



## Review article

# A critical review of existing strategies for emission control in the monoethanolamine-based carbon capture process and some recommendations for improved strategies



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## ABSTRACT

Exit streams of decarbonated flue gas and carbon dioxide from monoethanolamine (MEA)-based post-combustion carbon capture (PCC) units may emit amine and its degradation products as vapor and as dissolved in fine droplets of liquid. Conventional scrubbing, cooling, adsorption and mist elimination processes used with PCC units are not sufficient to eliminate these emissions. Further attempts to eliminate these emissions could be challenging, because the available options to control them are limited. Such emissions appear to be an environmental concern and more sophisticated methods are required to capture a these emissions, if the amine based PCC process is to be widely used in coal fired power stations. Since MEA, its degradation products and various corrosion reactions in liquid phase are precursors of all gaseous emission, an ideal approach to reduce emissions would be to maintain a low concentration of degradation products in the liquid phase, which would also reduce the concentration of degradation products in fine droplets. Further improvements in process design may also eliminate vapor emissions. This paper summarizes various emission control methods, including their limitations and further scope for their improvement and use in the amine-based PCC process.

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## Contents

1. Introduction	178
2. Effect of feed flue gas impurities	179
3. Emissions from different amine based solvents	179
4. Current gaseous emission control methods	180
4.1. Fine droplet emissions	180
5. Limitations and further improvements	181
5.1. Absorption column and demister design	181
5.2. Water consumption, sludge production and toxic emissions	181
6. Advanced emission control strategies	183
7. Recommendations	186
Acknowledgements	187
References	187

## 1. Introduction

Post-combustion capture (PCC) of carbon dioxide (CO<sub>2</sub>) is one of several feasible options to reduce emissions from coal-fired power plants. Alkanolamine-based CO<sub>2</sub> separation, which was originally a

natural gas sweetening process, could easily be deployed for this purpose. Commonly used alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), methyl-diethanolamine (MDEA), piperazine (PIPA), 2-amino-2-methyl propanol (AMP) and 2-methylaminoethanol. Out of these, MEA is considered as the most suitable [1,2], due to its biodegradability, relatively lower toxicity and superior CO<sub>2</sub> absorption [2] characteristics compared with amines such as 2-amino-2-methyl propanol (AMP), N-methyl

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diethanolamine (MDEA) and piperazine (PIPA) [1]. However, thermal and oxidative degradation of MEA produces potentially toxic emissions, including aldehydes, organic acids and nitrogen-containing compounds such as other amines, amides, nitrogen oxides, ammonia and N-nitroso compounds. Some of these degradation products are high-molecular-weight compounds that tend to accumulate in the solvent phase, while other volatile degradation products with limited solubility remain in the gas phase and are emitted along with the flue gas or CO<sub>2</sub> product stream. MEA degradation is a vast topic, and is therefore considered as beyond the scope of this paper, which only discusses emission control methods. The current state-of-the-art PCC process uses several stages of scrubbing with water [3–5], acid [6] or proprietary chemicals [7,8] along with demisters to arrest entrained vapors and fine droplets.

Mimura et al. [3] showed that single-stage scrubbing with water is not very effective in arresting vapors. A minimum of three stages of water scrubbing could effectively separate vapors, but this requires more wash water and larger equipment [3]. The quantity of water and equipment size could be reduced with an acid wash stage [6] using different acids and a proprietary chemical wash [7,8]. Depending on the type of acid used, the products of the acid wash may be either regenerated to amine or disposed of. The mechanism of the proprietary chemical wash is not disclosed in the literature [7,8]. Methods such as cooling and adsorption have also been used for separating vapors, but these have not been specifically tested in a PCC process. However, cooling could only capture condensable vapors, and would not be effective for ammonia, which is the main component of PCC unit emissions [6,9]. An adsorption system could remove most of the vapors, but the large equipment size and costs [10] are unattractive for commercial-scale power plants.

The entrainment of fine liquid droplets into exit streams can be minimized by demisters on the top sections of the absorber and stripper [11]. Out of the available types of demisters (inertial impaction, Brownian diffusion and direct interception), none are recognized as suitable for PCC. This may be because the demisters are optimized for minimizing operating and capital costs [12], and therefore may not be as effective as required for emission control.

Specific methods to minimize the concentration of degradation product in the liquid phase have been deployed [13–15,8,3,9]. This paper summarizes different methods used in the existing designs of absorbers and strippers to minimize the entrainment of vapor and fine droplets in exit streams. The paper also presents the main limitations of the existing basis of and methodologies for demister design, highlights the importance of reducing degradation product concentration in liquid phase, and examines prospective methods for separating liquid degradation products. Finally, a set of recommendations are drawn for further improvement in the MEA-based PCC process.

## 2. Effect of feed flue gas impurities

The MEA-based PCC process was originally developed for natural gas sweetening, which mainly involves removal of H<sub>2</sub>S, CO<sub>2</sub> and water. The flue gas from coal-fired power plants contains several impurities (PM<sub>10</sub>, SO<sub>x</sub>, NO<sub>x</sub>, CO, HCl, HF, CH<sub>4</sub>, N<sub>2</sub>O, Sb, As, Be, Cd, Co, Pb, Mn and Ni), which have to be removed by scrubbing with water prior to the CO<sub>2</sub> absorption step, to prevent corrosion of equipment, contamination, and degradation of MEA solvent [16–19]. Although the capture process effectively removes SO<sub>2</sub> and NO<sub>x</sub>, it generates emissions of NH<sub>3</sub>, MEA, and other compounds resulting from thermal [20] as well as oxidative [21,22] degradation of MEA. Certain concentrations of PM<sub>10</sub>, SO<sub>x</sub>, NO<sub>x</sub>, CO, HCl, HF, etc., promote MEA degradation and emission of some

degradation products. For example, up to 60 ppm of SO<sub>2</sub> can inhibit the degradation of MEA by scavenging oxidative radicals in absorber condition. A higher concentration of SO<sub>2</sub> does not inhibit degradation, but increases corrosion of equipment alloy [17] and the corrosion products can promote degradation of MEA [9]. As mentioned above, MEA degradation is a vast topic; therefore, only aspects relevant to the emission control are briefly presented in this paper. However, the determination of emissions from PCC units into gas and liquid streams is important, because liquid-phase emissions (or impurities) may also have some adverse effects on MEA solvent.

## 3. Emissions from different amine based solvents

The best amine-based CO<sub>2</sub> capture unit would have the minimum energy requirements, a high degree of CO<sub>2</sub> capture, and minimum liquid waste and emissions to air. Amines are toxic, but human health risks related to the amines used for CO<sub>2</sub> capture are unknown. Health risks are strongly dependent on the type of amine used and the actual amount of emission. MEA is the most commonly used amine for CO<sub>2</sub> capture and is nontoxic and biodegradable, whereas amines such as AMP, MDEA and PIPA are ecotoxic and have comparatively low biodegradability [1]. The CO<sub>2</sub> absorption characteristics of MEA are also superior to the other amines [2]. However, thermal and oxidative degradation of MEA produces a number of toxic emissions, such as: ammonia, nitrosamines, N-acetyl ethanolamine (C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>), N-glycylglycine, (C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>), N-(hydroxyethyl)-succinimide (C<sub>6</sub>H<sub>8</sub>NO<sub>3</sub>), 1-(2-hydroxyethyl)-2-imidazolinone (C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>), 1-(2-hydroxyethyl)-2-imidazolidone (HEIA) [20] (C<sub>6</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>), N-(2-hydroxyethyl)-ethylenediamine (HEEDA) [20] (C<sub>4</sub>H<sub>13</sub>N<sub>2</sub>O), N,N'-di(hydroxyethyl)urea (DHU) [20], (C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>), N,N-diacetylanolamine, (C<sub>6</sub>H<sub>11</sub>NO<sub>3</sub>), 2,6-dimethyl-4-pyridinamine (C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>), 2-imidazolecarboxaldehyde (C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>O) and 2-oxazolidone (OXA) (C<sub>3</sub>H<sub>5</sub>NO<sub>2</sub>).

CO<sub>2</sub> capture processes that use amino acid salt [23] solutions have a relatively fast rate of CO<sub>2</sub> absorption, high CO<sub>2</sub> absorption capacity, high stability towards oxygen and a more favorable binding energy than MEA solution. Many amino acid salts are naturally occurring and have favorable biodegradation properties. Due to these favorable properties, amino acid salts have been deployed for commercial-scale acid gas removal processes [24], and also in membrane contactors, which are compact and cost effective [25]. The oxygen resistance of amino acid salts makes them suitable for CO<sub>2</sub> separation from flue gas generated from coal combustion [26,27].

Aqueous amino acid salt solutions (AAS) have low enthalpy and near zero vapor pressure, which makes them suitable for an economical and emission-free capture process. The energy requirement for the regeneration of amino acid salt solution is 2.7 GJ/tonne of CO<sub>2</sub>, which compares favorably with the MEA process. Amino acid salt is stable under thermal stress and oxygen environments that appear under real operating conditions. The total loss of solvent per year due to oxidative and thermal degradation is estimated around <20% of the amount originally used in a standard MEA process. Only 1 ppm ammonia emission was reported during 4000 h of operation at Staudinger Power Plant, which uses amino acid salt solution for PCC, and emissions of volatile organic compounds, formaldehydes, methylamine and nitrosamines were not detectable [28,29].

In the amino acid salt PCC process, as CO<sub>2</sub> concentration rises above a certain value in salt solution, an equilibrium proportion of CO<sub>2</sub> is precipitated either as neutral amino acid molecule or a bicarbonate salt [27,30]. Therefore, a constant concentration of CO<sub>2</sub> in the salt solution phase is maintained at equilibrium. As a result, the driving force for absorption is maintained at a constant

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