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## Results from MEA Degradation and Reclaiming Processes at the CO<sub>2</sub> Technology Centre Mongstad

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### Abstract

In 2015, the CO<sub>2</sub> Technology Center Mongstad (TCM DA), operated a test campaign using aqueous monoethanolamine (MEA) solvent at 30 wt%. The main objective was to demonstrate and document the performance of the TCM DA Amine Plant located in Mongstad, Norway. As part of the test campaign, thermal reclaiming was performed in order to eliminate accumulated degradation products and improve the solvent performance. This paper presents results and discussions concerning formation and monitoring of amine degradation products along with experiences related to the thermal reclaiming process and its operational procedure. Evaluations of the efficiency of thermal reclaiming and the solvent improvement after reclaiming are also presented.

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## 1. Introduction

The CO<sub>2</sub> Technology Centre Mongstad (TCM DA) is located next to the Statoil refinery in Mongstad, Norway. TCM DA is a joint venture set up by Gassnova representing the Norwegian state, Statoil, Shell, and Sasol. The facility run by TCM DA entered the operational phase in August 2012 and it is one of the largest post-combustion CO<sub>2</sub> capture test centres in the world. A unique aspect of the facility is that either a flue gas slipstream from a natural gas turbine based combined heat and power (CHP) plant or an equivalent volumetric flow from a residual fluidized catalytic cracker (RFCC) unit can be used for CO<sub>2</sub> capture. The CHP flue gas contains about 3.5% CO<sub>2</sub> and the RFCC flue gas contains about 13-14% CO<sub>2</sub>. One of the main test plants at TCM DA is a highly flexible and well-instrumented amine plant. The amine plant was designed and constructed by Aker Solutions and Kværner to accommodate a variety of technologies, with capabilities of treating flue gas streams of up to 60,000 standard cubic meters per hour. The plant is being offered to vendors of solvent based CO<sub>2</sub> capture technologies to, among others, test; (1) the performance of their solvent technology, and (2) technologies aimed to reduce the atmospheric emissions and environmental impact of amines and amine based degradation products from such solvent based CO<sub>2</sub> capture processes. The objective of TCM DA is to test, verify, and demonstrate CO<sub>2</sub> capture technologies suitable for deployment at full-scale. Up to now the vendors Aker Solutions, Alstom, Shell Cansolv Technologies Inc. and Carbon Clean Solutions Ltd. have successfully used the TCM DA facilities to verify their CO<sub>2</sub> capture technologies.

From July to October 2015 TCM DA, in collaboration with partners, operated a test campaign using the non-proprietary aqueous monoethanolamine (MEA) solvent at 30 wt%. After testing a variety of process conditions for a total of 1843 hours, clear evidence of solvent degradation was observed. The test campaign proceeded with thermal reclaiming of the solvent in order to eliminate accumulated degradation products and demonstrate improvement of solvent performance. This work presents results concerning MEA degradation monitoring and reclaiming operation at TCM DA. Various design and operational factors that affect degradation rates are discussed, the efficiency of thermal reclaiming is estimated and experiences related to the reclaiming process and its operational procedure is shared.

### 1.1. Solvent degradation mechanisms

Amine solvents degrade due to exposure to heat (thermal degradation), presence of oxygen (oxidative degradation) and reactions of the amine with flue gas contaminants such as SO<sub>x</sub>, NO<sub>x</sub>, halogenated compounds, hydrocarbons and other impurities. Thermal degradation occurs mainly in the stripper section and is strongly dependent on the stripper operating temperature. The main thermal degradation products in MEA are Oxazolidin-2-one (OZD), MEA urea, HEIA, HEEDA [1]. The rate of formation of these products depend on the operating temperature (faster kinetics), CO<sub>2</sub> loading (more carbamate present) and MEA concentration. Oxidative degradation is mainly an issue for post-combustion CO<sub>2</sub> capture where the solvent is exposed to oxygen present in the flue gas. This occurs mainly in the absorber, where the level of oxygen is significant. Amine oxidation is also shown to be catalyzed by transition metal ions and will typically results in formation of ammonia and different organic acids [2]. In a second step, the organic acids will form heat stable salts (HSS) which are difficult to regenerate under normal regeneration conditions (atmospheric pressure and temperature around 120°C) [1]. These salts will therefore remain and accumulate in the circulated solvent. Amine degradation may also be induced by flue gas contaminants such as sulfur, polysulfide and CO. This issue has become especially evident for oil refinery flue gases such as gas originating from RFCC units [2]. Nonvolatile contaminants causing amine degradation can also arise from other sources such as make-up water, anti-foam agents, lubricants and corrosion inhibitors [2].

Several degradation processes often occur simultaneously to produce a wide range of degradation products. Accumulation of amine degradation products affects the solvent properties. They are known to increase the solvent viscosity and surface tension which again affects heat transfer coefficients, diffusion coefficients, and mass transfer rates [3]. This will again lead to loss of solvent capacity and increased energy numbers. Further, degradation products might lead to corrosion, fouling and foaming [2], which again increases operational and maintenance costs and might cause long-term technical integrity issues. Dissolved metal elements originating from corrosion are also as mentioned above expected to contribute as catalysts for oxidative degradation [1].

## 1.2. Solvent refreshing options

In order to reduce the impact of unwanted impurities and minimize the operational and maintenance issues listed above, a number of techniques have been suggested. Wang et al. (2015) have published an extensive review of amine reclaiming technologies and other techniques to handle this issue, including purging (bleed and feed), neutralization, ion exchange, adsorption, electrodialysis, and different thermal reclamation techniques [4]. Dumée et al. (2012) also presents a thorough comparison of the most promising techniques [1]. A summary is provided below.

- **Bleed and feed**

Bleed and feed is a simple operational procedure where a portion of the degraded solvent is continuously or periodically purged and replaced with fresh solvent. However, amine replacement and disposal might make this technique rather costly, particularly for specialized and expensive solvents. Further, a certain level of degradation products needs to build up before effecting bleed and feed in order to minimize replacement and disposal costs.

- **Neutralization**

Neutralization converts amine HSS to sodium or potassium HSS by addition of NaOH or KOH, according to the following reaction using NaOH as an example:



Neutralization maintains the amine capacity; however, there is no reduction in salt content of the solvent. The amine becomes more and more contaminated by salts that contribute to higher solvent density and viscosity, reduced surface tension, and possibly foaming and fouling. Eventually, the solvent needs to be discarded.

- **Ion exchange**

Ion exchange is a technology where the amine HSS ion is replaced with a friendlier ion. For example, an anion exchange removes HSS anions, replacing them with hydroxide ions, which frees the amine and let it return together with water to the process. The HSS anions are later removed from the resin by regeneration with NaOH. The practice of removing HSS from amine systems by ion exchange has presented many technical and operational challenges, and several researchers report doubt in the practical efficiency for amine applications. High consumption of chemical and water for resin regeneration together with generation of large amounts of waste are mentioned as other disadvantages. Further, ion exchangers are not capable of removing uncharged contaminants, i.e. degradation products originating from thermal degradation. It is still regarded a relatively economical method, especially for low levels of contaminants. However, if poorly designed and/or operated it can cause significant solvent losses and sodium slippage into the main amine process.

- **Adsorption**

Adsorption on activated carbon is a widely used method to remove high-boiling or surface active organic compounds [5]. However, activated carbon it is not able to remove significant amount of degradation products [2].

- **Electrodialysis**

Electrodialysis has also been suggested as a method to purify amine solutions. It uses a stack of alternating anionic and cationic ion-exchange membranes to selectively remove charged contaminants from the solvent [1]. The main disadvantage also for this method is inability to remove uncharged amine degradation products originating from thermal degradation and hydrocarbons [2].

- **Thermal reclaiming**

Thermal reclaiming is usually conducted on a small slipstream extracted from the stripper reboiler on a semi-continuous basis [2, 5]. The amine solution is vaporized in the reclaimer vessel and returned as vapour to the main process, while the less volatile degradation products and other contaminants accumulate in the reclaimer vessel bottoms. Stoichiometric addition of NaOH during thermal reclaiming allows recovery of the amine from the amine heat stable salts by conversion to sodium salts, according to Reaction (1). Thermal reclaiming has long been a recognized reclamation method for MEA. Compared with secondary and tertiary amines, MEA has a low normal boiling point allowing it to vaporize without degrading significantly. For other amines with higher boiling points vacuum might be required in order to prevent thermal degradation during reclaiming. The fact that MEA reclaiming units can be operated at the stripper pressure eliminates the need for a separate condenser for the reclaiming system and reduces the overall energy demand. In this approach the reclaimer product vapour which contains MEA is directly sent to the stripper [1, 5]. A major disadvantage of thermal reclaiming is the formation of an aqueous slurry waste whose disposal poses a challenge for the CO<sub>2</sub> capture process. The amount of waste depends on various parameters such as the flow rate of the slip stream fed to the reclaimer, the amount of basic solution used to liberate

MEA from heat stable salts, solvent conditions and overall operating conditions of the plant. According to the International Energy Agency (IEA) about 3.2 kg of amine reclaimer waste is generated per ton of CO<sub>2</sub> captured from coal fired flue gases using MEA [3]. However, depending on gas pre-treatment, combustion fuel, the type of amine used and the capture process itself, the reclaimer waste generation can vary in the range of 0.1-14.9 kg waste/ton CO<sub>2</sub> [3]. Collecting representative samples of reclaimer waste is complicated and so far there is limited information in the public domain that fully represents amine reclaiming waste for CO<sub>2</sub> capture processes. Using the Flour Econamine FG<sup>SM</sup> system as a reference, Nurrokhmah et al. (2013) have investigated methods to characterize MEA reclaiming waste along with possible waste treatment and reuse options. Thermal reclaiming is also mentioned to be energy extensive. However, alternative reclaiming technologies such as ion exchange and electrodialysis are not able to remove metals and non-ionic products and the potential efficiency of HSS removal is not as high as for thermal reclaiming [1].

### Nomenclature

CHP	Combined Heat and Power
DCC	Direct Contact Cooler
HSS	Heat Stable Salts
IBC	Intermediate Bulk Container
IEA	International Energy Agency
MEA	Monoethanolamine
MP	Medium Pressure
RFCC	Residue Fluidized Catalytic Cracker
SRD	Specific Reboiler Duty
TCM	CO <sub>2</sub> Technology Centre Mongstad

## 2. The TCM DA amine plant

An illustration of the TCM DA amine test unit is presented in Figure 1, and a short description is given in the following. Flue gas is cooled down and saturated with water in a direct contact cooler (DCC) before it enters the absorber. At TCM DA there are two possible sources of flue gas, i.e. exhaust gas originating from the natural gas fired combined heat and power plant and industry gas originating from the residue fluidized catalytic cracker. Both flue gas sources have their individual flue gas fans and DCCs as illustrated in Figure 1. Product CO<sub>2</sub> can also be recirculated back to the CHP gas absorber inlet to adjust the CO<sub>2</sub> content. For RFCC gas there is an option of mixing in air to adjust the CO<sub>2</sub> content. The conditioned flue gas is contacted counter-currently with the amine solvent in the absorber tower. CO<sub>2</sub> from the flue gas is absorbed yielding a solvent rich in CO<sub>2</sub> and a depleted flue gas with low CO<sub>2</sub> content. The depleted flue gas is released to the atmosphere after passing two sections of water wash. Typical absorber conditions are close to ambient pressure and temperatures of 40 - 80 °C, depending on the CO<sub>2</sub> content in the incoming flue gas. The CO<sub>2</sub> rich solvent is pre-heated in the lean/rich cross heat exchanger before it enters the stripper column where the chemical reactions are reversed to desorb CO<sub>2</sub> and regenerate the solvent. Heat is provided through steam in a thermosiphon reboiler to maintain regeneration conditions, i.e. 100 - 120 °C and pressure around 1 barg. The product CO<sub>2</sub> is released to the atmosphere, while the regenerated lean solvent is pumped back to the absorber via the lean/rich cross heat exchanger and the lean cooler.

The TCM DA amine test unit is also equipped with a thermal reclaimer which treats a slip stream of the lean solvent coming from the stripper. The thermal reclaimer uses additional heat provided by steam to separate the useful solvent from the degradation products which are accumulated in the solvent over time. The reclaimer vapour contains useful solvent which is recycled back to the main process, while the waste remains in the reclaimer and is periodically discharged. Water and NaOH can be added to the reclaimer unit on demand. The operating pressure corresponds to the stripper pressure.

The reclaiming system consists of a flash vessel and a steam heater, as illustrated in Figure 1. The dimensions of the reclaiming vessel is 2.3m x 3.0 m (IDxTT) and it is designed for an operating volume of 1 – 7 m<sup>3</sup>, which corresponds to approximately 2 – 14 % of the total solvent inventory of the plant.

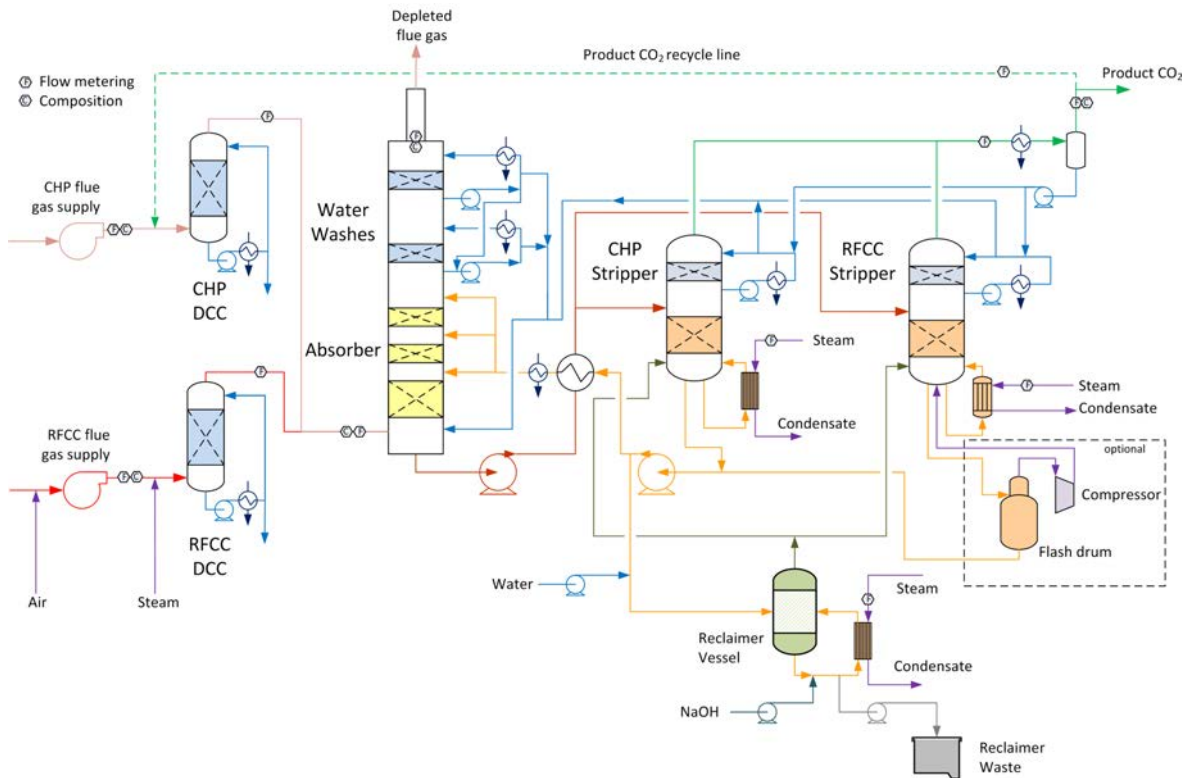


Figure 1: Schematic illustration of the TCM DA amine plant

### 2.1. MEA campaign overview

The MEA test campaign was conducted from 06/07/2015 to 17/10/2015. During the total 1960 hours of operation a wide range of operational process conditions were executed and a total of 4941 tons of CO<sub>2</sub> was captured. The variation of gas and solvent flow rates and stripper bottom temperatures are presented in Figure 2, while further details on typical operating process conditions are presented in Table 1 of Gjernes et al. (2017) [7]. The test campaign was operating on 30 ± 2 wt% MEA and the ranges of the lean and rich CO<sub>2</sub> loadings during the campaign was 0.19 - 0.29 and 0.46 - 0.53 mol CO<sub>2</sub>/mol MEA, respectively. The majority of the campaign was operated with CHP flue gas; however, for a shorter period of 9 days from 16/09/2015 to 24/09/2015 it was operated on a mixture of CHP and RFCC gas, as indicated in Figure 2. Thermal reclaiming was performed towards the end of the campaign, after 1838 hours of operation. Reclaiming was performed for 92 hours, and the plant was run for an additional 28 hours after the reclaiming period before the campaign was concluded 17/10/2015.

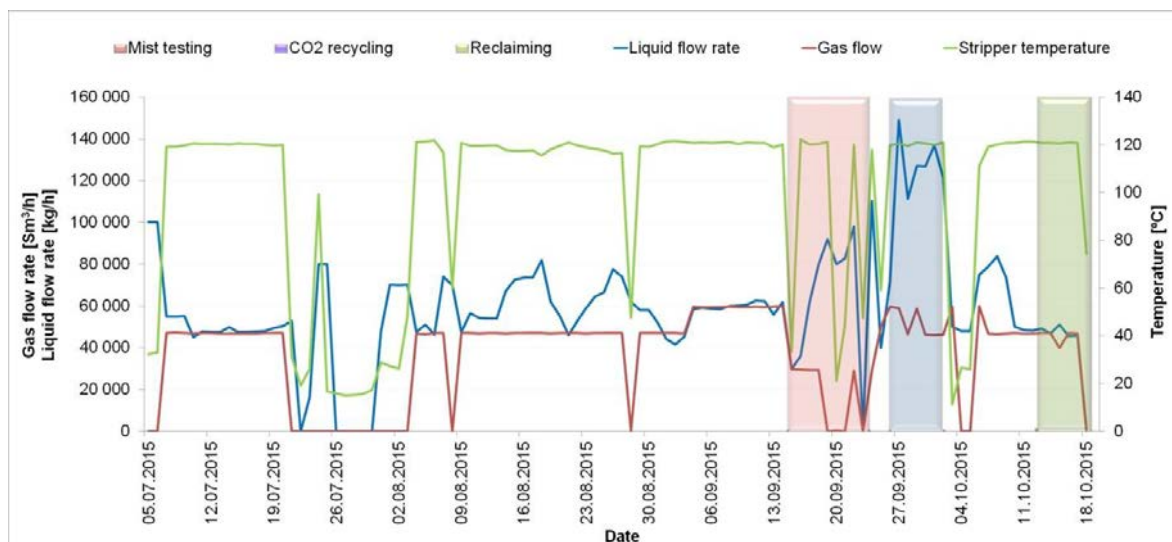


Figure 2: Overview of the daily gas and solvent flow rates and stripper temperatures during the MEA test campaign

### 3. Solvent degradation during the test campaign

#### 3.1. Process conditions that influenced solvent degradation

The MEA test campaign was conducted by executing a wide range of process conditions with frequent operational set-point changes. Such a shifting operating environment might accelerate solvent degradation. The average stripper bottom temperature was 120 °C, with a maximum of 122.5 °C. Superheated MP steam in the temperature range of 130 - 150 °C was used as heat source in the stripper reboiler. The reboiler skin temperature for which the solvent is exposed to, can therefore be assumed to be around 130°C. The solvent will undergo thermal degradation when exposed to temperatures at this level.

The majority of the campaign was operated with CHP flue gas. However, as part of specific mist testing where the aim was to induce formation of aerosols and study its effect on emissions, the plant was operated on a mixture of CHP and RFCC gas [8]. The mist testing where more specifically conducted by;

1. Increasing the concentration of CO<sub>2</sub> in the feed flue gas up to 12 vol% by recycling parts of the captured CO<sub>2</sub> to the absorber flue gas inlet.
2. Mixing portions of the RFCC flue gas with the CHP flue gas.

Up to 10 % mixing of RFCC gas in CHP gas was tested. Typical CHP and RFCC gas concentrations downstream the DCCs are presented in Table 1. As seen in the table, the CHP flue gas contains significant amounts of oxygen which causes oxidative degradation. Exposure to higher concentrations of CO<sub>2</sub> and RFCC gas impurities during the mist testing accelerated the rate of solvent degradation. Further, metal particulate material present in the RFCC gas might have contributed as catalysts for oxidative degradation.

Table 1: Typical CHP and RFCC flue gas conditions downstream DCC conditioning at TCM DA.

Description	Unit	Conditioned CHP gas	Conditioned RFCC gas
Temperature	°C	25 - 50	15 - 50 <sup>(1)</sup>
Pressure	mbar g	Up to 250	Up to 250
Nitrogen	mol %	73 - 79	73 - 79
Oxygen	mol %	13 - 14	3 - 8
CO <sub>2</sub>	mol %	3.5 - 4.0 <sup>(2)</sup>	13.0 - 14.5 <sup>(3)</sup>
H <sub>2</sub> O	mol %	Saturated	Saturated
SO <sub>2</sub>	ppmv	<0.3	<5
NO <sub>x</sub>	ppmv	<5	60
NH <sub>3</sub>	ppmv	<5	<1
CO	ppmv		<3
Particulates	mg/Nm <sup>3</sup>		<sup>(4)</sup>

**Note:**

1. With steam injection.
2. Facility is provided to enable CO<sub>2</sub> recycling, thereby allowing tests with CO<sub>2</sub> concentrations up to about 15 vol%.
3. Facility is provided to enable air dilution, thereby allowing tests with CO<sub>2</sub> concentrations down to about 2.5 vol %.
4. H<sub>2</sub>SO<sub>4</sub>: 10-25 mg/Sm<sup>3</sup>; Other soluble salts (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>+NH<sub>4</sub>HSO<sub>4</sub>+NaCl: 5-10 mg/Sm<sup>3</sup>; Non water soluble salts SiO<sub>2</sub>+Ca and other metals: 0-2 mg/Sm<sup>3</sup>

### 3.2. The impact of process design on solvent degradation

As mentioned above, the main factors causing solvent degradation was elevated operating temperature in the stripper section and exposure to oxygen and contaminants in the flue gas. The effect of thermal and oxidative degradation will not only depend on these factors themselves, but also on the solvent residence times in the sections of the plant where these factors are significant, i.e. the part of the plant where the solvent is exposed to higher temperatures and oxygen and gas contaminants.

The hot solvent inventory (desorber packing, desorber sump, reboiler, hot part of the lean/rich cross heat exchanger and the hot lean and rich solvent piping) calculated for CHP baseline operating conditions are presented in Table 2. For details about the CHP baseline operating conditions it is referred to Faramarzi et al. (2017) [9]. The total of 13.4 m<sup>3</sup> hot solvent inventory is quite significant and corresponds to about 35% of the total solvent inventory. The corresponding solvent residence time is about 20 minutes for CHP baseline operating conditions. The main contributor to the hot solvent inventory is clearly the rather long hot lean solvent pipe, which contributes to 60% of the total hot solvent inventory. The reboiler itself has a rather low solvent residence time; however, the beforementioned reboiler skin temperature of about 130 °C might also contribute to significant thermal degradation as degradation increases exponentially with the temperature.

The solvent inventory exposed to oxygen and the corresponding oxygen exposure time is also presented in Table 2. It is expected that the largest effect of oxygen exposure is seen in the absorber packing, where the actual inventory and exposure time is estimated to about 8 m<sup>3</sup> and 12 minutes, respectively, considering CHP baseline operating conditions. This abovementioned exposure time is also relevant for flue gas contaminants when operating on CHP/RFCC gas mixture.

In order to minimize solvent degradation it is clearly of interest to perform plant design such that the exposure times to oxygen and elevated temperatures are limited. For scale-up purposes it is therefore of specific importance to minimize solvent hold-up in hot parts of the plant.

Table 2: Estimated solvent inventory and residence times for solvent exposed to oxygen and elevated temperatures based on CHP baseline operating conditions (for details about the CHP baseline conditions it is referred to Faramarzi et al (2017) [9]).

Section of the plant	Solvent inventory [m <sup>3</sup> ]		Exposure/residence time [min]	
	Exposed to oxygen	Exposed to temperature > 100°C	Oxygen	Temperature > 100°C
Absorber packing	7.8		11.5	
Absorber sump	9.0		13.3	
Desorber packing		0.9		1.3
Desorber sump		2.3		3.4
Reboiler		0.4		0.6
Lean/rich cross heat exchanger		0.5		0.7
Hot rich solvent piping		1.1		1.6
Hot lean solvent piping		8.2		12.1
Total	16.8	13.4	24.8	19.8

### 3.3. Monitoring of solvent degradation

Solvent degradation was observed and monitored by a number of parameters during the test campaign. Lean and rich solvent samples were frequently withdrawn for solvent analysis. The analytical methods are described by Morken et al (2017) [10]. Firstly the physical properties of the solvent changed during the campaign as shown by the increase of solvent viscosity in Figure 3. The viscosity was measured in TCM DA lab and reported at two different temperatures (30°C and 60°C) and a clear increase of about 50% is observed from the test campaign start until reclaiming started on 12/10/2015.

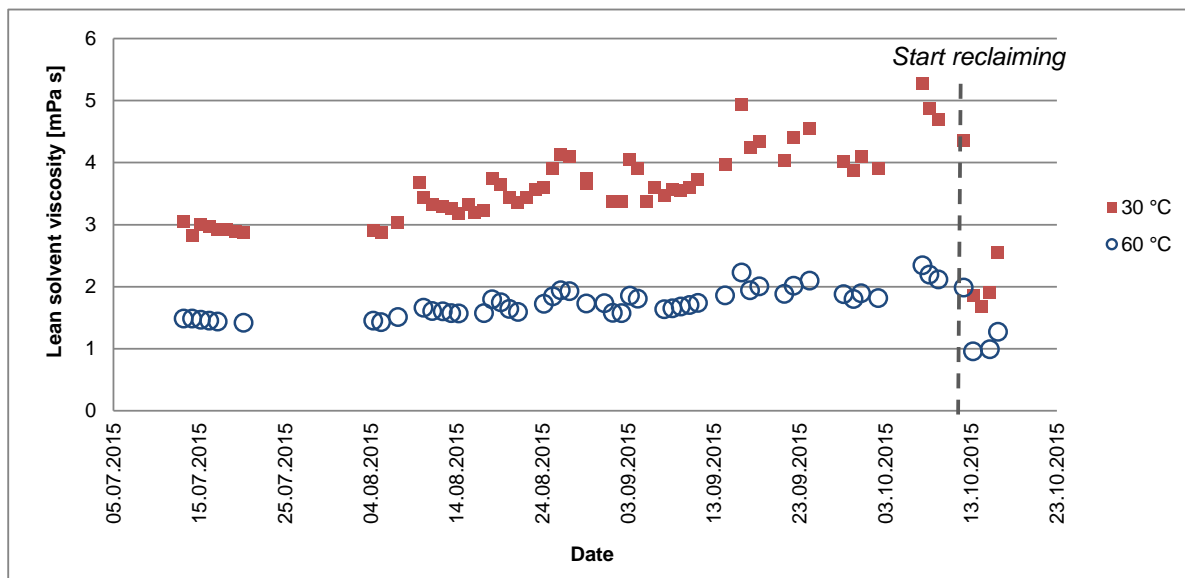


Figure 3: Change in solvent viscosity during the MEA test campaign



A clear observation of solvent degradation was also the change of solvent color during the test campaign. The fresh 30 wt% MEA solvent started out as a clear liquid, which changed color quite fast after contact with flue gas. The solvent became gradually darker during the campaign, until it reached the dark brown color illustrated by the third sample glass from 11/10/2015 in Figure 4.



Figure 4: Picture of solvent samples taken during the campaign. The color change indicates solvent degradation.

Further, the level of volatile degradation products in the gas phase increased significantly during the period of Mist testing. Morken et al (2017) presents detailed results regarding ammonia emissions, which is associated with presence of ammonia in the solvent originating from solvent degradation [10]. Emission of ammonia is also highly dependent on operating conditions; however the observed build-up of ammonia in the solvent is regarded as a clear sign of solvent degradation.

Heat stable salts started building up in the solvent as shown in Table 3 before it reached a maximum of 0.203 mol/kg just before reclaiming started on 12/10/15. More detailed results concerning HSS analysis are presented by Morken et al (2017) [10]. The concentration of main degradation products was also monitored continuously and shows a significant increase as the test campaign progressed. It is referred to Morken et al (2017) for details [10].

Table 3: Total concentration of heat stable salts (HSS) during the campaign.

Date	Concentration of heat stable salts (HSS) [mol/kg]
13.07.2015	0.011
20.07.2015	0.038
10.08.2015	0.052
17.08.2015	0.069
24.08.2015	0.083
31.08.2015	0.120
07.09.2015	0.108
14.09.2015	0.141
21.09.2015	0.149
28.09.2015	0.138
12.10.2015	0.203

Additional parameters which are important to monitor during operation of the amine plant are solvent foaming tendency and metal ion concentration. The latter gives indications of plant corrosion and was also monitored during the test campaign. The results are presented by Hjelmaas et al. (2017) [11].

#### 4. Reclaiming procedure and operational experience.

The reclaimer was operated in a semi-continuous operation mode, meaning that solvent was continuously fed to the reclaimer vessel, while the reclaimer waste was allowed to accumulate and was only disposed at the end of the test campaign. The process was operated continuously for 3 days with exception of one unexpected plant stoppage for about 3 hours on the 13/10/2015.

The reclaimer vessel was initially filled with water. Water circulation and steam heating was started before the solvent feed to the reclaimer vessel. The rather large volume of initial water evaporated during the reclaiming operation and resulted in dilution of the solvent as shown in Figure 5.

The reclaimer liquid was circulated in the reclaiming system loop through the steam heat exchanger at a circulation rate of approximately 165 m<sup>3</sup>/h. No boiling occurs in the steam heater, but the liquid flashes when it enters the evaporator vessel. The evaporating level was controlled by adjusting the steam rate supply. As the liquid became more concentrated, its boiling temperature increased and the rate of evaporation was reduced. The percentage of degradation products in the reclaimer, and the resulting temperature were slowly increasing. Upon reaching high temperature, high viscosities and high amounts of precipitates, the reclaimer feed was stopped.

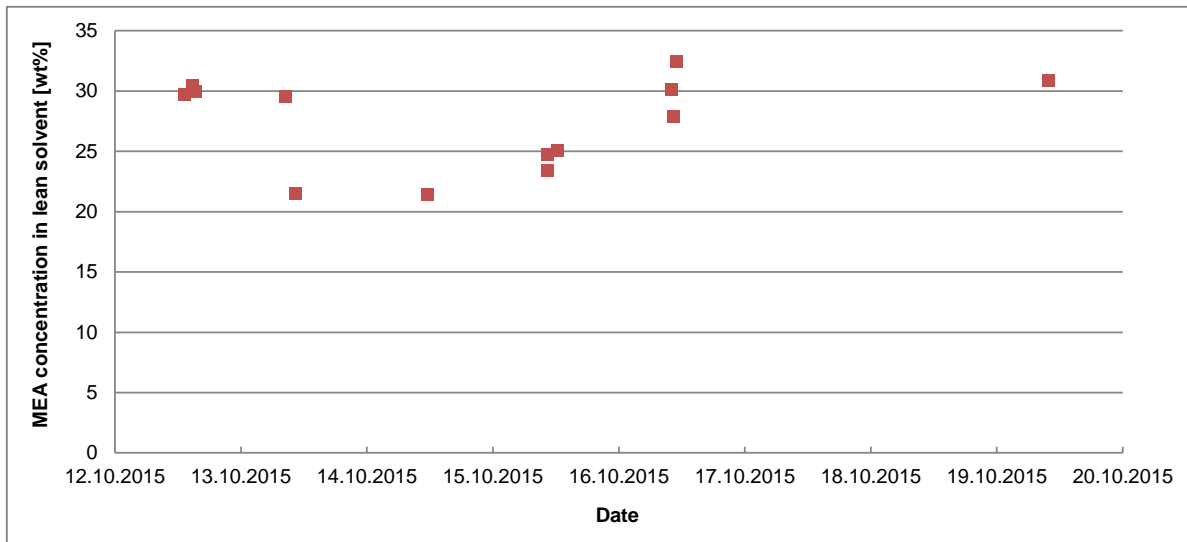


Figure 5: MEA concentration in the lean solvent during reclaiming

#### 4.1. Solvent and water feed rate.

The reclamation unit was fed with a continuous slip stream of the lean amine solvent from downstream the stripper. The reclaiming unit was also fed simultaneously with water in order to control the boiling temperature of the reclaiming fluid below 160 °C. Figure 6 presents the solvent and water flow rates along with the reclaiming liquid temperature.

The solvent slip stream corresponded to 4 - 5 % of the lean solvent circulation and was up to a maximum of about 3 000 kg/h as illustrated in Figure 6. A total accumulated amount of 46 000 kg solvent was fed to the reclaiming unit during the whole period of 3 days. This corresponds to about 110 % of the total solvent inventory.

#### 4.2. Steam consumption

The reclaiming heat duty variations were according to the changing amount of the lean solvent slip stream directed to the reclaiming vessel. As shown in Figure 7, in order to vaporize MEA in the reclaiming unit a significant amount of heat was required. At times, the amount of heat used for reclaiming was almost equal to the heat used to regenerate the solvent in the stripper. As reclaiming of MEA is energy intensive, it is important to optimize the amount of lean amine slip stream sent to the reclaiming unit. However, as shown in Figure 6 the flow of slip stream varied due to the fluctuations in the process conditions and it was not possible to achieve a constant flow during the reclaiming procedure.

The reboiler heat duty increased significantly when the reclaiming unit was brought on stream and then plateaued at about 2 500 kW. This was due to the large amount of water that was initially added to reclaiming unit, which evaporated from the reclaiming vessel and caused dilution of the solvent. The concentration of MEA was consequently reduced to about 21 wt% as shown in Figure 5. Thus the amount of water to be boiled off in the stripper was much larger, causing higher energy numbers.

The reclaiming liquid circulation and steam heating continued for 2 days after the solvent feed was stopped in order to evaporate as much as possible of the useful MEA solvent and concentrate the waste.

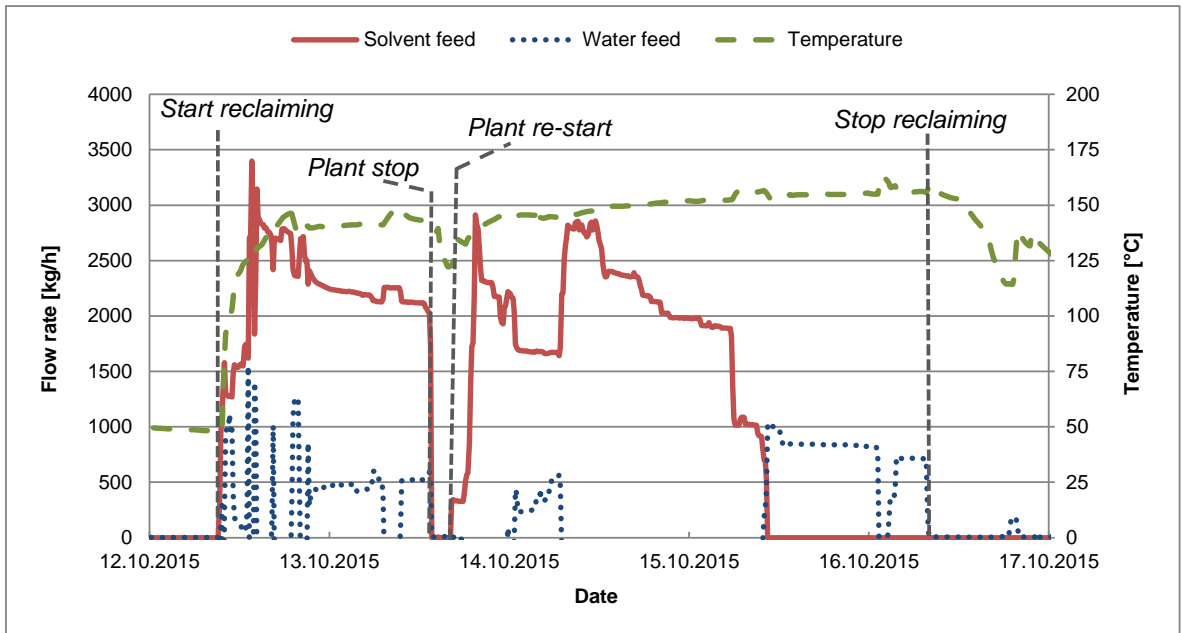


Figure 6: Reclaimer solvent slip stream, water feed rate and reclaimer liquid temperature.

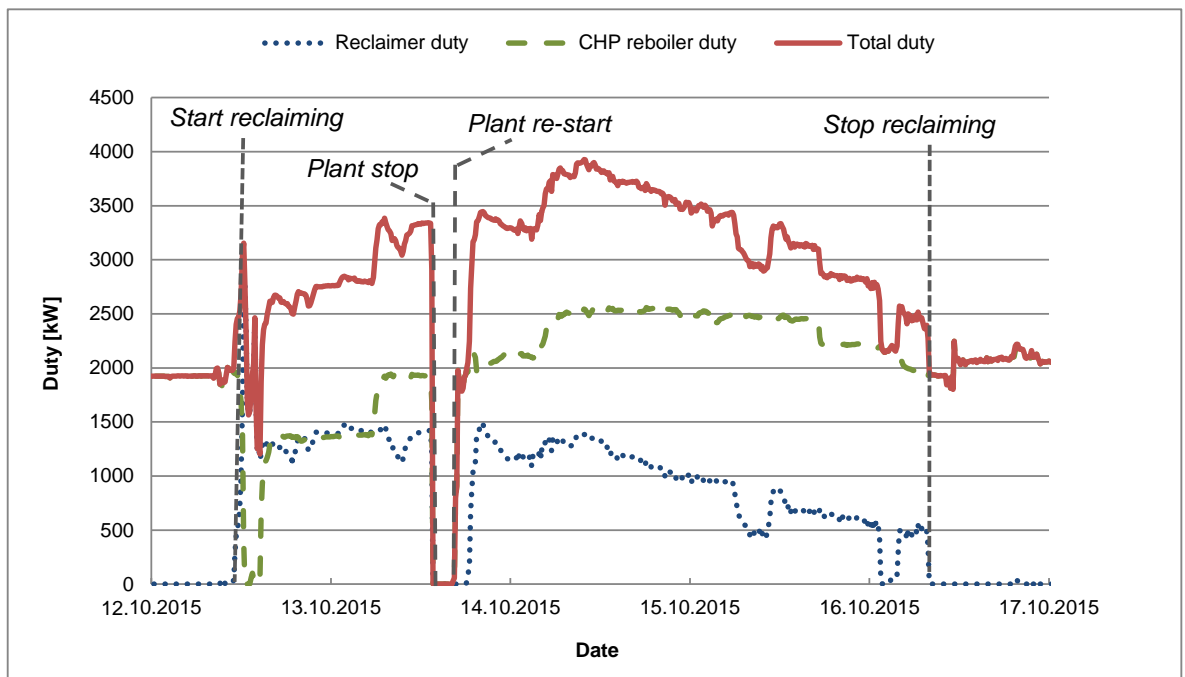


Figure 7: Steam consumption during reclaiming.

### 4.3. Dosage of NaOH

Aqueous solution of 50 wt% NaOH was added to the reclaimer vessel via the reclaimer liquid circulation loop in order to stabilize anions of amine heat stable salts by converting them to sodium salts and liberating the amine according to Reaction (1). The recovered amine and water vapor was returned to the stripper sump.

A dosage rate of 3 L NaOH/m<sup>3</sup> solvent was applied during reclaiming based on previous experience at TCM DA. In total 227 liters 50% NaOH was added, which corresponds to 4299 mol Na<sup>+</sup>.

According to Reaction (1), the stoichiometric ratio of NaOH to HSS should ideally be 1:1. This is a very rough estimate since the actual ratio depends on the electrical charge of the anions. The concentration of HSS components was 0.203 mol MEA-eq/kg solvent at the point of reclaiming start 12.10.15 (see Table 3). With a total solvent inventory of 40 800 kg in the plant at the time, this corresponds to 8282 mol HSS. A stoichiometric check shows excess HSS compared to NaOH, which might cause additional MEA loss in the reclaimer waste.

### 4.4. Reclaimer waste

After the reclaiming operation was concluded the majority of the concentrated waste was drawn off to the flushing line and passed through the sea water cooler to the IBC (Intermediate Bulk Container) drainage system. The reclaimer fluid was quite concentrated and viscous at the time, thus some water was added in order to dilute the waste and enable unloading of the vessel. The total concentrated waste was collected in IBCs and added up to a total of about 6 m<sup>3</sup>. This corresponds to about 1.3 kg reclaimer waste/ton CO<sub>2</sub> captured during the overall campaign, which is well below reported numbers in the literature. Further, the reclaiming process was initiated when HSS concentration reached 0.203 mol/kg, as beforementioned. The actual necessity of reclaiming at this level of HSS must be considered based on the actual solvent condition and potential plant corrosion issues, i.e. at this moment the reclaiming campaign was not necessary but rather conducted for demonstration purposes in the test campaign. The waste/ton CO<sub>2</sub> capture would thus be even lower in an actual necessary reclaimer case. The reclaimer vessel and piping was afterwards flushed with water.

## 5. Efficiency of thermal reclaiming

In order to investigate the reclaiming efficiency and demonstrate how the solvent quality is recovered and maintained by the reclaiming process, samples were frequently taken from the lean amine solvent, the reclaimer liquid and reclaimer vapor. The samples were analyzed for MEA, degradation products, HSS and metals, and the results are summarized in Table 4.

The concentration of degradation products in lean amine was analyzed throughout the test campaign and the results are presented by Morken et al (2017) [10]. Figure 8 below shows the concentration of degradation products in the lean amine solvent during the reclaiming operation. It is seen that the degradation products is efficiently cleaned from the lean amine and about 95% percent of the degradation products was removed. A small increase in concentration from day three indicates that degradation is significant during reclaiming, likely due to thermal degradation due to operation at elevated temperatures inside the reclaimer vessel.

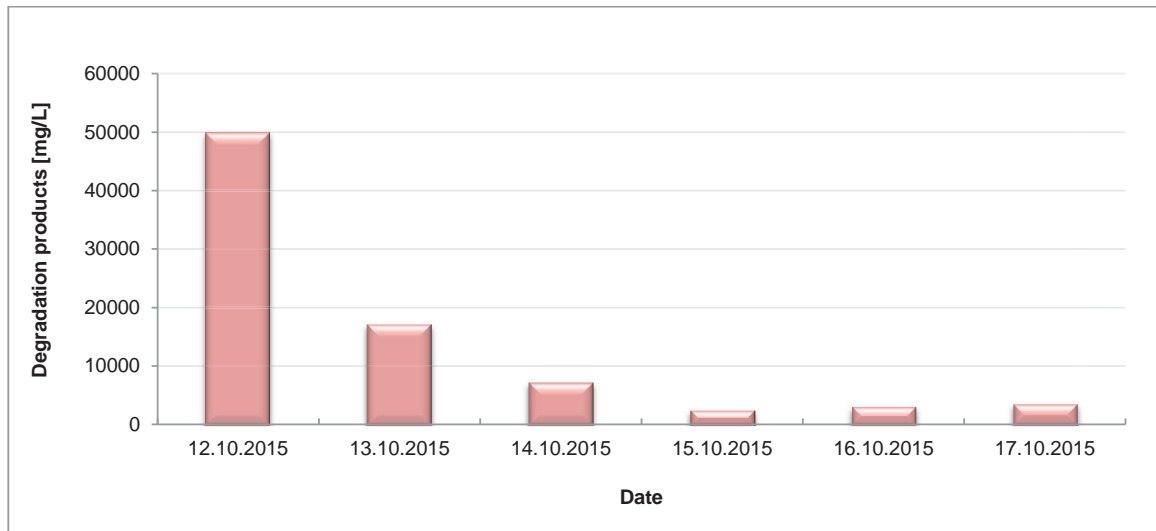


Figure 8: Concentration of degradation products (D-mix) in lean amine during reclaiming

A very similar trend is seen for the concentration of metal elements iron (Fe), Nickel (Ni) and Chromium (Cr) in Figure 9 below. The concentration is reduced by more than 95% after reclaiming.

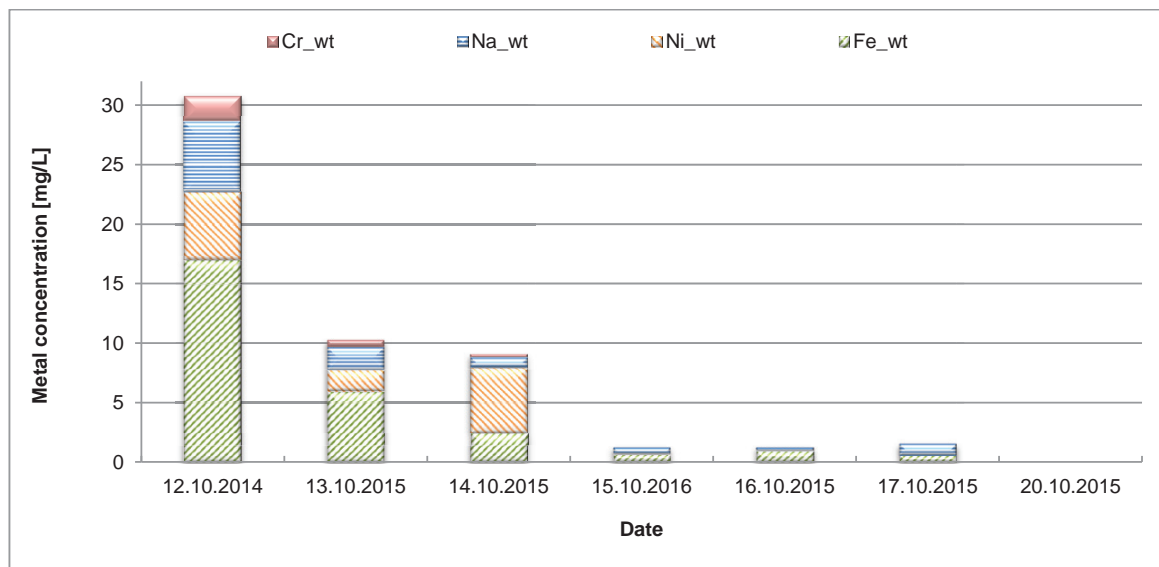


Figure 9: Concentration of metal elements in lean amine during reclaiming

The trends for heat stable salts in the lean solvent, reclaimer liquid and the reclaimer vapor are shown in Figure 10. Again, the concentration of HSS in lean amine is rapidly reduced to less than 5% of the start concentration, as shown by the blue columns in the graph. The accumulation of HSS in the reclaimer liquid is also clearly seen by the

red columns. HSS could not be detected in the reclaiming vapor return to stripper, as expected. Figure 11 presents the concentration of MEA, NaOH and HSS in the reclaiming liquid during the reclaiming process. Most of the MEA is evaporated during the period as seen in the figure. HSS and Na<sup>+</sup> is accumulated, however MEA seems to be in excess, also at the end of the reclaiming.

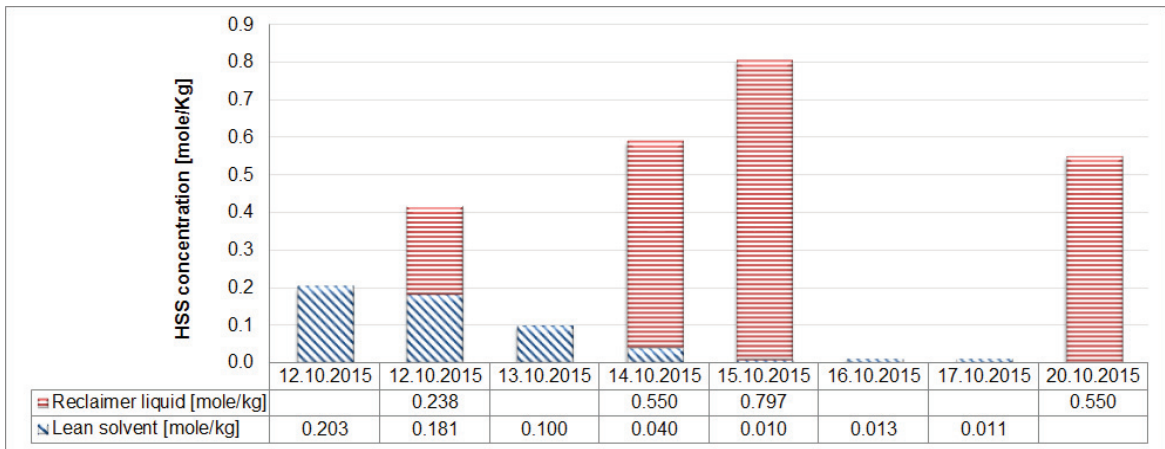


Figure 10: Concentration of HSS in lean amine and the reclaiming liquid

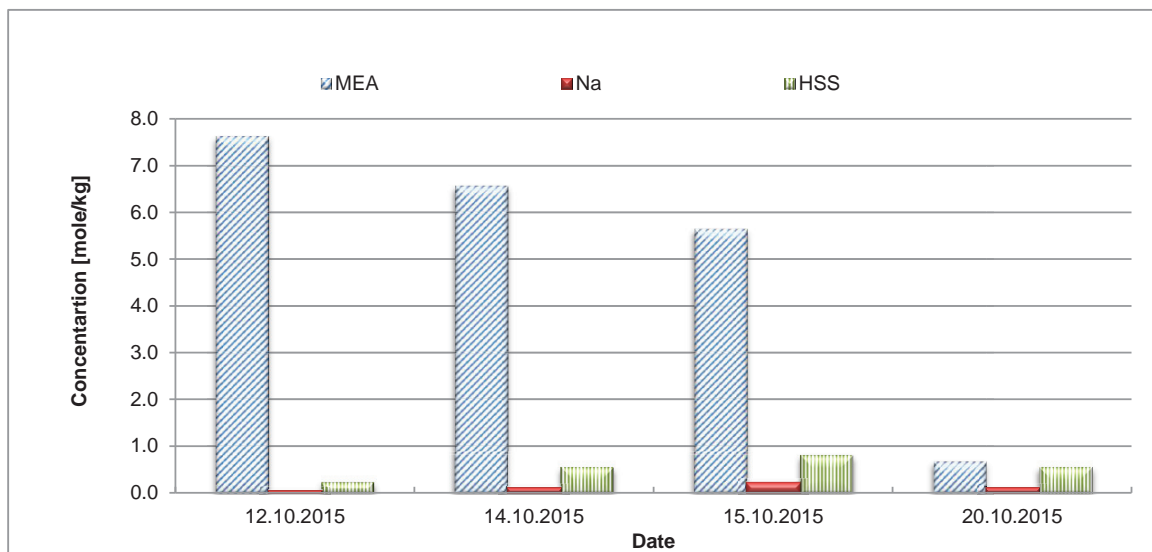


Figure 11: Concentration of MEA, NaOH and HSS in the reclaiming liquid

The color of the solvent changed back to a lighter color after reclaiming as illustrated by the fifth sample glass from 15/10/2015 in Figure 4. Based on analysis of the reclaiming waste and assessment of the total MEA inventory in the plant before and after reclaiming, it is estimated that about 500-550 kg MEA was lost to waste during

reclaiming. This corresponds to 4% of the total inventory (according to Table 4) and 0.11 kg MEA/ton CO<sub>2</sub> captured.

Table 4: Amount of HSS, degradation products and metals removed from the solvent and MEA lost in reclaimer waste

		12.10.2015	17.10.2015	
		Before reclaiming	After reclaiming	Removal
Total solvent inventory	[kg]	40800	37600	
MEA	[kmol]	199	191	4 %
HSS	[mol]	8280	413	95 %
Degradation products	[kg]	1837	129	93 %
Metals	[g]	1133	56	95 %

## 6. Solvent performance after reclaiming

After the reclaiming operation had been concluded the plant was operated for another 28 hours at a flue gas flow rate of 47,000 Sm<sup>3</sup>/h. Two test cases were conducted during this period, and these are used for comparison to other similar tests conducted previously in the campaign with a fresh solvent. The two test cases after reclaiming is designated “T4” and “T5”, while the optimum energy case with the use of anti-foam (case 2B6) from previously in the campaign is used for comparison. The total operating hours at the point in time when case 2B6 was conducted was approximately 950 hours. The overall 2015 MEA campaign and the entire specific test series carried out to investigate the capture plant performance is described by Gjernes et al. (2017) [7].

Figure 12 summarizes the operation before and after reclaiming. T4 and T5 were operated with 24 and 18 m absorber packing height, respectively. During T4 the amine plant was a bit unstable while there were stable conditions during T5. Case 2B6 was operated with 24 meters of packing height. The plant performance after reclaiming was comparable to the optimum performance achieved earlier in the campaign and there were no significant indications of reduced solvent quality.

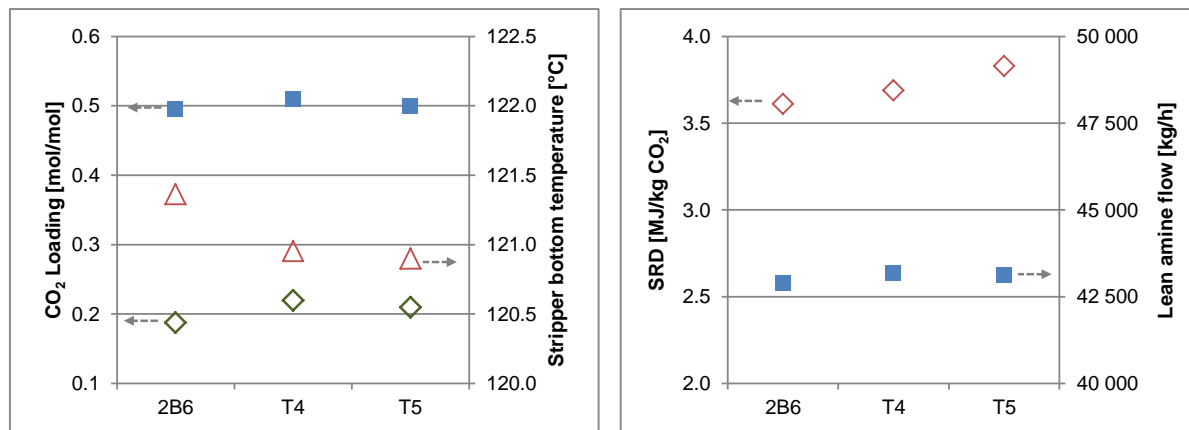


Figure 12: Results for test cases 2B6, T4 and T5: To the left rich- (squares) and lean-loading (diamonds) and stripper bottom temperature (triangles) and to the right SRD (diamonds) and lean amine flow (squares).



## 7. Discussion and future work

Monitoring the amine concentration and CO<sub>2</sub> loading is very important for optimal operation. At TCM DA the solvent concentrations are mainly followed on a daily basis with manual samples and analysis. Further, a number of analyzers are available for real-time online monitoring, i.e. conductivity, density and pH analyzers. These online results can be correlated to enable a closer follow-up of the solvent condition.

As an effect of reclaiming start-up, the solvent in the main process was diluted by water evaporating from the reclaiming vessel. In future campaigns, extra care will be taken not to disrupt the main process during reclaiming. The deviation in solvent concentration could have been corrected at an earlier stage with an online estimate of solvent concentration.

The reclaiming environment is very harsh to the solvent due to high temperatures (up to 160 °C). The elevated temperatures represent a risk of additional thermal degradation. Care must therefore be taken in order to limit the residence time of the reclaiming solvent and thereby unnecessary degradation. Thus frequent manual solvent sampling or online analyses are required in order to monitor the progress of reclaiming and terminate the reclaiming process when the target is reached. In this test campaign it was very successfully demonstrated a 95 % cleaning efficiency when circulation a 4-5 % slip stream through the reclaiming vessel for three days, which added up to an accumulated reclaimed volume of about 110% of the total solvent inventory.

The total HSS analysis indicates that the amount of NaOH added during reclaiming was on the stoichiometric low side to limit the MEA loss in the reclaiming waste. It is therefore reasonable to believe that additional MEA was lost in HSS to the waste. Thus, the total MEA loss of 4% could be reduced even further by optimizing the NaOH dosage. However, the actual effect of NaOH addition on MEA release from HSS should be investigated more in detail.

There is little information available in the literature that addresses how the build-up of impurities impacts the energy demand for regenerating MEA in the stripper i.e. reboiler heat duty. However, the density and viscosity of the solvent increased with the increasing level of contaminants as discussed in Section 3. This will cause reduction of the solvent heat transfer coefficient and consequently the heat transfer efficiency in the reboiler. The impact of accumulation of the contaminants on the specific heat capacity of amines is also very little addressed in the literature. However, it is expected that degraded MEA has higher specific heat capacity than MEA which in turn could increase the sensible heat needed to regenerate the solvent in the stripper. It is recommended to investigate these effects in the future.

As the amine plant was only operated for 28 hours after solvent reclaiming, a very limited investigation of the effect of removing the aqueous phase contaminants on the energy requirement of the stripper reboiler was performed. In future tests, sufficient time should be allowed to investigate in detail and compare the solvent performance at the beginning of the test campaign to the performance just before reclaiming and just after reclaiming.

In order to further optimize the process and reduce disposal problems both the reclaiming procedure itself and the collection and drainage of the reclaiming waste can be improved. The rapid cleaning of the lean solvent suggests running the reclaiming vessel more frequently for shorter time periods (for example 12 hours a week) as one option to avoid degraded solvent to accumulate in lean amine. In this way the acceleration of degradation reactions could also be minimized. The draining and flushing operation can be improved by using less water or even small amounts of steam for keeping the reclaiming vessel fit for purpose. This will reduce the amounts of waste.

## 8. Conclusions

A test campaign with 30 wt% MEA has been conducted for a total of 1960 hours at the CO<sub>2</sub> Technology Centre Mongstad. The present paper discusses main causes of solvent degradation and various parameters for monitoring degradation products. Further, the effect of process design and operating conditions on solvent degradation is discussed, and thermal reclaiming is evaluated as a technique for removal of degradation products and other contaminants in the MEA solution.

The solvent condition was closely monitored during the test campaign and several observations such as increasing solvent viscosity and darker solvent color indicated solvent degradation. Solvent exposure to oxygen and flue gas contaminants in the absorber and operation at elevated temperatures (above 100 °C) in the stripper section are highlighted as main causes for degradation. When performing scale-up to commercial CO<sub>2</sub> capture units it is recommended to minimize the hot solvent residence time in the plant, in order to minimize solvent degradation.

Thermal reclaiming has demonstrated an efficient clean-up of the MEA solvent. The cleaning efficiency was about 95% with respect to degradation products, HSS and metal elements. The solvent viscosity returned to normal values and the solvent color was normalized to a clearer and more yellow appearance. The quality recovery of the solvent was further assessed by an evaluation of the capture process after the reclaiming was concluded by comparing the solvent performance to results obtained at earlier stages of the test campaign and there were no significant indications of reduced solvent quality.

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