Review

A review of degradation and emissions in post-combustion CO_2 capture pilot plants

Vanja Buvik [a], Karen K. Høisæter [a], Sorun J. Vevelstad [b], Hanna K. Knuutila [a],*

[a] Department of Chemical Engineering, NTNU, NO-7491 Trondheim, Norway
[b] SINTEF Industry, NO-7465 Trondheim, Norway

A B S T R A C T

Pilot plant testing of amine solvents for post-combustion CO_2 capture is an essential tool for fully understanding degradation behaviour and emission profiles under realistic process conditions. This review aims to summarise the lessons learned in different pilot campaigns, as well as to give recommendations how solvent stability and emissions can be monitored and assessed. A total of 18 different pilot plants and 29 individual campaigns were studied, of which the majority used ethanolamine and flue gas from coal-fired power plants.

The findings of the review are that solvent stability data from different pilot plants show significantly higher operation time in which the solvent is stable, when extensive flue gas pretreatment is implemented. It was also found that no single degradation compound seems to suffice for the assessment of the degradation of a solvent, even for the widely studied ethanolamine process. Monitoring of the total liquid-phase heat stable salt concentration, as well as gas phase ammonia concentration may, however, give an informative picture of the state and degradation of the solvent. There seems to be a lack of universally applied analytical methods, which makes it difficult to compare one campaign or location to another. The implementation of validated and documented analytical standards in this regard will facilitate production of reproducible, reliable and comparable data for future solvent stability assessment.

1. Introduction

Removal of CO_2 from gas streams has been performed industrially for almost a century to provide pure CO_2 for industrial purposes, as well as sales-quality natural gas. CO_2 capture and storage is also predicted to be vital for achieving the goals of the Paris agreement and combat anthropogenically caused global warming (Rogelj et al., 2018). In recent years, several new solvents have been developed (Feron et al., 2020) and the interest towards a safe and optimised operation of the plants has increased due to the potential use of the technology for large-scale capture of CO_2 from power plants and other industries. As a consequence of the scaling up, however, various challenges have arisen. In a large-scale plant, solvent degradation, energy consumption, and potential emissions of the solvent or degradation compounds, can have significant environmental and economic consequences. Therefore, to gain a better understanding of the large-scale operation, the process and operating conditions are first studied through a pilot campaign allowing investigation of the effect of flue gas composition, impurities, and solvent performance, including degradation, corrosion, and emissions, on the process performance and costs.

Degradation, as well as corrosion, are considerable challenges in amine-based CO_2 capture. As the degradation increases, the amount of make-up solvent that needs to be added throughout the campaigns increases. Among other, Moser et al. (2020) summarised that solvent-make-up required in 12 campaigns performed with 30 wt% (aq.) ethanolamine (MEA) varied from 0.3 to 3.6 kg $t_{CO_2}^{-1}$, showing a 10-fold difference. Furthermore, a feature that is often observed in pilot campaigns using MEA is that after stable operation for a certain amount of time, a sudden and rapid increase in degradation product formation and concentration of dissolved metals occurs (Dhingra et al., 2017; Rieder and Unterberger, 2013). What causes this abrupt spike in degradation rate has not yet been fully understood and prediction of when it will take place is therefore not possible. This effect has also been seen in laboratory-scale studies and it is therefore commonly assumed that dissolved iron and other metals catalyse the oxidative amine degradation in the absorption process also in pilot-scale (Bello and Idem, 2005; Chi and Rochelle, 2002; Strazisar et al., 2003; Léonard et al., 2014). Furthermore, certain degradation products also affect corrosion rates both positively and negatively, as they can act as chelators or inhibit the build-up of a protective film on the metal surface of the plant (Kohl and Nielsen, 1997; Tanthapanichakoon et al., 2006).

The identification of high concentrations of typical primary oxidative degradation products (formed in the first stages of degradation) in solvents used in pilots with real flue gas has shown that oxidative degradation indeed is a dominant degradation mechanism in the

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* Corresponding author.
  E-mail address: hanna.knuutila@ntnu.no (H.K. Knuutila).

Abbreviations

abs	absolute
AMP	2-amino-2- methyl-1-propanol
aq.	aqueous
ATR	attenuated total reflectance
CHP	combined heat and power
CCS	carbon capture and storage
DeSOx	removal of SO_X
DeNOx	removal of nitrogen oxides (NO_X)
DNPH	2,4- dinitrophenylhydrazine
ED	electrodialysis
EDX	energy dispersive X-ray microanalysis
ELPI	electrical low pressure impactor
ESP	electrostatic precipitator
FGD	flue gas desulphurisation
FMPS	fast mobility particle sizer
FT-IR	Fourier- transform infrared spectroscopy
GC	gas chromatography
HSE	Health, Safety and Environment
HSS	heat stable salts
IC	ion chromatography
ICP	inductively coupled plasma
LC	liquid chromatography
MDEA	*N*-methyl diethanolamine
MS	mass spectrometry
NDIR	non- dispersive infrared
NG	natural gas
OES	optical emission spectroscopy
OPC	optical particle counter
ppb	parts per billion
ppm	parts per million
PR	particulate removal
PTR	proton- transfer reaction
Pz	piperazine
RFCC	residual fluidised cracker
SCR	selective catalytic reduction
SEM	scanning electron microscope
TONO	total nitrosamine
VOC	volatile organic compounds
WESP	wet electrostatic precipitator
WFGD	wet flue gas desulphurisation
QTOF	quad time of flight

absorption process (Vega et al., 2014). Typical concentrations of oxygen in the flue gas is generally between 4% and 15% and lower in flue gases originating from coal-fired power plants than gas-fired power plants. Since the solvent has direct contact with the flue gas oxygen in the absorber and since the solubility of oxygen decreases with increasing temperature, the concentration of dissolved oxygen is the highest in the absorber and the absorber sump. Oxidative degradation is therefore assumed to primarily take place here, although the elevated temperatures in the rich solution also could increase the reactivity despite of low oxygen concentrations (Chi and Rochelle, 2002).

Thermal degradation primarily takes place during the solvent regeneration, at elevated temperatures and in the presence of CO_2 (Davis and Rochelle, 2009). Products of the thermal degradation process, as well as some of the oxidative degradation products, are often more volatile than the amines themselves and are likely to evaporate in the absorber. This increases the chance of emission to the atmosphere together with the purified flue gas, unless emission reduction technologies are in place (Rochelle, 2012).

There are well known methods to reduce degradation. Flue gas pretreatment technologies, removing impurities such as SO_x and NO_X gases, as well as particulate matter such as fly ash are implemented to some extent in most pilot campaigns. Methods such as "Bleed and Feed", removal of a part of the degraded solvent and refilling with fresh solvent throughout the process, have recently been thoroughly tested without success (Moser et al., 2020). Apart from the "Bleed and Feed", solvent reclaiming is often used to limit the amount of makeup solvent and maintaining the operation.

The purpose of this review is to summarise available data from pilot tests using amine solvents for post-combustion CO_2 capture and real flue gas or industrial gases. It covers traditional bench-mark amine 30 wt% MEA as well as new amines and amine blends proposed for post-combustion CO_2 capture. The emphasis will be put on solvent stability, emissions and corrosion and how these aspects are monitored, and the three concepts are seen in light of one another. The review aims to be of help for future pilot campaigns and how these concepts can and should be monitored. Although a large number pilots and campaigns for post-combustion capture of CO_2 exist (Idem et al., 2015) and have taken place, those from which reported solvent stability or emission data are not available, are also not included here.

Furthermore, most of the data given originates from journal papers and conference proceedings, but to give a complete picture and overview of the pilot plants and campaigns as possible, some of the given data has been found in conference presentations. The campaigns included have also been limited to the latest decade, to provide up-to-date information about current developments and trends.

2. Overview of pilot plants and campaigns

Table 2.1 lists the pilot plants included in this review. Most of the pilots use a slip-stream of the flue gas from power plants or industrial sources. Furthermore, the table includes only pilot plants where data for emissions or degradation has been published. A more extensive overview of pilots and demonstration plants for post-combustion CO_2 capture can be found elsewhere (Cousins et al., 2016; Idem et al., 2015).

As expected, the CO_2 capture capacity correlates with the absorber diameter, so that the pilot with the smallest absorption capacity (kg CO_2 h^{-1}) also has the smallest absorber diameter. The absorber packing heights vary from 3 to 24 m. Most of the plants have at least one water wash section on the top of the absorber to limit the emissions of volatile solvent components and degradation compounds.

Table 2.2 presents an overview of the gas compositions of the pilot campaigns included in this study. It also shows the gas pretreatment performed before the amine scrubbing. Altogether 19 different flue gas sources were studied, of which 16 originated from coal-fired power plants. The concentrations of CO_2 are between 11 and 14 vol% (dry) for coal-fired power plants, whereas for gas burners, it is typically lower. Pilot campaigns performed in connection to the cement industry have to deal with CO_2 concentrations up to 18 vol%. The pilot plant at Tiller in Norway, receives flue gas from a propane burner, and the gas can be diluted with air or CO_2 to simulate different industrial cases. Technology Centre Mongstad DA (TCM) has a possibility to use a slip-stream from natural gas-fired combined heat and power plant (CHP) or a slip-stream from residual fluidised cracker unit (RFCC). Similarly, the National Carbon Capture Center (NCCC) in Alabama, USA, has two available gas streams for solvent testing, one coal, and one simulated natural gas stream. Therefore, gas streams of both TCM and NCCC vary in their concentrations of H_2O, CO_2, O_2, NO_x and SO_2, depending on the choice of flue gas source. The Mobile Test Unit (MTU), built and operated by Aker Solutions, has been used at three different test locations in Norway, Scotland and the USA, two with coal-derived flue gas and one time with

CHP flue gas at TCM, where degradation data is available from the first two.

In spite of this being a review focusing on pilot scale studies using real flue gas, some additional studies using synthetic flue gas have been included in the evaluation of how amine solvents degrade. These campaigns are given separately in Table 4.8, and have been included because of their extensive analytical work, giving interesting insights on solvent stability, to support trends or shed light on topics included in the discussion.

2.1. Pretreatment technologies

As mentioned in the introduction, removal of contaminants before the CO_2 capture process, limits the possibility of unwanted side reactions of the amine solvent taking place, leading to solvent degradation and deterioration of the overall process performance. The need for pretreatment varies with the type of flue gas, which contaminants it typically contains and in which concentrations they are present. It also depends on the solvent itself. As some of these contaminants are causes of respiratory problems and of environmental concern, systems for removal of these from flue gas have been in use for half a century already. As shown in Table 2.2, in most of the pilot locations at least some pretreatment is used. Here, we separate the contaminants into three categories: particulate matter (ash, soot and catalyst fines), NO_x and SO_2/SO_X, and treatment technologies for each category will be briefly presented below (Meuleman et al., 2016).

Particulate matter is usually removed by wet or dry electrostatic precipitation (ESP). The ESP applies a negative charge to the particulate matter, facilitating their attachment to a positively charge electrode. The dry ESP then removes the particulates from the electrode by mechanical or magnetic impact whereas the wet ESP uses a water wash. It is also possible to apply a filter for the removal of particles. Pressure drops when particulates start accumulating in the filter and this limitation weighs against the otherwise high removal efficiencies (>99.95%) and simplicity of the method (Nicol, 2013; Meuleman et al., 2016).

NO_X gases are typically removed either by selective catalytic reduction (SCR) or a non-catalytic reduction (SNCR), reducing them to N_2 and water, where SCR holds the largest market share. The SCR process takes place at temperatures between 160 and 350 °C, whereas SNCR has a temperature requirement closer to 1000 °C (Meuleman et al., 2016).

SO_2/SO_X gas is not just a contaminant deriving from the combustion process itself, but is also formed when sulphur components pass through a NO_x-removal unit. It is even occasionally added to the ESP for reducing the resistivity of the fly ash. SO_2/SO_x can be removed in a wet flue gas desulphurisation (WFGD) unit, where the acidic nature of SO_x allows it to be scrubbed out by an alkaline lime stone ($CaCO_3$) solution. There are also dry or semi-dry FGD systems available, relying on dry alkaline sorbents, but the WFGD systems have approximately 84% of the market. The FGD step has the additional benefit of removing chloride from the flue gas, washing it out with the sulphur loaded lime stone (Zhu, 2010; Meuleman et al., 2016).

3. Analytical methods used in pilot campaigns

In amine-based post-combustion CO_2-capture, one of the main challenges is solvent degradation (Rochelle et al., 2001), which requires a reliable solvent monitoring strategy. The main goal of this monitoring is often to quantify the concentration of the intact starting amines. In laboratory scale experiments, knowing the change in amine concentration over time allows assessment of the stability of the solvent system. However, in pilot scale, where the amines chosen are often relatively stable, the amine concentration is also measured to ensure that the amine and water concentrations stay constant. In both cases the analytical method used has to be fast, accurate, and straightforward (Cuccia et al., 2018).

Another target for the monitoring of the solvents is to identify the degradation products of the amines. Degradation products are typically categorised into five main classes: amine derivatives, acids, aldehydes, amides, and nitrosamines. Compared to the analysis of the starting solvent components, the study of degradation compounds is a more challenging endeavour (Cuccia et al., 2018). Firstly, many of them have an unknown structure. Moreover, the high concentration of the starting amine in the solvent can make it hard to detect degradation compounds that are typically present at low levels and even at trace amounts (da Silva et al., 2012). There are multiple analytical methods to choose from when analysing these species, with different advantages and disadvantages. When choosing an analytical method, nature of the compounds, matrix and concentration ranges of the analytes must be regarded. Dissolved metal species can also be found in the solvents and these are measured to monitor corrosion. Many monitoring technologies for gaseous emission have been reported (Kolderup et al., 2020) and a large number of publications studying aerosol formation mechanisms, as well as aerosol reduction technologies, have been published in the last five

Table 2.1
An overview of the dimensions of the different pilot plants studied and compared in this review. (Y = yes)

Pilot plant	CO_2 cap. rate [kg h^{-1}]	Water/acid wash	Abs. diameter [m]	Abs. packed height [m]	Reference
Aioi Works	830	Y	0.85	15	Nakamura et al. (2013, 2014), Okuno et al. (2017)
Brindisi	2500	Y	1.5	22	Rieder et al. (2017), Mangiaracina et al. (2014), Kamijo et al. (2013), Enaasen et al. (2014)
CAER 0.1 MWth	10		0.1	3.25	Thompson et al. (2014), Frimpong et al. (2013), Cousins et al. (2016)
CAER 0.7 MWe					Thompson et al. (2017a)
Changchun	100		0.35	8	Feron et al. (2014)
Esbjerg	1000	Y	1.1	17	Knudsen et al. (2009)
Ferrybridge	4167	Y			Fitzgerald et al. (2014)
Heilbronn	300		0.6	23.9	Rieder et al. (2017), Dhingra et al. (2017), Rieder and Unterberger (2013)
Lasziska		Y	0.33	8.4	Spietz et al. (2018)
Loy Yang	20		0.21	2.7	Artanto et al. (2012), Dhingra et al. (2017), Reynolds et al. (2015a)
Maasvlakte	250	Y	0.65	8	Rieder et al. (2017), Dhingra et al. (2017), Khakharia et al. (2015)
Mikawa	420	Y		15	Saito et al. (2014, 2015
MTU	180	Y	0.4	18	da Silva et al. (2012), Morton et al. (2013), de Koeijer et al. (2011), Bade et al. (2014)
NCCC	Various	Y	0.64	6	Brown et al. (2017), Gao et al. (2019)
Niederaussem	300	Y			Moser et al. (2011a,b)
Tarong	100		0.35	7.14	Cousin et al. (2012)
TCM	5200	Y	3.5×2	12–24	Gorset et al. (2014), Morken et al. (2017), de Koeijer et al. (2011), Brigman et al. (2014)
Tiller	50	Y	0.2	19.5	Mejdell et al. (2011)

Table 2.2
A summary of the flue gas sources and compositions at different locations, where post-combustion CO_2 capture campaigns have been performed. SR: SO_x removal, NR: NO_X, PR: particle removal. Further details on pretreatment can be found in the Appendix, Table 5.2.

Location	Flue gas source	Pretreatment	cO_2 (vol%) Wet	/	Dry	cCO_2 (vol%) Wet	/	Dry	cSO_X ppm	/	mg m$_N^{-3}$	cNO_X ppm	/	mg m$_N^{-3}$	Reference
Aioi Works (IHI), Japan	Coal or propane boiler		–	/	–	–	/	–	–	/	–	–	/	–	Nakamura et al. (2013, 2014)
Breivik, Norway	Cement		7.5	/	9.2	17.8	/	21.8	–	/	<130 mg	–	/	180–250	Knudsen et al. (2014)
Brindisi, Italy	Coal	SR, PR, NR	–	/	6.3–8.2	–	/	11–13	–	/	0–20	–	/	24–68	Rieder et al. (2017), Mangiaracina et al. (2014)
CAER 0.1 MWth, USA	Coal	SR, PR	6	/	–	14	/	–	170–250	/	–	80–90	/	–	Frimpong et al. (2013), Thompson et al. (2014)
CAER 0.7 MWe, USA	Coal	SR, PR, NR	8	/	-	10-16	/	-	<5	/	-	<50	/	-	Thompson et al. (2017a)
Changchun, China	Coal	PR, SR, NR	5.8	/	6.4	10.8	/	12.0	–	/	<50	–	/	<160	Feron et al. (2014)
Esbjerg, Denmark	Coal	PR, SR, NR	–	/	5–9	12	/	–	<10	/	–	<65	/	–	Knudsen et al. (2009)
Ferrybridge, UK	Coal	PR, SR, NR	–	/	–	–	/	–	–	/	–	–	/	–	Fitzgerald et al. (2014)
Heilbronn, Germany	Coal	PR, SR, NR	–	/	6.4	12–14	/	–	–	/	–	–	/	–	Dhingra et al. (2017), Rieder et al. (2017), Mejdell et al. (2017)
Laziska, Poland	Coal	SR	–	/	–	13.1–13.3	/	–	–	/	<10	–	/	–	Spietz et al. (2018)
Longannet, Scotland	Coal		~10	/	–	12	/	–	–	/	–	80–170	/	–	da Silva et al. (2012), Graff (2010)
Loy Yang, Australia	Coal	PR, SR, NR	4–5	/	–	10–11	/	–	120–200	/	–	150–250	/	–	Reynolds et al. (2015a), Artanto et al. (2012), Dhingra et al. (2017), Bui et al. (2016)
Maasvlakte The Netherlands	Coal	SR	–	/	7.4	13	/	–	–	/	–	–	/	–	Khakharia et al. (2015), Dhingra et al. (2017), Rieder et al. (2017)
Mikawa, Japan	Coal	PR, SR	–	/	–	–	/	12	<5	/	–	100	/	–	Saito et al. (2014, 2015)
Niederaussem, Germany	Coal	PR, SR, NR	–	/	5.0	–	/	14.2	–	/	<1	–	/	120–200	Moser et al. (2011a,b, 2020)
Tarong, Australia	Coal	PR, SR	6	/	–	10	/	–	200	/	–	150	/	–	Cousin et al. (2012), Cousins et al. (2016)
TCM, Norway	CPH	PR, SR	14	/	15	3.6	/	3.8	<1	/	–	–	/	3	Gorset et al. (2014), Morken et al. (2017), Shah et al. (2018)
	RFCC		3.2	/	3.3	15	/	15	5	/	–	–	/	60	
Tiller, Norway	Propane burner		<15	/	–	4.5–14	/	–	Very low			–	/	20	da Silva et al. (2012), Mejdell et al. (2011)
Wilsonville (NCCC) USA	Coal	PR, SR, NR	–	/	4.5	–	/	14	2.5 (dry)	/	–	1–3 (dry)	/	–	Bumb et al. (2017), Morton et al. (2013), Brown et al. (2017)
	Simulated NG		–	/	15.9	–	/	4.5							

years using various analytical methods. The most frequently used analytical methods during pilot campaigns are described below and an overview of the methods can be found in Table 3.1 .

Titration is a quick tool that can give valuable information of different aspects of a solvent. In CCS, titration is most commonly used to find total alkalinity, the CO_2-loading and amounts of heat stable salts (HSS). Total alkalinity is a measurement of the total concentration of base in a solution. It is determined by titrating a basic solution with an acid (e.g. sulphuric or hydrochloric) until the equivalence point, at which the base is neutralised, is reached (Somridhivej and Boyd, 2016).

This method is a quick and inexpensive way of getting an estimate of amine concentration, and thus an easy way of gaining insight into the stability of the amine (Matin et al., 2012). It is, however, important to differentiate between the actual concentration of the starting amine and the total alkalinity as some degradation products are alkaline. Therefore, the result from a total alkalinity measurement incorporates the concentration of the starting amine, as well as possible alkaline degradation products that also have CO_2 binding abilities.

Titration used to find CO_2-loading or HSS concentration works in a similar way as that of the total alkalinity measurements. The difference is that bases are used instead of an acid and the solutions have to be pretreated before the titration. For CO_2-loading measurements, the CO_2 in the solution is first extracted using $BaCl_2$, before titration with NaOH (Hilliard, 2008). To get the HSS concentration, the solution is first treated with a cation exchange resin and then titrated with a base (Aronu et al., 2014; Reynolds et al., 2015a). Both of these methods are more time-consuming than the total alkalinity measurement. Nevertheless, if other, more expensive, analytical techniques are unavailable, these two methods can be a less costly alternative that provide important information.

Liquid chromatography–mass spectroscopy (LC–MS) is an analytical method used to separate molecules based on their chemical and physical properties. The liquid sample passes through an LC-column, and the different species separate as a result of their varying affinity towards a stationary phase in the column. The mass spectrometer ionises the compounds, and a magnetic field separates the ions based on their mass-to-charge ratio (Lundanes et al., 2014). There are multiple additions that can be included, like an additional step for compound separation. An example of this is QTOF (quad time of flight).

LC–MS is a common choice for both quantitative and qualitative analysis of degradation compounds, as this technique can analyse most of the classes of degradation compounds (amine derivatives, acids, amides, and nitrous amines) (Chahen et al., 2016; Vevelstad et al., 2013; Cuzuel et al., 2014). In the quantitative analysis, the remaining concentration of starting amine can be determined with high accuracy using an internal standard. Known degradation compounds can also be quantified, if internal standards are available and their application can also allow for qualitative analysis to identify unknown degradation products (da Silva et al., 2012; Lepaumier et al., 2011). An approach for identifying and semi-quantifying degradation compounds using TOF-MS has been described (Thompson et al., 2017a,d).

There are some disadvantages to the LC–MS technique. The equipment and maintenance are very costly and require skilled operators. It is, therefore, seldom found on site, which can give rise to challenges regarding the stability of the samples. However, published data on reanalysing samples have shown a good agreement between the analysed samples right after experiments and one month later (Knuutila et al., 2014a). There is also no library with which to compare any unknown peaks (Lepaumier et al., 2011). Identification of unknown peaks in the degraded mixtures will, therefore, start with the prediction of potential degradation compounds based on chemistry, after which deuterated standards will be purchased. These can be expensive, and in some cases, they are even not commercially available (da Silva et al., 2012).

Ion chromatography (IC) is a sub- category of liquid chromatography, and a useful method for analysing ionic species. Since many

Table 3.1
Summary of the main analytical methods used. *Offline measurement.

Method	Compounds analysed	Solvent amine	Water wash liquid	Emission	Remarks
LC–MS	Amine and amine degradation products.	x	x	x*	The equipment and maintenance are costly. Requires skilled operator, often off site. However, up-concentration possible and is able to detect compounds in low concentration.
GC–MS	Amine and amine degradation products.	x	x	x*	The compounds need to have boiling point below 300-500 °C and the analytes have to be stable at these high temperatures. High-quality spectra achieved and extensive library of pure compounds available to compare against.
IC	Amine and amine degradation products.	x	x		Relatively inexpensive but requires regular use and maintenance. Only ionic compound could be analysed.
FT-IR	Amine gas effluents, e.g. aldehydes, ammonia, water NO_x, SO_x, CO and CO_2	x	x	x	Online CO_2 analysis possible; both liquid and gas phase analysis possible, often preferred for emission monitoring; liquid phase analyses more challenging due to degradation; also used for speciation.
Titration	Total alkalinity in the solvent and in the water wash liquid; the CO_2-loading analyses; heat stable salts (HSS) analyses	x	x		Simple method and inexpensive.
PTR-MS	Amine and volatile organic compounds (VOCs).			x	Gas phase – could be used online; Quantitative data obtained without gas standard and

Table 3.1 (*continued*)

Method	Compounds analysed	Solvent amine	Water wash liquid	Emission	Remarks
ICP-MS	Atoms	x			calibration; high detection sensitivity (pptV range) ppm levels can be measured; expensive instrument with high operation cost
TOC/TN	Carbon and nitrogen	x	x		Relatively simple and inexpensive; could be placed onsite; often used to measure CO_2 in a liquid sample
FMPS	Particle size distribution			x	Fast response; not robust in demanding industrial surroundings
OPC	Particle size distribution and total particle number			x	Detects particles down to 50 nm in diameter; Properties of aerosol like density and shape not accounted for
SEM/EDX	Particle size distribution and structure, size and composition of solids in the aerosol particles			x*	Offline method
ELPI+	Particle size distribution and particle number concentration			x	Online method

degradation products are known to have ionic properties, the IC is well-suited for amine degradation studies (Wang and Jens, 2012). Similar to normal liquid chromatography, the separation of the species occurs due to their different affinity to a stationary phase; in IC this difference is caused by the species different columbic interaction with the ion-exchanger (Lundanes et al., 2014).

There are two types of ion chromatography, namely anion- exchange and cation-exchange (Lundanes et al., 2014). Anion-exchange is commonly used to analyse for degradation products in anionic forms, such as carboxylates, nitrate, and nitrite (Wang and Jens, 2014; Kadnar and Rieder, 1995). It is also one of the most described methods for analysing the total amide content by converting the amides to their corresponding carboxylic acid through amide hydrolysis (Freeman, 2011; Sexton, 2008). The generated carboxylic acids can then be analysed with the anion-exchange, and the surplus of carboxylic acids presents the carbamate concentration. Cation-exchange, on the other hand, is commonly used to quantify solvent amines, as well as to identify and to quantify amine degradation products, like alkyl amines, in the form of heat stable salts (Thompson et al., 2014; Moser et al., 2020; Reynolds et al., 2015b; da Silva et al., 2012). Quantitative IC-analysis requires chemical standards.

IC is a relatively inexpensive analytical method. Compared to LC-MS, the equipment is cheaper and requires less maintenance. Furthermore,

the implementation is also somewhat more straightforward, as dilution is the only sample preparation needed (Cuccia et al., 2018). The limitation of the IC method is that non-ionic compounds cannot be analysed. Therefore, IC is often used in combination with other analytical methods. The IC instrumentation requires both regular use and maintenance to deliver reliable results.

Gas chromatography–mass spectroscopy (GC–MS) works similarly as LC–MS, but as the name implies, the analysis occurs in a gas phase. GC–MS can be used both for quantitative analyses as well as to identify some degradation products (Wang and Jens, 2012). However, only compounds that have boiling points below 300–500 °C, can be analysed. At the same time, the analytes also have to be stable at these high temperatures. This limits the number of degradation compounds that can be analysed.

On the other hand, very high-quality spectra can be achieved as the gaseous eluate allows for the solvent to be removed before entering the MS and as the analytes are easily ionisable in the gas phase. An extensive library of various pure compounds is available, and any unknown spectra can be compared to the library (Lepaumier et al., 2011). The existence of this library is one of the main advantages for this method.

Fourier transform infrared spectroscopy (FT-IR) is a method that utilises molecular bonds' ability to oscillate when exposed to infrared radiation. In principle, FT-IR allows for the simultaneous analysis of up to 50 compounds with a low detection limit (~1 ppm). FT-IR can be used both for analyses of the liquid and gas phases. However, in aqueous solvent solutions, the detection of degradation compounds is challenging, if not impossible, due to low concentrations of degradation compounds, complex chemical matrix, as well as the high concentrations of amine and water (Cuccia et al., 2018; Macbride et al., 1997).

FT-IR is mostly employed as a gas phase on-line analytical method. The method is mostly used to monitor gas effluents, e.g. NO_X, SO_X, CO, and CO_2, and to quantify amines (like Pz, MEA, MDEA and ammonia) present in the gas leaving the absorber/water wash (Khakharia et al., 2013, 2015; Knudsen et al., 2013, 2014; Bade et al., 2014; Mertens et al., 2012). FT-IR can also be used to quantify aldehydes (formaldehyde and acetaldehydes).The advantage of applying on-line FT-IR is that the only preconditioning needed is heating the gas sample to prevent condensation. However, work should be done to ensure that the heating does not induce further thermal degradation of the amine. The ability to detect aldehydes is an essential advantage for this method, as other analytical methods are often limited in this regard.

FT-IR can also be used to analyse the liquid phase. Here, FT-IR together with attenuated total reflectance (ATR) is typically used to monitor the loading and solvent amine concentrations in the solvent loop. When specific degradation compounds are found in high enough concentrations, they can also be quantified and monitored. The main challenge is that degradation compounds will change the spectra, and the results will become more inaccurate overtime, requiring calibration with degraded solvent (Grimstvedt et al., 2019). In recent years, method, where FT-IR with ATR is used to analyse the speciation in the solvent has also been developed (Richner and Puxty, 2012; Diab et al., 2012).

Proton-transfer reaction mass spectroscopy (PTR- MS) is a technique used for online measurement of volatile organic compounds (VOCs) in a gas-stream. In the PTR-MS instrument, gas-phase VOCs are ionised as a proton is transferred from an ion reagent, typically H_3O^+, to the sample molecules. The ionised molecules are then mass analysed in the MS-part of the equipment (Hansel et al., 1995). For the proton transfer to take place, the analysed molecules must have higher proton affinity than water. This gives some restrictions to which compounds can be analysed. To overcome this, instruments have in later years been modified to be able to switch between H_3O^+ and for example NO^+ as reagent ions, which has increased the amount of detectable compounds (Jordan et al., 2009).

The PTR-MS can give both quantitative and qualitative measurement results. One of the main advantages of this method is that neither gas

standards, nor calibration for different gases, are necessary to get a precise quantification of the different species. Another advantage is the outstanding detection sensitivity of this method. The detection limit varies for different apparatuses, but it is typically in the pptV range (Lindinger et al., 1998). A drawback in this regard is that there is a maximum measurable concentration limit. The equations that are used in the analysis are based on the assumption that the decrease of reagent ions can be neglected. With a concentration at about 10 ppmV and up, this no longer holds and the results will be incorrect. A solution is to dilute the gas with air.

Inductively coupled plasma mass spectroscopy/optical emission spectroscopy (ICP-MS/-OES) are elemental analytical techniques, which enables detection of most atoms at ppm levels. This is done by atomising and ionising the molecules in the studied mixture by passing it through an inductively heated plasma, often argon (Sheppard et al., 1990). Using an ICP-MS instrument, the atomic ions that are created are then analysed with MS. The ICP-OES uses the fact that some of the atoms/ions that are created are also excited. The intensity of the radiation is proportional with the concentration of each atom, and so this technique can be used for both quantitative and qualitative analysis (Thomas, 2004).

These techniques demand sample preparation, where one usually has to add an internal standard, primarily deionised water with nitric or hydrochloric acid. The drawback is that the equipment is expensive, and the analysis has a high operation cost because it employs argon gas (Todoli and Mermet, 2008). In the field of CCS, this technique is used to monitor the amounts of trace metals in solutions. This gives an indication of corrosivity of the studied solvent. It should be noted that the method has not been validated. ICP-MS can also be used for measuring the total amount of carbon in a solution, but this is not widely used in the field of CCS.

Total organic carbon (TOC) analyser can measure amounts of carbon in a solution. It has different modes and can also be used for analysis of the total amount of inorganic carbon, total carbon and total nitrogen. In the field of CCS, it is often used to measure amount of CO_2 in a liquid sample (Knudsen et al., 2014; Bernhardsen et al., 2019).

The analyses happens over three steps, namely acidification, oxidation, and non-dispersive infrared (NDIR) detection. In the acidification step, acid is added, which then converts all bicarbonate and carbonate ions to carbon dioxide. The measurement of the resulting gas gives the amount of inorganic carbon in the sample, corresponding to the CO_2 loading. Catalytic combustion oxidises all carbon in the sample to CO_2, so that this also can be quantified by NDIR. Other oxidation processes are also available for the quantification of organic carbon (Shimadzu Corporation, 2014).

Fast mobility particle sizer (FMPS) is a fast response technique, enabling rapid detection of particle size distribution of aerosols. The gas-streams carrying aerosols is let into the FMPS and through a cyclone that removes particles bigger than 1 µm. The aerosols then continues through a region, in which they are charged with a known charge. The positively charged particles are then separated in an electric field based on their diameter and charge-state. The size distribution is measured in 32 channels, ranging from 5.6 to 560 nm (Jeong and Evans, 2009; Levin et al., 2015). Disadvantages of this technique is that it is not very robust in very demanding industrial surroundings (Kero and Jørgensen, 2016).

Optical particle counter (OPC) is an online measuring technique that is used to find aerosol size distribution and total particle number. In the OPC, particles are passed through a laser-light, which results in scattering of this light. The scattering is then classified and this gives a size spectrum (Burkart et al., 2010). OPCs can detect particles as small as 50 nm in diameter, and for smaller particles than this is simply not detected. Particles with a diameter of several hundred µm can also be detected, though not with the same instrument. If the particle size exceeds the detection limit for a certain instrument, it will simply be counted as the maximum diameter (Eliasson and Watson, 2016; Welker, 2012). A drawback of this method is that properties of the aerosols, such

as density, shape, refractive index and absorption, is not accounted for (Welker, 2012).

Scanning electron microscope with energy dispersive X-ray microanalysis (SEM/EDX) is an elemental microanalysis technique. The SEM part of the instrument is a microscope that can magnify from about 10 to 3,000,000 times. It is an offline method, so samples must first be collected from for example filters or films (Li and Shao, 2009; Byers1 et al., 1971). The surface of your sample is scanned with a focused beam of electrons. These electrons react with the atoms in the sample, resulting in various signals. The detection of these by SEM and by EDX can map out both the composition and the topography of the sample surface (Newbury and Ritchie, 2013; Goldstein et al., 2003). The resulting SEM image is quite analogous to normal vision (Byers1 et al., 1971), and the resulting image can give the structure, the size and the composition of solids in the aerosol particles. It can also be processed with different approaches to give size distribution (Sun et al., 2012; Brostrøm et al., 2020; Goldstein et al., 2003; Moser et al., 2017).

Electron low pressure impactor (ELPI+) is a real-time particle detection technique, which combines electrical detection of charged particles and a 15-stage cascade impactor. When the aerosol enters the ELPI+, a unipolar diffusion charger first charges the particles of the aerosol. The unipolarly charged particles are then deposited in the various impactor stages depending on their aerodynamic size. In the impactor stages, electrometers are used to measure signals from the charged particles, which can then be converted to particle size distribution. In the end, this measurement gives particle number concentration and size distribution in real-time. The particle size distribution ranges from 6 nm to 10 µm (Lamminen, 2011; Järvinen et al., 2014).

Iso-kinetic sampling using impingers is the most common way of manual sampling of emissions (Mertens et al., 2012, 2013; Morken et al., 2014, 2017; Bade et al., 2014; Lombardo et al., 2017; Gjernes et al., 2017). Typically, multiple impingers are installed in series to avoid breakthrough. The first impinger is often empty, whereas in the following impingers different absorbents, like dilute sulphuric acid or 2, 4- dinitrophenylhydrazine (DNPH), are used. Sulphuric acid is often used for collection ammonia and amine samples, while 2,4-dinitrophenylhydrazine is used to sample acetaldehyde and formaldehyde (Mertens et al., 2012, 2013; Bade et al., 2014). A good overview of standard methods for manual sampling, mainly developed for monitoring of the working environment, can be found elsewhere (SEPA, 2015; Azzi et al., 2010; Wittgens et al., 2010). A disadvantage of the iso-kinetic sampling is that it is an offline method, used periodically. FTIR, discussed earlier, is therefore often used to continuously monitor amine and ammonia emissions in the gas phase.

4. Results

4.1. Solvent stability and corrosion

Both oxidative and thermal degradation may take place with the carbamates formed in a reversible reaction between amine and CO_2. In the case of thermal degradation the mechanism often goes through carbamate polymerisation reactions (Rochelle, 2012; Davis and Rochelle, 2009; Lepaumier et al., 2009a). Oxidative degradation mechanisms, which are widely studied but extremely complex and therefore less understood, are assumed to start with radical reactions on the amine or carbamate. Once the reactions have initiated and primary degradation compounds are formed, these can react further with other degradation compounds, carbamates and amine in the solution to form secondary degradation compounds (Eide-Haugmo et al., 2011; Bello and Idem, 2005; Lepaumier et al., 2009b). These reactions are catalysed by the presence of dissolved metals in the aqueous amine solvent (Blachly and Ravner, 1963; Goff, 2005). The chemical structure of some typical degradation compounds identified and/or quantified in pilot plant and lab scale studies can be found in the appendix, in Table 5.4.

A total of 29 individual campaigns in 18 different pilot plants, where

Table 4.1

List of all the 30 wt% MEA (*aq.*) campaigns studied in this review.

Location	Time [h]	Remarks	Campaign focus	References
Brindisi	550	40 m^3 of 30 wt% MEA added during campaign. Typically 1 mg m$_N^{-3}$ of particulate matter at inlet.	Assessment of different operation modes and conditions. Establish guidelines with relevant data on emissions, HSE, and other operability, flexibility and cost aspects.	Rieder et al. (2017), Mangiaracina et al. (2014)
CAER 0.1 MWth	100		Comparison of MEA 30 wt% and the proprietary solvent CAER B2	Thompson et al. (2014)
CAER 0.7 MWe	1316	Thermal reclaiming was performed from 880 to 970 h.	Understand the impact on the solvent of flue gas constituents and potential higher oxygen content in the solvent due to secondary air stripper	Thompson et al. (2017a,b,c)
Changchun	1063		Performance trials; comparison with different solvent blends	Feron et al. (2014, 2015)
Esbjerg (a)	6000	Samples analysed after 500 h. Solvent partly degraded before start (0.5 wt% HSS content). 6 ppm S in flue gas.	Demonstrate the post combustion capture technology in conjunction with a coal-fired power station. Comparison with CASTOR 2, additionally comparing sulphur accumulation properties.	Dhingra et al. (2017), Knudsen et al. (2009)
Esbjerg (b)	3360	Samples from 1850 h (11 weeks) studied in degradation study.	Test campaign	da Silva et al. (2012)
Ferrybridge	>600		Benchmarking with MEA, before testing of a proprietary solvent. Assessment of solvent durability, perform process optimisation and to provide data on plant design and scale-up.	Fitzgerald et al. (2014)
Heilbronn (a)	1600	Campaign in 2011.	Benchmarking campaign.	Rieder and Unterberger (2013), Dhingra et al. (2017)
Heilbronn (b)	1500	760 kg MEA added after 952 h, water added at end, reducing the MEA concentration to ~25 wt%. Concentrations of degradation products given here are from sampling at 535 h. Campaign took place in 2013/2014.	Establish guidelines with relevant data on emissions, HSE, and other operability, flexibility and cost aspects. ED reclaiming tests performed offline, with degraded solution.	Rieder et al. (2017), Bazhenov et al. (2014, 2015)
Longannet, MTU	ca. 4400	Reclaiming after 3 months, total time 6 months		da Silva et al. (2012)
Loy Yang	834	MEA pre-used 639 or 700 h, for capture of CO$_2$ from a black coal-fired PP (Tarong).	Performance trials; comparison with different solvent blends	Dhingra et al. (2017), Reynolds et al. (2015b), Artanto et al. (2012)
Maasvlakte (a)	3500	Reclaimed after 3000 h	Study corrosion in relation to solvent degradation and ammonia emissions.	Dhingra et al. (2017), Khakharia et al. (2015)
Maasvlakte (b)	890		Establish guidelines with relevant data on emissions, HSE, and other operability, flexibility and cost aspects.	Rieder et al. (2017)
Niederaussem (a)	5000		Performance validation and investigation of time-dependence of MEA degradation and organic acid formation. Test of optimised process configurations.	Moser et al. (2011a)
Niederaussem (b)	12,000		Study solvent degradation	Moser et al. (2018)
Niederaussem (c)	13,000		Study time-dependent degradation products and trace components and how they can act as catalysts for degradation. Confirm threshold concentrations of iron from literature. Testing of "Bleed and Feed" as a degradation management strategy.	Moser et al. (2020)
TCM (a)	2162	Campaign duration 20.11.13–24.02.14	Verify Aker Solutions' Advanced Carbon Capture® process including two proprietary advanced amine solvents	Gorset et al. (2014), Morken et al. (2014)
TCM (b)	2000	Reclaimed after 1852 h	Demonstrate and document the performance of the TCM DA Amine Plant	Morken et al. (2017)
Tiller	2350		Benchmarking campaign	da Silva et al. (2012), Mejdell et al. (2011)

Table 4.2
List of all the campaigns using proprietary or other solvents than MEA 30 wt% (*aq.*) studied in this review.

Location	Time [h]	Solvent	Remarks	Reference(s)
Austin		8m PZ		Nielsen et al. (2013)
CAER 0.1 MWth	185	CAER B2		Thompson et al. (2014)
Changchun	306	blend 5		Feron et al. (2014)
Esbjerg	1000	CASTOR 2	Sampling after 500 h, stripper pressure 2.0 bar	Knudsen et al. (2009)
Ferrybridge	>600	RS-2®		Fitzgerald et al. (2014)
Laziska		40 wt% AEEA		Spietz et al. (2018)
Mikawa	840	Solvent A	Sterically hindered, secondary amine	Saito et al. (2014, 2015)
Mikawa	740	TS-1		Saito et al. (2014)
TCM	4029	S21	03.10.12–01.04.13, reclaiming after 3600 h	Gorset et al. (2014)
TCM	3507	S26	03.03.14–16.08.14, reclaiming after 3300 h	Gorset et al. (2014)

solvent degradation was studied, were found. 30 wt% MEA (*aq.*) was used in 19 of these (Table 4.1) and 10 were campaigns testing proprietary or other amine solvents (Table 4.2). A total of about 40 different compounds or compound groups were found measured in the liquid phase of the different campaigns, some just once, while others reoccur in several studies. A summary of the most frequently occurring liquid phase degradation components, as well as in which campaigns they have been analysed, can be found in Table 4.3 for campaigns using 30 wt% MEA (*aq.*) and Table 4.4 for other, including proprietary, solvents.

Despite of pretreating the flue gas to remove reactive contaminants, amine degradation does take place in large scale CO_2 capture. This is sometimes a terminal problem, resulting in the need for solvent replacement and interrupted operation. Some technologies are being studied, to limit degradation after it has begun to take place, such as solvent reclaiming, removing irreversibly formed heat stable salts. Reclaiming technologies aim to keep as much of the non-degraded amine as possible and only remove formed contaminants from the solvent. Reclaiming can typically be either thermal, by ion exchange or through electrodialysis and may be performed on- or offline (Kentish, 2016; Wang et al., 2015). The "Bleed and Feed" strategy involves the removal of parts of the degraded solvent and replacing it with fresh solvent (Moser et al., 2020). If any known degradation limiting technologies have been applied throughout the campaign, this is also given in Table 4.1.

Formate, as well as other organic acids, have long been regarded as primary indicators of oxidative degradation in the liquid phase and are therefore among the most reported degradation compounds of MEA degradation. Of the 19 campaigns shown in Table 4.3, formate is quantified in nearly two thirds, and half of the campaigns also analysed for oxalate. These two as well as acetate and glycolate, are formed in the first steps of the degradation process by electron or hydrogen abstraction before they react with the amine or other degradation products to form other degradation compounds (Rooney et al., 1998).

A summary of reported concentrations of organic acids can be seen in Fig. 4.1, as well as total concentration of other (in some cases unknown) HSS, where that has been reported. One MEA-campaign from the 0.1 MWth CAER pilot (Thompson et al., 2014) of only 100 h and one campaign from the Esbjerg pilot (Knudsen et al., 2009) of unclear total operation time prior to HSS analysis, were omitted. Fig. 4.1 shows a large span in the concentrations of heat stable salts found in various 30 wt% MEA (*aq.*) campaigns when normalised per time in operation. Normalisation of this data does not give a complete picture of the degradation processes and may not be an ideal way of comparing different pilot campaigns and locations to one another, but it gives a visual representation of the degradation compounds observed. Surprisingly, one of the highest HSS concentrations is actually found in the shortest campaigns. A correlation between the amount of pretreatment technologies applied prior to CO_2 removal is apparent, when comparing Fig. 4.1 with Table 2.2. Esbjerg, Heilbronn and Niederaussem all operate with coal as their flue gas sources and have an extensive pretreatment set up. TCM also observe relatively low concentrations of HSS. The flue gas originates from sources with less contaminants and the degradation

here is comparable to pretreated flues gas from coal-fired power plants.

Furthermore, it can be observed that most campaigns see relatively high concentrations of organic acids and HSS at the campaign end, or when samples have been analysed before solvent reclaiming has taken place, but that the ratio between the four organic acids are inconsistent. Acetate and formate are most often the dominant degradation product of those analysed, but it varies which one of the two is found in the highest concentrations. It therefore seems like process conditions play a very important role for which degradation pathways will take place within the solvent. The average concentration of liquid phase formate in Fig. 4.1 is 2500 mg kg^{-1} (1000 h)$^{-1}$, whereas acetate, oxalate and glycolate both have an average of 800 and glycolate of 500 mg kg^{-1} (1000 h)$^{-1}$, respectively.

All the compounds previously discussed are typical products of oxidative degradation. Thermal degradation products have been reported in many campaigns and include *N*-(2-hydroxyethyl)-2-imidazolidone (HEIA), which is a product of a carbamate polymerisation reaction, and 2-(2-hydroxyethylamino)ethanol (HEEDA), which is a product of an addition reaction. These degradation compounds are typically seen in lower concentrations than the oxidative degradation products. Measured concentrations of thermal (HEIA), as well as secondary oxidative degradation compounds (HEA, HEF, HEI, HEGly, HEPO, OZD, BHEOX) in MEA- campaigns are summarised in Table 4.5, the degradation product bicine is also presented here, assumed to be formed upon oxidation of DEA/MDEA or TEA derivatives (Lepaumier et al., 2009b; Gouedard et al., 2012). It is evident that secondary oxidative degradation compounds, formed when primary degradation compounds proceed to react, also occur in relatively high concentrations, especially HEF, HEGly and HEPO. The average concentrations of both HEGly and HEPO are twice that of formate when considering all campaigns, with about 5000 and 7000 mg kg^{-1} (1000 h)$^{-1}$, respectively. This same trend, of much higher concentrations of HEPO and HEGly in the solvent than formate, is seen also in studies with synthetic flue gas (Knuutila et al., 2014a; Chahen et al., 2016).

Thermal degradation compounds tend, however, to occur in lower concentrations. For example, the concentration of HEEDA are very low and rarely reported, and it has not been included in this table. The highest reported concentration of HEEDA is 246 mg L^{-1}, in one of the MEA 30 wt% (*aq.*) pilot campaigns (Thompson et al., 2017c). Some pilot campaigns even observe that the concentrations of some thermal degradation compounds (HEIA and HEEDA) decline after an initial increase, throughout the operation time, making it apparent that they further react, or degrade themselves. (Moser et al., 2020; Thompson et al., 2017c) A campaign using synthetic flue gas and 30 wt% MEA (*aq.*), also saw OZD reaching a threshold concentration after a certain time of operation, and thereafter no further change, despite of the overall degradation rate sustaining (Chahen et al., 2016). Equally for Pz, thermal degradation products such as ethylenediamine and *N*-(hydroxyethyl)-piperazine have been found to initially increase and then decrease (Nielsen et al., 2013).

Inorganic compounds originating from the flue gas or construction material, like oxidised metal ions and elementary sulphur, are also

Table 4.3

An overview of the campaigns, which have studied degradation in MEA 30 wt% (*aq.*) and which degradation product and dissolved inorganic compound concentrations have been reported. x = identified and quantified, nd = not detected, t = tentative.

Campaign	Total HSS	Acetate	Formate	Glycolate	Oxalate	HEA	HEI	HEF	HEGly	HEIA	HEPO	BHEOX	OZD	NDELA	HEEDA	Bicine	DEA	Fe	Ni	Cl⁻	SO₄²⁻	NO₃⁻	Reference
Brindisi																		x					Rieder et al. (2017), Mangiaracina et al. (2014)
CAER 0.1 MWth	x		x																	x	x	x	Thompson et al. (2014)
CAER 0.7 MWe	x	x	x	x	x		x		x	x			x		x			x	x	x	x	x	Thompson et al. (2017a,c)
Changchun	x		x		x																		Feron et al. (2014, 2015)
Esbjerg (a)	x																	x					Knudsen et al. (2009), Dhingra et al. (2017)
Esbjerg (b)			x		x	x	x	x	x		x	nd	nd								x		da Silva et al. (2012)
Heilbronn (a)			x		x													x	x	x	x	x	Rieder and Unterberger (2013), Dhingra et al. (2017)
Heilbronn (b)	x	x	x	x	x													x		x	x	x	Rieder et al. (2017), Bazhenov et al. (2015)
Longannet, MTU						x	x						x										da Silva et al. (2012)
Loy Yang	x	x	x		x		x		t	x	t	x	x	nd	x	nd							Reynolds et al. (2015b), Artanto et al. (2012), Dhingra et al. (2017)
Maasvlakte (a)																		x					Dhingra et al. (2017), Khakharia et al. (2015)
Maasvlakte (b)																		x					Rieder et al. (2017)
Niederaussem (a)		x	x							x								x	x	x			Moser et al. (2011a)
Niederaussem (b)		x	x		x													x	x	x	x		Moser et al. (2018)
Niederaussem (c)		x	x		x					x			x		x			x	x	x	x	x	Moser et al. (2020)
TCM (a)	x		x	x	x	x	x	x	x		x		x	x								x	Gorset et al. (2014), Morken et al. (2014)
TCM (b)	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				x	x	Morken et al. (2017)
Tiller						x	x	x	x		x	x	x	x	x	x	nd						da Silva et al. (2012), Mejdell et al. (2011)
SUM	8	7	12	4	10	4	7	5	5	5	5	4	7	3	5	3	3	10	5	7	8	7	

Table 4.4

An overview of the campaigns, which have studied degradation in various solvents (*aq.*) and which degradation product and dissolved inorganic compound concentrations have been reported.

Pilot	Solvent	Degradation comp.	Inorganics	Reference(s)
Austin	8m PZ	Formate, acetate, oxalate + more	Cr^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+}	Nielsen et al. (2013)
CAER 0.1 MWth	CAER-B2	Total HSS and formate	SO_4^{2-}	Thompson et al. (2014)
Esbjerg	CASTOR 2	Total HSS	S	Knudsen et al. (2009)
Changchun	"blend 5"	Formate	SO_4^{2-}	Feron et al. (2014)
TCM	S21	Total HSS and TONO		Gorset et al. (2014)
TCM	S26	Total HSS and TONO		Gorset et al. (2014)
Mikawa	"tertiary solvent A"	Formate, acetate and oxalate		Saito et al. (2014)
Mikawa	"TS-1"	Formate		Saito et al. (2014)

found in the degraded solvents. Keeping track of dissolved metal concentrations allows for a simple assessment of corrosion of the equipment. The presence of NO_x, SO_2, and chlorine in the flue gas are the reasons why these are found in the solvent. The accumulation of these species is likely to influence degradation rates and mechanisms and therefore give valuable insights about the processes taking place within the degrading solvent. Fig. 4.2 shows that there is no immediate correlation between operation time and the accumulation of iron in the

MEA solvent.

NO_x are known to form nitrosamines with several amine species. Nitrosamines are toxic already in low concentrations and have therefore been of great concern for the operation of an amine-based CO_2 capture process. They are, however, readily degradable in sunlight (de Koeijer et al., 2013). The formation of nitrosamines in pilot plants has been a concern, both with NO_x present in the flue gas and particularly when using secondary amines, which are known to be highly prone to the
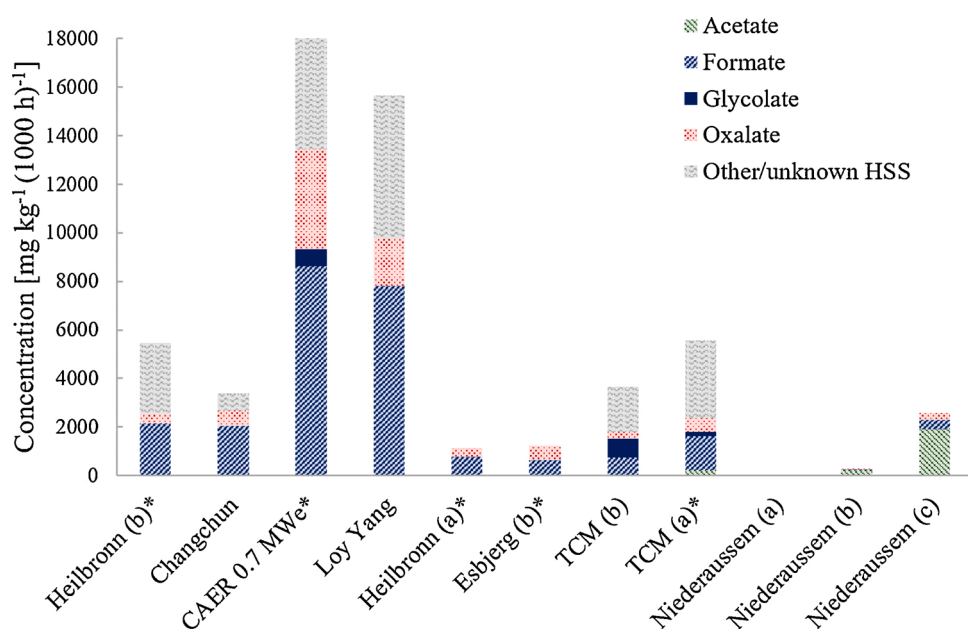

Fig. 4.1. Heat stable salt/organic acid concentrations measured in post-combustion CO_2 capture pilot campaigns using 30 wt% MEA, at the end of the campaign or right before reclaiming the solvent. Concentrations converted to concentration per 1000 h, to facilitate comparison of different campaigns and pilots. Keep in mind that where no concentration is given, reported data for the given compounds is not available. All references are given in Table 4.3. *Mass concentration converted to mass fraction under the assumption that $\rho = 1 \, kg \, L^{-1}$.

Table 4.5

Measured concentrations of degradation compounds in mg L^{-1}, which are not inorganic components nor organic acids, in post-combustion CO_2 capture pilot campaigns using 30 wt% MEA, at the end of the campaign or right before reclaiming of the solvent. *Mass fraction in original publication converted to mass concentration under the assumption that $\rho = 1 \, kg \, L^{-1}$.

| Campaign	HEA	HEF	HEI	HEGly	HEPO	BHEOX	OZD	HEIA	NDELA	Bicine	Reference
CAER 0.7 MWe			4800	1047			<10	1712			Thompson et al. (2017a)
Esbjerg (b)	590	440	440	7610	2320						da Silva et al. (2012)
Longannet		8580	160				23				da Silva et al. (2012)
Loy Yang			2030*			3400*	350*	960*		270*	Reynolds et al. (2015b)
Niederaussem (a)								200*			Moser et al. (2011a)
Niederaussem (c)							96*	380*			Moser et al. (2020)
TCM (a)	4580	5200	2070	8000	11,140			1150	31 μmol L^{-1}		Morken et al. (2014)
TCM (b)	4963	5062	1826	18,922	18,788	274	82	181	4.9	62	Morken et al. (2017)
Tiller	731	721	1758	7295	27,691	35.2	8.7		0.536	32.6	da Silva et al. (2012)
Average/1000 h	1321	1505	839	4821	6940	672	131	435	1	32	
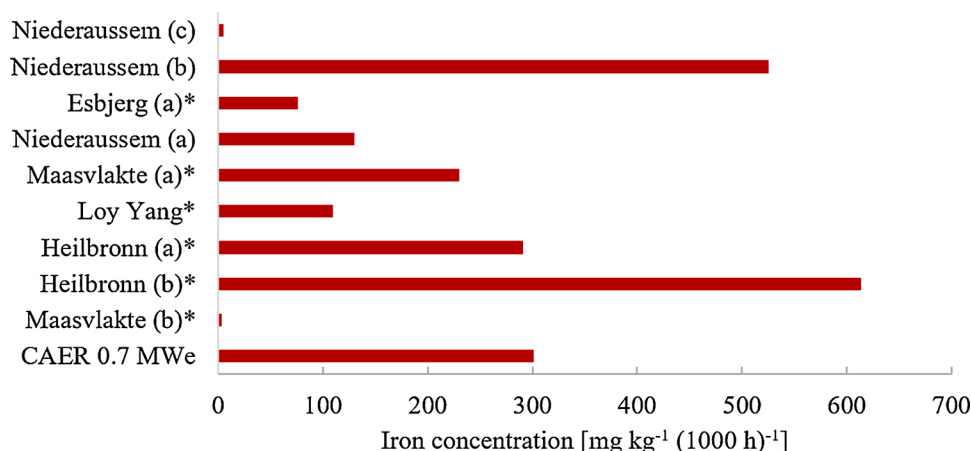
Fig. 4.2. Accumulated concentrations of iron during pilot campaigns using MEA 30 wt% (*aq.*). All references are given in Table 4.3. *Mass concentration in original publication converted to mass fraction under the assumption that $\rho = 1\,kg\,L^{-1}$.

Table 4.6
Measured concentrations of inorganic compounds in mg kg^{-1}, including metals, in post-combustion CO_2 capture pilot campaigns using 30 wt% MEA as solvent, at the end of the campaign or right before reclaiming of the solvent. *Mass concentration in original publication converted to mass fraction under the assumption that $\rho = 1\,kg\,L^{-1}$.

Campaign	Nitrate (NO$_3^-$)	Sulphate (SO$_4^{2-}$)	Chloride (Cl$^-$)	Nickel (Ni)	Sulphur (S)	Reference
CAER 0.1 MWth	720	3400	40			Thompson et al. (2014)
CAER 0.7 MWe	1115*	3640*	193*	28		Thompson et al. (2017a,c)
Esbjerg (b)		5100*				da Silva et al. (2012)
Heilbronn (a)	150*	370*	10*	180*		Rieder and Unterberger (2013)
Heilbronn (b)	600*	820*	70*			Bazhenov et al. (2014)
Niederaussem (a)			1800	200	100	Moser et al. (2011a)
Niederaussem (b)	270	85	8300		20	Moser et al. (2018)
Niederaussem (c)	2200	800	83	0	200	Moser et al. (2020)
TCM (b)	1173*	70*				Morken et al. (2017)

Table 4.7
Accumulated concentrations of degradation compounds and sulphate during pilot campaigns using other solvents and blends than MEA 30 wt%. *Mass concentration in original publication converted to mass fraction under the assumption that $\rho = 1\,kg\,L^{-1}$. **Sum of formate, oxalate and acetate.

Pilot	Solvent	HSS [mg kg^{-1}(1000 h)$^{-1}$]	Formate [mg kg^{-1}]	Sulfate (SO$_4^{2-}$) [mg kg^{-1}]	Reference
Austin	8m Pz	5648**	3273		Nielsen et al. (2013)
CAER 0.1 MWth	CAER-B2	22,162	1694	2929	Thompson et al. (2014)
Changchun	Blend 5	4085	215	980	Feron et al. (2015)
Esbjerg	CASTOR-2	4000			Knudsen et al. (2009)
Mikawa	Tertiary solvent A	313*	5*		Saito et al. (2014)
Mikawa	TS-1	644*			Saito et al. (2014)
TCM	S21	28 mmol/mg			Gorset et al. (2014)
TCM	S26	6 mmol/mg			Gorset et al. (2014)

formation of nitrosamines (Fine, 2015; Knuutila et al., 2014b). A thorough lab-scale pilot test of addition of NO and NO$_2$ to MEA (primary amine) and diethanolamine (DEA; secondary amine) showed this, also testing the UV-radiation as a removal technology (Table 4.8) (Knuutila et al., 2014a,b). Where measured, the concentrations of the nitrosamine NDELA is found in Table 4.5. Other nitrosamines, which are quantified less often than NDELA in the liquid phase and gas phase emissions in pilot campaigns are No-HEGly and NDMA. Morken et al. (2014) found 15 times more No-HEGly than NDELA, accounting for about half of the total nitrosamine (TONO) content. This finding indicates that the focus when studying nitrosamines in the amine solutions may not have been on the right compounds. Furthermore, a comparative study quantifying nitrosamines in identical solutions, a large variation in results from different laboratories has been reported (Fraboulet et al., 2016).

The reported concentrations of inorganic compounds quantified in the solvent during pilot campaigns are summarised in Table 4.6 for MEA and Table 4.7 for other amines and proprietary solvents. Some additional compounds, in addition to those given in Table 4.3 and Table 4.4, can be found quantified for the campaigns described in da Silva et al. (2012), Morken et al. (2017), Thompson et al. (2014), Reynolds et al. (2015b), Rieder and Unterberger (2013) and Saito et al. (2014). Since these compounds are not widely analysed and thus cannot not be used in search for general trends, they are not given here.

Dhingra et al. (2017) already showed that the concentration of dissolved iron in the 30 wt% (*aq.*) solvent tends to reach a sudden spike over a short period of time in four different pilot campaigns. It therefore comes as no surprise, that there is no correlation between operation time and iron concentration in the solvent when studying Fig. 4.2. The campaigns at Niederaussem (c) (Moser et al., 2020) and at Maasvlakte (b) (Rieder et al., 2017) have significantly lower iron concentrations compared to the seven other campaigns where data is available, despite of at least the pilots in Maasvlakte, Loy Yang and Esbjerg all being constructed in stainless steel 304/316L (Dhingra et al., 2017). These numbers indicate that no severe corrosion had taken place during the

Table 4.8

An overview of some relevant pilot studies using synthetic flue gas and aqueous amine solutions.

Pilot	Solvent	Time [h]	Compounds studied	Campaign focus	Reference(s)
Austin (SRP)	8m Pz	1350	Formate, oxalate, acetate, Cr^{3+}, Fe^{2+}, Ni^{2+}, Cu^{2+} + more		Nielsen et al. (2013)
IFPEN	30 wt% MEA	1700	Formate, glycolate, acetate, SO_4^{2-}, NO_3^-, NO_2^-, HEGly, DEA, OZD, HEF, HEA, HEI, HEPO + more	Study MEA degradation and predict degradation product emissions.	Chahen et al. (2016)
Gløshaugen	30 wt% MEA	990	Formate, NO_3^-, HEGly, DEA, OZD, HEF, HEPO, HEA, NDELA		Knuutila et al. (2014a,b)
Gløshaugen	50 wt% DEA	410	OZD, HEF, HEPO, HEA, HEI, NDELA	Study formation and destruction of nitrosamines.	Knuutila et al. (2014a,b)

campaign. Comparing the seven campaigns with relatively high iron concentrations, we may still not be able to say much about degradability and corrosivity of the system, since degradation and corrosivity do not increase linearly, instead we can expect a rapid spike after corrosion and solvent degradation have reached a certain level.

When comparing the degradation of the proprietary solvents in Table 4.7, specific characteristics of the solvent have to be compared to MEA. Formed degradation compounds are solvent specific, making it impossible to compare solvents of unknown amines to any benchmark by comparing single degradation components. However, the formation of HSS over time makes an interesting comparison since total HSS-measurement takes into account all different HSS compounds that are present. For example, HSS formation rate appears to be halved with CAER-B2 compared to 30 wt% MEA (*aq.*) under the same conditions (Thompson et al., 2014), whereas when CASTOR-2 is compared to 30 wt % MEA (*aq.*), it is reduced to a fourth (Knudsen et al., 2009). In "Blend 5" tested at Changchun, the HSS formation rate is more or less the same as for 30 wt% MEA (*aq.*) (Feron et al., 2015). It should be remembered that comparing total HSS, or solvent make-up-rate, discussed earlier, does not tell anything about the formation of potentially toxic degradation compounds or the formation of volatile degradation products, which can have a huge effect on the design of emission countermeasures and monitoring emissions. A detailed understanding of the degradation compounds formed for all amines is always needed.

4.2. Emissions

In a CO_2 capture plant, it can be distinguished between three different types of emissions; gas-phase (vapour), liquid entrainment, and aerosol/mist emission (Knudsen et al., 2013; Spietz et al., 2018). Factors influencing the gas-phase emission are the volatility of the amine, CO_2 loading, and gas temperature. Often, a well- designed water wash is enough to minimise these emissions. Liquid entrainment emissions are liquid droplets that are carried by the gas flow, however, water wash sections can remove these. Aerosols and mist are small droplets suspended in the gas. The formation of these depend to a large extent on the flue gas composition upstream the CO_2 capture plant and on the capture plant's operation conditions (Mertens et al., 2015) and presence of condensation nuclei (<1 μm) as for example particulate matter, soot, SO_2, SO_3, NO_2 or H_2SO_4 (Mertens et al., 2012; Spietz et al., 2018; Moser et al., 2015). When formed, mist penetrates wash sections and conventional demisters, and therefore, additional mitigation techniques are required.

Several studies have been conducted in the last years to better understand and control emissions and mist/aerosol formation. A summary of the components contained in emissions can be found in Table 4.9 . The table shows that the most commonly monitored emission is the solvent amine, followed by ammonia. Ammonia is one of the primary degradation compounds of MEA and is highly volatile. Nitrosamine concentrations are also often monitored due to their harmful nature. Concentration of nitramines in water wash have also been measured, but in both of them the nitramines were below the detection limit in the water wash water (Khakharia et al., 2014a; Morken et al., 2014). Further volatile degradation compounds, such as allylamines, (form) aldehydes, and some ketones, have been studied only in a few campaigns.

The concentrations of the main degradation species detected in the gas phase can be found in Table 4.10 , where it can be observed that there is no universal standard for the reporting of concentrations of compounds in emissions. Variation in practice, insufficient information and the different units makes it challenging to compare the results in detail. The MEA emissions are below one ppm in three out of the six campaigns. In the pilot campaigns with high MEA emissions, the emissions are measured after the absorber and no water wash sections are used. For proprietary solvents, the solvent emissions are, in all cases, lower compared to those of MEA campaigns. This could mean that the proprietary solvent components are less volatile than MEA, or well-

Table 4.9

Emissions monitored at different pilot locations/campaigns. Emission monitoring given here does not necessarily mean that concentrations of emissions are published.

Pilot plant	Solvent amine	NH₃	Nitrosamine	Aldehydes	Alkylamine	Nitramine	Ketones	Reference(s)
CAER 0.7 MWe	x	x	x	x			x	(Thompson et al., 2017b,c)
Esbjerg	x	x		x				(Mertens et al., 2012, 2013; Khakharia et al., 2014a; Aas and da Silva, 2010)
Ferrybridge	x	x	x					(Fitzgerald et al., 2014)
Łaziska		x		x				(Spietz et al., 2018)
Maasvlakte	x	x	x			x		(Khakharia et al., 2014a; Da Silva et al., 2013)
Mitsubishi		x						(Kamijo et al., 2013)
MTU - Breivik	x	x	x					(Knudsen et al., 2014)
MTU - Longannet	x							(Graff, 2010)
MTU - NCCC	x	x			x			(Knudsen et al., 2013)
NCCC	x	x	x	x	x			(Dahlin et al., 2013)
Niederaussem	x							(Moser et al., 2013, 2014, 2017)
TCM	x	x	x	x		x	x	(Bade et al., 2014; Gorset et al., 2014; Morken et al., 2014, 2017; Lombardo et al., 2017)
Tiller	x	x	x		x			(Mejdell et al., 2011)
Toshiba	x							(Fujita et al., 2013)

Table 4.10

Concentrations of emissions in different campaigns and locations, where given in literature.

Pilot plant	Solvent	Solvent amine	NH_3	TONO	Formaldehyde	Reference(s)
Mitsubishi [ppm]	MEA		14			(Kamijo et al., 2013)
TCM [ppm]	MEA MEA	<1	20	$<8\times10^{-8}$		(Morken et al., 2014)
Tiller [ppm]		<0.4	20	nd		(Mejdell et al., 2011)
CAER 0.7 MWe* [ppmV]	MEA	5-1385	12-282	< LOQ	35-73	(Thompson et al., 2017b, c)
MTU - NCCC [ppmV]	MEA	10-50/0[b]	10-40			(Knudsen et al., 2013)
NCCC [ppmV]	MEA (water wash)	2.13	1.74		0.0031	(Dahlin et al., 2013)
NCCC [ppmV]	MEA (acid wash)	3.02	4.75		0.0020	(Dahlin et al., 2013)
Ferrybridge* [mg m^{-3}]	MEA			0.020		(Fitzgerald et al., 2014)
Maasvlakte [mg m$_N^3$]	MEA	250/1[a]	10-70	(5 to 75)×10^{-6}		(Khakharia et al., 2014a; Da Silva et al., 2013)
MTU - Longannet* [mg m$_N^{-3}$]	MEA	<4	50-80			(Graff, 2010)
Łaziska [ppm]	AEEA		27-50		0.11	(Spietz et al., 2018)
Mitsubishi [ppm]	KS-1		<1.5			(Kamijo et al., 2013)
MTU - NCCC [ppmV]	ACC novel solvent	20/0[b]	1-4			(Knudsen et al., 2013)
Toshiba [ppmV]	TS-1		18/5.6[c]			(Fujita et al., 2013)
Esbjerg [mg m$_N^3$]	CASTOR/CESAR	0.02-0.7			0.059-1.1	(Mertens et al., 2012; Khakharia et al., 2014a; Aas and da Silva, 2010)
MTU - Breivik [mg m$_N^{-3}$]	S26	<0.46[b]	<4.0[b]	<0.03[b,d]		(Knudsen et al., 2014)
MTU - TCM* [mg m$_N^{-3}$]	S21	0.031	0.14	<0.83[e]		(Gorset et al., 2014)
MTU - TCM* [mg m$_N^{-3}$]	S26	0.09[b]	0.01[b]	<0.05[e]		(Gorset et al., 2014)
NCCC [ppm]	Pz	<1d	3.1	<0.34[e]		(Akinpelumi et al., 2019)
TCM* [mg m$_N^{-3}$]	S21	0.5	3.1	<0.34[e]		(Gorset et al., 2014)
TCM* [mg m$_N^{-3}$]	S26	1.8/0.09[b]	1.9/0.01[b]	<0.02[e]		(Gorset et al., 2014)

* Reclaiming was, or may have been performed in the duration of the campaign.
[a] Reduced after water wash and BDU.
[b] Reduced with ACC™ emission control system.
[c] Reduced by cooling lean temperature.
[d] Reduced by higher lean temperature and two- stage water wash.
[e] μmol m$_N^{-3}$ nd = not detected.

designed emission mitigation methods are used.

Ammonia emissions, as seen in Table 4.10, are larger than MEA emissions due to the high volatility of ammonia. Also ammonia emissions can be controlled with water wash systems, partly explaining the lower emissions at TCM, Tiller, Maasvlakte and Mitsubishi compared to CAER. Furthermore, as the ammonia concentrations are often at ppm-levels in the gas phase, it is an attractive compound to monitor as a sign of degradation. Proprietary solvents seem to degrade less to ammonia as, in all cases, the ammonia emissions are significantly lower than those of MEA. However, since ammonia is highly volatile, the ammonia emissions are very dependent on the operating time, temperatures in the water wash sections and process conditions. The solvent degradation also influences emissions. As solvent degradation increases, the emission of ammonia has been reported to increase in MEA (Mertens et al., 2012, 2013). However, no dedicated studies were found looking at the effect of degradation on emissions.

As seen in Table 4.10 nitrosamines are generally observed only in the lower ppm to ppb range. The same is true for aldehydes with one exception: a laboratory pilot study by Chahen et al. (2016) using 30 wt% MEA (aq.) and a synthetic flue gas. In this study, acetaldehyde was measured in the range of 1 mg m^{-3}. This is a nearly 80 times higher concentration than formaldehyde in this particular study. This study also found relatively high concentrations of ethylene glycol and the nitrosamine NDMA, but these in the range of <0.5 mg m^{-3} (Chahen et al., 2016).

Based on the pilot results it is clear that for MEA, the wash water section can limit the MEA emission to a few hundred ppb, ammonia in the low ppm range, methylamine at low ppb range in case no mist is present (Morken et al., 2017; Lombardo et al., 2017; Gjernes et al., 2017). Furthermore, in these cases, there is no observation of nitrosamine and nitramine emissions over the detection limit. The solvent emissions of the tested proprietary solvents can be controlled to similar levels as seen with 30 wt% MEA (aq.). This is in line with reported numbers for commercially available proprietary solvents (Singh and Stéphenne, 2014; Feron et al., 2020).

As mentioned earlier, the presence of mist can increase the emissions significantly and thus, extensive work has been conducted to study aerosol emissions, their formation, mechanisms, and countermeasures. Mist can be formed via two different nucleation mechanisms, homogeneous and heterogeneous (Kolderup et al., 2020) and both mechanisms are important. Avoiding homogeneous nucleation by removing SO_3 and avoiding H_2SO_4 will not entirely eliminate aerosol formation, since heterogeneous nucleation and growth by condensation have been reported to be the main mechanisms leading to aerosol-based emissions in a CO_2 capture column (Khakharia et al., 2015; Kolderup et al., 2020; Moser et al., 2011b, 2014). Also, both the concentration of particles and sulphuric acid has an impact on the formation of aerosol emissions (Khakharia et al., 2013, 2015). For cases with low particle numbers before the absorber, typically seen for natural gas-fired power plants, mist is often not detected (Morken et al., 2017). For TCM, a 500 000 particles cm^{-3} was deemed acceptable to stay below the local emission permit (Lombardo et al., 2017). Several publications discuss the influence of flue gas cleaning before the absorption column (Knudsen et al., 2013; Khakharia et al., 2013) and different process changes (Moser et al., 2011b, 2013, 2014; Khakharia et al., 2013, 2014b, 2015) as the flue gas composition and operational settings influence the particle number, size, size distribution, composition, and physical/chemical properties of the mist.

Effects of water wash temperature, acid wash, dry bed, flue gas pretreatment, and wet electric precipitator have been tested alone or in coupled operation. They all showed a reduction up to an order of magnitude of amine emission (Moser et al., 2014). A wet electrostatic precipitator (WESP), often seen as an option to avoid mist formation, could also cause aerosol formation by increasing the number

concentration of ultra-fine particles or droplets in the flue gas (Moser et al., 2015). A gas-gas heater installed up- or downstream of the wet flue gas desulphurisation (WFGD) prevents amine mist formation inside the absorber (Mertens et al., 2015; Lombardo et al., 2017; Khakharia et al., 2014b, 2015; Majeed et al., 2017; Harsha et al., 2019).

Having a dry bed between the absorber and the water wash reduces the emission of amine compounds (Moser et al., 2014). Furthermore, lean MEA inlet temperature to the absorber influencing the absorber temperature profile and flue gas temperature at the top of the absorber, flue gas temperature difference over the washing section, flow rate of water in wash sections as well as the amount of make-up water to these sections have a significant impact on the amine and ammonia emissions (Lombardo et al., 2017; Spietz et al., 2018; Akinpelumi et al., 2019). Demisters are an efficient way to reduce amine emissions when mist is present, and further testing of impaction candles and high efficiency demisters is proposed to identify options with low pressure drop and high efficiency (Lombardo et al., 2017). Finally, proprietary emission control concept (ACC™), combining a novel absorber design to prevent amine mist formation and a final pH-controlled wash stage is reported to reduce the emission of alkylamines, ammonia and solvent amine(s) (Bade et al., 2014; Knudsen et al., 2013).

4.3. Analytical methods

For the monitoring of both the solvent degradation and the emissions in the pilot plants, many different analytical methods are being deployed. The amount of information given about these, however, is varying. How much information is given can for example be dependent on the purpose of the given paper/report, if the analysis is done internally or externally, or if the specific method used is disclosed or not. In this section, the analytical methods that are most frequently deployed in the pilots and how they are used will be presented. These include FT-IR, LC–MS, GC–MS, IC, titration, PTR-MS and ICP-MS/-OES. Note that results from papers that only reports their findings, without stating which analytical method is being used, are not included.

When monitoring the emissions from the pilot plants, online FT-IR is often the preferred method (Bade et al., 2014; Knudsen et al., 2013, 2014; de Koeijer et al., 2011; Mertens et al., 2012; Khakharia et al., 2013, 2014; Moser et al., 2018; Artanto et al., 2012; Fitzgerald et al., 2014; Thompson et al., 2017b). Here, the FT-IR is used to analyse the emissions from the absorber, and can detect and quantify various amines and aldehydes, water content, as well as standard inorganic components such as NH_3, SO_2, NO_x, etc.. The detection limit is usually 1 ppmV. When the solvent amine emission concentration dips below this limit, manual sampling campaigns have been conducted (Gorset et al., 2014).

LC–MS has also been frequently used to monitor emissions in many of the pilot plants (Khakharia et al., 2014; Knudsen et al., 2013, 2014; Bade et al., 2014; Fujita et al., 2013; da Silva et al., 2012). This is however not done online, but through absorption in impingers. Different absorption medias are utilised, but sulphuric and sulfamic acid are the most common. At Norcem, DNPH cartridges was also used (Knudsen et al., 2014). These can capture condensate and aldehydes/ketones which is not captured in the acid absorbers. Sampling in the impingers are usually done for 1-2 hours. The impinger methods used are often well documented in the publications. The LC-MS results are, also, often used to verify FT-IR results. As manual sampling combined with LC–MS analyses is based on up- concentrating the degradation compounds into the impingers, it can be used to detect compounds present in low concentrations, and can therefore give a more overall picture of the composition of the emissions. LC–MS is also used to study the solvent degradation and quantify degradation components (Knuutila et al., 2014b; Moser et al., 2020; Thompson et al., 2017a). Unfortunately, in general very little information is given about the LC-MS methods used by the pilot plants.

Like LC–MS, GC–MS is also used to monitor both the emissions and the solvent degradation in various pilots (Moser et al., 2011b; Fujita et al., 2013; Artanto et al., 2012; Knudsen et al., 2009, 2013; da Silva et al., 2012; Thompson et al., 2017a). The samples are often the same as the ones analysed with LC–MS, and so these two methods combined gives a comprehensive overview of the sample composition. But like with LC–MS, the methods used is in most cases under reported or not reported at all. There are however exceptions, where the method used is thoroughly rendered (Reynolds et al., 2015b).

Compared to the methods mentioned above, the information gained from IC is restricted to ionic species. This results in that that its use varies a lot in the different pilot plants. In some cases, it is used to analyse HSS in the solvent samples (Thompson et al., 2014, 2017a,b; Moser et al., 2020; Reynolds et al., 2015b; da Silva et al., 2012; Fitzgerald et al., 2014), while in some cases only inorganic anions such as sulphate is analysed (Mertens et al., 2015; Moser et al., 2020; Knuutila et al., 2014b). How well the methods are rendered seems to depend on where the analysis has been conducted. For the ones performed in-house, the method is described well, while when external laboratories have been used it is usually not described.

Titration is a quick and cheap method, but is nevertheless not extensively used in the pilots. Under titration measurements of total amine concentration (total alkalinity), measurement of the CO_2-loading, or measurement of HSS is included. When titration is used to analyse samples from the pilots, many or all of these are usually performed (Moser et al., 2011a; Artanto et al., 2012; Knudsen et al., 2009, 2014; Fitzgerald et al., 2014).

The last two analytical methods included are PTR-MS and ICP-MS/-OES. PTR-MS is used in some of the plants as an online analysis tool for amine concentration and volatile components (Moser et al., 2014; Bumb et al., 2017). In these cases, it is often used to study volatile degradation products in the emission stream (Fujita et al., 2013). ICP-MS/-OES is an offline method, and is used by some pilots to detect and quantify metals and trace elements in a solution (Moser et al., 2020; Knudsen et al., 2014; Thompson et al., 2017a). Little information is shared about the instruments or methods being used for both these analyses.

5. Discussion and recommendations

Most of the pilots are not in continuous operation. Furthermore, the different campaigns typically focus on various aspects of the process to reduce risk, costs, and close knowledge gaps. As the pilot campaigns are costly, data on a lot of different aspects of the process is collected simultaneously. The campaign's focus may be on process performance of a promising solvent or solvent blend, and large changes in the process parameters are done throughout the campaign duration. At the same time as the process itself is optimised, data related to solvent degradation can be collected for stability assessment. These different focus points of the different campaigns make it more challenging to compare them to one another, when it comes to degradation and emission. Degradation depends on many factors as well as process parameters, including flue gas composition, temperatures in the absorber and desorber, construction material of the plant, and the solvent residence times in the absorber and desorber. This means that for a clear and unambiguous comparison, all these factors need to be taken into consideration, when they mostly are reported in varying detail, depending on the campaign emphasis. Finally, the reported degradation, the analytical methods, sampling frequency and type of compounds analysed, also vary a lot from campaigns to campaign. All these factors lead to a situation, where a comparison of degradation in different campaigns, even when operated with the same solvent, is intricate. The gathered learning from all these campaigns together does, however, give an overall picture of the degradation that has been and can be observed when operating a post-combustion CO_2 capture plant using MEA.

Below, the main findings related to flue gas treatment, degradation and emission are discussed.

Flue gas pretreatment. Sufficient flue gas pretreatment before entering the absorber column plays a vital role in the solvent stability in

connection with coal-fired power plants. For example, the pilot plants in Niederaussem, Esbjerg and Heilbronn, which have extensive setups for pretreatment, have much lower formation rates of HSS than those, like Loy Yang and the 0.1 MWth CAER pilot, where more limited flue gas pretreatment is performed. There is a good agreement that removing SO_x, NO_X and particulates from the flue gas a positive effect on solvent degradation and therefore emissions of degradation compounds.

Solvent degradation. When reading the summaries of degradation and corrosion products quantified in Table 4.3 to Table 4.7 it is important to keep in mind that a plethora of process conditions may play decisive roles in the degradation mechanisms and rates that take place. Usually, limited information is reported when it comes to changes in process conditions during the campaign, and detailed process design, like residence time of the solvent in the absorber sump. Knowledge of these details could give additional insights on what influences solvent stability.

Organic acids have often been used as an indication of MEA degradation, but no studies have yet found a direct correlation between their concentration and the total degradation in an arbitrary MEA campaign. In addition to the organic acids being precursors for the formation of other degradation compounds, HEF being formed from formic acid, HEA from acetic acid etc., different campaigns have showed different acids as primary degradation products. At the pilot plant in Niederaussem, acetate is measured in higher concentrations than formate (Moser et al., 2011a, 2018, 2020), but in the Loy Yang and TCM pilots the opposite is seen (Reynolds et al., 2015b; Morken et al., 2017) (Fig. 4.1). Furthermore, as some (thermal) degradation compounds tend to increase in concentration in the beginning of a campaign and then steadily decrease later in the campaign (Moser et al., 2020), reacting to further degradation compounds or decomposing, it is important to be aware of what one is measuring. These compounds should therefore not be used for assessing the state of the amine solvent.

Because organic acids react further to form other degradation compounds throughout the operation time, their concentrations do not always increase linearly. It is less common to quantify other degradation compounds, since they typically require more complicated analytical methods, which are time-consuming and costly. Based on the results of the studied pilot campaigns, there doesn't seem to be any single degradation product that quantitatively correlates with the overall amine degradation. Despite of some of the HSS being of inorganic origin, coming from the flue gas itself (SO_4^{2-}, Cl^-, NO_3^-, etc.) and some from the degradation of the amine, it is still an important parameter so consider when assessing the state of the solvent. It has been seen that despite of extensive flue gas pretreatment, remaining concentrations of inorganic contaminants increases steadily with operation time (Thompson et al., 2017a). However, in several cases the total amount of heat stable salts (HSS) in the solvent increases nearly linearly throughout the operation time, regardless of other process parameters and this might give a good indication of the solvent degradation rate (Reynolds et al., 2015b; Thompson et al., 2014; Feron et al., 2015). The total amount of HSS is often not given in articles describing pilot campaigns and instead, the monitoring focuses on selected organic acids. In these cases, knowing how well the monitored compounds describe the solvent's degree of degradation can be challenging. If one still wants to study single organic acids, an assessment should probably still be made to the total amount of HSS.

Also, although organic acids are some of the typical main degradation products of MEA, this is most likely not the same for other amines. Despite of these products often being denominated as *primary* degradation products, this does not state anything about their importance, merely the order in which they are formed. Using an organic acid, such as, i.e. formic acid as a proxy to assess overall degradation should therefore be done with caution, regardless of which amine is studied. Nevertheless, the concentrations of heat stable salts and inorganics from the flue gas and corrosion can still indicate the properties and stability of the different solvents. Iron is a frequently monitored inorganic species in the solvent and a correlation between ammonia formation and iron concentration in the solvent has been clearly observed (Dhingra et al., 2017). Despite of this correlation, it is not clear which effects cause this, whether it is the increasing corrosivity with increasing degradation or an increased iron solubility caused by pH changes (Nordstrom and Alpers, 1997) or iron complex formation with a more degraded solution. A combination of these explanations is also likely. An explanation for the rapid spike observed both for ammonia formation and iron concentration has not been found. Further and thorough analytical work will be needed to fully understand these phenomena in degraded amine solvents.

Most studies choose a factor to compare a new solvent blend to benchmark 30 wt% MEA (*aq.*), like total concentration of HSS or total concentration of nitrosamines in the solvent (TONO). These give insights about specific degradation properties of the solvent and is useful for solvent stability assessment. Comparing single property of solvent, like TONO-concentration can be a way to address specific issues, like safety of the operators. However, it does not say anything about the overall solvent stability. Comparing the amount of dissolved inorganic components in the same pilot but for different solvent systems may indicate the suitability of a certain solvent in certain application (Thompson et al., 2014; Feron et al., 2015).

There is no guideline for how to monitor amine degradation in a carbon capture plant. This has resulted in the use of various methods in different pilot campaigns, with no common consensus in terms of what compounds to analyse for and how this is done. A determining factor in the choice of analytical method is often the availability and cost of the analytical methods. Some methods might be more readily available but give less information, for example total alkalinity, while others are very costly and unavailable, and might therefore not be chosen, like for example LC-MS.

Combination of measurement of NH_3 by FT-IR combined with determination of NH_3 concentrating in the water wash, as well as total HSS concentration in the liquid solvent could be a relatively easy and solvent independent way of monitoring the state of degradation in the plant. It should be remembered, that specific analyses should be performed to monitor the accumulation of toxic and harmful degradation compounds in the solvent loop. Additionally, specific methods to monitor the emission of volatile degradation compounds and solvent amine will always be needed.

Analytical methods. Few of the analytical methods applied in monitoring the amine degradation have been sufficiently validated. Validation of a method ensures that the analytical system used is suitable for its purpose and that it provides legitimate data. Ideally, an analytical method should be validated against another method, which is independent of its measurement principle. For instance, the quantification of MEA by LC-MS should agree with the concentration measured by cation IC, as these methods depend on entirely different measurement principles.

Furthermore, in many cases, very little information has been published regarding the parameters of the analytical methods used, e.g. flow rate and retention time, in the chromatographic methods. This is unfortunate, as it makes it impossible for others to validate the reliability of the claims given regarding the results of these analyses. In combination with, and maybe as a result of, the restricted information given about the analytical methods is the under-reporting of uncertainties and detection limits. Both these parameters are important in handling the data given, and the lack thereof therefore impairs the results.

It is widely seen that some external laboratories are processing the samples from different campaigns and pilots. In these cases, accredited, validated methods for the specific compounds in question are crucial. Use of round robin tests could be an effective way to ensure the consistence of the reported analyses of degradation compounds. Published round robin tests have, for example, highlighted the challenges in analyses of nitrosamines (Fraboulet et al., 2016).

Emissions. As emissions are site and solvent specific, direct comparison of actual emissions from different pilot plants is therefore not an option. The emission of highly volatile degradation compounds, like ammonia, can usually be controlled with water or acid wash (Mertens et al., 2013; Knudsen et al., 2013). The same applies to many solvent compounds, as long as the aerosol formation is limited. For example, the gaseous MEA emission could be abated by single well- designed water wash (Mertens et al., 2012, 2013). In the presence of aerosol, the solvent emissions can be significant, and aerosol mitigation techniques are needed to reduce the emissions to acceptable levels. The emissions through aerosol particles can be reduced by eliminating the mist precursors upstream from the absorber, or by controlling the growth of the aerosol particles in the absorber. The proposed ways to control the aerosol growth, are reducing the temperature gradients in the absorber or accelerating the particle growth to form large, easily removable aerosols (Moser et al., 2014; Mertens et al., 2013; Knudsen et al., 2013). Operation of the presence of some upstream equipment like wet flue gas desulphurisation unit, gas heater, and wet electrostatic precipitator can have a crucial influence on the aerosol formation (Moser et al., 2015; Mertens et al., 2015). In general, the installation of a Brownian demister unit reduces the aerosol emissions (Khakharia et al., 2014; Bade et al., 2014; Lombardo et al., 2017).

Emissions of both the solvent itself and its degradation products has to be considered and monitored, but the available information about the pilots and performed campaigns varies. For example, data related to solvent emissions and descriptions of emission reduction technologies are often missing. Besides, the emission reduction technologies used are sometimes proprietary, and details are therefore not given in the publication. A reliable monitoring strategy is required to keep track of the degradation and emission in pilot-plants. There is, however, no set standard to follow. Instead, multiple analytical methods are being used, and this choice is often dependent on the desired information, available resources and know-how as well as the availability of equipment.

Finally, all full-scale plants will need an emission permit, and these depend on local regulations where the plant is located. In Norway, for example, the emission permit for TCM regulates the emission levels for solvent amine, alkylamines aldehydes and ammonia (Morken et al., 2014). The regulation also includes nitrosamine and nitramine.

The following take-home-messages and trends summarise the main findings:

- Flue gas pretreatment including SO_x, NO_X and particle removal significantly increases solvent stability. Pilot plants containing an excessive flue gas pretreatment system tend to experience significantly less degradation than those with a limited or no such system. However, the type of flue gas pre-treatment also impacts the emissions, as some flue gas pretreatments can increase the risk of amine mist formation by increasing the presence of nuclei in the flue gas.
- Monitoring of any single known degradation compound is not a universal way of assessing solvent stability, not even for the comprehensively studied MEA. The organic compounds formate and acetate, for example, seem to vary in their relative abundance in different pilot plants and campaigns. Some compounds even decrease in concentration after a certain time of operation and therefore, the monitoring of single compounds should be done with caution and this knowledge in mind.
- A relatively simple, and to some extent, solvent independent method to monitor solvent degradation could be a combination of measurement of gas- phase NH_3 by FT-IR with total HSS concentration in the liquid solvent. However, monitoring of NH_3 or the total HSS concentration is not always the best solution. But for solvents that produce NH_3 and HSS as one of their primary degradation compounds, such as MEA, this is a straight-forward and informative monitoring approach. Knowledge of the main degradation compounds are therefore always needed.

- There is no universal standard for measurement of emission from large-scale capture plant. An international standard is also lacking for sampling, conditioning, and analysis of volatile trace elements in flue gas, leaving the CO_2 capture plant (Moser et al., 2013). These issues should be addressed in future works and development of such a standard would enhance the comparability and certainty in the measurements on site.
- There is a general lack in reporting of analytical methods and their uncertainties, when emission and degradation data is published. To facilitate reproducible and comparable results, documented methods should be applied for the quantification of species both in gas and liquid phase, including all parameters for chromatographic analyses.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.ijggc.2020.103246.

References

Aas, N., da Silva, E.F., 2010. Emission measurements at Dong's Emission measurements at Dong's pilot plant for CO_2 capture in Esbjerg. Technical report. SINTEF. Materials and Chemistry, Oslo.

Akinpelumi, Korede, Saha, Chiranjib, Rochelle, Gary T., 2019. Piperazine aerosol mitigation for post-combustion carbon capture. Int. J. Greenhouse Gas Control 91, 102845. https://doi.org/10.1016/j.ijggc.2019.102845.

Aronu, U.E., Lauritsen, K.G., Grimstvedt, A., Mejdell, T., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 1781–1794.

Artanto, Y., Jansen, J., Pearson, P., Do, T., Cottrell, A., Meuleman, E., Feron, P., 2012. Fuel 101, 264–275.

Azzi, M., Day, S., French, D., Halliburton, B., Jackson, P., Lavrencic, S., Riley, K., Tibbett, A., 2010. CO2 Capture Mongstad-Project A-Establishing sampling and Analytical Procedures for Potentially Harmful Components From Post-Combustion Amine Based CO2 Capture Task 2: Procedures for Manual Sampling.

Bade, O.M., Knudsen, J.N., Gorset, O., Askestad, I., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 884–892.

Bazhenov, S., Vasilevsky, V., Rieder, A., Unterberger, S., Grushevenko, E., Volkov, V., Schallert, B., Volkov, A., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 6349–6356.

Bazhenov, S., Rieder, A., Schallert, B., Vasilevsky, V., Unterberger, S., Grushevenko, E., Volkov, V., Volkov, A., 2015. Int. J. Greenhouse Gas Control 42, 593–601.

Bello, A., Idem, R.O., 2005. Ind. Eng. Chem. Res. 44, 945–969.

Bernhardsen, I.M., Trollebø, A.A., Perinu, C., Knuutila, H.K., 2019. J. Chem. Thermodyn. 138, 211–228.

Blachly, C.H., Ravner, H., 1963. The Effect of Trace Amounts of Copper on the Stability of Monoethanolamine Scrubber Solutions. Naval Research Lab Washington DC, Washington DC.

Brigman, N., Shah, M.I., Falk-Pedersen, O., Cents, T., Smith, V., De Cazenove, T., Morken, A.K., Hvidsten, O.A., Chhaganlal, M., Feste, J.K., Lombardo, G., Bade, O.M., Knudsen, J., Subramoney, S.C., Fostås, B.F., De Koeijer, G., Hamborg, E.S., 2014. Energy Proc. 63, 6012–6022.

Brostrøm, A., Kling, K.I., Hougaard, K.S., Mølhave, K., 2020. Complex Aerosol Characterization by Scanning Electron Microscopy Coupled with Energy Dispersive X-ray Spectroscopy.

Brown, N., Heller, G., Staab, G., Silverman, T., Kupfer, R., Brown, R., Brown, A., 2017. Energy Proc. 114, 1075–1086.

Bui, M., Gunawan, I., Verheyen, V., Feron, P., Meuleman, E., 2016. Int. J. Greenhouse Gas Control 48, 188–203.

Bumb, P., Patkar, P.E., Mather, R., Kumar, R., Hall, J., Morton, F., Anthony, J., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1087–1099.

Burkart, J., Steiner, G., Reischl, G., Moshammer, H., Neuberger, M., Hitzenberger, R., 2010. J. Aerosol Sci. 41, 953–962.

Byers1, R.L., Davis, J.W., White, E.W., Mcmillan, R.E., 1971. A Computerized Method for Size Characterization of Atmospheric Aerosols by the Scanning Electron Microscope, p. 6.

Chahen, L., Huard, T., Cuccia, L., Cuzuel, V., Dugay, J., Pichon, V., Vial, J., Gouedard, C., Bonnard, L., Cellier, N., Carrette, P.L., 2016. Int. J. Greenhouse Gas Control 51, 305–316.

Chi, S., Rochelle, G.T., 2002. Ind. Eng. Chem. Res. 41, 4178–4186.

Cousin, A., Cottrell, A., Huang, S., Feron, P.H.M., Lawson, A., 2012. Energy Generation, pp. 16–17.

Cousins, A., Wardhaugh, L., Cottrell, A., 2016. Absorption-Based Post-Combustion Capture of Carbon Dioxide. Elsevier Inc, pp. 649–684 (Chapter 26).

Cuccia, L., Dugay, J., Bontemps, D., Louis-Louisy, M., Vial, J., 2018. Int. J. Greenhouse Gas Control 72, 138–151.

Cuzuel, V., Brunet, J., Rey, A., Dugay, J., Vial, J., Pichon, V., Carrette, P.L., 2014. Oil Gas Sci. Technol. 69, 821–832.

Dahlin, R.S., Landham, E.C., Kelinske, M.L., Wheeldon, J.M., Love, D.H., 2013. Amine Losses and Formation of Degradation Products in Post-Combustion CO2 Capture. In: July38th International Technical Conference on Clean Coal & Fuel Systems 2013: The Clearwater Clean Coal Conference, 651.

da Silva, E.F., Lepaumier, H., Grimstvedt, A., Vevelstad, S.J., Einbu, A., Vernstad, K., Svendsen, H.F., Zahlsen, K., 2012. Ind. Eng. Chem. Res. 51, 13329–13338.

Da Silva, E., Kolderup, H., Goetheer, E., Hjarbo, K.W., Huizinga, A., Khakharia, P., Tuinman, I., Mejdell, T., Zahlsen, K., Vernstad, K., Hyldbakk, A., Holten, T., Kvamsdal, H.M., Van Os, P., Einbu, A., 2013. Energy Procedia, pp. 778–783.

Davis, J., Rochelle, G., 2009. Energy Proc. 1, 327–333.

de Koeijer, G., Enge, Y., Sanden, K., Graff, O.F., Falk-Pedersen, O., Amundsen, T., Overå, S., 2011. Energy Procedia, pp. 1207–1213.

de Koeijer, G., Talstad, V.R., Nepstad, S., Tønnessen, D., Falk-Pedersen, O., Maree, Y., Nielsen, C., 2013. Int. J. Greenhouse Gas Control 18, 200–207.

Dhingra, S., Khakharia, P., Rieder, A., Cousins, A., Reynolds, A., Knudsen, J., Andersen, J., Irons, R., Mertens, J., Abu Zahra, M., Van Os, P., Goetheer, E., 2017. Energies 10.

Diab, F., Provost, E., Laloué, N., Alix, P., Souchon, V., Delpoux, O., Fürst, W., 2012. Fluid Phase Equilib. 325, 90–99.

Eide-Haugmo, I., Lepaumier, H., da Silva, E.F., Einbu, A., Vernstad, K., Svendsen, H.F., 2011. 1st Post Combustion Capture Conference, pp. 17–19.

Eliasson, J., Watson, I.M.K., 2016. Weber in Volcanic Ash: Hazard Observation. Elsevier Inc, pp. 89–94.

Enaasen, N., Zangrilli, L., Mangiaracina, A., Mejdell, T., Kvamsdal, H.M., Hillestad, M., 2014. Energy Proc. 63, 1040–1054.

Feron, P., Conway, W., Puxty, G., Wardhaugh, L., Green, P., Maher, D., Fernandes, D., Cousins, A., Shiwang, G., Lianbo, L., 2014. Energy Proc. 63, 1399–1406.

Feron, P., Conway, W., Puxty, G., Wardhaugh, L., Green, P., Maher, D., Fernandes, D., Cousins, A., Cottrell, A., Li, K., Shiwang, G., Lianbo, L., Hongwei, N., Hang, S., Jinyi, W., Shiqing, W., Dongfang, G., Maeder, M., Clifford, S., 2015. Comparative Evaluation of A New Liquid Absorbent in A PCC Pilot Plant in China.

Feron, P.H., Cousins, A., Jiang, K., Zhai, R., Garcia, M., 2020. Fuel 273, 117776.

Fine, N.A., 2015. Ph.D. Thesis. The University of Texas at Austin.

Fitzgerald, F.D., Hume, S.A., McGough, G., Damen, K., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 6239–6251.

Fraboulet, I., Chahen, L., Lestremau, F., Grimstvedt, A., Schallert, B., Moeller, B.C., Järvinen, A., 2016. Energy Procedia, Vol. 86. Elsevier Ltd, pp. 252–261.

Freeman, S.A., 2011. Ph.D. Thesis. The University of Texas in Austin.

Frimpong, R.A., Johnson, D., Richburg, L., Hogston, B., Remias, J.E., Neathery, J.K., Liu, K., 2013. Chem. Eng. Res. Des. 91, 963–969.

Fujita, K., Muraoka, D., Ogawa, T., Kitamura, H., Suzuki, K., Saito, S., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 727–734.

Gao, T., Selinger, J.L., Rochelle, G.T., 2019. Int. J. Greenhouse Gas Control 83, 236–244.

Gjernes, E., Pedersen, S., Cents, T., Watson, G., Fostås, B.F., Shah, M.I., Lombardo, G., Desvignes, C., Flø, N.E., Morken, A.K., De Cazenove, T., Faramarzi, L., Hamborg, E. S., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1146–1157.

Goff, G.S., 2005. Oxidative Degradation of Aqueous Monoethanolamine in CO2 Capture Processes: Iron and Copper Catalysis, Inhibition, and O2 Mass Transfer.

Goldstein, J., Newbury, D., Joy, D., Lyman, C.E., Echlin, P., Lifshin, E., Sawyer, L., Michael, J., 2003. Scanning Electron Microscopy and X-ray Microanalysis – | Joseph Goldstein | Springer. Springer US, p. 690. XIX.

Gorset, O., Knudsen, J.N., Bade, O.M., Askestad, I., 2014. Energy Procedia, Vol. 63, pp. 6267–6280. Elsevier Ltd.

Gouedard, C., Picq, D., Launay, F., Carrette, P.-L., 2012. Int. J. Greenhouse Gas Control 10, 244–270.

Graff, O.F., 2010. Advanced CO2 Capture With Bio Aker Clean Carbon-Emission Measurement and Analysis from Mobile Carbon Capture Test Facility.

Grimstvedt, A., Wiig, M., Einbu, A., Vevelstad, S.J., 2019. Int. J. Greenhouse Gas Control 83, 293–307.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., Lindinger, W., 1995. Int. J. Mass Spectrom. Ion Process. 149-150, 609–619.

Harsha, S., Khakharia, P., Huizinga, A., Monteiro, J., Goetheer, E., Vlugt, T.J.H., 2019. Int. J. Greenhouse Gas Control 85, 86–99.

Hilliard, M.D., 2008. Ph.D. Thesis. The University of Texas at Austin.

Idem, R., Supap, T., Shi, H., Gelowitz, D., Ball, M., Campbell, C., Tontiwachwuthikul, P., 2015. Int. J. Greenhouse Gas Control 40, 6–25.

Järvinen, A., Aitomaa, M., Rostedt, A., Keskinen, J., Yli- Ojanperä, J., 2014. J. Aerosol Sci. 69, 150–159.

Jeong, C.-H., Evans, G.J., 2009. Aerosol Sci. Technol. 43, 364–373.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Herbig, J., Märk, L., Schottkowsky, R., Seehauser, H., Sulzer, P., Märk, T.D., 2009. Int. J. Mass Spectrom. 286, 32–38.

Kadnar, R., Rieder, J., 1995. J. Chromatogr. A 706, 339–343.

Kamijo, T., Sorimachi, Y., Shimada, D., Miyamoto, O., Endo, T., Nagayasu, H., Mangiaracina, A., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 813–816.

Kentish, S.E., 2016. Absorption-Based Post-Combustion Capture of Carbon Dioxide. Woodhead Publishing, pp. 426–438. Chapter 17.

Kero, I., Jørgensen, R., 2016. Int. J. Environ. Res. Public Health 13, 871.

Khakharia, P., Brachert, L., Mertens, J., Huizinga, A., Schallert, B., Schaber, K., Vlugt, T. J., Goetheer, E., 2013. Int. J. Greenhouse Gas Control 19, 138–144.

Khakharia, P., Kvamsdal, H.M., Da Silva, E.F., Vlugt, T.J.H., Goetheer, E., 2014a. Int. J. Greenhouse Gas Control 28, 57–64.

Khakharia, P., Mertens, J., Vlugt, T.J.H., Goetheer, E., 2014b. Energy Proc. 63, 911–925. Elsevier Ltd.

Khakharia, P., Brachert, L., Mertens, J., Anderlohr, C., Huizinga, A., Fernandez, E.S., Schallert, B., Schaber, K., Vlugt, T.J., Goetheer, E., 2015. Int. J. Greenhouse Gas Control 34, 63–74.

Knudsen, J.N., Jensen, J.N., Vilhelmsen, P.-J., Biede, O., 2009. Energy Proc. 1, 783–790.

Knudsen, J.N., Bade, O.M., Anheden, M., Bjorklund, R., Gorset, O., Woodhouse, S., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 1804–1813.

Knudsen, J.N., Bade, O.M., Askestad, I., Gorset, O., Mejdell, T., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 6464–6475.

Knuutila, H., Svendsen, H.F., Asif, N., 2014a. Int. J. Greenhouse Gas Control 31, 182–191.

Knuutila, H., Asif, N., Vevelstad, S.J., Svendsen, H.F., 2014b. Oil Gas Sci. Technol. [[Revue d'IFP Energies nouvelles]] 69, 805–820.

Kohl, A.L., Nielsen, R.B., 1997. In: Kohl, A.L., Nielsen, R.B. (Eds.), Gas Purification, 5th ed.). Gulf Professional Publishing, Houston, pp. 187–227 (Chapter 3).

Kolderup, H., da Silva, E., Mejdell, T., Tobiesen, A., Haugen, G., Hoff, K.A., Josefsen, K., Strøm, T., Furuseth, O., Hanssen, K.F., Myhrvold, T., Johnsen, K., 2020. SINTEF REPORT Emission Reducing Technologies H&ETQP Amine6 SINTEF Materials and Chemistry.

Léonard, G., Voice, A., Toye, D., Heyen, G., 2014. Ind. Eng. Chem. Res. 53, 18121–18129.

Lamminen, E., 2011. J. Phys.: Conf. Ser. 12064.

Lepaumier, H., Picq, D., Carrette, P.L., 2009a. Ind. Eng. Chem. Res. 48, 9061–9067.

Lepaumier, H., Picq, D., Carrette, P.L., 2009b. Ind. Eng. Chem. Res. 48, 9068–9075.

Lepaumier, H., Grimstvedt, A., Vernstad, K., Zahlsen, K., Svendsen, H.F., 2011. Chem. Eng. Sci. 66, 3491–3498.

Levin, M., Gudmundsson, A., Pagels, J.H., Fierz, M., Mølhave, K., Löndahl, J., Jensen, K. A., Koponen, I.K., L, J., 2015. Aerosol Sci. Technol. 49, 556–565.

Li, W., Shao, L., 2009. J. Geophys. Res. 114, D09302.

Lindinger, W., Hansel, A., Jordan, A., 1998. Int. J. Mass Spectrom. Ion Process. 173, 191–241.

Lombardo, G., Fostås, B.F., Shah, M.I., Morken, A.K., Hvidsten, O.A., Mertens, J., Hamborg, E.S., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1210–1230.

Lundanes, E., Reubsaet, L., Greibrokk, T., 2014. Chromatography: Basic Principles, Sample Preparations and Related Methods, 1st ed. Wiley-VCH, Weiman.

Macbride, D.M., Malone, C.G., Hebb, J.P., Cravalho, E.G., 1997. Effect of Temperature Variation on FT-IR Spectrometer Stability, p. 1.

Majeed, H., Knuutila, H., Hillestad, M., Svendsen, H.F., 2017. Effect of amine volatility on aerosol droplet development in absorption columns. Energy Proc. 114, 977–986. Elsevier Ltd.

Mangiaracina, A., Zangrilli, L., Robinson, L., Kvamsdal, H.M., Os, P.V., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 1617–1636.

Matin, N.S., Remias, J.E., Neathery, J.K., Liu, K., 2012. Ind. Eng. Chem. Res. 51, 6613–6618.

Mejdell, T., Vassbotn, T., Juliussen, O., Tobiesen, A., Einbu, A., Knuutila, H., Hoff, K.A., Andersson, V., Svendsen, H.F., 2011. Energy Procedia, Vol. 4. Elsevier Ltd, pp. 1753–1760.

Mejdell, T., Haugen, G., Rieder, A., Kvamsdal, H.M., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1231–1244.

Mertens, J., Knudsen, J., Thielens, M.L., Andersen, J., 2012. Int. J. Greenhouse Gas Control 6, 2–11.

Mertens, J., Lepaumier, H., Desagher, D., Thielens, M.L., 2013. Int. J. Greenhouse Gas Control 13, 72–77.

Mertens, J., Bruns, R., Schallert, B., Faniel, N., Khakharia, P., Albrecht, W., Goetheer, E., Blondeau, J., Schaber, K., 2015. Int. J. Greenhouse Gas Control 39, 470–477.

Meuleman, E., Cottrell, A., Ghayur, A., 2016. Absorption-Based Post-Combustion Capture of Carbon Dioxide. Woodhead Publishing, pp. 519–551 (Chapter 22).

Morken, A.K., Nenseter, B., Pedersen, S., Chhaganlal, M., Feste, J.K., Tyborgnes, R.B., Ullestad, y., Ulvatn, H., Zhu, L., Mikoviny, T., Wisthaler, A., Cents, T., Bade, O.M., Knudsen, J., De Koeijer, G., Falk-Pedersen, O., Hamborg, E.S., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 6023–6038.

Morken, A.K., Pedersen, S., Kleppe, E.R., Wisthaler, A., Vernstad, K., Ullestad, y., Flø, N. E., Faramarzi, L., Hamborg, E.S., 2017. Energy Procedia, Vol. 114, pp. 1245–1262. Elsevier Ltd.

Morton, F., Laird, R., Northington, J., 2013. Energy Proc. 37, 525–539.

Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T., 2011a. Int. J. Greenhouse Gas Control 5, 620–627.

Moser, P., Schmidt, S., Sieder, G., Garcia, H., Stoffregen, T., Stamatov, V., 2011b. Energy Procedia, Vol. 4. Elsevier Ltd, pp. 1310–1316.

Moser, P., Schmidt, S., Wallus, S., Ginsberg, T., Sieder, G., Clausen, I., Palacios, J.G., Stoffregen, T., Mihailowitsch, D., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 2377–2388.

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G.A., Stoffregen, T., Rösler, F., 2014. Energy Procedia, Vol. 63. Elsevier Ltd, pp. 902–910.

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G.A., Stoffregen, T., Richter, T., 2015. Int. J. Greenhouse Gas Control 41, 229–238.

Moser, P., Wiechers, G., Stahl, K., Stoffregen, T., Vorberg, G., Lozano, G.A., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1000–1016.

Moser, P., Wiechers, G., Schmidt, S., Elsen, R., Khakharia, P., Garcia, J., Monteiro, M.-S., Jens, K.-J., Solli, K.-A., Sanchez Fernandez, E., Garcia, S., Maroto-Valer, M., Barrio, J., Kvamsdal, M., 2018. GHGT-14. Melbourne, Australia.

Moser, P., Wiechers, G., Schmidt, S., Garcia Moretz-Sohn Monteiro, J., Charalambous, C., Garcia, S., Sanchez Fernandez, E., 2020. Int. J. Greenhouse Gas Control 95, 102945.

Nakamura, S., Yamanaka, Y., Matsuyama, T., Okuno, S., Sato, H., 2013. Energy Proc. 37, 1897–1903.

Nakamura, S., Yamanaka, Y., Matsuyama, T., Okuno, S., Sato, H., Iso, Y., Huang, J., 2014. Energy Proc. 63, 687–692.

Newbury, D.E., Ritchie, N.W.M., 2013. Scanning 35, 141–168.

Nicol, K., 2013. Recent Developments in Particulate Control. IEA Clean Coal Centre Technical Report. IEA Clean Coal Centre, pp. 1–54.

Nielsen, P.T., Li, L., Rochelle, G.T., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 1912–1923.

Nordstrom, D.K., Alpers, C.N., 1997. Reviews in Economic Geology. Vol. 6A. The Environmental Geochemistry of Mineral Deposits, January 1999. Society of Economic Geologists, Inc, pp. 133–160 (Chapter 6).

Okuno, S., Nakamura, S., Yamanaka, Y., Matsuyama, T., Sato, H., Ikeda, R., 2017. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 1282–1287.

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A.L., Meuleman, E., 2015a. Int. J. Greenhouse Gas Control 39, 407–419.

Reynolds, A.J., Verheyen, T.V., Adeloju, S.B., Chaffee, A.L., Meuleman, E., 2015b. Energy Fuels 29, 7441–7455.

Richner, G., Puxty, G., 2012. Ind. Eng. Chem. Res. 51, 14317–14324.

Rieder, A., Unterberger, S., 2013. Energy Procedia, Vol. 37. Elsevier Ltd, pp. 6464–6472.

Rieder, A., Dhingra, S., Khakharia, P., Zangrilli, L., Schallert, B., Irons, R., Unterberger, S., van Os, P., Goetheer, E., 2017. Energy Proc. 114, 1195–1209.

Rochelle, G., Bishnoi, S., Chi, S., Dang, H., Santos, J., 2001. Research Needs for CO2 Capture From Flue Gas by Aqueous Absorption/Stripping.

Rochelle, G.T., 2012. Curr. Opin. Chem. Eng. 1, 183–190.

Rogelj, J., Shindell, D., Jiang, K., Fifita, S., Forster, P., Ginzburg, V., Handa, C., Kheshgi, H., Kobayashi, S., Kriegler, E., 2018. Mitigation pathways compatible with 1.5°C in the context of sustainable development. Global Warming of 1.5°C. Intergovernmental Panel on Climate Change.

Rooney, P.C., Dupart, M.S., Bacon, T.R., 1998. Hydrocarbon Process. Int. Ed. 77, 109–113.

Saito, S., Udatsu, M., Kitamura, H., Murai, S., Kato, Y., Maezawa, Y., Watando, H., 2014. Energy Proc. 51, 176–183.

Saito, S., Udatsu, M., Kitamuraa, H., Murai, S., 2015. PCCC-3.

SEPA, 2015. Review of Amine Emissions From Carbon Capture Systems, Version 2.01.

Sexton, A.J., 2008. Ph.D. Thesis. The University of Texas in Austin.

Shah, M.I., Lombardo, G., Fostås, B., Benquet, C., Kolstad Morken, A., De Cazenove, T., 2018. 14th International Conference on Greenhouse Gas Control Technologies GHGT-14.

Sheppard, B.S., Shen, W.-L., Davidson, T.M., Carusot, J.A., 1990. J. Anal. Atom. Spectrom. 5, 700–967.

Shimadzu Corporation, 2014. Manual TOC Shimadzu.

Singh, A., Stéphenne, K., 2014. Shell Cansolv CO_2 capture technology: Achievement from first commercial plant. Energy Proc. 63, 1678–1685.

Somridhivej, B., Boyd, C.E., 2016. Aquaculture 459, 99–109.

Spietz, T., Chwoła, T., Krótki, A., Tatarczuk, A., Wi̧ecław-Solny, L., Wilk, A., 2018. Int. J. Environ. Sci. Technol. 15, 1085–1092.

Strazisar, B.R., Anderson, R.R., White, C.M., 2003. Energy Fuels 17, 1034–1039.

Sun, K., Lu, L., Jiang, H., 2012. Thermal Sci. 16, 1437–1441.

Tanthapanichakoon, W., Veawab, A., McGarvey, B., 2006. Ind. Eng. Chem. Res. 45, 2586–2593.

Thomas, R., 2004. Practical Guide to ICP-MS. Marcel Dekker, New York.

Thompson, J.G., Frimpong, R., Remias, J.E., Neathery, J.K., Liu, K., 2014. Aerosol Air Qual. Res. 14, 550–558.

Thompson, J.G., Bhatnagar, S., Combs, M., Abad, K., Onneweer, F., Pelgen, J., Link, D., Figueroa, J., Nikolic, H., Liu, K., 2017a. Int. J. Greenhouse Gas Control 64, 23–33.

Thompson, J.G., Combs, M., Abad, K., Bhatnagar, S., Pelgen, J., Beaudry, M., Rochelle, G., Hume, S., Link, D., Figueroa, J., Nikolic, H., Liu, K., 2017b. Int. J. Greenhouse Gas Control 64, 267–275.

Thompson, J., Nikolic, H., Combs, M., Bhatnagar, S., Pelgen, J., Abad, K., Liu, K., 2017c. Energy Proc. 114, 1297–1306.

Thompson, J., Richburg, H., Liu, K., 2017d. Energy Procedia, Vol. 114. Elsevier Ltd, pp. 2030–2038.

Todoli, J.L., Mermet, J.M., 2008. Liquid Sample Introduction in ICP Spectrometry. Elsevier.

Vega, F., Sanna, A., Navarrete, B., Maroto-Valer, M.M., Cortés, V.J., 2014. Greenhouse Gases: Sci. Technol. 4, 707–733.

Vevelstad, S.J., Grimstvedt, A., Elnan, J., da Silva, E.F., Svendsen, H.F., 2013. Int. J. Greenhouse Gas Control 18, 88–100.

Wang, T., Jens, K.-J., 2012. Ind. Eng. Chem. Res. 51, 6529–6536.

Wang, T., Jens, K.J., 2014. Int. J. Greenhouse Gas Control 24, 98–105.

Wang, T., Hovland, J., Jens, K.J., 2015. J. Environ. Sci. (China) 27, 276–289.

Welker, R.W., 2012. Developments in Surface Contamination and Cleaning: Detection, Characterization, and Analysis of Contaminants. Elsevier Inc, pp. 179–213.

Wittgens, B., Einbu, A., Brunsvik, A., Zahlsen, K., 2010. H&E TQP 1D1: Establish Sampling and Analytical Procedures for Potentially Harmful Components Post Combustion Amine Based CO2 Capture.Subtask 3: Online Sampling and Analysis. FM07-AJZ00-Z-RA-0002-03.

Zhu, Q., 2010. Non- Calcium Desulphurisation Technologies. IEA Clean Coal Centre Technical Report. IEA Clean Coal Centre, pp. 1–42.