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Predicting amine mist formation based on aerosol number concentration and size measurements in flue gas

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Abstract

Amine based solvent used for CO₂ capture can be lost during the process due to: degradation, vaporization, mechanical losses and aerosol (mist) formation. Only recently, studies have appeared pointing out that aerosols can dominate the total amine emission at pilot plant scale behind coal fired power plants. Future full scale amine scrubber installations will be imposed emission limit values (ELV) for a number of components including NH₃ and the amine itself. Most likely these ELV will be expressed as maximum concentrations tolerated in the CO₂ poor flue gas leaving the stack so it is important to prevent or cure amine aerosol emission. The study presents a novel combination of two existing measurement techniques, that measure: (i) amine emissions from the top of the absorber using FTIR and (ii) PSD of the incoming flue gas using the ELPI⁺. The study is the first to show how combining these two measurement techniques allows to predict the presence or absence of mist formation. This hypothesis is based on information obtained during several measurement campaigns on different pilot plants.

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1. Introduction

Post combustion carbon capture (PCCC) is based on the removal of CO_2 after the combustion of a fossil fuel. Reactive absorption is one of the most important techniques for the removal of CO_2 from flue gas. This reactive absorption process makes use of the reversible nature of the chemical reaction of an aqueous alkaline solvent (usually an amine) with an acid gas (CO_2). The amine based solvent can be lost during the process due to: degradation, vaporization, mechanical losses and aerosol (mist) formation. Studies on emission processes such as vaporization and mist formation exist at laboratory conditions [1, 2, 3]. Only recently, studies have appeared pointing out that aerosols can dominate the total amine emission at pilot plant scale [4, 5, 6, 7, 8, 9, 10, 11, 12].

The origin and driving factors of the NH_3 and monoethanolamine (MEA) emissions including mist formation phenomena as measured at different pilot plants using a Fourier Transformed Infra Red (FTIR) analyser were recently published [10]. Mist precursors can be ultrafine liquid or solid particles of sulphuric acid, salts or any form of particulate matter in the flue gas entering the absorber from for example a coal fired power plant [4, 11]. Submicron ($< 1 \mu\text{m}$) particulate matter or H_2SO_4 aerosols may serve as nuclei for the formation of amine aerosols [4]. Particles in the form of soot (10^6 number of particles per cm^3) can cause MEA emissions in the order of 200 mg Nm^{-3} [11]. H_2SO_4 aerosols with a particle number concentration in the order of 10^8 per cm^3 can lead to MEA emissions in the range of $600\text{--}1100 \text{ mg Nm}^{-3}$.

Future full scale amine scrubber installations will be imposed emission limit values (ELV) for a number of components including NH_3 and the amine itself. Most likely these ELV will be expressed as maximum concentrations tolerated in the CO_2 poor flue gas leaving the stack. The exact value of the ELV will depend on the local authorities but it is clear that the high amine concentrations measured during mist formation phenomena will not be tolerated. Therefore, countermeasures need to be implemented. For the design of different countermeasures types and location (upstream or downstream the amine plant), it is crucial to have an idea of the aerosol size distribution and number concentration entering or leaving the absorber.

Recently, a relation between measurements of the aerosol sizes and numbers entering and leaving a MEA mini-pilot absorber was published [13]. These data can serve future installations when designing aerosol emission countermeasures. The generated H_2SO_4 aerosols sent into the mini-pilot absorber are observed to be extremely small (i.e. $< 0.2 \mu\text{m}$) with number concentrations exceeding $1\text{E}8 \text{ cm}^{-3}$. The aerosols grow in size as they travel through the mini-pilot absorber through the taking up of water and amine to sizes close to but staying below $1 \mu\text{m}$. However, despite the fact that most of the aerosols (expressed in number concentrations) are well below $1 \mu\text{m}$, most of the water (and thus amine) is found in the aerosol sizes between 0.5 and $2 \mu\text{m}$. Therefore, if one aims at designing efficient countermeasures, eliminating this size fraction is crucial.

The work presented here builds further on the lessons learned in previous work and presents Particle Size Distributions (PSD) and corresponding total number concentrations measured upstream of different carbon capture pilot installations around the world. The combination of amine measurements using FTIR behind the absorber and linking it to PSD measurements in front of the absorber is novel. The objective of the paper is apart from presenting these novel data, the formulation of a hypothesis that allows to predict mist formation based on the PSD of the incoming flue gas. It is important to note that throughout this work, MEA was used as a solvent.

2. Materials and Methods

The presence or absence of mist formation inside the absorber is observed through amine measurements carried out by a Fourier Transformed Infra Red (FTIR) analyser in the flue gas leaving the absorber. These amine concentrations are then linked to the incoming (i.e. in front of absorber) PSD and total number concentration as measured by an Electrostatic Low Pressure Impactor (ELPI⁺). Both analyser systems and sampling-set-ups are shortly presented below.

2.1. Fourier Transformed Infra Red (FTIR) measurements of amines leaving the absorber

A FTIR analyser (GASMET CX 4000) is used to analyse the gas phase leaving the absorber at the different pilot plants. The sampled flue gas is heated to 180°C using a trace heated transfer line. At this temperature the aerosol phase is vaporised implying that the concentration of amine measured by FTIR is the sum of vapour phase MEA and MEA that was present in the aerosols [9, 10]. The FTIR analyzer was specifically calibrated for the amine of interest at the different locations (in this study always MEA). The uncertainty of the components measured by the FTIR depends on the chemical composition (and thus possible interferences) of the matrix in which it is measured. Therefore, stating detection and quantification limits is difficult; however they are in the low mg Nm⁻³ range at the applied conditions (for more information, [9,10]).

2.2. Electrostatic Low Pressure Impactor (ELPI⁺) measurements of particle size distribution and total number concentrations

The PSD and total number concentrations in the incoming flue gas are measured using DEKATI's Electrical Low Pressure Impactor, ELPI⁺. The particles are charged by corona charging and subsequently separated in a low pressure cascade impactor with 14 electrically insulated collection stages. The measured current signals are proportional to the number concentration and size. By using kernel functions in order to account for the charging efficiency dependency on diameter and for the collection efficiencies of the different stages, the number concentration in every channel can be calculated. A more precise description of the original ELPI can be found in [14, 15]. The ELPI⁺ features an additional impactor stage which enlarges the measurement range covered by impactor stages from a cut-off of 30 nm down to a cut-off of 16.7 nm [16]. Additionally, a filter stage has been added which collects all the particles that aren't trapped in one of the impactor stages. The charging efficiency decreases strongly with the particle size, so that below 6 nm no charging is expected anymore. Thereby, particles down to 6 nm can be measured. The maximum number concentrations that are detectable in every stage as indicated in the manual are not reached during any of the pilot testing described here.

A last important remark concerns the non-isokinetic sampling of the aerosols and the effect this may have on the observed aerosol sizes. This effect is only important for aerosols that are larger than a few µm [17, 10]. The absence of the effect of iso-kinetic sampling on the measured MEA concentrations using the FTIR was presented in [10]. This was explained by the fact that the aerosols should be smaller than 1 µm which is confirmed by a study [13] in which the PSD of the incoming flue gas and the PSD of the flue gas leaving the absorber are compared. Therefore, it was judged not necessary to iso-kinetically sample the aerosols for both the FTIR and ELPI⁺ measurements at the different pilots visited in the framework of this study. Measured ELPI⁺ total number concentrations of H₂SO₄ aerosols were compared with measurements using a condensation particle counter (UF-CPC 200 PALAS GmbH) [18]. The usage of these two different principles for the measurement of the volatile sulfuric acid aerosol shows that both devices confirm high number concentrations above 10⁸ cm⁻³. In case where the flue gas contains a very high

number of aerosols smaller than 6 nm, an overestimation of number concentrations measured by the ELPI⁺ filter stage (< 6nm), which has been noted in literature before for the original ELPI, has been observed.

It is impossible to use the ELPI⁺ on saturated flue gas since condensation on the impactor plates of the ELPI⁺ would imply short-circuiting between impactor plates and thus falsify the measurement. This means that the flue gas must be diluted before entering the ELPI⁺. This study uses a one-stage heated dilution step to dilute the flue gas to make ELPI⁺ measurements possible as depicted in figure 1. The flue gas behind the absorber is usually found at a temperature close to 50 °C. The sampling probe as well as the dilutor is therefore heated up to a temperature slightly higher (eg. 80 °C) to avoid condensation along the sampling system. Inside the heated box with the dilutor, the sampled flue gas is diluted with heated, particle and moisture free air. Controlling the flow through the mass flow controller allows applying different dilution ratios and by doing so, the effect of the dilution on the measured PSD can be investigated.

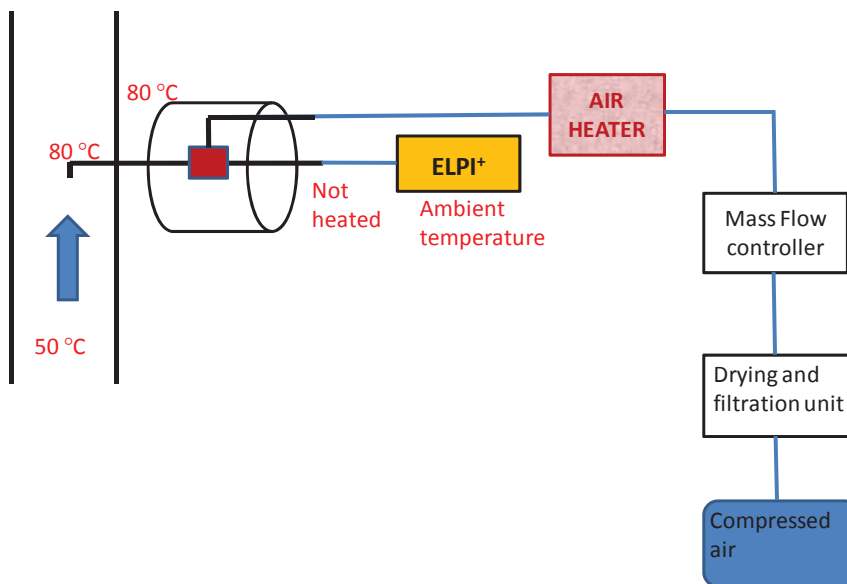


Fig. 1. Sampling set-up of the ELPI⁺ including the one-stage heated dilution step

3. Results and discussion

3.1. Effect of dilution on the measured ELPI⁺ PSD measurements

Similarly to the effect described in [13] for the case of H₂SO₄ aerosols, shrinking of MEA aerosols behind the absorber with increasing dilution ratios is observed here due to the evaporation of water from the aerosol. Figure 2 presents this phenomenon for one of the locations during a period where high MEA mist formation was taking place. Increasing the dilution increases the fraction of PM/aerosols in the smallest size fractions. The extent to which the shrinking occurs is very much function of the nature of the PM/aerosols. At some of the locations, hardly any shrinking was observed suggesting the absence of high water content inside the PM/aerosols. This reduces the

potential for water evaporation and thus shrinking of the PM/aerosols. One must be aware that the measured PSD may not be the true PSD and this difference may be larger in cases where aerosols with large water contents are present. In these conditions, the true PSD will be shifted towards larger sizes as compared to the measured PSD (with dilution) and this shift is very much a function of the dilution ratio as can be seen in figure 2.

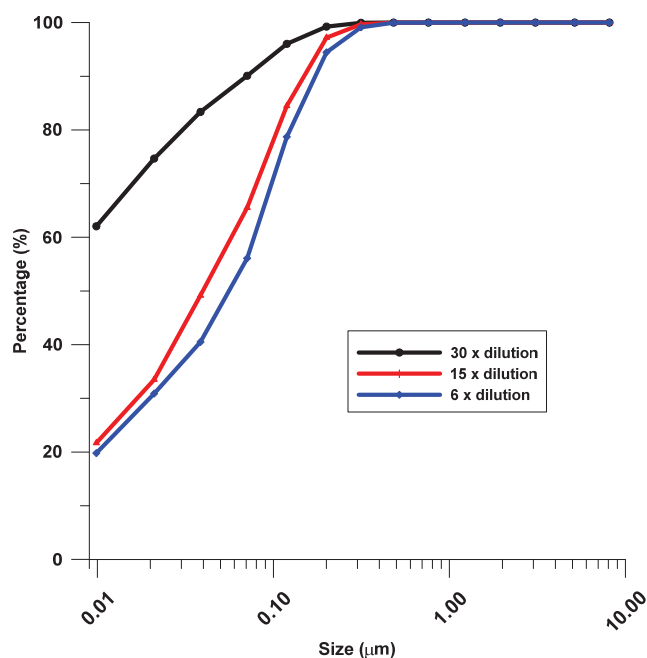


Fig. 2. Increasing dilution reduces the apparent aerosol size and thus shifts the measured PSD towards smaller sizes in cases where aerosols/PM with high water content are present

3.2. Filtering PM/aerosols from the flue gas prevents mist formation inside the absorber

At different pilot plants, the effect of filtering of the incoming flue gas on the MEA mist formation process was evaluated. Filtering the flue gas targets to reduce the number concentration of the mist precursors (PM/aerosols) entering the absorber and thus reducing the chances of mist formation. Figure 3 presents this effect for 3 different flue gases sent into a MEA absorber. For reasons of confidentiality, the number concentrations on the y-axis are removed. As a comparison, the measured ambient PM/aerosol PSD of the ambient air at one of the locations is also presented. Flue gas 1 and 2 contain a high number of PM/aerosols and at these locations, MEA mist formation took place leading to high MEA emissions from the top of the absorber. ELPI⁺ measurements of the flue gas 3 however, revealed significant lower PM/aerosol numbers. Using this flue gas, no MEA mist formation process took place and only volatile MEA emissions were measured by the FTIR (< few ppm). In order to confirm the fact that it is indeed the presence of a high number of mist precursors that induces the mist formation and not something else inside the flue gas, a filtering of flue gas 2 was carried out (keeping all other operational parameters constant). The filtering resulted in a PSD measured by the ELPI⁺ similar to the PSD of flue gas 3 with even slightly lower numbers than in

flue gas 3. The filtering prevented MEA mist formation and the FTIR revealed very low MEA emissions leaving the absorber. This experiment reveals that indeed, the presence of mist precursors in the form of nuclei (PM/aerosols) in great numbers leads to mist formation and thus high amine emissions. Filtering the flue gas is therefore considered as a possible countermeasure to avoid mist formation.

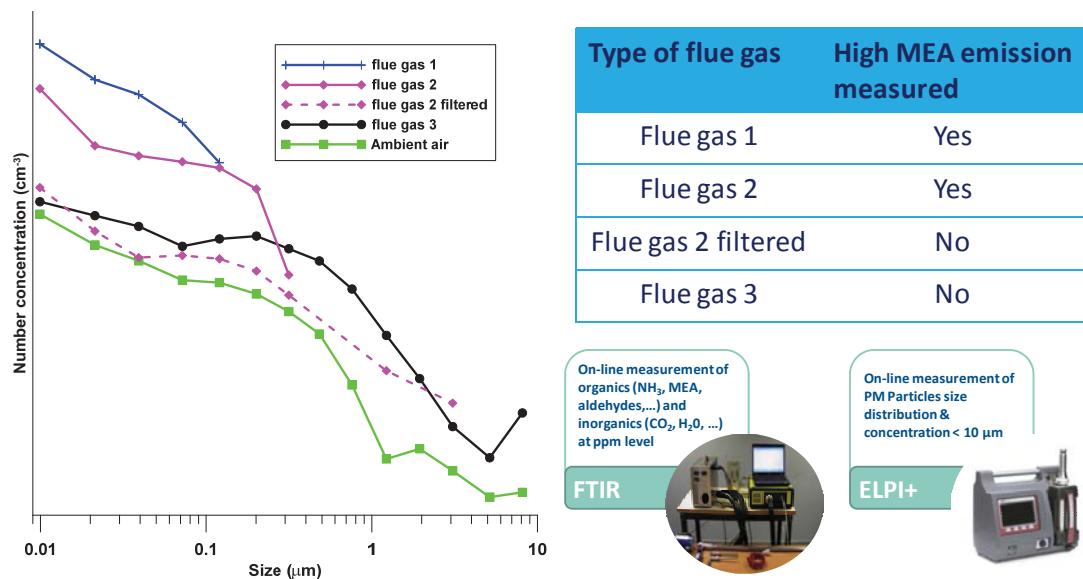


Fig. 3. Filtering PM/aerosols out of the flue gas prevents mist formation inside the MEA carbon capture absorber

3.3. Relating measured PM/aerosols concentrations upstream of different pilot plants to the presence/absence of mist formation

Based on several measurement campaigns at different pilot plants during which experiments were carried out where the flue gas was filtered, we managed to come to the hypothesis presented in figure 4. We noted that above a certain threshold number concentration, MEA mist formation takes place and that below a certain value, no MEA formation issues were encountered. In between these values, there is a grey zone. Flue gas with a total number concentration that falls within this grey zone was observed to lead during some periods to mist formation and during other periods not. This may be related to variations in numbers of PM/aerosols entering the absorber as well as to changes in operational settings of the pilot plant varying throughout the day. It must be repeated that this work was done only using MEA as a scrubbing solvent and therefore, the thresholds observed in this study may not be valid for other solvent systems.

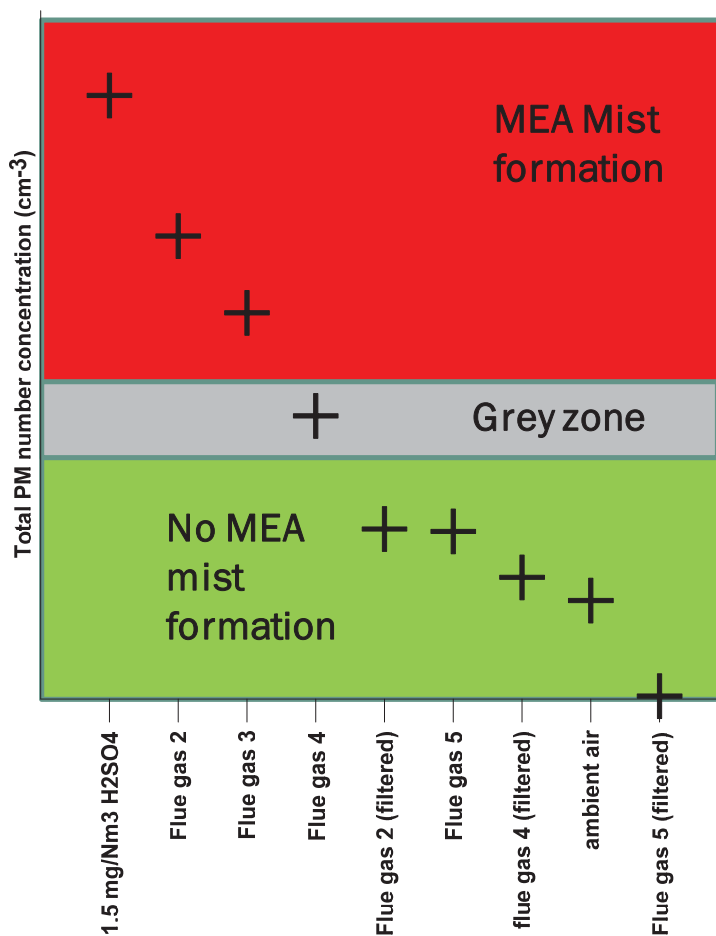


Fig. 4. Relating number concentrations measured upstream of different MEA capture pilots to the presence or absence of MEA mist formation

4. Conclusions and future research

The study presents a novel combination of two existing measurement techniques, that measure: (i) amine emissions from the top of the absorber using FTIR and (ii) PSD of the incoming flue gas using the ELPI⁺. The ELPI⁺ measurement is challenging because dilution of the saturated flue gas is necessary to avoid condensation inside the equipment which would falsify the readings. Dilution can impact the apparent PSD since if the PM/aerosols of interest contain a lot of water, increasing the dilution shrinks the PM/aerosols and thus will affect the measured PSD.

The study presents a case whereby high MEA emissions were present because of MEA mist formation. Filtering this flue gas reduced the MEA emissions to very low numbers. This experiment reveals that indeed, the presence of mist precursors in the form of high number concentrations of nuclei (PM/aerosols) leads to mist formation and thus high MEA emissions.

The study is the first to show how combining these two measurement techniques (amine emissions from the top of the absorber and PSD of the incoming flue gas) allows to predict the presence or absence of mist. This hypothesis is based on information obtained during several measurement campaigns on different pilots. Above a certain threshold number concentration, MEA mist formation takes place whereas below a certain value, no MEA mist formation issues were encountered. In between these values, there is a grey zone.

Currently, research is going-on to identify the best possible countermeasures (upstream, inside and downstream of the absorber) to avoid or cure (i.e. precipitate the formed aerosols) this mist formation. We require a high efficiency countermeasure but at the lowest CAPEX and OPEX cost possible since this will be extremely important for future demo and full scale installations.

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