported for storage. Several technologies, such as absorption, adsorption, chemical looping and membrane separation, exist and are described below.

In an absorption process a liquid sorbent is used to separate the CO<sub>2</sub> from the flue gas. The flue gas is passed through an absorption column where it comes in contact with the sorbent and CO<sub>2</sub> is separated from the rest of the flue gas. The CO<sub>2</sub>-rich sorbent then goes through a regenerative process where either the temperature and/or the pressure is changed to facilitate the release of CO<sub>2</sub>. Various sorbents can be employed, with an amine system being a common choice. Sorbents like aqueous solutions of monoethanolamine (MEA) or diethanolamine (DEA) are frequently utilized [13]. Another common alternative is utilizing potassium carbonate as a sorbent. [10]

In an adsorption process a solid sorbent is used to separate CO<sub>2</sub> from the flue gas. The flue gas is passed through an adsorption system where it comes in contact with the sorbent which

captures the CO<sub>2</sub>. The captured CO<sub>2</sub> can then be recovered through swinging the temperature or the pressure of the adsorption system, which also regenerates the sorbent. Several sorbents can be used and some of them are activated carbon, zeolites, calcium oxides or lithium zirconated. [10]

In chemical looping, the combustion system is similar to that of the oxyfuel combustion with the difference being that instead of pure oxygen, a metal oxide is used during the combustion of the fuel. The metal oxide will reduce to metal while oxidizing the fuel to CO<sub>2</sub> and water, which can easily be separated with condensation; leaving a pure CO<sub>2</sub> gas stream. [10]

In a membrane separation system, a thin layer of CO<sub>2</sub>-selective material is bonded with a thicker, non-selective and cheaper material that acts as mechanical support [14]. The flue gas is passed through the CO<sub>2</sub>-selective membrane and the CO<sub>2</sub> is separated. [10]

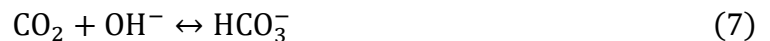
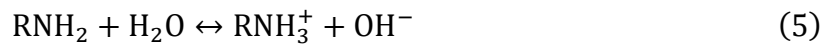
All these separation technologies are promising but this work uses an amine-based absorption technology to separate CO<sub>2</sub> from flue gases.

### 2.3 Amine absorption systems

Amines are beneficial as sorbents because they can reversibly and selectively bind to CO<sub>2</sub>, which makes them ideal for the separation of CO<sub>2</sub> from many CO<sub>2</sub>-containing gases, including flue gases. When a primary amine, RNH<sub>2</sub>, reacts with CO<sub>2</sub> they form the zwitterion RNH<sub>2</sub><sup>+</sup>COO<sup>-</sup>. In contact with another primary amine, the zwitterion reacts and forms a carbamate, RNHCOO<sup>-</sup>. In the presence of water, such as in an aqueous solution, the zwitterion can also react with water to form bicarbonate, HCO<sub>3</sub><sup>-</sup>. Which can also be formed if the carbamate reacts with water. The reactions are shown in Reaction 1-4. [6]



When water is present in the solution the primary amine will react and form bicarbonate, HCO<sub>3</sub><sup>-</sup>, as shown by Reaction 5-8. [6]

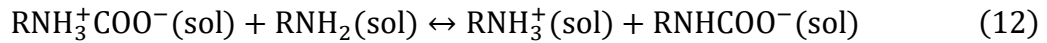
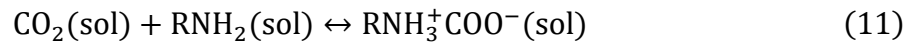


The formation of carbamate, as opposed to bicarbonate depends on the stability of the carbamate that is formed. A sterically hindered amine will form a sterically hindered carbamate that is less stable which means that the formation of bicarbonate will be favored in aqueous solutions. The reaction of a sterically hindered amine in an aqueous solution can be summarized as Reaction 9. [6]



Conventional amine absorption systems typically use aqueous amine solutions. The drawback with implementing an aqueous amine absorption system, such as monoethanolamine (MEA), is that the energy required to regenerate the amine is large; sometimes as large as a third of the total energy output of an energy plant [15]. This is, in part, due to the need to also increase the temperature of the solvent that the amine is solved in during the regeneration. For an aqueous system where water is used, large amounts of energy are needed due to both the high specific heat capacity and the high heat of vaporization of water. To reduce the energy demand of absorption systems organic solvents have been explored.

Interestingly, research has found that when the amine 2-amino-2-methyl-1-propanol (AMP) reacts with CO<sub>2</sub> in a non-aqueous solution, a reaction that forms a solid carbamate salt, RNH<sub>3</sub><sup>+</sup>RNHCOO<sup>-</sup>, takes place. The carbamate salt will precipitate and create a two-phase system. This phenomenon has been researched at Lund University extensively. The reactions are shown in Reaction 10-13 below. [6]



Since there is no water, the carbamate salt, RNH<sub>3</sub><sup>+</sup>RNHCOO<sup>-</sup>, is the only product that can form. The two-phase system consists of a CO<sub>2</sub>-rich phase made up of the reaction products and a CO<sub>2</sub>-lean phase made up of the solvent and physically absorbed CO<sub>2</sub>.

## 2.4 AMP/DMSO

The pilot plant described in this work, which is explained in the section below, uses a phase-changing non-aqueous amine absorption system that utilizes the sterically hindered amine 2-amino-2-methyl-1-propanol (AMP) in the organic solvent dimethyl sulfoxide, DMSO. This system is researched as an alternative to an aqueous MEA solution. Based on research at Lund University it has been suggested that 25 wt-% AMP in DMSO should be used. [6]

Load,  $\alpha$ , is a way to measure the performance of an absorption system. It is defined as the amount of carbon dioxide that is solved per molar amount of AMP, as shown in Equation 14:

$$\frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}} = \alpha \quad (14)$$

An important aspect to consider when evaluating absorption systems is the cyclic capacity, which is defined as the amount of CO<sub>2</sub> that can be separated each cycle of regeneration. The cyclic capacity can be estimated based on solubility data as the difference between the rich loading and the lean loading. Based on Reactions 10-13, the theoretical maximum loading for non-aqueous AMP is 0.5 and for 0.5 for aqueous MEA. Showing that similar cyclic capacities can be achieved [6].

The absorption of CO<sub>2</sub> in an amine absorption system is an exothermic process, meaning that heat is released. The amount of heat that is released from the absorption is determined by the heat of dissolution ( $\Delta H_{\text{sol}}$ ) and the heat of reaction ( $\Delta H_{\text{reaction}}$ ) shown in Equation 15 below. [6]



$$\Delta H_{\text{abs}} = \Delta H_{\text{sol}} + \Delta H_{\text{reaction}} \quad (15)$$

In the regeneration step when the reaction needs to be reversed, the desorption and regeneration of the absorbent, requires heat. The amount of heat needed is determined by the heat needed to increase the temperature,  $\Delta H_{\text{sens}}$ , the energy to evaporate water/solvent,  $\Delta H_{\text{vap}}$ , and the heat of phase change  $\Delta H_{\text{phase}}$  shown in Equation below. [6]

$$\Delta H_{\text{reg}} = \Delta H_{\text{abs}} + \Delta H_{\text{sens}} + \Delta H_{\text{vap}} + \Delta H_{\text{phase}} \quad (15)$$

One of the main advantages with this absorption system is that the sterically hindered carbamate that is formed with AMP is less stable and prevents the formation of more stable products. This means that lower regeneration temperatures are needed to reverse the absorption, around 70-90°C. The carbamate that is formed with MEA is, on the other hand, stable and requires temperatures of >120°C to reverse the absorption. As water evaporates at 100°C, a lot of the energy needed to regenerate MEA is used to vaporize the water. DMSO however, has boiling point of 189°C and its vaporization will only be a small part of the energy consumption when regenerating the AMP/DMSO system. Which also means that less DMSO will be lost due to evaporation. [6]

Another advantage is that the solid carbamate salt that is formed during the reactions can be separated from the rest of the liquid. In doing so, the amount of liquid that is heated up during the regeneration step, and consequently the energy needed to regenerate it, could be reduced.

Based on the research on this technology and encouraged by the promising results, a pilot plant to assess this technology on a larger scale has been built.

## 2.5 Pilot plant

Based on the promising results from research conducted at Lund University, Energimyndigheten granted funding for a project in collaboration with Växjö Energi AB (VEAB), Sydsånes Avfallsaktiebolag (SYSAV), Öresundskraft and Granitor, to assess this technology at a pilot scale. To facilitate this evaluation, Granitor designed and built a pilot plant which was installed at VEAB in Växjö for the duration of this master thesis.

The pilot is a post combustion implementation that utilizes a 25 wt-% AMP/DMSO amine absorption system for CO<sub>2</sub> separation and is in principle divided into two different unit operations: absorption and regeneration. A simplified schematic overview of the process can be seen in Figure 1 below.

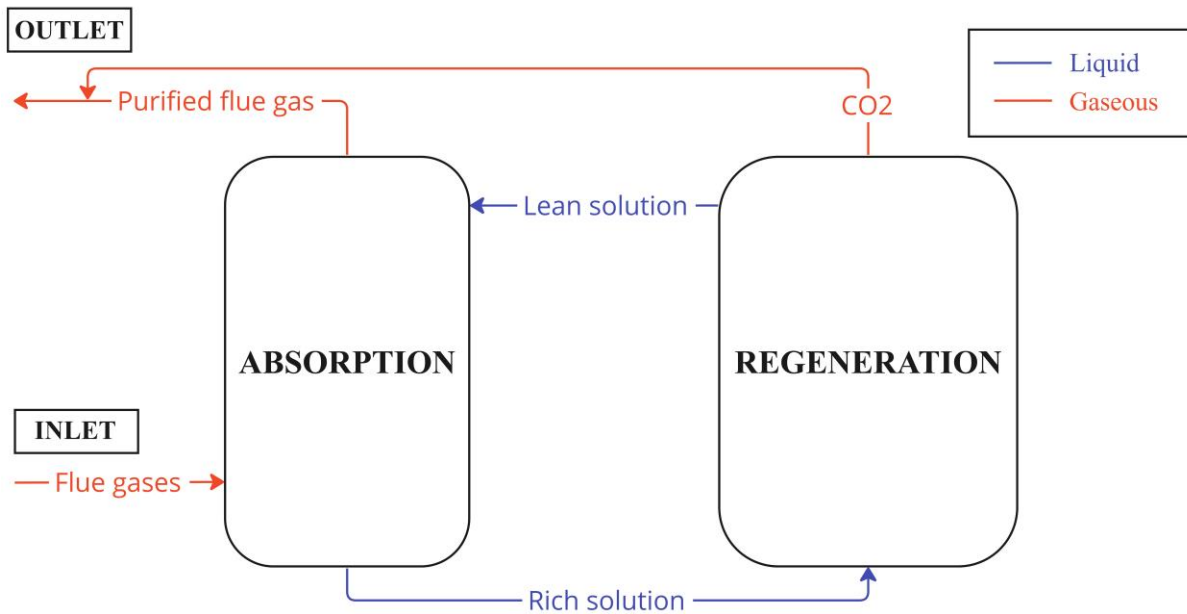


Figure 1 - A schematic view of the design of the pilot plant with the two main sections: absorption and regeneration. The orange streams are gaseous streams, and the blue streams are liquid streams.

The absorption process takes place in an absorption column that is 9 m tall with a diameter of 0.5 m. The column contains a 5-meter-high randomly packed bed made of polypropen (PP) that facilitates absorption by increasing the contact area and flow-through time through the absorption tower. The CO<sub>2</sub>-containing flue gas enters at the bottom of the tower and moves upwards, while the solvent enters at the top and moves downwards. The CO<sub>2</sub> is absorbed into the solution, reacts with the amine which transfers CO<sub>2</sub> from the gas-phase into the liquid-phase. The CO<sub>2</sub>-lean flue gas exits at the top of the column, while the CO<sub>2</sub>-rich solution exits at the bottom.

The CO<sub>2</sub>-rich solution is then transported to the regeneration tank, where the temperature is increased and the CO<sub>2</sub> is released. The solvent is then circulated back into the absorption tower. To reduce the energy needs of the system, a separation unit could be installed between the absorption and regeneration step. This unit would separate the CO<sub>2</sub>-rich slurry from the CO<sub>2</sub>-lean solvent and reduce the volume that requires regeneration.

Lower temperatures promote absorption and in the pilot plant, temperatures of approximately 25-40°C were utilized. Prior to entering the absorption tower, an external cooling system was employed to cool down both the flue gases and the lean solution. During continuous operation, the exothermic reaction between AMP and CO<sub>2</sub> will generate heat which causes the solution in the absorption tower to heat up. This increase in temperature could have a negative effect on the cyclic capacity since the solubility of CO<sub>2</sub> decreases with an increase in temperature. To counteract this, intercooling of the absorption tower could be installed.

The regeneration step consists of two stirred tanks that are heated with an electric boiler system through internal heating coils. To maintain a continuous operation, the flow of rich solution will be diverted so that one tank is regenerating while the other is being filled. When the regeneration step is active the temperature in the tank will be 80°C and the CO<sub>2</sub> that desorbs will be transported away from the tank with a fan. The fan generates a pressure of – 10 mbarg

inside of the tank that facilitates desorption. Following regeneration, the now lean solution is recirculated back to the absorption tower to repeat the process.

To comply with Swedish emission regulations, the separated CO<sub>2</sub> stream is combined with the purified flue gas stream and rejoins the flue gas stack at its location. In addition to CO<sub>2</sub> there will also be small concentrations of AMP, DMSO and nitrosamines in the exhaust gas from the pilot plant. These concentrations must be monitored and will be monitored through sampling.

## 2.6 Sampling

Amine-based post-combustion capture technology, such as the one described here, is a mature technology and is considered the most reasonable near-term technology that can help reduce the CO<sub>2</sub> from the energy sector. As such, amines are also considered to be an emerging class of atmospheric pollutants as it is expected that CO<sub>2</sub> capture plants will result in increased emission of amines and secondary product formations into the atmosphere. Its atmospheric chemistry is poorly understood but what is expected is however that they will form nitrosamines when in contact with NO<sub>x</sub> and/or volatile organic compounds. Nitrosamines are carcinogenic to animals and are anticipated to be carcinogenic to humans as well. [16, 17]

Due to both interests out of a research perspective and because of potential future regulations from Swedish agencies, the emission of AMP, DMSO and nitrosamines (N-Nitrosodimethylamine, (NDMA)) must be monitored. There are several ways that the compounds could be emitted from the pilot plant. One is that the liquid phase of AMP/DMSO will naturally be in equilibrium with its gaseous phase and will escape via both the purified flue gas stream and the separated CO<sub>2</sub> stream. Another is that during circulation of AMP/DMSO, aerosols will form and eventually make their way out of the pilot plant via either the purified flue gas stream or the separated CO<sub>2</sub> stream. And the third is that nitrosamines will form when NO<sub>x</sub> from the flue gas reacts with AMP and escape via the gas streams. The technology described in this work is a post-combustion technology and VEAB, where the pilot plant is situated during the writing of this work, purifies its flue gas from NO<sub>x</sub>. It is however expected that low concentrations of NO<sub>x</sub> is present in the flue gas and that nitrosamines will form when NO<sub>x</sub> encounters AMP in the pilot plant.

### **3. Aim**

The objective of this master thesis has been to support the startup of the pilot plant installed at VEAB in Växjö, which utilizes the AMP/DMSO carbon capture technology developed at Lund University. This report aims to:

- Provide instructions on how to operate the pilot plant.
- Develop sampling methods to monitor emissions of AMP, DMSO and NDMA.
- Provide further insight regarding what the best regeneration conditions are.

## 4. Method

This work was divided into three parts: operating procedures at the pilot plant, sampling of flue gases and regeneration.

### 4.1 Materials

The chemicals used in the lab in this study were 2-amino-2-methyl-1-propanol, AMP, (99%, Thermo Fisher Scientific), dimethyl sulfoxide, DMSO, (99.9%, Acros Organics), carbon dioxide (99.99%, AGA) and nitrogen gas.

The chemicals used at the pilot plant had a different supplier to those used in the lab and they were 2-amino-2-methyl-1-propanol, AMP, (>88%, Lehmanns&Voss&Co) and dimethyl sulfoxide, DMSO, (99,9%, Toray Fine Chemicals Co.).

### 4.2 Preparation of stock mixture

To perform experiments on regeneration of the absorbent, a stock mixture from which to take samples from was prepared. The composition of the stock mixture used in the experiments was 25 wt-% AMP and 75 wt-% DMSO, which was the same composition that was used in the pilot plant. The amount of stock mixture that was prepared was based of on how much was needed for each experiment. First, the amount of AMP needed was decided. A 500 ml blue cap bottle was then weighed with and without the cap, the AMP was then poured into the bottle. Based on the amount of AMP that was poured, the required amount of DMSO was calculated, to achieve a 1:3 weight ratio, and poured into the bottle. The cap was screwed on and the bottle was shaken to ensure proper mixing. Worth noting is that AMP is not liquid at room temperature and needs to be stored in an oven at 50°C for a few hours before a stock solution is prepared.

For the experiments that needed CO<sub>2</sub>-loaded AMP/DMSO samples, each sample was loaded with CO<sub>2</sub> separately. The amount of AMP/DMSO required for the experiment was transferred from the stock mixture to a smaller container. The weight of CO<sub>2</sub> needed for each experiment was calculated using Equation 13 in Section 2.4. The sample was then placed on a scale with the tube from the CO<sub>2</sub> container inserted into the mixture. The container was loosely sealed with parafilm and CO<sub>2</sub> was then bubbled carefully into the mixture until the desired weight of CO<sub>2</sub> had been added.

Table 1 - Stock mixtures included in the experiments. The table shows the sampe size and the composition of 2-amino-2-methyl-1-propanol (AMP) and dimethyl sulfoxide (DMSO) prior to CO<sub>2</sub>-loading.

Sample size (g)	AMP (wt-%)	DMSO (wt-%)	$\alpha$ (mol CO <sub>2</sub> /mol AMP)
50	25	75	0, 0.38, 0.50-0.55

### 4.3 Writing instructions on how to operate the pilot plant

The instructions on how to operate the pilot plant are based on three aspects; 1), technical knowledge of the pilot plants design that was learnt from reading the ‘Operation and maintenance manual’ and ‘Piping and instrumentation diagram’ written by the process engineers who designed the pilot plant [18, 19]; 2) spending time with operators who were familiar with the pilot plant or processes like it and observing and learning from them; 3) knowledge gained by spending time at the pilot plant and getting hands-on experience.

The writing process started by getting familiar with the pilot plant and its design by reading the technical documentation and visiting the pilot plant. Once a basic understanding of how the different unit operations were connected and how the pilot plant was controlled, every procedure, problem and solution was documented. As more procedures were documented, a sense of which procedures were missing to be able to operate the pilot plant formed. Each of the missing procedures were performed and documented until a manual on how to operate the pilot plant was completed.

#### 4.4 Gaseous sampling of AMP, DMSO and nitrosamines (NDMA) at the pilot plant

To sample the flue gas at the pilot plant, an impinger and an adsorption setup was used. The impinger setup consisted of a 25 ml midget impinger with sulfuric acid that was used to sample AMP. The adsorption setup consisted of an adsorption cartridge (Ellutia Termosorb-N) that was used to sample nitrosamines (NDMA) and DMSO. The sampling devices were connected to a pump arrangement built with a pump (Casella Apex2 IS), flow meter (TSI 4100 series), dust filter and tubing. The schematic view of the setup is shown in Figure 2. Instructions for sampling are found in Appendix A.

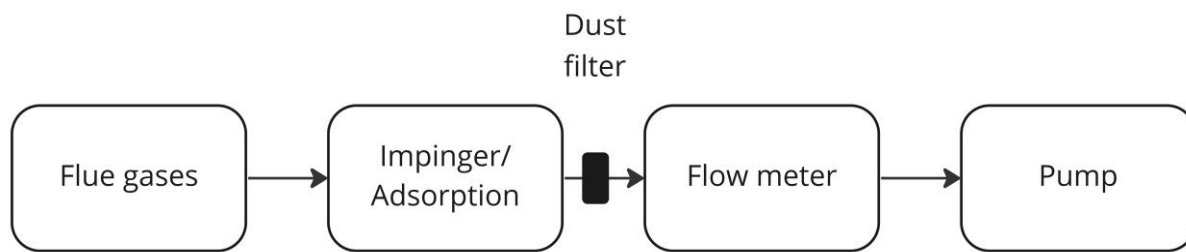


Figure 2 - A schematic view of the sampling setup used to sample gas streams at the pilot plant.

The flue gas was sampled before it entered and exited the pilot plant at the sample sites shown in Figure 3. The flue gas sampled at the inlet had not been in contact with the amine absorption system and consisted only of the flue gas emitted from the cogeneration plant at VEAB. At the outlet, the flue gas had circulated through the absorption system and the flue gas had been in contact with the AMP/DMSO solution.

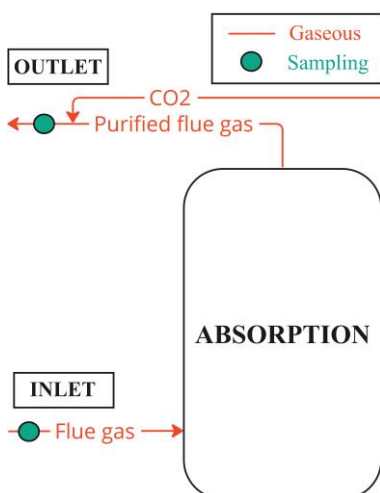


Figure 3 – Schematic overview of the gaseous sampling sites and their location in relation to the absorption process.

Before the sampling started, the setup was built and attached to one of the sampling sites. In Figure 4 the experimental setup for sampling of NDMA and DMSO at the inlet sampling site is shown. After a sampling run with an impinger setup, the contents along with the filter of the impinger was transferred to a different container and stored in a fridge until analysis. After an adsorption sampling run, the adsorption cartridge was put in its original package and stored in a freezer until analysis. The samples were sent to credited labs (EHS Analytics (AMP), AMM-lab (NDMA)) for analysis.



Figure 4 - A picture of the sampling setup at the pilot plant. A Thermosorb-N cartridge is connected to the setup to sample the concentration of nitrosamines at the inlet of flue gases to the absorption tower.

#### **4.5 Liquid sampling of AMP/DMSO at the pilot plant**

Liquid samples from the pilot plant were taken from sampling sites installed in the pilot plant, shown in Figure 5. At the 'Lean solution' site, liquid that had been regenerated was sampled. At the 'Rich solution' site, liquid that had been in contact with CO<sub>2</sub> was sampled and at the 'Purified flue gas' site, condensate from the absorption tower was sampled. These samples were later analyzed at Lund University.

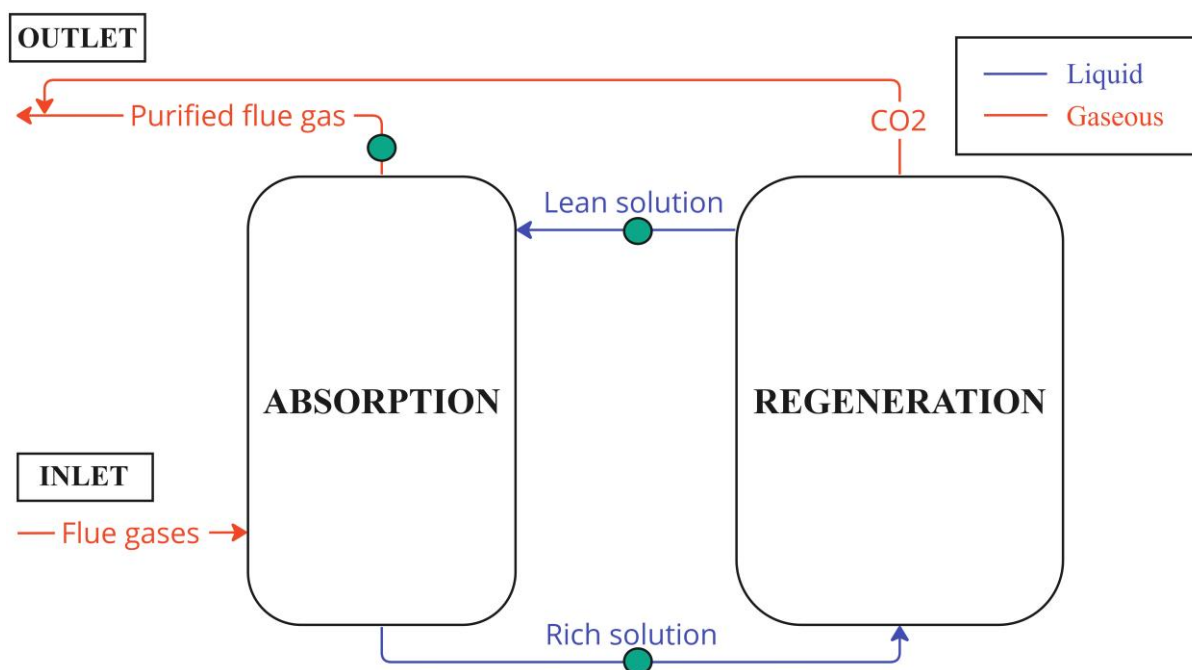


Figure 5 - Liquid sampling sites at the pilot plant and their location in relation to the absorption system.

## 4.6 Regeneration

Regeneration at the pilot plant was conducted at a pressure of -10 mbarg, produced by a fan that forced gas out of the regeneration tanks. To try and evaluate the regeneration at the pilot plant, experiments using a pressure of -10 mbarg and a stripper gas was tested. The stripper gas was evaluated as an alternative to using -10 mbarg. The reasoning behind utilizing a stripper gas was to increase the driving force of CO<sub>2</sub> desorption, by pushing away the gas phase above the liquid phase and decreasing the partial pressure of CO<sub>2</sub>.

An experiment was also conducted with a 30°C water bath to see how the precipitate in the AMP/DMSO solution would respond to temperature after it had been regenerated, i.e., the lean solution.

### 4.6.1 Regeneration with stripper gas

To evaluate regeneration conditions with or without a stripper gas, a setup consisting of a plate heater (IKA-COMBIMAG RET), magnetic stirrer bar, glass condenser, two-neck round bottom flask, 1 L beaker, thermocouple (ANRITSU TYPE K), mass flow controller (MFC, Bronkhorst EL-FLOW select), power source (HI-TEC MODEL E-), tubing and cables was used.

An experiment started with setting up a water bath, consisting of the 1 L beaker, a hot plate stirrer, a magnetic stirrer, a thermocouple and a metal retort stand as shown in Figure 6. The 1 L beaker was filled with water and heated to 80-90°C. During heating, the samples were prepared and loaded in the two-neck round bottom flask with CO<sub>2</sub> according to Section 4.2. The two-neck round bottom flask was weighed empty, with AMP/DMSO solution and with CO<sub>2</sub>-loaded AMP/DMSO solution. When the water bath had reached the desired temperature the CO<sub>2</sub>-loaded solution in the two-neck round bottom flask was connected to the gas condenser and submerged in the water bath and fastened with the metal retort stand. If stripper gas was used, it was pumped through the two-neck round bottom flask at a flowrate of 1 l/min via the MFC. After the experiment, the two-neck round bottom was weighed and the regenerated AMP/DMSO solution was transferred to a 50 ml blue cap bottle.



The efficiency of the regeneration was evaluated based on the weight difference of the sample before and after regeneration. The weight loss was attributed to the desorption of CO<sub>2</sub> from the sample and provided a quantifiable measure of the regeneration efficiency. In addition to this, a visual inspection of the sample was conducted after regeneration to assess extent of regeneration. The amount of precipitate after the regeneration could indicate how well the sample had been regenerated.

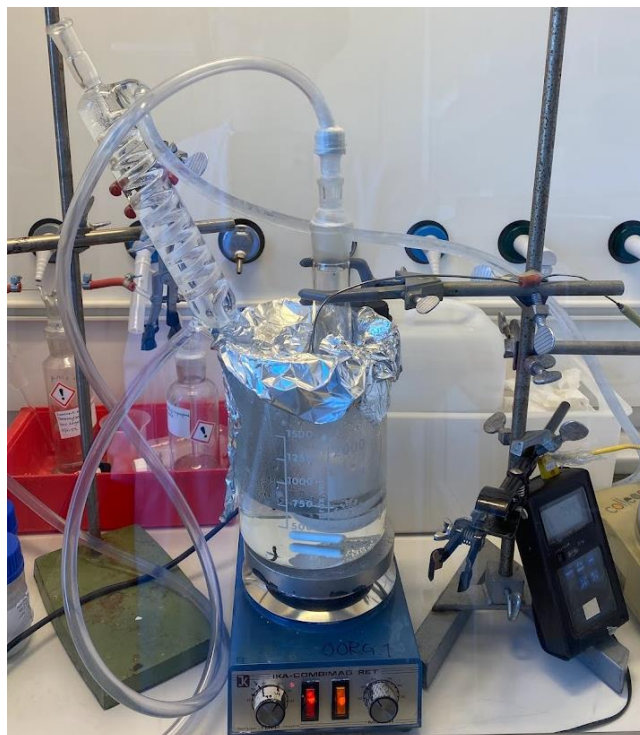


Figure 6 - A picture of the setup used during the regeneration experiments with and without stripper gas.

#### 4.6.2 Regeneration with negative pressure

The regeneration experiments with negative pressure were conducted using a setup consisting of a multi-flask evaporator (BUCHI Multivapor P-6), cooling system (NESLAB RTE-111), vacuum pump (BUCHI Vacuum Pump V-700), tubing and glassware. The setup is shown in Figure 7.

An experiment started with starting the cooling system to let the gas condenser cool down before the multi-flask evaporator was started. At the same time samples were prepared in evaporation flasks and loaded with CO<sub>2</sub> according to section 4.2. The evaporation flasks were weighed empty, with AMP/DMSO solution and with CO<sub>2</sub>-loaded AMP/DMSO solution. The flasks were then placed in the multi-flask evaporator, the temperature was set to 87°C with a rotation speed of 500 rpm and the vacuum pump was started. After the experiment the evaporation flasks were weighed and the regenerated AMP/DMSO solution was transferred to 50 ml blue cap bottles.

The efficiency of the regeneration was evaluated based on the weight difference of the sample before and after regeneration. The weight loss was attributed to the desorption of CO<sub>2</sub> from the sample and provided a quantifiable measure of the regeneration efficiency. In addition to this, a visual inspection of the sample was conducted after regeneration to assess extent of

regeneration. The amount of precipitate after the regeneration could indicate how well the sample had been regenerated.

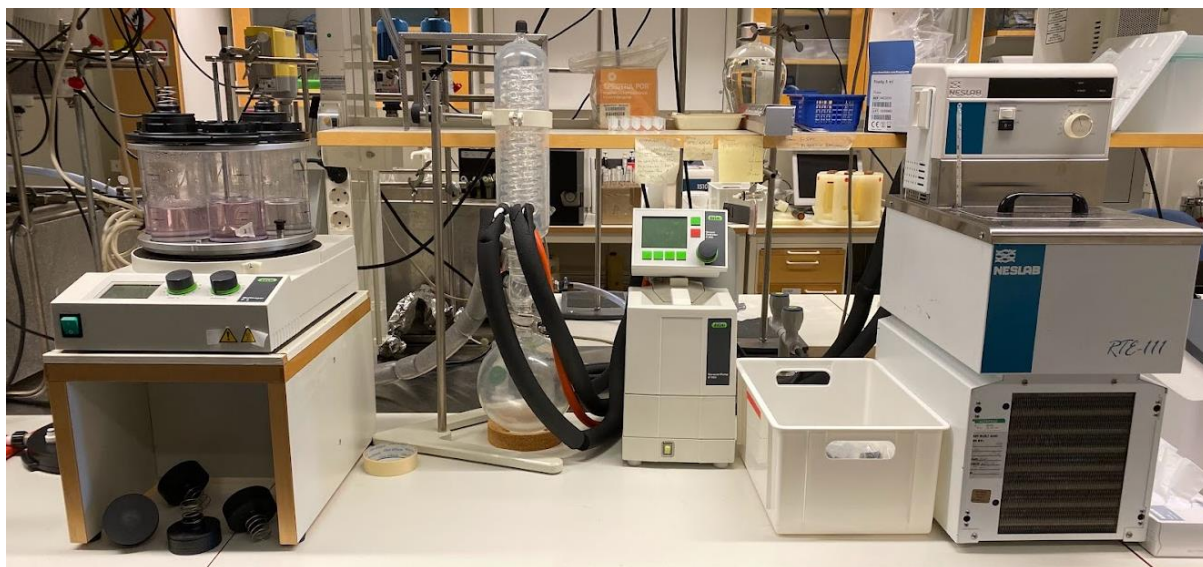


Figure 7 - A picture of the setup used during the -10 mbarg pressure experiments.

#### 4.6.3 Regeneration in a water bath

To assess the behavior of a regenerated AMP/DMSO at 30°C, a set up comprising a water bath and a thermocouple (ANRITSU TYPE K) was utilized. The setup is shown in Figure 8 and the samples were obtained from the experiment done in Section 4.6.

To conduct the experiment, the water bath was started and set to 30°C with agitation. The thermocouple was inserted to monitor the temperature and when the temperature had reached 30°C, the samples were then submerged and weighed down with weights. The samples were kept underwater for 41 minutes before being taken out. After the experiment, the samples were evaluated visually to check for differences in the appearance of the precipitate compared to before they had been submerged in 30°C water.

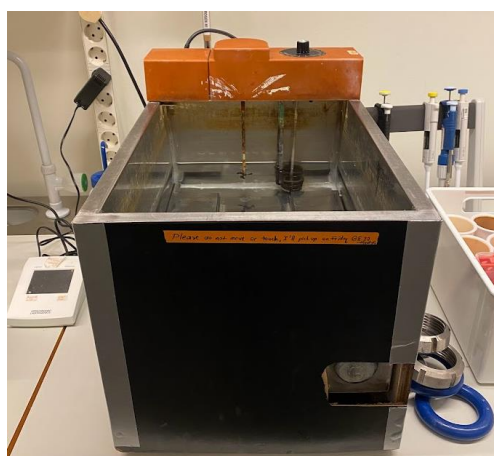


Figure 8 - A picture of the setup used during the water bath experiment. The weights that were used to submerge the blue cap bottles are seen in the bottom right of the picture.

## 5. Results and discussion

The results and discussion section is divided into three parts: the work at the pilot plant, the concentration of the emitted chemicals (AMP, DMSO, NDMA) and the results of the lab-scale regeneration experiments.

### 5.1 Pilot plant

During the five-week period spent at the pilot plant to understand its operation and write instructions on how to run it, several problems and opportunities of improvement were identified. The biggest problem faced at the pilot plant was clogging, which was likely caused by either low temperatures and/or insufficient regeneration of the solution. Some of the problems have been solved while others await solving, both of which will be presented and discussed here. The instructions for how to run, operate the pilot plant and what to do if things go wrong are found in Appendix A.

The regeneration unit of the pilot plant is housed in a half container and when the five-week period started, it was winter with temperatures below 0°C. This posed several problems. Firstly, the pilot plant was not temperature secured and when the temperature fell below 0°C, the water in the electric boiler system froze and the piping was damaged in several places. A temporary solution to this was to install an external heating system that kept the container heated, which solved the problem. An improvement would be to install a permanent air heat pump to be able to keep the temperature constant both in winter and in summer.

Secondly, depending on the water content and the CO<sub>2</sub>-load in the AMP/DMSO solution, the freezing point varies between -19.6°C to 15.8°C [6]. One of the reasons for this is that when the AMP/DMSO solution is loaded with CO<sub>2</sub>, the concentration of AMP in the liquid phase decreases as it forms a carbamate and precipitates. The freezing point of pure DMSO is 19°C and when its concentration increases, the risk of the solution freezing increases. This could be a contributing factor to the clogging issues that have been encountered.

During pilot plant operation, the absorption tower is heated by the flue gases, while the piping inside the container is heated by the solution from the stripper tanks. However, problems arise when the solution is circulated from the stripper tanks to the top of the absorption tower. In cold weather the solution is rapidly cooled down in the small pipe, seen in Figure 9, and at risk of clogging the system which would force the pilot plant to shut down. To address this issue, it is recommended to install some form of heating device around the pipe, possibly a heating cable, to eliminate the risk of clogging.

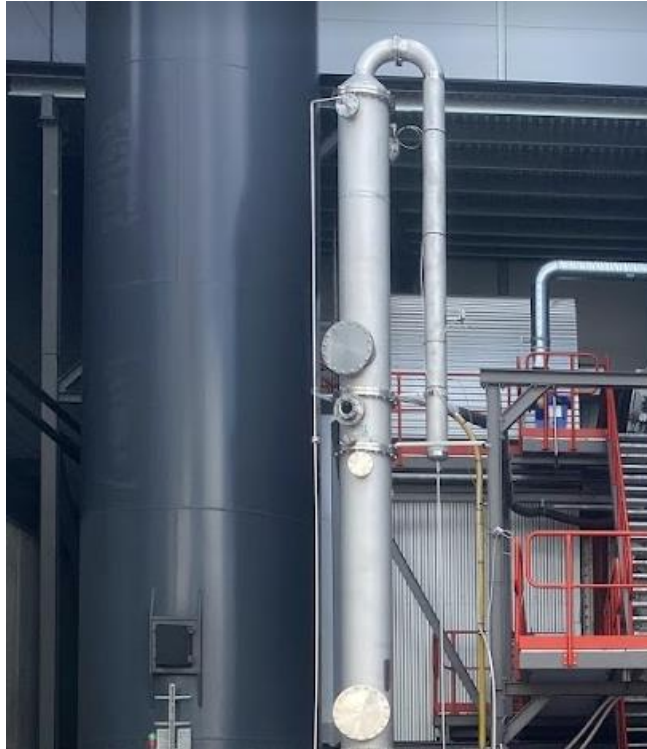


Figure 9 - A picture of the absorption tower present at the pilot plant. The small pipe to the left of the adsorption tower is the pipe that transports the solvent from the regeneration tanks to the top of the absorption tower. To the right of the absorption tower the valve to release excess condensation water can be seen.

The other probable cause for clogging is insufficient regeneration of the AMP/DMSO solution, which would result in more precipitation being circulated through the pilot plant, increasing the risk of clogging. Another problem with insufficient regeneration is that it raises the freezing point of the AMP/DMSO solution and increases the amount of DMSO that can freeze, which further amplifies the difficulties with avoiding clogging [6]. It is therefore imperative to avoid both low temperature and insufficient regeneration at the pilot plant.

When trying to evaluate regeneration at the pilot plant and see if it was sufficient, some obstacles were encountered. Currently, it's only possible to do a mass balance of the captured CO<sub>2</sub> based on the liquid streams. It is however essential to be able to perform a mass balance for the gas streams as well to compare and confirm the results. As the pilot plant is primarily a research facility designed to gather data on this carbon capture technology, having more data points would be advantageous. The missing information is the concentration of CO<sub>2</sub> and the gas flow for some of the CO<sub>2</sub> gas streams. Before an accurate evaluation can be made, two CO<sub>2</sub> meters and one flow meter needs to be installed according to Figure 10.

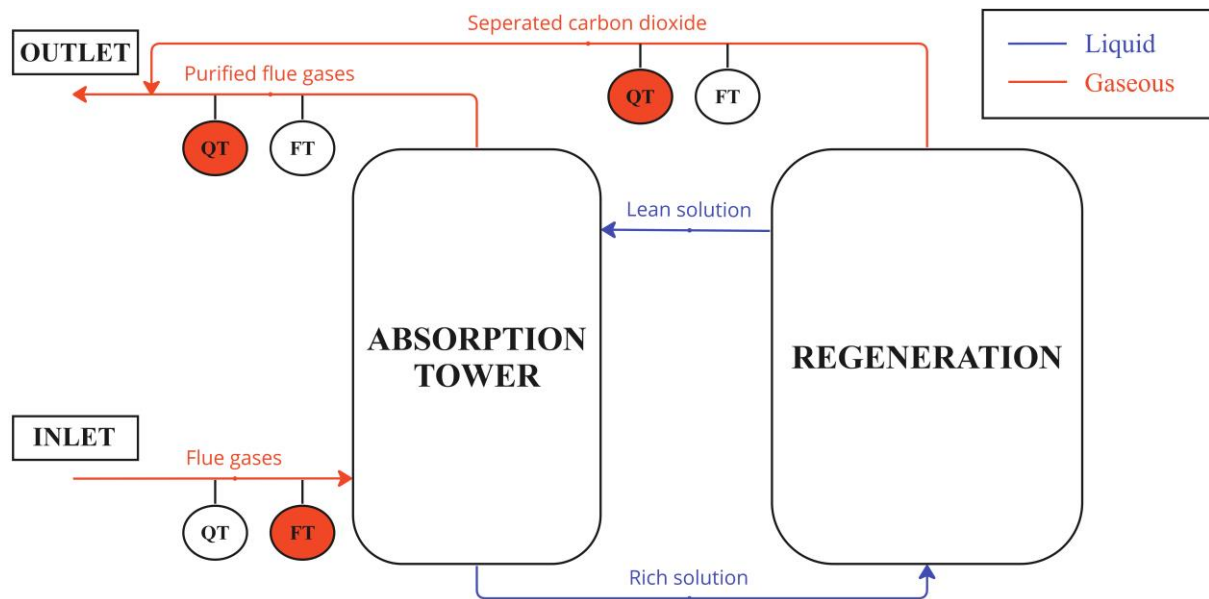


Figure 10 - A schematic view of the pilot plant and the existent and missing measuring points that are needed to do a CO<sub>2</sub> mass balance. "QT" stands for CO<sub>2</sub> meter and "FT" stands for flow meter.

Another issue related to the CO<sub>2</sub> mass balance is that it is unclear whether the pipes of the gas stream leaving the stripper tanks are sealed airtight. If the pipes are not airtight, air will be sucked in, and the flow meter readings would be misleading. Confirmation on this is needed before an accurate mass balance can be made.

If it is established that the solution is not regenerated enough, two conditions can be altered to increase the regeneration: increasing the temperature and/or decreasing the pressure. However, increasing the temperature is not recommended due to fire safety issues that can occur above 87°C. To decrease the pressure, the pipes in connection to the stripper tanks need to be airtight and a more powerful fan might need to be installed to decrease the vapor pressure of and increase the driving force of CO<sub>2</sub> desorption.

Another potential issue is the accumulation of water in the system. Water enters the pilot plant via the flue gases which despite going through a gas condenser and heat exchanger still contain water that accumulates in the system. Other than opening the condensation valve, seen in Figure 9, there is no good way of getting rid of water that has accumulated in the system. While it is not clear how water affects the pilot plant and its efficiency, more research needs to be conducted to investigate whether something needs to be implemented to handle the accumulation of water or not.

Regarding a separation unit, focus has instead been on getting the process working before adding the separation step, which if it works, could improve the effectivity of the pilot plant. When the problems described above are solved and the pilot plant can be running continuously without problems, a separation step can be considered.

During operations at the pilot plant, two pieces of equipment were damaged and need replacing. A flow meter was broken and the HKH20AA01 valve, seen in Appendix A, could not be controlled via the command center and had to be manually opened/closed.



## 5.2 Concentration of emitted AMP, DMSO and NDMA

Sampling of AMP, DMSO and nitrosamines (NDMA) were conducted under different conditions at the pilot plant, as shown in Table 2. The samples are differentiated and the impinger samples are annotated “A” while the adsorption samples are annotated “N”. ‘Attempted pilot run’ refers to when it was attempted to circulate AMP/DMSO through the pilot plant but when it was interrupted due to clogging. ‘Attempted water run’ refers to when it was attempted to circulate water through the pilot plant without success, also due to clogging. The impinger samples were obtained from the flue gas using a gas flow of 1 l/min, while the adsorption samples were obtained using a gas flow of 2.5 l/min.

Table 2 – Gaseous samples of AMP, DMSO and nitrosamines (NDMA) that were taken at the pilot plant and the conditions under which they were taken.

Sample	Sample site	CO <sub>2</sub> fan flow (l/min)	Conditions during sampling
A1	Outlet	174	<ul style="list-style-type: none"> <li>• Regeneration at 80°C.</li> <li>• Attempted pilot run.</li> </ul>
N1	Inlet	-	<ul style="list-style-type: none"> <li>• Blank.</li> </ul>
A2	Outlet	206	<ul style="list-style-type: none"> <li>• Regeneration at 60°C.</li> </ul>
N2	Outlet	176	<ul style="list-style-type: none"> <li>• Regeneration at 80°C.</li> <li>• Attempted pilot run.</li> <li>• Attempted water run.</li> </ul>
A3, N3	Outlet	287	<ul style="list-style-type: none"> <li>• Regeneration at 80°C.</li> <li>• Impinging started 2 hours and 56 minutes after regeneration started.</li> </ul>

The impinger samples were sent to EHS ANALYTICS for analysis of the AMP concentration, the results are shown in Table 3. The analyses were conducted using liquid chromatography-mass spectrometry-mass spectrometry (LC-MS-MS-ES+) with a limit of quantification (LOQ) of 0.5 µg/ml reagent solution [20].

Table 3 – The laboratory result from the certified lab EHS ANALYTICS regarding the AMP content in the gas samples sampled at the pilot plant. The samples were collected at the outlet of the pilot plant using the impinger setup found in section 4.4. [20]

Sample	Sampling site	AMP total (µg)	Time (min)	Volume flue gas (l)	Flow (ng/l*min)
A1	Outlet	290	77.75	77.75	47.973
A2	Outlet	86	30.43	30.43	92.874
A3	Outlet	8.6	58.47	58.47	2.516

The absorption samples were sent to AMM-lab for analysis of the NDMA concentration and the results are shown in Table 4. The analyses were conducted using Liquid chromatography-mass spectrometry (LC-MS) [21].

Table 4 – The laboratory result from the certified lab AMM-lab regarding the AMP content in the gas samples sampled at the pilot plant. The samples were collected at the outlet of the pilot plant using the adsorption set up found in Section 4.4. [21]

Sample	Sampling site	NDM A (ng)	Time (min)	Volume flue gas (l)	Flow (pg/l*min)
<b>N1 Blank</b>	- Inlet	<20	120.37	300.92	<0.552
<b>N2</b>	Outlet	31	62.67	156.67	3.157
<b>N3</b>	Outlet	<20	126.23	315.58	<0.502

The absorption samples came back from AMM-lab solved in acetonitrile and were analyzed for the concentration of DMSO at Lund University, the results are shown in Table 5. The analyses were conducted using gas chromatography (GC). [21]

Table 5 - The laboratory result from the certified lab Amm-lab regarding the AMP content in the gas samples sampled at the pilot plant. The samples were collected at the outlet of the pilot plant using the adsorption set up found in Section 4.4.[22]

Sample	Sampling site	DMSO (mg)	Time (min)	Volume flue gas (l)	Flow (µg/l*min)
<b>N1 Blank</b>	- Inlet	-	120.37	300.92	-
<b>N2</b>	Outlet	6.5	62.67	156.67	0.662
<b>N3</b>	Outlet	1.6	126.23	315.58	0.0401

### 5.2.1 AMP

Regarding the concentrations of AMP emitted from the pilot plant, sample **A1** shows a significantly larger amount of AMP than the other samples **A2** and **A3**. However, sample **A2** shows a higher concentration of AMP because of the shorter sampling time. The reason for this most likely due to different operational conditions during sampling. During sampling of **A1**, an attempt was made to circulate AMP/DMSO through the pilot plant to absorb CO<sub>2</sub>. Although the circulation attempt failed, AMP/DMSO was still pumped into the system, and it is possible that AMP/DMSO reached the absorption tower before the system clogged and the circulation attempt was cancelled. If AMP/DMSO reached the absorption tower it would mean that AMP/DMSO would have a larger area of contact with the flue gas and therefore also greater possibility of being emitted. During the sampling of **A2** and **A3** no “attempted pilot run” was made and water was circulated through the pilot plant the operational day before the sampling, reducing the amount of AMP/DMSO present in the pilot plant. The majority of emitted AMP/DMSO would from sample **A2** and **A3** would have originated from the stripper tanks where the CO<sub>2</sub>-fan drives off regenerated CO<sub>2</sub>.

Besides sampling time and sampling conditions, the biggest difference is the CO<sub>2</sub>-fan flow rates. From sample **A1** to **A3** the CO<sub>2</sub>-fan flow increased, and it would be reasonable to assume that if more volume leaves the stripper tank, more AMP should also be detected in the impinger sample. But the results show the opposite. The reason is unknown but between the first sample **A1** and the last sample **A3**, 22 days had passed. When the first sample **A1** was taken, the chemicals had only been in the pilot plant for 5 days. When the pilot plant is running and flue gases are going through the system, water accumulates. This is partly attributed to the

hygroscopic nature of DMSO as well as water from the flue gases condensing. During these 22 days, it would be safe to assume that more and more water had accumulated in the system and that the AMP/DMSO solution has been diluted. Whether this is the reason for the decrease in detected AMP in the impinger samples or not is unknown, but it might play a role. It is also worth noting that it is not confirmed whether the pipes in conjunction to the stripper tanks are sealed airtight or not. If they are not, the CO<sub>2</sub>-fan flow rates could be affected by air being sucked into the system, misrepresenting the CO<sub>2</sub> flow rate.

Amine degradation could also play a part in the reduction of AMP emitted throughout the time spent at the pilot plant. As mentioned before, amines degrade in the presence of NO<sub>x</sub> but they can also degrade in the presence of O<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub> [23]. All of which are present in the flue gas to varying degrees of concentration. More research is needed to investigate the degree of amine degradation at the pilot plant.

### 5.2.2 NDMA

Regarding the concentration of NDMA, sample **N1** shows <20 ng, below the detection level, which is not unexpected since it was sampled at the inlet of the flue gas to the pilot plant and had not yet been in contact with any amines in the pilot plant. Moreover, the flue gas had already passed through a gas purification process at VEAB. The reason for the sample was to sample a blank to see the baseline NDMA concentration in the flue gas.

Sample **N2** and sample **N3** were however taken at the outlet but show different results. For NDMA to form, NO<sub>x</sub> must come in contact with amines and thus depends on whether AMP is in the system. For sample **N2** which shows the highest concentration of NDMA, AMP/DMSO was circulated the operational day before, as well as during the day of the sampling. It is therefore reasonable to assume that there was a higher concentration of AMP in the system that NO<sub>x</sub> from the flue gas could react with that day. For sample **N3** which shows a low concentration of NDMA, the results from sample **A3** indicate that there were not a lot of AMP in the system at the time of sampling and thus not a lot of AMP that NO<sub>x</sub> could react with. This could be because water was circulated through the pilot plant the operational day before, as it would have reduced the amount of AMP/DMSO in the absorption tower.

### 5.2.3 DMSO

Regarding the concentration of DMSO, the reason that **N2** shows a larger amount and concentration of DMSO follows the same reasoning as to why **N2** shows a larger concentration of NDMA; they are the same sample. AMP/DMSO was circulated the operational day before and at the day of sampling, meaning that more DMSO would reasonably be present in the absorption tower. Sample **N3** was taken on the same day as sample **A1**, which showed the lowest concentration of AMP, which would also indicate that the amount of DMSO that could be emitted was also low. The reason for this could be that water was circulated through the pilot plant on the operational day before.

Sample **A3** and **N3** were taken on the same day and an estimate can be made for the ratio of emission of AMP/DMSO. Comparing the concentrations of AMP in sample **A3** with the concentration of **N3** gives an estimate that 16 times more DMSO is being emitted than AMP. This could however be dependent on the sampling, analytical methods, vapor pressure, degradation of AMP and more reasons. The ratio should thus not be taken as a fact, just an indication. More research would be necessary to get a better estimate.



### 5.3 Liquid samples sampled at the pilot plant

The liquid samples taken at the pilot plant, along with sampling point and how they were analyzed are listed in Table 6 below. The samples were taken at the sampling sites shown in Figure 5, according to the instructions “Chemical solution sampling” found in Appendix A under Section 9.1.11.3. Most of the liquid samples taken in this report were analyzed by David Wedin in his master thesis [22].

Table 6 – Liquid samples taken at the pilot plant, which day, which sampling point (Figure 5) and how they were analyzed. ST1 stands for stripper tank 1.

Sample	Date	Sampling point	Analysis method	Results
Solvent sample ST1	9 Mars	Lean solution	GC	[22]
Solvent sample ST1	28 Mars	Lean solution	GC	[22]
Condensate from absorption tower	28 Mars	Purified flue gas	GC	[22]
Solvent sample ST1	4 April	Lean solution	None	None
Pilot sample ST1- bottom part	11 April	Lean solution	GC, this work	Section 5.6, [22]
Pilot sample ST1 - middle part	12 April	Lean solution	GC	[22]

### 5.4 Regeneration at 80°C

Experiments on regeneration of CO<sub>2</sub>-loaded AMP/DMSO at 80°C were conducted in three different ways with duplicates. Without a stripper gas, with a stripper gas and at a lower pressure of -10 mbarg to evaluate the impact the different methods had on the regeneration of CO<sub>2</sub>-loaded AMP/DMSO. The experiments with stripper gas were conducted in a water bath according to Section 4.6.1 and the experiments at a lower regeneration pressure were conducted with a multi-evaporator according to Section 4.6.2.

For the experiments that were conducted with a stripper gas, the samples were CO<sub>2</sub>-loaded to  $0.5-0.55 \frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}}$  while the samples with -10 mbarg were loaded to  $0.38 \frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}}$ , according to Section 4.2. The latter load is what is estimated to be the load of the AMP/DMSO CO<sub>2</sub>-rich solution in the pilot plant during operation [6]. The results of the experiments are shown in

Table 7.

Table 7 – The results from the regeneration experiments done without stripper gas, with stripper gas and -10 mbarg that were conducted at 80°C for 30 or 120 minutes. The weights and CO<sub>2</sub>-loads before and after the regeneration are shown and used as a measure to assess the regeneration.

<b>80°C</b>	<b>0 ln/min gas</b>		<b>1 ln/min gas</b>		<b>-10 mbarg</b>	<b>-10 mbarg</b>
	<b>120 min</b>	<b>30 min</b>	<b>120 min</b>	<b>30 min</b>	<b>30 min</b>	<b>20 min</b>
<u>Experiment 1</u>						
Solution (g)	50.05	50.2	49.97	49.99	45.48	50.46
Amount CO <sub>2</sub> loaded (g)	3.25	3.17	3.38	3.08	2.31	2.46
Regenerated solution (g)	51.07	51.32	49.2	50.18	45.99	51.71
$Load_{Before} \left( \frac{mol_{CO_2}}{mol_{AMP}} \right)$	0.526	0.512	0.548	0.499	0.411	0.395
$Load_{After} \left( \frac{mol_{CO_2}}{mol_{AMP}} \right)$	0.165	0.181	-0.125	0.031	0.091	0.201
<u>Experiment 2</u>						
Solution (g)	49.76	50.21	50.27	50.29	47.94	50.6
Amount CO <sub>2</sub> loaded (g)	3.28	3.08	3.43	3.13	2.44	2.47
Regenerated solution (g)	50.06	51.35	50.15	49.54	48.67	51.85
$Load_{Before} \left( \frac{mol_{CO_2}}{mol_{AMP}} \right)$	0.534	0.497	0.553	0.504	0.412	0.395
$Load_{After} \left( \frac{mol_{CO_2}}{mol_{AMP}} \right)$	0.049	0.184	-0.019	-0.121	0.123	0.200

The regeneration results were based on the assumption that all the weight that was lost during the experiment was CO<sub>2</sub> desorbing from the AMP/DMSO solution. The results, shown in

Table 7, were compared with solubility data of CO<sub>2</sub> in 25 wt-% AMP/DMSO, shown in Figure 11. [6] The solubility data shows the lowest level of CO<sub>2</sub>-saturation that can be achieved, i.e., the best results that can be achieved at a certain pressure level. The regeneration results of the experiments conducted with stripper gas were not included due to misleading (negative) values of regeneration. The reasons will be discussed further below.

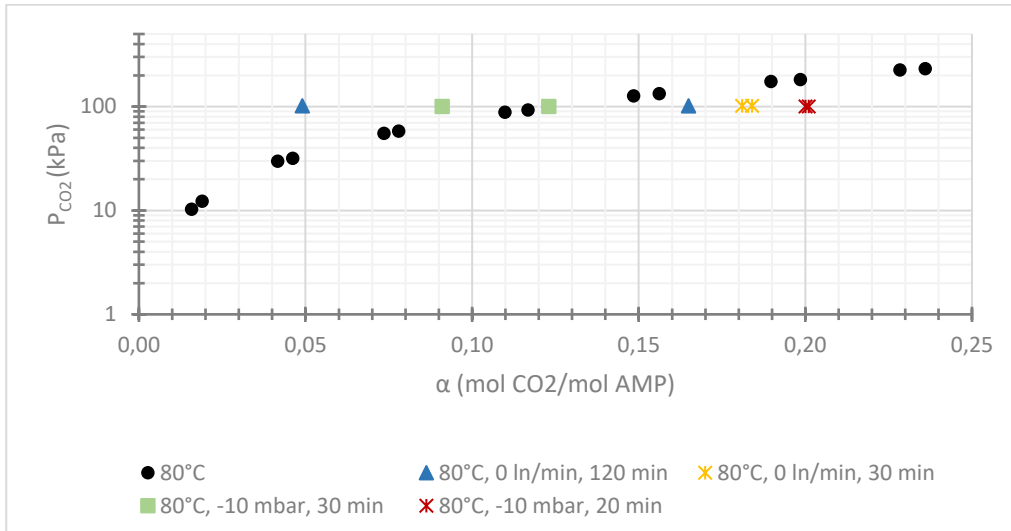


Figure 11 - The solubility of CO<sub>2</sub> in AMP shown as load from the regeneration experiment in comparison with solubility equilibrium data of CO<sub>2</sub> in AMP at 80°C.[6]

In combination with regeneration, visual data was gathered after each regeneration experiment. Pictures of the regenerated solutions after the stripper gas experiments are shown in Figure 12. The picture on the left are the samples from experiment 1 and the picture on the right are the samples from experiment 2.

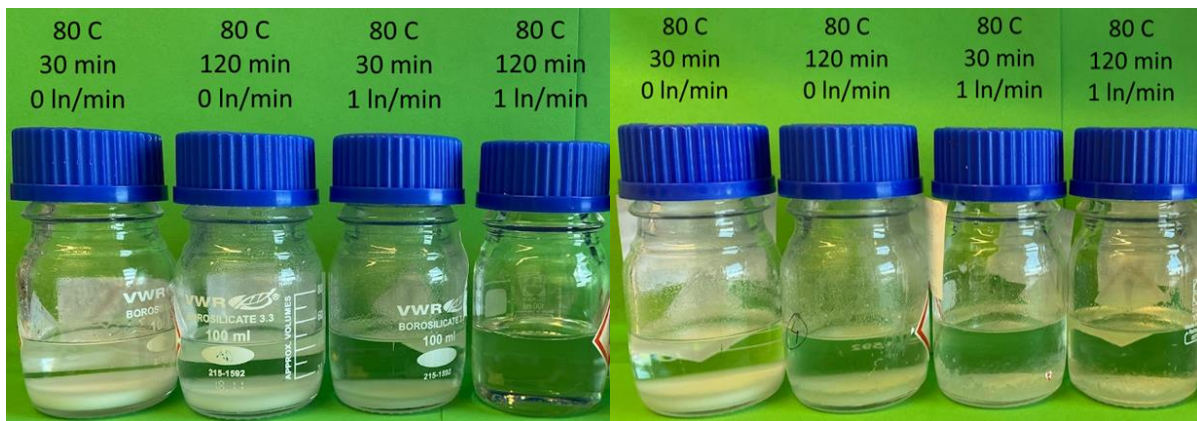


Figure 12 – Pictures of the samples after they had been regenerated at 80°C for 30 or 120 minutes with stripper gas, without stripper gas.

### 5.4.1 Stripper gas

The regeneration data from the experiments with a stripper gas, showed that the weight loss after regeneration exceeded the amount of CO<sub>2</sub> loaded before the experiment. Therefore, as the load was measured as a weight difference before and after the experiments, the results were therefore deemed inconclusive in terms of expected cyclic capacities. Nonetheless, Figure 12 suggests that more CO<sub>2</sub> can be regenerated if a stripper gas is used, as opposed to not using anything. This is indicated by the amount of precipitate (white) in the sample, shown in Figure

12. This is no surprise as the purpose of the stripper gas was to lower the partial pressure of  $\text{CO}_2$  and drive of the gas phase above the liquid. Which increases the driving force so that the  $\text{CO}_2$  that is solved in the liquid phase can desorb easier. In the experiment without the stripper gas,  $\text{CO}_2$  is removed solely due to convection and the equilibrium of  $\text{CO}_2$  to the local atmosphere. This lowers the driving force of  $\text{CO}_2$  desorption, leading to a larger amount of precipitate in the regenerated samples, as shown in Figure 12.

However, it is worth noting that based on the solubility data presented in Figure 11, regenerating at  $80^\circ\text{C}$  without any measures to improve the driving force of  $\text{CO}_2$  desorption can yield results close to the equilibrium curve. This indicates that even without a stripper gas, a cyclic capacity of 0.32 can be obtained, which is comparable to the cyclic capacity of the conventional aqueous 30 wt-% MEA solution [6].

The challenge with using the stripper gas was that it also lowered the vapor pressure of AMP/DMSO, leading to more AMP/DMSO evaporation, as shown in

Table 8. This affects the regeneration data as it is measured as a weight difference, before and after each experiment.

Table 8 - The loss of unloaded AMP/DMSO due to only evaporation after 30 min at 80°C with a 1 or 0 l/min gas flow of N<sub>2</sub>. The weight of the samples were around 50 g before each experiment.

NO CO <sub>2</sub> -LOAD	80°C, 1 l/min		80°C, 0 l/min	
	30 min	30 min	30 min	30 min
Temperature (C)	79.4 - 80.6	79.7 - 82.0	79.8 - 80.9	77.1 - 81.9
Gas flow (l/min)	1.00	1.00	0.00	0.00
Loss (g)	0.44	0.34	0.15	0.07

Because of the lowered vapor pressure, AMP and DMSO more readily evaporated and travelled upwards, aided by the gas flow, into the gas condenser where it cooled down and condensed into small droplets. Similarly, the CO<sub>2</sub> being regenerated also travelled upwards in the gas condenser, aided by the stripper gas flow. However, instead of simply passing through the gas condenser and exiting the experimental setup, the CO<sub>2</sub> was absorbed by the droplets of AMP/DMSO that had condensed within the gas condenser. This created a layer of precipitate inside of the gas condenser. A picture of the lower part of the gas condenser after “test 1 – 120 min” can be seen in Figure 13 below, where the precipitation layer is clearly visible. The same thing occurred during the other experiments that utilized the same setup, but to a much lesser extent.



Figure 13 – Precipitation is visible in the gas condenser after the "test 1 - 120 min - 80°C, 1 l/min".

#### 5.4.2 Regeneration below atmospheric pressure

The main difference between the experiments conducted with negative pressure and those with a stripper gas was the duration they were regenerated at 80°C for. The -10 mbarg experiment samples were heated in a multi evaporator from room temperature to 80°C during the experiment. However, the multi evaporator required 12 minutes to reach the desired temperature, whereas the stripper gas samples were placed in an 80°C water bath at the start of the experiment, allowing them to spend more time at 80°C compared with the -10 mbarg samples.

The results of the -10 mbarg regeneration experiments suggests that it is possible to regenerate the solution to the CO<sub>2</sub> solubility equilibrium curve within 30 minutes, as seen in Figure 11, indicating the maximum regeneration attainable at these conditions (temperature, pressure, load). However, more experiments should be conducted to confirm the data, as these are only duplicates.

These findings suggest that a cyclic capacity of  $0.3 \frac{\text{mol}_{\text{AMP}}}{\text{mol}_{\text{DMSO}}}$ , similar to that of a conventional 30 wt-% aqueous MEA solution, could be obtained at the pilot plant, if the rich CO<sub>2</sub>-loading are around  $0.4 \frac{\text{mol}_{\text{AMP}}}{\text{mol}_{\text{DMSO}}}$ . [6] Assuming that the data is correct, the regenerated AMP/DMSO solution's settled appearance should look like the solutions shown in Figure 14.

The 20-minute regeneration experiments showed that 20 minutes were not enough time for the CO<sub>2</sub>-rich AMP/DMSO solution to reach the equilibrium curve. This can be attributed to the sample being at 80°C for only 8 minutes when the experiment ended, which was not enough time to regenerate the solution. As shown in Figure 11, regenerating for 20 minutes with -10 mbarg yields a slightly different final CO<sub>2</sub>-load than without a stripper gas for 30 minutes (around 0.2 compared to 0.18). Keeping in mind that the samples without a stripper gas were loaded to around 0.5 compared to 0.4 for the -10 mbarg samples. However, since the -10 mbarg sample was at 80°C for only 8 minutes compared to 30 minutes, it suggests that regeneration is more efficient at -10 mbarg.

The regeneration conditions at the pilot plant were -10 mbarg and 80°C. These results suggest that the temperature and means to drive of CO<sub>2</sub> should be enough to regenerate the AMP/DMSO solution, indicating that another problem is causing the clogging. The experiments demonstrated that the samples could be regenerated to the maximum regeneration point (i.e., the equilibrium curve) at lab scale using the pilot plant conditions but that there is still precipitate in the solution. These findings provide insight into the initial suspicions regarding the root causes of clogging, which were insufficient regeneration or low temperatures causing the solution to precipitate or freeze in the pipe and suggests that there might be another cause.

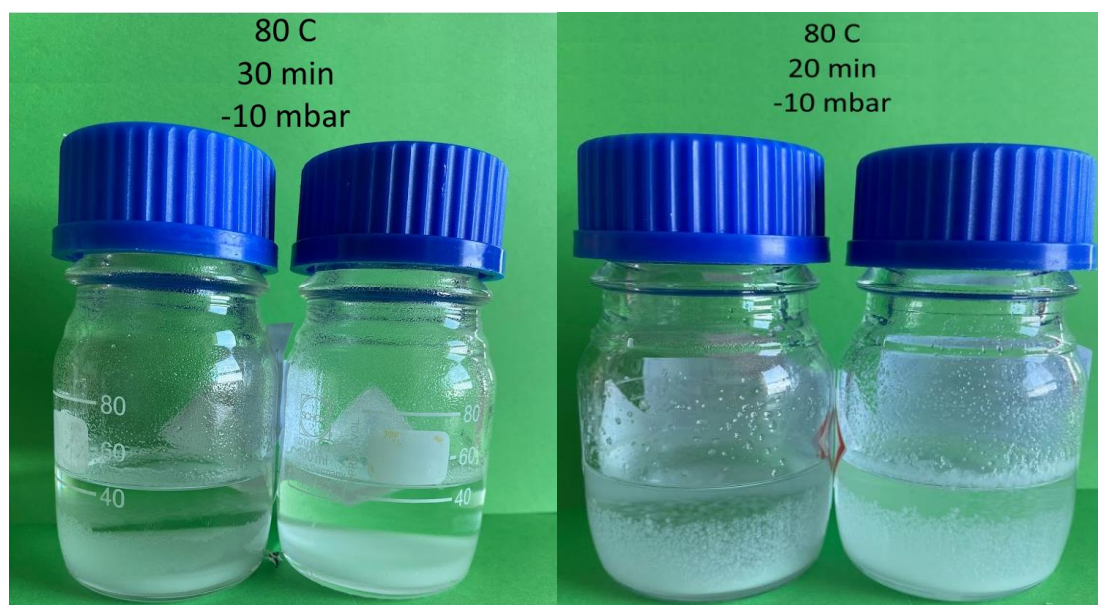


Figure 14 - Pictures of the samples after they had been regenerated at 80°C for 30 or 20 minutes at -10 mbarg.



### 5.4.3 Residence time during regeneration

The results from the experiments conducted with -10 mbarg pressure suggests that an increase in regeneration duration leads to a larger amount of CO<sub>2</sub> being desorbed from the sample, as shown in both Figure 11 and Figure 14. However, the experiment without a stripper gas indicate that this is only true to a certain point since the level of regeneration between 30 and 120 minutes did not show a large increase in desorbed CO<sub>2</sub>. The results of the 120-minute experiment without a stripper gas are however uncertain due to the unreasonable data of the second experiment, as shown in Figure 11. The data point is considered an outlier as it achieved a regeneration far beyond the equilibrium curve, which is impossible. This could be due to an abnormal amount of AMP/DMSO evaporating due to some unknown fault. Consequently, more experiments are needed to confirm the regeneration data for the 120-minute experiments without a stripper gas.

### 5.5 Regeneration at 90°C

To assess the impact of increasing the regeneration temperature from 80°C to 90°C, experiments were conducted with CO<sub>2</sub>-loaded AMP/DMSO at 90°C. As previous experiments demonstrated issues with precipitate forming in the gas condenser when utilizing a stripper gas, the 90°C experiments were conducted without a stripper gas. The experiments were conducted in a water bath, according to Section 4.6.1, and the samples were CO<sub>2</sub>-loaded to  $0.5\text{-}0.53 \frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}}$ . The results of the regenerations are presented in Table 9.

Table 9 - The results from the regeneration experiments done without stripper gas that were conducted at 90°C for 30 or 120 minutes. The weights and CO<sub>2</sub>-loads before and after the regeneration are shown and used as a measure to assess the regeneration.

	90°C		0 ln/min	
	120 min		30 min	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2
Solution (g)	50.03	50.03	49.89	50.74
Amount CO <sub>2</sub> loaded (g)	3.19	3.15	3.21	3.29
Regenerated solution (g)	50.76	50.93	50.54	51.47
$Load_{Before} \left( \frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}} \right)$	0.517	0.51	0.521	0.525
$Load_{After} \left( \frac{\text{mol}_{\text{CO}_2}}{\text{mol}_{\text{AMP}}} \right)$	0.118	0.146	0.106	0.117

The CO<sub>2</sub>-loading results obtained after regeneration, presented in Table 9, were compared with solubility data of CO<sub>2</sub> in 25 wt-% AMP/DMSO, shown in Figure 15. [6] The solubility data shows the lowest level of CO<sub>2</sub>-saturation that can be attained, i.e., the best results that can be achieved at a certain pressure level.

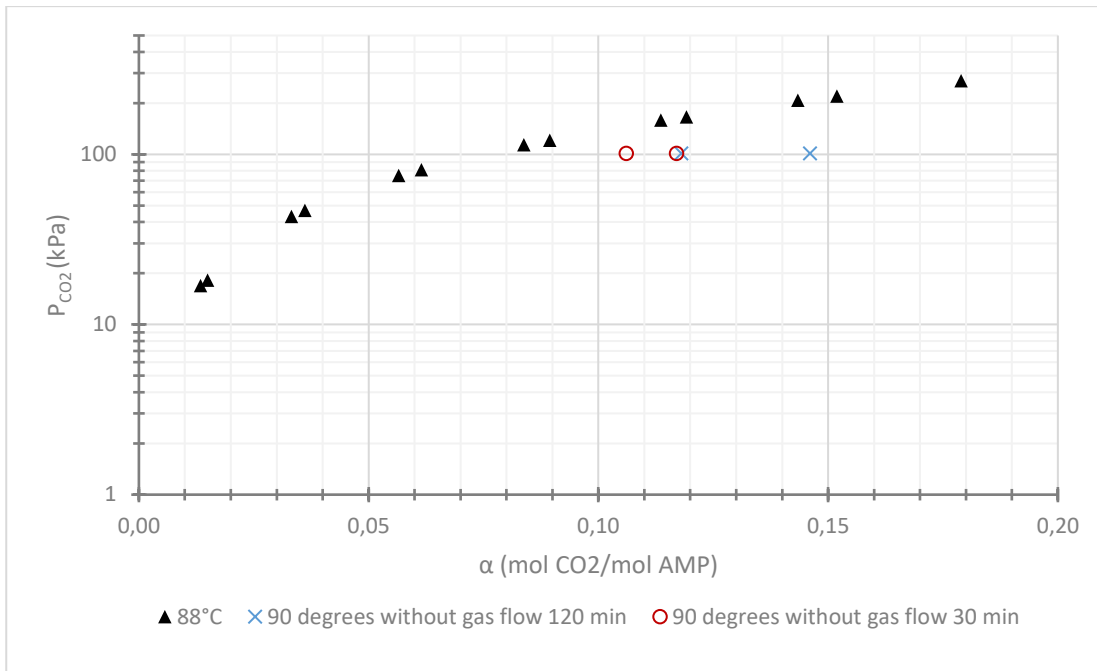


Figure 15 – The solubility of CO<sub>2</sub> in AMP shown as load from the regeneration experiment in comparison with solubility equilibrium data of CO<sub>2</sub> in AMP at 88°C.[6]

In addition to the regeneration data, visual data was gathered after each experiment. Pictures of the regenerated solutions are shown in Figure 16 below with the picture on the left representing samples from experiment 1 and the picture to the right samples from experiment 2. Regarding the 120-minute experiment, presented in the Figure 16A, a small amount of water accidentally got into sample at the end of the experiment. Interestingly this altered the entire appearance of the precipitate, causing it to become more cloudy, occupying more space, as opposed to appearing compact.

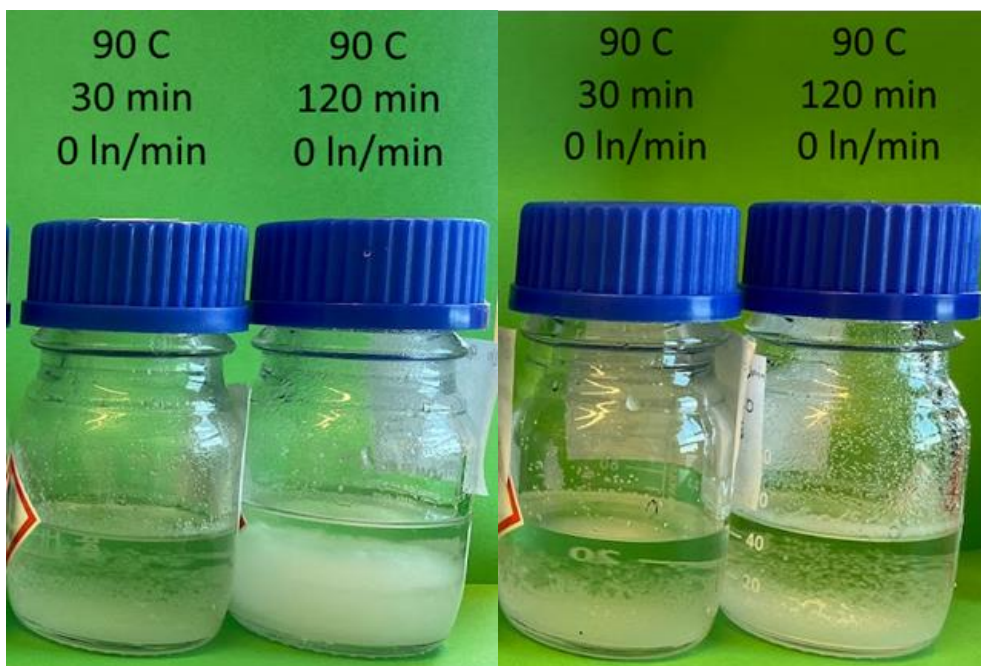


Figure 16 – Pictures of the samples after they had been regenerated at 90°C for 120 or 30 minutes with or without a stripper gas. A to the left, B to the right.

When comparing the cyclic capacities achieved at different regeneration temperatures, Table 9 shows that utilizing a temperature of 90°C instead of 80°C without a stripper gas increased the cyclic capacity to 0.4. This stands in contrast with the cyclic capacity of 0.3 obtained at 80°C. The regeneration experiments conducted at -10 mbarg also demonstrated a cyclic capacity of 0.3, but those samples were only loaded to 0.4 as opposed to 0.5 for the experiments with/without a stripper gas. It is therefore possible that a larger cyclic capacity could be obtained if they were loaded with more CO<sub>2</sub> prior to the experiments as the samples reached their equilibrium point and could not be regenerated further. These results do however indicate that a higher temperature during regeneration yields a better cyclic capacity.

Depending on the pilot plant requirements, the AMP/DMSO solution may not need to be regenerated to the extent achieved during the 90°C experiments. There is a tradeoff between the amount of CO<sub>2</sub> regenerated and the energy required to regenerate it. Further experiments are needed to determine the degree to which the AMP/DMSO solution needs to be regenerated, and which CO<sub>2</sub>-load the pilot plant can handle without experiencing clogging issues.

### **5.5.1 Residence time during regeneration**

According to the solubility data in Figure 15, regenerating for 120 minutes did not result in a significant improvement in regeneration. The samples appear to reach similar levels of regeneration to the 30-minute experiments, apart from the first 120-minute experiment where the weight slightly increased because of an accidental addition of a small amount of water. This reinforces the notion that regenerating for 120 minutes does not significantly improve the degree of regeneration.

### **5.5.2 Water content in AMP/DMSO**

Water will be present in the pilot plant due to both the water content in the flue gas and the hygroscopic nature of DMSO. Additional experiments should be conducted to investigate the AMP/DMSO/H<sub>2</sub>O system, given the drastic change in appearance of sample “Experiment 1 - 90°, 0 l/min, 120 min” seen in Figure 16 following the accidental addition of a small amount of water. While the regeneration values shown in Table 9 indicate that the sample is regenerated similarly to the other samples, the precipitate occupies a considerably larger space. The findings suggest that the AMP/DMSO solution behaves differently in water than previously thought. If the precipitate occupies more space, it could be contributing to the clogging observed in the pilot plant.

The mechanism behind this new system behavior is unknown. However, based on the reaction mechanism described in Section 2.3, it is understood that in the presence of water, AMP can be involved in more reactions, and these products could potentially contribute to the formation of the new precipitate. Alternatively, the carbamate salt that is formed when AMP reacts with CO<sub>2</sub> could form a different crystal structure in water. Another possibility is that DMSO precipitates since the phase diagram of DMSO in water indicates that there is a small range between 10-20°C and 0-10 wt-% water where DMSO could precipitate [24]. In the presence of AMP, the behavior is however unknown.

Something, although unexplained, evidently happens and additional experiments are needed to study how an AMP/DMSO/H<sub>2</sub>O system behaves given the potential impact it has on the performance of the pilot plant.

## 5.6 Regeneration of pilot sample

An experiment was conducted, according to Section 4.6.2, using a sample from the pilot plant (Pilot sample ST1 – Bottom part - Section 5.3) to assess the degree of regeneration achieved and to determine if more CO<sub>2</sub> could be regenerated. At the same time an experiment was conducted using unloaded AMP/DMSO to determine whether the loss of AMP/DMSO due to evaporation was significant. The sample, shown in Figure 17, was extracted from the bottom of the stripper tank at the pilot plant, following a regeneration phase. After the extraction, uncertainties regarding the degree of regeneration had arisen following visual examination of the sample.

The behavior of the precipitate was again found to be peculiar and distinct from the regenerated lab samples observed earlier. As seen in Figure 17, a part of the solution is suspended in the supernatant, while another part has sedimented. The reason for this strange appearance could be attributed to the influence of water or DMSO, as has been discussed in the section above. The AMP utilized at the pilot plant and in the lab originate from different suppliers, and the purity and composition of the AMP could contribute to this new phenomenon. The AMP used at the pilot plant contains less than 7% 2-methyl-2-(methylamino)-1-propanol, which may affect the solution's behavior. As mentioned above, more experiments are needed to study and understand the phenomenon.



Figure 17 - Sample from the regenerated AMP/DMSO solution taken from the bottom of stripper tank 1 at the pilot plant. The sample in the picture on the right had been shaken prior to the photograph to visualise how the sample would look at the pilot plant under agitation.

Table 10 shows that it was not possible to regenerate the pilot sample further, implying that this is how the AMP/DMSO solution would appear inside of the pilot plant after the regeneration stage. Furthermore, it also showed that the loss of AMP/DMSO during the evaporation experiments were not significant. The weights of the sample are close to their starting weight and the difference could be attributed to inaccuracies of the scale.

Table 10 - The results from the 30 min evaporation experiment with non-loaded 25w% AMP/DMSO and the pilot plant sample seen in Figure 17.

30 min	AMP/DMSO without CO <sub>2</sub> load		Pilot plant sample	
	Sample 1	Sample 2	Sample 1	Sample 2
<b>Difference (g)</b>	-0.03	-0.09	0.14	0.09
<b>Difference (%)</b>	0.01%	0.03%	-0.05%	-0.03%

The sample, (Pilot sample ST1 – Bottom part - Section 5.3), does however not look like the regenerated samples from the laboratory regeneration experiments after being regenerated, as shown in Figure 18. The precipitate looks very different, almost like miniature ice shards. The reason for that might be attributed to the presence of water in the sample, which may lead to the formation of a new precipitate structure.



Figure 18 – Pictures of the pilot samples after they had been regenerated at 80°C and -10 mbar for 30 minutes. On the picture on the right, it is possible to see precipitation that looks different than what it does at in the lab. The picture on the right is tilted to show the precipitate more clearly.

To quantify the amount of water in the sample, the pilot plant sample was evaporated, see Section 4.6.2. The pressure was continuously lowered from atmospheric pressure to 35 mbar at 58°C to evaporate the water. The pressure-drop to 35 mbar lasted 108 minutes, after which the samples were evaporated for an additional 60 minutes.

Table 11 reveals that 25% of the sample was water which most likely originates from the flue gases or residual water remaining when water was pumped through the pilot plant to unclog it. Gas chromatography (GC) analysis indicates a water concentration of 20-30% [22]. At 20-25 wt-% water the DMSO should, according to its phase diagram, not precipitate at room temperature [24]. Nevertheless, the behavior of DMSO precipitation in an AMP/DMSO/H<sub>2</sub>O system remains unknown. There is however a strong indication that water is a contributing factor to the distinct appearance of the precipitate in the pilot sample.



Table 11 – Amount of water in the pilot plant sample “Pilot sample ST1- bottom part, Section 5.3”

35 mbar, 58°C	Pilot sample	
	Sample 1	Sample 2
<b>Before evaporation (g)</b>	63.6	57.4
<b>After evaporation (g)</b>	47.7	42.8
<b>Evaporated (%)</b>	25.0	25.5

Numerous indications suggest that water alters the dynamics of the AMP/DMSO precipitating system. To gain a better understanding of this phenomenon, additional experiments regarding water in the AMP/DMSO system must be conducted.

### 5.7 Solubility of the precipitate at 30°C

Upon cooling down to room temperature, the laboratory regeneration samples precipitated. Given that the lean solvent stream will be at 30°C, an experiment was conducted to observe how the precipitate behaves at this temperature. The 30-minute samples from Section 4.6.1 were submerged in a 30°C water bath for 41 minutes to determine whether the precipitate dissolves at a slightly higher temperature. As seen in Figure 19, the precipitate did not dissolve, and the samples maintained the same appearance as they had at room temperature. The reason that sample ‘(1) 80°C at 0 ln/min for 30 min’ is different is because it was accidentally shaken before the picture was taken. After it had time to settle, its appearance went back to how it looked before the water bath.

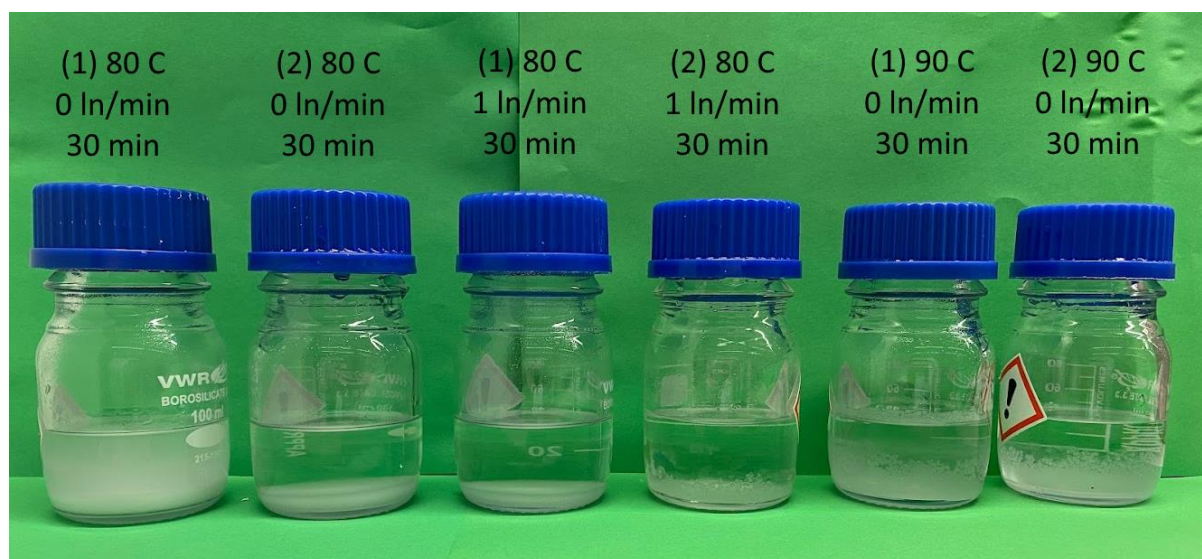


Figure 19 – The 30-minute samples from section 4.6.1 after being placed in a water bath for 41 minutes at 30°C.

## 6. Conclusion

Clogging was the main issue during the time spent at the pilot plant trying to get it operational, and it must be resolved before pursuing further research. The pilot plant's clogging prevented continuous carbon capture operation and limited the amount of data that was gathered. In the early stages of this master's thesis, two potential causes were hypothesized: 1) Low temperatures, which caused the AMP/DMSO solution to freeze/precipitate and clog the pipes and equipment or 2) Inadequate regeneration of the AMP/DMSO solution, resulting in precipitate clogging the pipes and equipment.

To address the issue of low temperatures in the pilot plant container it is suggested to implement an air heat pump to maintain a constant temperature. It is also recommended to install a heating device, possibly a heating cable, around the crucial pipe seen in Figure 9 that transports the lean AMP/DMSO solvent to the top of the absorption tower to avoid freezing and clogging.

Several laboratory experiments were conducted to assess whether the regeneration was adequate, revealing that the of 80°C at – 10 mbarg could regenerate the AMP/DMSO solution to equilibrium within 30 minutes, at least in laboratory scale. However, during the liquid sampling at the pilot plant, it was observed that the solvent does not behave as it does in laboratory scale. It is suspected that the precipitate found in the pilot plant sample may be different than from what have been encountered in the lab.

Potential reasons for this could be the accumulation of water in the pilot plant, which was estimated to be around 25% of the AMP/DMSO solution. When water was accidentally added to a sample in the lab, the appearance of the precipitate changed and became cloudy instead of compact, similar to the precipitate sampled at the pilot plant. It might be that the presence of water generates a different carbamate salt crystal structure. Another possibility is that DMSO precipitates, as it known that DMSO can precipitate in a DMSO/H<sub>2</sub>O system at 10-20°C with low concentrations of water. If precipitation of DMSO occurs in an AMP/DMSO/H<sub>2</sub>O system, is however unknown.

In order to evaluate the performance of the pilot plant, measuring equipment is needed and it was found that measuring equipment (flow and CO<sub>2</sub> meters) was missing from the gas streams. These instruments are needed to assess the performance of the pilot plant during continuous operation. Without the measuring equipment, it is not possible to do a CO<sub>2</sub> mass balance for the gas stream and therefore difficult to evaluate the performance of the pilot plant. Moreover, it would not be possible to compare the mass balance of the gas streams with the mass balance of the liquid streams to verify the findings.

Another important aspect of assessing the performance of the pilot plant is monitoring the emissions of AMP, DMSO and NDMA. Sampling revealed that the sampled concentrations were lower than the estimated emissions. However, the pilot plant was not operated continuously due to problems with clogging which renders the results not representative for emissions during continuous pilot plant operation.

As mentioned previously, the accumulated water in the pilot plant was 20-25% of the solution. Since the pilot plant was not operated continuously, it is difficult to say whether similar water accumulation will be observed during normal operation. There is however a strong suspicion that water accumulation will be a problem and that it is something that needs to be addressed.

Not the least to save energy by avoiding the need to heat up water during the regeneration phase but also to prevent potential issues if the new precipitate structure causes problems.

The conditions at the pilot plant were shown to be sufficient for regeneration of CO<sub>2</sub>. However, it was also demonstrated that higher temperatures (90°C vs 80°C), lower pressures and longer residence times made the regeneration more efficient. Regeneration times over 30 minutes did however not significantly improve the regeneration, as there was only a slight increase in cyclic capacity. Supported by solubility data it was further demonstrated that lower pressures enabled more CO<sub>2</sub> desorption. These factors are important to consider if there is a decision to alter the regeneration conditions in the future.



## 7. Future work

Once the challenges at the pilot plant are resolved, efforts to make it operational should continue. When a baseline of operations has been established, equipment tuning experiments to optimize the performance of the plant should start. Effort should be made on finding the optimal time/temperature/pressure combination for the best regeneration contra energy expenditure and the cyclic capacity of the pilot plant.

To further improve the pilot plant, a separation unit that separates the CO<sub>2</sub>-rich stream from the CO<sub>2</sub>-lean stream should be used during operation to reduce the volume that needs to be regenerated. To evaluate the separation unit, the efficiency of separation and energy savings/losses should be investigated.

More research should be conducted to understand the precipitation phenomenon that was observed in the pilot plant sample, and whether it is a problem or not. If it is dependent on water, more research should be conducted to explore options to prevent the accumulation of water. Regardless of whether water is the cause of the new precipitation or not, options to reduce water accumulation should be explored to potentially save energy by avoiding to heat water during the regeneration stage.

When it is possible to operate the pilot plant continuously, more sampling should be conducted to get representable samples of AMP, DMSO and NDMA emissions from the gas stream.

It could be worthwhile to examine the extent of AMP degradation, as it has been observed in other amine absorption processes that the presence of NO<sub>x</sub> can cause degradation. This degradation could result in the need to occasionally add amines to maintain a 25 wt-% solution, leading to additional costs during plant operation.

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## 9. Appendix

### 9.1 Appendix A – Pilot plant operating handbook

In the following text below, instructions for how to operate and troubleshoot the pilot plant will be explained. A simplified schematic overview of the pilot plant is shown in Figure 20 which shows the absorption and regeneration unit (electric boiler system), which will be explained in more detail below.

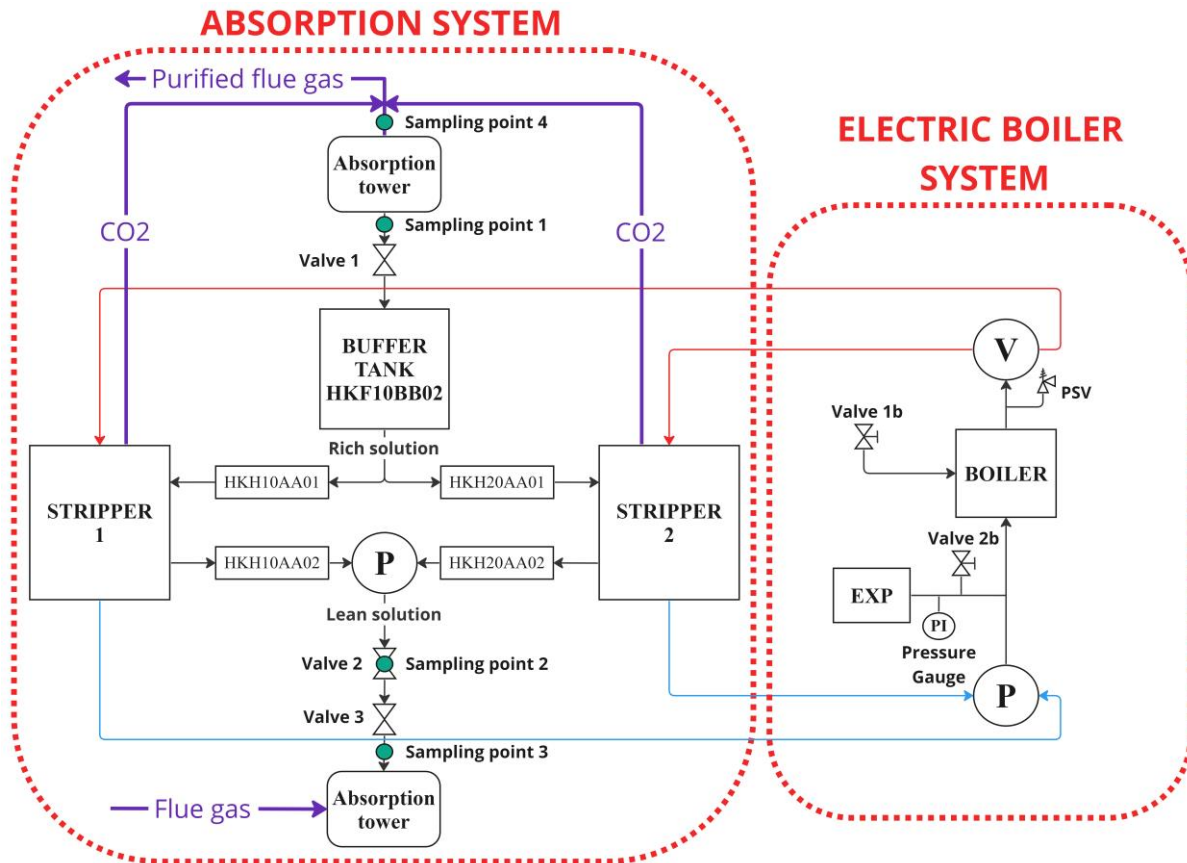


Figure 20 – A schematic overview of the pilot plant.

### 9.1.1 Pilot plant startup

For simplicity, the pilot plant instructions are divided into three zones: zone 1 that represents the area where the CO<sub>2</sub> capture system is located, zone 2 where the flue gas inlet/outlet is located and zone 3 where the external cooler system is located.

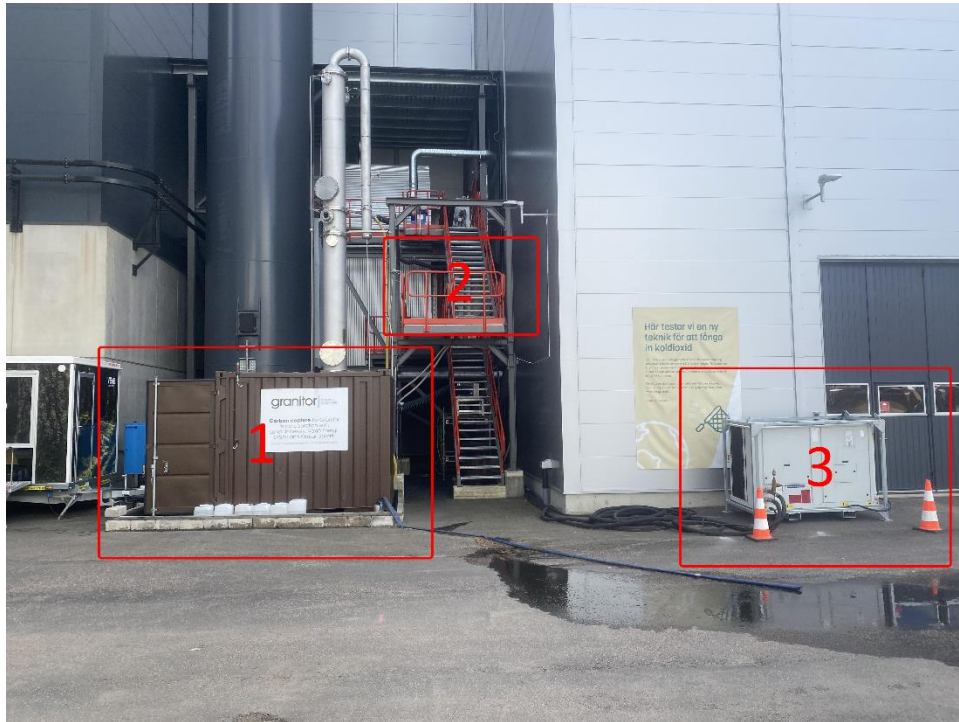


Figure 21 - An overview of the pilot plant placed at VEAB AB in Växjö. Zone 1: Pilot plant. Zone 2: Inlet and outlet of flue gases. Zone 3: External cooling.

Some of the equipment in the pilot plant is controlled via a computer that is referred to as the “command center” in the instructions, shown in Figure 22 below. At the command center the menu seen below can be used to access control of the equipment under “Frekvensomriktare” or the valves under “Ventiler”. It can also display measurement values if the button “Mätvärden” is pressed.

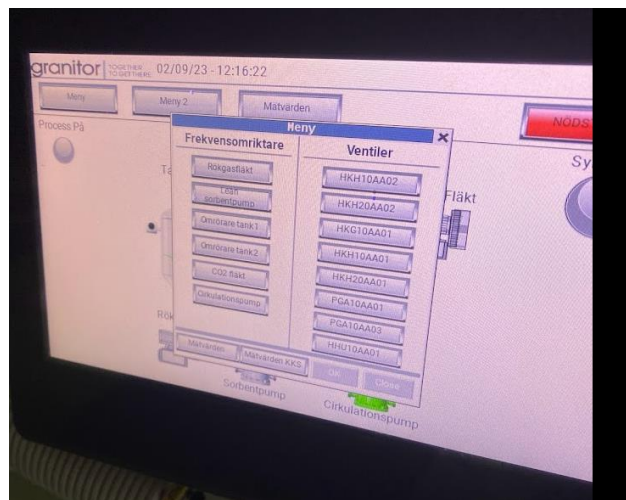


Figure 22 – The display of the computer “command center” that is used to control some of the equipment and valves at the pilot plant. The computer also shows the measurement values of the measurement probes installed at the pilot plant.

Two scenarios are possible at the startup of the pilot plant.

#### 9.1.1.1 There are no chemicals in the system

1. Start the electric boiler according to “9.1.5 Electric boiler”.
2. Fill the system according to “9.1.7 Load the system with chemicals”.

#### 9.1.1.2 There are chemicals in the system

1. Start the external cooling system according to “9.1.2.1 External cooling system – Power on”.
2. Open the flue gas stream according to “9.1.3.1 Flue gases – Turn on flue gas flow”.
3. Start the flue gas circulation fan according to “9.1.4.1 Flue gas circulation fan – Power on”.

#### 9.1.2 External cooling system



Go to zone 3 according to Figure 21.



Figure 23 - The external cooling device in Zone 3.

The instruction below for how to operate the external cooling device use the interface seen in Figure 24.

#### 9.1.2.1 Power on

1. Turn power on by switching the lever seen in Figure 23 to on “I”.
2. Push and hold  until the screen light up (approx. 4 seconds).
3. Push .



### 9.1.2.2 Power off



1. Push and hold .
2. Push .
3. Turn off power by switching the lever in Figure 23 to off “O”.



Figure 24 - The interface of the external cooling control panel.

### 9.1.3 Flue gases

Go to zone 2 according to Figure 21.

#### 9.1.3.1 Turn on flue gas flow

1. Open inlet valve.
2. Open outlet valve.

#### 9.1.3.2 Turn of flue gas flow

1. Close inlet valve.
2. Close outlet valve.



Figure 25 - The inlet and outlet of the flue gases found in zone 2.

### 9.1.4 Flue gas circulation fan

The instruction below for how to operate the flue gas circulation fan uses the interface seen in Figure 26.

#### 9.1.4.1 Power on

1. Adjust the knob to zero.
2. Press the “Hand On” button.
3. Adjust the fan speed with the knob to 40 Hz to let the fan start. Raise the fan speed to 50+ Hz when the fan has stabilized.

#### 9.1.4.2 Power off

1. Adjust the fan speed to zero with the knob.
2. Press the “Off Reset” button.

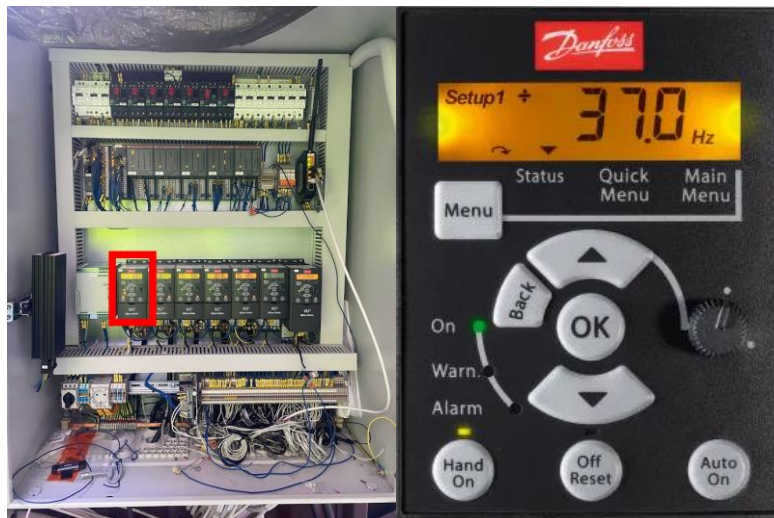


Figure 26 - An overview and close up of the interface used to control the flue gas circulation fan, found at the back of the pilot plant container in zone 1.

### 9.1.5 Electric boiler

The schematic overview of the electric boiler is shown below in Figure 27. The “P” stands for circulation pump, the “V” stands for the valve that adjusts the flow of heat between stripper tank 1 and stripper tank 2, the “PSV” stands for pressure safety valve, the “EXP” stands for expansion vessel. The electric boiler is the unit that provides the heat for the stripper tanks and make it possible to regenerate CO<sub>2</sub>.



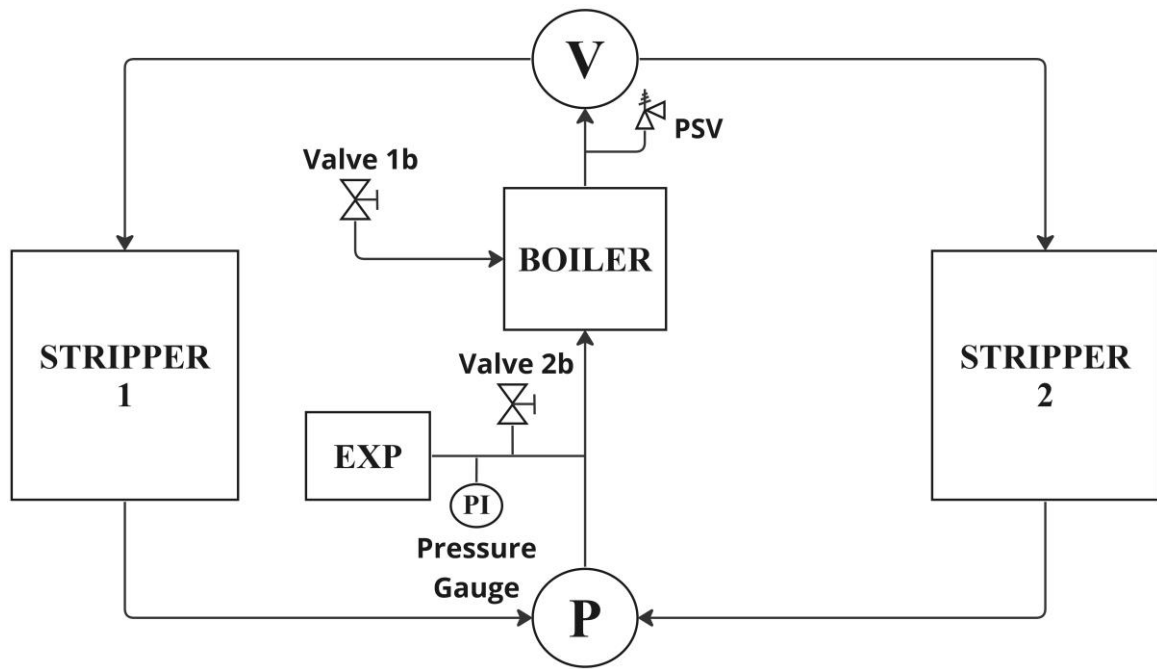


Figure 27 - A schematic overview of the electric boiler system found in zone 1. The “P” stands for circulation pump, the “V” stands for the valve that adjusts the flow of heat between stripper tank 1 and stripper tank 2, the “PSV” stands for pressure safety valve, the “EXP” stands for expansion vessel.

The valves “Valve 1b” and “Valve 2b” from Figure 27 are shown in Figure 28 below.

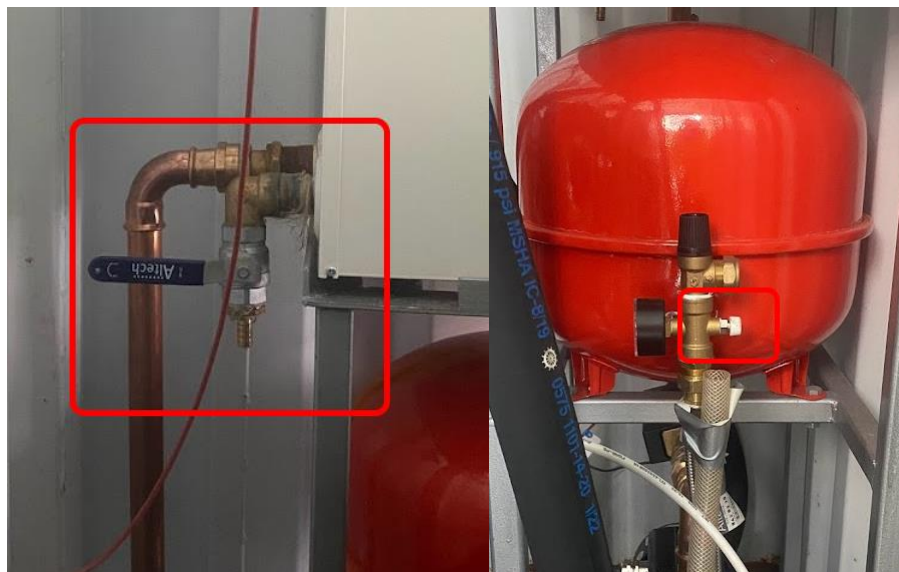


Figure 28 - The valves of the electric boiler. To the left: valve 1b which is used to fill the system with water. On the right: valve 2b which is used to release air from the system.

The instruction below for how to operate the electric boiler use the interface seen in Figure 29. Three scenarios are possible at the startup of the pilot plant.

#### 9.1.5.1 System not filled with water

1. Connect an external pump via a hose to the valve 1b.
2. Open valve 1b, start the external pump and pump water until the pressure gage reaches 2 bar.
3. Close valve 1b and start the circulation pump via the command center.

4. Open valve 2b to release air stuck in the system and run until no air leaves the system.
5. Close valve 2b, stop the circulation pump and open valve 1 and pump water until the pressure gage reaches 2 bars again.
6. Close valve 1b and disconnect the hose to the external pump.

#### 9.1.5.2 System filled with water but not in standby

1. Start the circulation pump via the command center, adjust power of the pump according to the flow needed. During CO<sub>2</sub> absorption operations the power of the pump should be 100%.
2. Start the electric boiler by pushing **1** on the display connected to the boiler seen in Figure 29. The boiler is on when the status says “Till” or “Standby”.
3. Adjust the setpoint to the desired temperature via the **+** and **-** button.
4. Adjust the valve HHU10AA01 to decide which stripper tank will get heated, 0% for stripper tank 1 100% for stripper tank 2.

#### 9.1.5.3 System in standby

1. Adjust the set point “Börvärde” to 80°C.
2. Start the CO<sub>2</sub>-fan from the command center.
3. Adjust the valve HHU10AA01 to 0% to heat stripper tank 1 or 100% to heat stripper tank 2.

#### 9.1.5.4 System shutdown

1. Press **0** and check that the “Status” says “Från”.

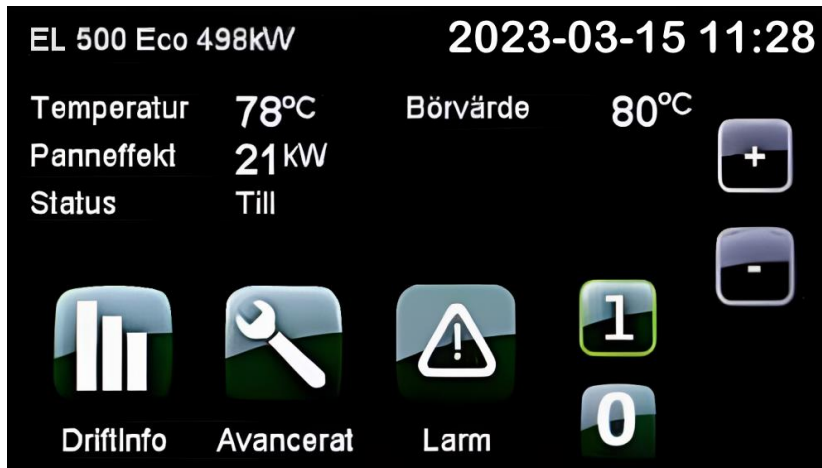


Figure 29 - The interface of the electric boiler control system found above the electric boiler.

#### 9.1.6 AMP/DMSO solvent system

The schematic overview of the AMP/DMSO system is shown below in Figure 30. “P” stands for the circulation pump. “HKH10AA01” and “HKH20AA01” are valves to control the flow of solvent into stripper tank 1 or stripper tank 2. “HKH10AA02” and “HKH20AA02” are valves that release solvent from stripper tank 1 or stripper tank 2 into the AMP/DMSO solvent system. Valves 1 and 3 are seen in Figure 31 and can restrict the flow into or out of the absorption tower. Valve 2 is seen in Figure 36 and can be used to take liquid samples from the stripper tanks or

to pump external fluids (i.e. water) into the AMP/DMSO solvent system. The AMP/DMSO solvent system is the unit that makes it possible to capture CO<sub>2</sub> from the pilot plant.

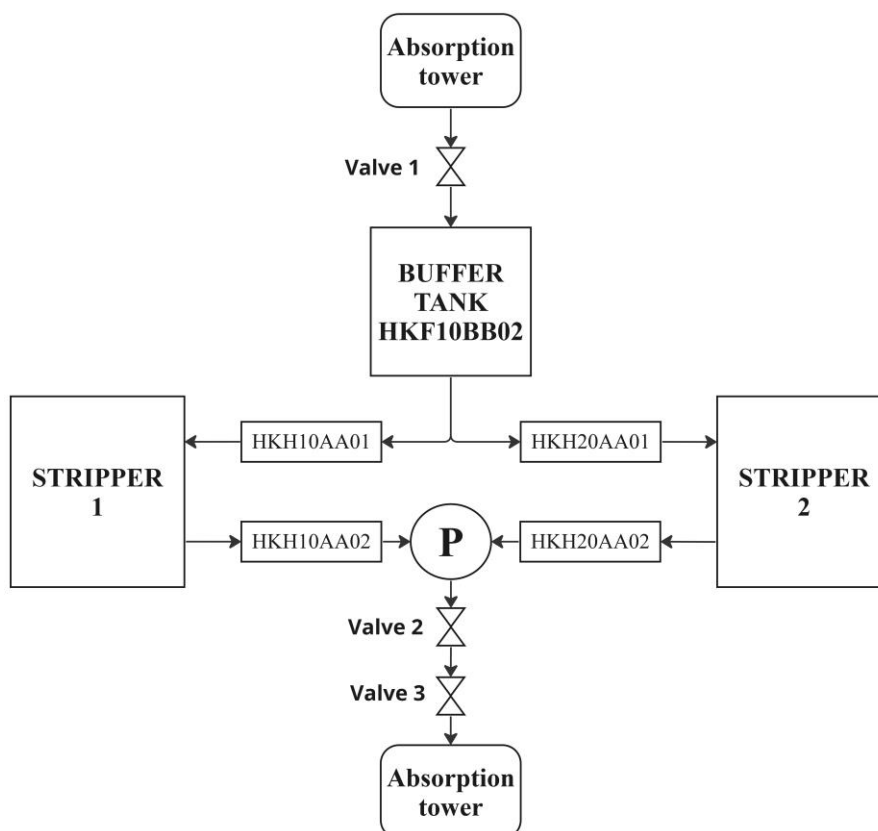


Figure 30 - The schematic overview of the AMP/DMSO system seen in zone 1 in Figure 21. “P” stands for the circulation pump. “HKH10AA01” and “HKH20AA01” are valves to control the flow of solvent into stripper tank 1 or stripper tank 2. “HKH10AA02” and “HKH20AA02” are valves that release solvent from stripper tank 1 or stripper tank 2 into the AMP/DMSO solvent system. Valves 1 and 3 are seen in Figure 31 and can restrict the flow into or out of the absorption tower. Valve 2 is seen in Figure 36 and can be used to take liquid samples from the stripper tanks or to pump external fluids (i.e. water) into the AMP/DMSO solvent system.

Before the pilot plant can be used, it must be filled with chemicals.

### 9.1.7 Load the system with chemicals

1. Close valve HKH10AA02 and HKH20AA02 via the command center.
2. Close valve HKH10AA01 and HKH20AA01 via the command center.
3. Turn on stirrer HKH10AM01 (stripper tank 1) or HKH20AM01 (stripper tank 2) to the desired agitation via the command center.
4. Confirm that the temperature in the stripper tank is above 20°C in the command center via “Mätvärden”.

#### 9.1.7.1 Fill the buffer tank

1. Connect a hose via an external pump to the buffer tank HKF10BB02.
2. Begin pumping the chemical with the lowest freezing point to allow the hose to warm up and avoid that the chemical with the higher freezing point freezes in the hose when it is pumped.
3. Fill chemicals according to need and load stripper tank 1 or 2 according to “9.1.7.2 Load stripper tank 1” or ” 9.1.7.3 Load stripper tank 2”.

### **9.1.7.2 Load stripper tank 1**

1. Open the valve HKH10AA01.
2. When the buffer tank HKF10BB02 is empty, close the valve HKH10AA01.

### **9.1.7.3 Load stripper tank 2**

1. Open the valve HKH20AA01.
2. When the buffer tank HKF10BB02 is empty, close the valve HKH20AA01.

## **9.1.8 Regenerate chemicals**

### **9.1.8.1 System startup**

1. Check that the temperature is 80°C in the stripper tank where the chemicals are stored and let it regenerate for a minimum of 30 minutes.
2. Connect the outlet of valve 2 to a container.
3. If the chemicals are in stripper tank 1, open HKH10AA02. If the chemicals are in stripper tank 2, open HKH20AA02.
4. Open the valve 2 and collect 3-4 liter, close the valve.
5. Check if there is precipitate in the liquid.
6. Pour the collected liquid in HKF10BB02 and open HKH10AA01 to return it to stripper tank 1 or HKH20AA01 to return it to stripper tank 2.
7. If there was precipitate present in the collected liquid, continue the regeneration process and repeat step 2-6. If there was no precipitate the chemicals are ready.

### **9.1.8.2 System shutdown.**

1. Check that the temperature is above 80°C in the stripper tank where the chemicals are stored and let it regenerate for a minimum of 30 minutes.
2. Lower the set point "Börvärde" to 20°C.

## **9.1.9 Intermittent pilot run**

The pilot plant is not automated but continuous absorption and regeneration can be conducted if the pilot plant is manually operated intermittently.

1. Follow the "9.1.1 Pilot plant startup" procedures.
2. Check that the temperature "Rök top absorb" is above 20°C.
3. Check that the chemicals are regenerated according to "Regenerate chemicals".
4. Check that valve 1 and valve 3 are open.
5. Open HKH10AA02 if the chemicals are in stripper tank 1 or HKH20AA02 if the chemicals are in stripper tank 2.
6. Start the solvent pump via the command center and pump solvent until the level in the stripper tank reaches the desired level. Stop the solvent pump.
7. Close HKH10AA02 if the chemicals were in stripper tank 1 or HKH20AA02 if the chemicals were in stripper tank 2.
8. Close valve 1.
9. Open valve HKH10AA01 to return the chemicals to stripper tank 1 or open valve HKH20AA01 to return the chemicals to stripper tank 2 and close the valve after the buffer tank HKF10BB02 is empty.
10. Repeat step 2-10.

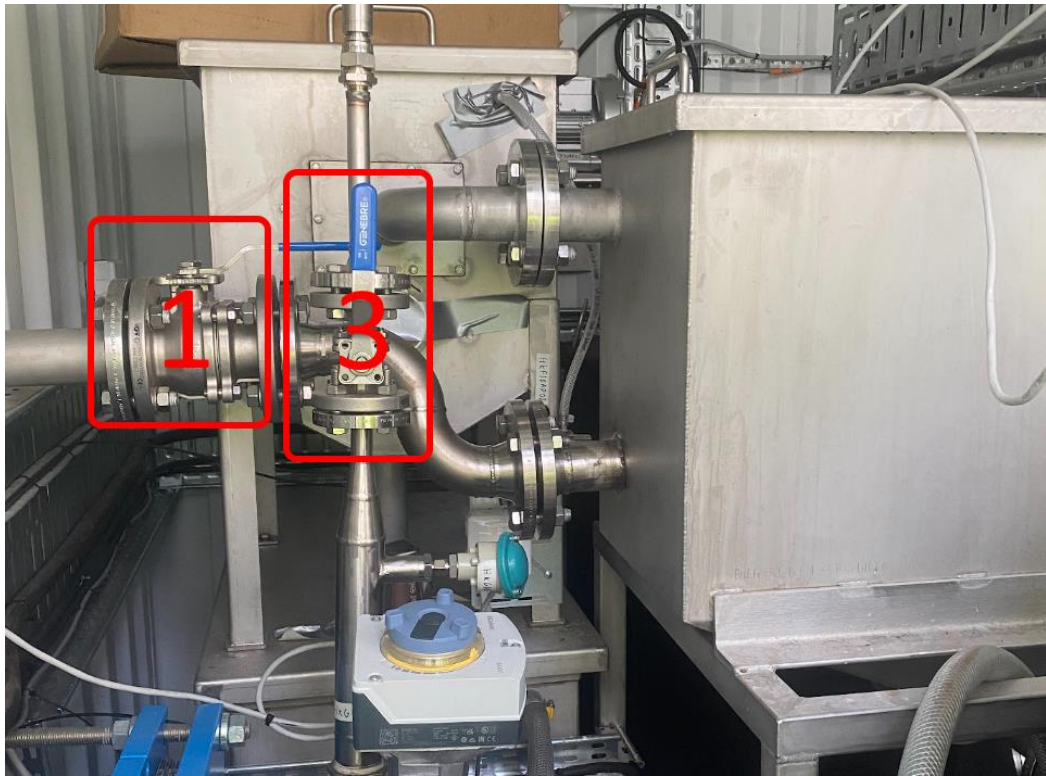


Figure 31 - The valves that control the flow out and in of the absorption tower, seen in Figure 30.

### 9.1.10 Gaseous sampling of AMP, DMSO and nitrosamines (NDMA)

To sample AMP, an impinger setup with sulfamic acid is used and to sample DMSO and NDMA, an adsorbent cassette is used. Take the samples during an intermittent pilot run, according to “intermittent pilot run”, to get a representative sample.

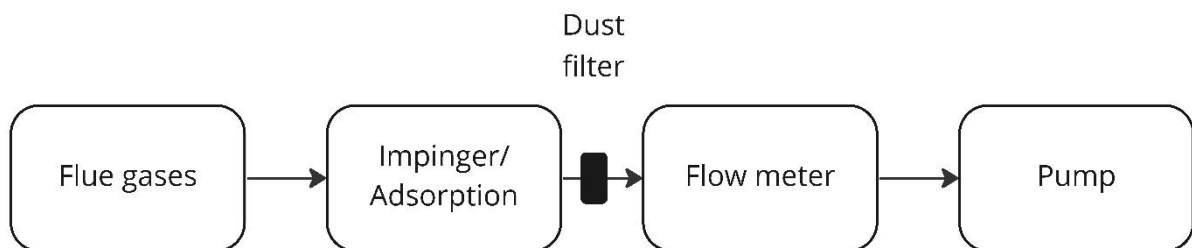


Figure 32 - A schematic overview on how the sampling setup should be connected.

1. Connect equipment according to Figure 32 and Figure 33.
2. Follow the instructions provided by the pump and flow meter.

#### 9.1.10.1 Impinger

1. Run the impinger at 1 ln/min for 30 min.

#### 9.1.10.2 Adsorber

1. Run the adsorber at 2,5 ln/min for >120 min.





Figure 33 - A picture of the adsorption setup in use at the inlet of flue gases to the absorption tower.

### 9.1.11 Liquidous sampling of AMP/DMSO at the pilot plant

Liquid samples can be sampled from the CO<sub>2</sub>-rich stream or the CO<sub>2</sub>-lean stream. Take the samples during an intermittent pilot run, according to “9.1.9 Intermittent pilot run”, to get a representative sample.

#### 9.1.11.1 Rich solution

1. Open the valve in Figure 34 and collect the amount of liquid needed.
2. Close the valve.

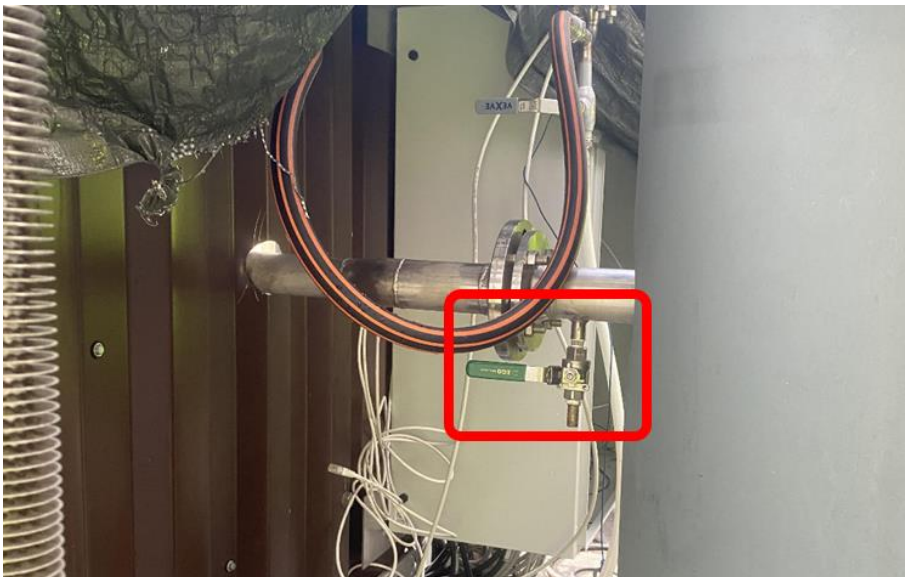


Figure 34 – The location of the sampling valve for CO<sub>2</sub>-rich solvent is found at the back of the pilot plant container in zone 1. It is positioned at the bottom of the absorption tower.

#### 9.1.11.2 Lean solution

1. Open the valve in Figure 35 and collect the amount of liquid needed.
2. Close the valve.

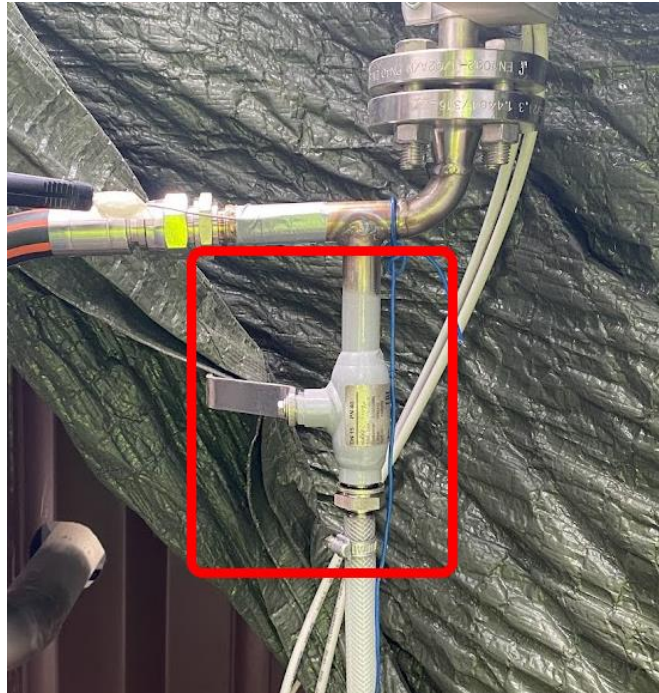


Figure 35 - The location of the sampling valve for CO<sub>2</sub>-lean solvent is found at the back of the pilot plant container in zone 1. It is positioned at the bottom of the absorption tower.

#### **9.1.11.3 Chemical solution sampling**

1. Open HKH10AA02 to sample from stripper tank 1, open HKH20AA02 to sample from stripper tank 2.
2. Connect the black hose in connection to the valve seen in Figure 36 to a container.
3. To get a representative sample, the pipes must first be flushed.
4. Open the valve and collect the liquid.
5. Close the valve and dispose of the collected liquid.
6. Open the valve and collect a sample.
7. Close the valve and close HKH10AA02 or HKH20AA02 depending on which was opened.

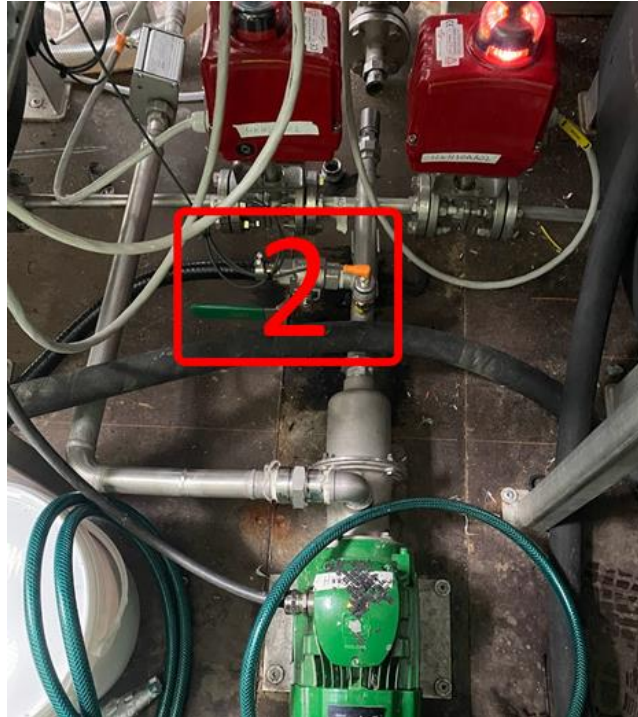


Figure 36 - The valve that is used to sample from the stripper tanks, empty the stripper tanks or to pump water through the system to get rid of clogging.

### 9.1.12 Empty chemicals

The system should not be run at the same time and the chemicals must keep a certain temperature to reduce risk of clogging the pipes. Wear protective equipment.

1. Check that the chemicals temperature is 30 °C.
2. Check if there are chemicals in the adsorption tower by opening valve 1 to the buffer tank HKF10BB02.
3. If there were chemicals: open HKH10AA01 to transfer the chemicals to stripper tank 1 or HKH20AA01 to transfer the chemicals to stripper tank 2.
4. Close HKH10AA01 if stripper tank 1 was used or HKH20AA01 if stripper tank 2 was used.
5. Open HKH10AA02 to empty stripper tank 1, open HKH20AA02 to empty stripper tank 2.
6. Connect the black hose in connection to the valve seen in Figure 36 to a container.

*Depending on what equipment is available, step five might have to be done in stages. A solution is to fill a bucket several times and empty it into an IBC tank. Another is to connect the black hose to a container and then connect a pump to the container to pump the chemicals to an IBC tank.*

7. Close KHK10AA02 if stripper tank 1 was emptied, close HKH20AA02 if stripper tank 2 was emptied.
8. Repeat step 1-6 to empty the other tank.
9. Check that valve HKH10AA01, HKH10AA02, HKH20AA01 and HKH20AA02 are closed.



*The system should be washed to ensure that there are not any chemicals left in the system. To wash the system, water will continuously be pumped through the system via one of the stripper tanks.*

10. Fill buffer tank HKF10BB02 with sufficient water.
11. Open HKH10AA01 to wash stripper tank 1 or HKH20AA01 to wash stripper tank 2.
12. Open HKH10AA02 if the water is in stripper tank 1, open HKH20AA02 if the water is in stripper tank 2.
13. Check that valve 1 and valve 3 are open.
14. Start the solvent pump via the command center and let the system run continuously for 10 minutes.
15. Stop the solvent pump via the command center and wait to let all water in the system settle in the stripper tank.
16. Repeat step 4-7.
17. Turn off the stripper tanks stirrer via the command center under “Omrörare tank1” if stripper tank 1 was emptied or “Omrörare tank” if stripper tank 2 was emptied.

*One of the stripper tanks and the absorption tower is now washed and the remaining stripper tank needs to be washed.*

18. Repeat step 10-12 for the remaining stripper tank.
19. Repeat step 4-7.
20. Turn off the stripper tank stirrer via the command center for the remaining stripper tank.

### **9.1.13 Pilot shutdown**

#### **9.1.13.1 Standby**

1. Turn off solvent pump.
2. Close valve HKH10AA02 and HKH20AA02.
3. Turn off flue gas circulation pump according to “9.1.4.2 Flue gas circulation fan - Power off”
4. Turn off flue gases according to “9.1.3.1 Flue gases -Turn off flue gas flow”.
5. Turn off the external cooling according to “9.1.2.2 External cooling system – Power off”.
6. Release the chemicals in the buffer tank HKF10BB02 to either stripper tank 1 via opening valve HKH10AA01 or stripper tank 2 via opening valve HKH20AA01. Close the valve when all liquids are gone.
7. Regenerate the chemicals and set the system in standby according to “9.1.8.2 Regenerate chemicals – System shutdown”.
8. Drain the systems pipes into a container via the rich solvent valve, lean solvent valve (see “9.1.11.1 rich solution sampling and 9.1.11.2 Lean solution sampling”) and the Figure 36 hose to prevent damage and clogging during standby.
9. Check that the external heating fan is on.

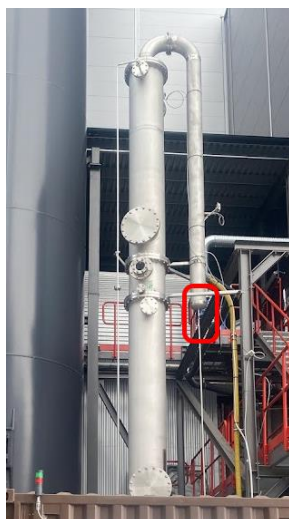


Figure 37 - The position of the valve that empties condensed water from the absorption tower. The valve can be reached from zone 2.

### 9.1.13.2 Complete shutdown

Do not proceed if there are still chemicals in the system, empty the chemicals according to “Empty chemicals”.

1. Check that the system is in standby according to “9.1.13.1 Pilot shutdown – Standby”.
2. Empty the system of chemicals according to “9.1.12 Empty chemicals”.
3. Turn off the heater system according to “9.1.5.4 Electric boiler – System shutdown”.
4. Turn of the heater circulation pump “Cirkulationspump” via the command center.
5. Check that valve 1, valve 3, HKH10A01, HKH20AA01, HKH10AA02 and HKH20AA02 are closed.
6. Check that all of the systems are turned off in the command center, no system icon should be colored green.
7. Drain all of the valves found outside of the pilot.
8. Turn off and disconnect the external heater.

### 9.1.14 Potential problems and solutions

#### 9.1.14.1 The solvent pump is not pumping

If the solvent pump is turned on, one of the stripper tanks are filled and either the valve HKH10AA02 or HKH20AA02 (depending on which stripper tank is filled) is open but the flow meter HKG10CF02 reads zero and no liquids are circulated through the system; the solvent pump is broken, the flow meter is broken or the system is clogged somewhere.

To facilitate troubleshooting it is easiest to have all of the chemicals in one stripper tank and water in the other stripper tank.

#### 9.1.14.2 The pipe after the stripper tank is clogged

To test and see if the pipe after the stripper tanks is clogged, open the valve to the stripper tank with water and open valve 2, seen in Figure 36. Have bucket ready to collect liquid coming out of valve 2.

If this section is clogged, the flow should either be nonexistent or very slow and thick with precipitation/frozen DMSO. Otherwise, if mostly water comes out this section is not clogged.

### 9.1.14.3 The VVX is clogged

Open the valve to the stripper tank with water in it, open valve 3 and open the valve after the VVX, seen in Figure 35. Have a bucket ready to collect potential liquids coming out. If a thick and precipitated/frozen DMSO liquid is coming out of the valve, it might be clogged. Turn the solvent pump on and try to pump water out of the valve. If mostly water comes out of this section it is not clogged.

### 9.1.14.4 The pipe after the VVX is clogged

Open the valve to the stripper tank with water in it, open valve 3 and open valve 1 to the buffer tank. Start the solvent pump and try to pump water through the system. If a thick liquid with precipitate/frozen DMSO comes out it might be clogged. If mostly water comes out it is not clogged. If the pressure gage HKG10CP02 is increasing and no water or liquid is coming out, it is probable that the VVX is clogged. Turn of the solvent pump.

Solutions that have proved most fruitful in unclogging the VVX has been to try and circulate water through the VVX multiple times, try to have the external heater pointed towards it to raise the temperature and reduce the amount of precipitate/frozen DMSO or to simply wait and try the next day.

### 9.1.14.5 The solvent pump is broken

If nothing of the above works, the solvent pump might be broken.

### 9.1.14.6 Electric boiler


#### 9.1.14.6.1 Overheating and/or not pumping

If the electric boiler is increasing in temperature but neither of the stripper tanks are increasing in temperature, it is possible that there is air in the electric boiler system. If this is not noticed fast enough the temperature will continue to increase until the safety fuse blows and an alarm is triggered.

1. Follow Section “9.1.14.6.3 An alarm has been triggered” if the light at the front of the display is blinking red.
2. Redo the steps in Section “System not filled with water”.


#### 9.1.14.6.2 Not heating

If the electric boiler is not heating it is either because the electric boiler is not turned on or because an alarm has been triggered. If the light at the front of the display is blinking red, an alarm has been triggered; see Section “9.1.14.6.3 An alarm has been triggered”

If the “Status” on the display says “Från” the electric boiler is not turned on and  must be pressed. If the status changes to “Standby” and “Till” and the “Panneffect” is increasing in effect, the electric boiler is turned on and is heating.

#### 9.1.14.6.3 An alarm has been triggered

If the light on the display of the electric boiler is red, an alarm has been triggered.

1. Press , read the alarm message and correct the fault and then remove the alarm message. When all of the alarm messages are fixed and removed, try to restart the electric boiler again.