

Degradation Products and Volatile Emissions in Post-Combustion Amine CO₂ Capture Processes

Abstract 452

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1.0 Introduction

This paper presents a synopsis of a literature review study performed by Trimeric Corporation on behalf of the Electric Power Research Institute. The objective of this study was to identify what impurities exist (or are expected to exist) in a post-combustion carbon dioxide (CO₂) capture process and to gather and summarize representative thermodynamic, chemical and environmental fate and transport data/properties on these species.

The topical scope of this review was limited to post-combustion coal-fired and natural gas-fired power plants equipped with aqueous-based solvent processes for CO₂ capture. This scope excludes related areas, such as capture of CO₂ from other anthropogenic sources such as cement kilns, fertilizer plants, refineries, ethanol plants, process furnaces, and other sources. Similarly, the study excludes consideration of alternate CO₂ capture technologies, such as membranes, solid sorbents, or enzyme-based technology.

The scope of investigation included all of the major categories of discharge streams that could potentially enter the CO₂ reservoir or the environment, including the following:

- The CO₂ capture solvent itself;
- Potential additives to the solvent (e.g. corrosion inhibitors);
- Oxidative and/or thermal degradation products;
- Vapor and/or liquid constituents exiting with the treated flue gas;
- Thermal reclaimer wastes;
- Solid filter cartridges and similar wastes;
- Process wastewater, and associated wastewater treatment sludges;
- Impurities present in the source CO₂ [e.g. Mercury (Hg), Selenium (Se), Nitrogen Oxides (NO_x), Sulfur Oxides (SO_x), etc.]; and
- Constituents originating from downstream of the capture process.

The initial search resulted in approximately 500 publications. The raw list of publications was screened by eliminating extraneous and duplicate publications and was narrowed to a list of 289 publications. Examples of extraneous publication topics are corrosion papers and papers that dealt with theoretical modeling of CO₂ capture systems. These remaining 289 publications comprised 119 conference papers, 110 journal articles, 39 government and industry reports, 11 patents, 6 academic theses and 4 books.

Information sought from these literature sources included ranges of concentrations for volatile components emitted to atmosphere, water solubility and partitioning, thermodynamic relationships and properties of degradation products, any other data that identifies or quantifies solvent degradation products that could enter groundwater or atmosphere, and existing analytical methods and capabilities for detecting these products.

The process described above resulted in identification of 314 individual chemical compounds that were reported in the literature as being associated with aqueous-based scrubbing of flue gas for CO₂ capture. The list of 314 chemicals was screened to focus on chemicals that were monoethanolamine (MEA) degradation products of thermal and oxidative degradation and from reactions with NO_x. These criteria narrowed the list of MEA degradation products for physical property review down to 76 compounds, which are shown in Table 1.

For these compounds, physical property databases were searched to identify physical property data sets relevant to the partitioning of the compounds between CO₂ and water phases. Sources of physical property data that were searched included DECHEMA's DETHERM® database and a comprehensive index of solubility data for chemicals in supercritical CO₂¹.

Table 1: MEA Degradation Products for Physical Property Review

Acetate [Acetic Acid, CH ₃ COOH]	Nitric Acid	3-hydroxyethylamino-N-hydroxyethyl propanamide
Methane [CH ₄]	Oxalate/Oxalic Acid	4-(2-hydroxyethyl)piperazine-2-one [HEPO]
Methanol	Piperazine	Amino acetaldehyde OR alpha-aminoacetaldehyde
2-butanol	Succinic Acid	Glycolamide [Hydroxyacetamide]
Acetaldehyde	Imidazole	Hydroxyacetaldehyde [Glycolaldehyde]
Acetone	Nitrosodiethylamine	Methyl dl-lactate
Ethanol	Oxamide [Oxalic Acid Amide]	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide [HEHEAA]
Ethylene Glycol	1-(2-hydroxyethyl)-2-imidazolidinone OR 1-(2-hydroxyethyl)imidazolidone-2 OR 1-(2-hydroxyethyl)-2-imidazolidone [HEIA]	N-(2-hydroxyethyl)acetamide OR N-acetylethylethanolamine OR N-(2-hydroxyethyl)acetate
Formate [Formic Acid]	1-(2-hydroxyethyl)piperazin-2-one	N-(2-hydroxyethyl)-diethylenetriamine [MEA trimer]
N-butyric Acid	1-(2-hydroxyethyl)piperazine-2-one [1-HEPO]	N-(2-hydroxyethyl)ethylenediamine [HEEDA, HEED]
Propionate/Propionic Acid	1-[(2-aminoethyl)amino]ethanol	N-(2-hydroxyethyl)imidazole [HEI]
Acetamide	1-[2-[(2-hydroxyethyl)amino]ethyl]-2-imidazolidone [Cyclic Urea of MEA Trimer]	N-(2-hydroxyethyl)lanthamide
Ammonia [NH ₃]	1-[2-[[2-[(2-hydroxyethyl)amino]ethyl]amino]ethyl]-2-imidazolidone [Cyclic Urea of MEA Quatramer]	N-(2-hydroxyethyl)oxamide
Diethanolamine	1-hydroxyethyl-2-piperazinone	N-(2-hydroxyethyl)succinimide OR N-(hydroxyethyl)succinimide
Diethylamine	1-hydroxyethyl-3-homopiperazine	N-(2-hydroxyethyl)triethylenetetramine [MEA Quatramer]
Dimethylamine [DMA]	1-methyl-2-imidazolecarboxaldehyde	N,N'-bis(2-hydroxyethyl)oxalamide [BHEOX]
Ethylamine	2-((2-[2-hydroxyethyl]amino)ethyl)-amino)ethanol [BHEEDA]	N,N'-di(hydroxyethyl)urea [DHU]
Ethylene [C ₂ H ₄]	2-(pyrrolidin-2-yl)ethanol	N-formylmethanolamine OR hydroxyethylformamide OR N-(2-hydroxyethyl)formamide [HEF]
Formaldehyde	2,6-dimethyl-4-pyridinamine	Nitrosodiethanolamine [NDELA]
Formamide	2-[(2-aminoethyl)amino]ethanol	Nitrosodimethylamine [NDMA]
Glycine	2-hydroxyacetamide	Nitrous acid
Glycolate/Glycolic Acid [Hydroxyacetic Acid]	2-hydroxyethylamino-N-hydroxyethyl acetamide	N-nitrosopiperazine
Methylamine	2-hydroxy-N-(2-hydroxyethyl)acetamide [HHEA]	Oxoacetic Acid
Monoethanolamine [MEA]	2-imidazolecarboxaldehyde	Trimethanolamine
Monomethylamine [MMA]	2-oxazolidone OR 2-oxazolidinone [OZD]	Vinyl Alcohol [Ethenol]
Nitrous Oxide [N ₂ O]		

This search revealed useful sets of published, raw, physical property data. Each of these potentially useful sources of data was tabulated, when found, for each of the chemical compounds of interest. Thirty-three sets of pure component physical property data, thirty sets of component/water binary data, twelve sets of component/CO₂ binary data, and three sets of component/water/CO₂ ternary data were found. Despite the available data, for the most widely studied solvent system for post-combustion capture, physical property data were not found for greater than 50% of the suspected degradation products.

2.0 Examples of Discharge Streams

Emissions to the atmosphere from an amine-based CO₂ capture unit may include some or all of the following: treated gas from the absorber, vent gas from the amine sump (or surge drum), carbon bed filter regeneration off gas, process heater exhaust gas, and the amine regenerator off gas.

The sources of liquid and solid waste discharged from amine units include used or spent amine including carryover from the absorber, spills (e.g., from filter element changeout operations), and blowdown (spent amine if not reclaimed). Condensed water from various sources in the amine unit and compressor interstage cooling can be classified as waste streams. Some amine units also generate sludges (wastes that have both solid and liquid constituents), typically from the reclaimer bottoms and filters. The presence of degradation products in all of the liquid and sludge waste streams is of potential environmental and health concern. Particles, salts, and corrosion products could also be present in the sludge material.

The list of products can be categorized into parent amines, oxidation products, thermal degradation products, atmospheric photo-oxidation products, upstream constituents and the products of reactions with upstream constituents-particularly NO_x and SO_x.

Oxidative degradation products include fragmented volatile products such as alkylamines, aldehydes and ammonia. Less volatile fragmented products include amino acids and carboxylic acids in the form of heat stable salts (HSS). Carboxylic acids, if present, can react with the parent amine to form a class of compounds known as amides. These amides can react with another molecule of the parent amine to form longer chain compounds. Most of these compounds have the potential to leave with the product CO₂ stream from the top of the regenerator.

Thermal degradation products are formed in the presence of CO₂ at elevated temperatures. A majority of primary and secondary amines react with CO₂ to form a carbamate structure. This carbamate structure can undergo a condensation reaction to form a group of compounds known as oxazolidones. Oxazolidones are reactive species that can further react with carbamates to form substituted ethylenediamines, substituted piperazines and other higher molecular weight species. Thermal degradation products are typically non-volatile and will tend to concentrate in the thermal reclaimer bottoms stream.

Some experimental studies have looked at the combined effect of oxidation and thermal degradation, because in a commercial CO₂ capture system the amine will be cycled through oxidation and thermal degradation reaction conditions in the absorber and regenerator, respectively. These combination products of oxidation and thermal degradation are also usually non-volatile.

Table 2 details the number of citations found for amine CO₂ capture systems, categorized by the type of degradation product. MEA is the most widely studied amine system, with the primary focus attributed to oxidative and thermal degradation. Publicly available information investigating the effects of volatile emissions and NO_x/SO_x degradation products on any amine capture systems is minimal.

Table 2: Number of Citations by Solvent System

	Oxidative Degradation	Thermal Degradation	NO_x/SO_x Degradation	Solvent Volatility
MEA	28	18	7	5
DEA	1	5	-	-
MDEA	3	4	-	-
Other Amines	33	24	8	8

3.0 Data Types

The literature sources that provide data on the performance of amine systems can be broken down into three categories: bench-scale studies, pilot plant studies, and analysis of amine samples from commercial facilities. Bench-scale studies are the most prevalent type of data available, because bench-scale experiments can be constructed with less effort, materials and cost when compared to pilot plant experiments. Amine solutions can be used in small quantities, and often times the experimental method can be set up to run multiple experiments concurrently.

A disadvantage regarding bench-scale experiments is that reaction conditions may not be representative of an actual CO₂ capture system. Often times, gas flow rate, temperature, pressure, oxygen concentration, or another reaction parameter has to be manipulated to simulate or accelerate amine degradation rates. In addition, mass transfer conditions that influence solvent degradation can be quite different in a bench-scale apparatus versus a packed tower with countercurrent gas and liquid flow. Assumptions must also be made to correlate degradation rates in a bench-scale system with contact residence times in a packed column.

A pilot plant experimental study may produce degradation products that are more representative of a commercial amine system. As mentioned before, a pilot plant facility requires a considerably larger investment, and access to a synthetic or actual flue gas source. Commercial facilities offer the greatest insight into amine degradation because these solvents have been exposed to flue gas impurities for a prolonged period of time over a wide range of operating conditions (normal operation, startup, shutdown, etc.).

Table 3 summarizes the ranges of experimental conditions for published benchscale degradation studies, while Table 4 lists the type of data available from pilot plant degradation studies. Tables 3 and 4 show that a wide range of benchscale experimental degradation studies have been performed over varying conditions, but pilot plant analyses are limited.

Table 3: Summary of Benchscale Degradation Experiment Types

# of Sources	Amine Systems	Degradation Type	Reactor Type	Agitation Rate (rpm)	Amine Volume (mL)	Temp (°C)	Pressure
3	MEA, MDEA, DEA, DGA™	Oxidative	Sparged	1000-1400	100-350	55-82	Atmospheric
2	MEA, DEA, MDEA, AMP	Oxidative	Autoclave	250	100	140	2 MPa
6	MEA, DEA, MDEA, AMP	Thermal	Autoclave	0-250	100-250	90-250	1.5-6.9 MPa
4	MEA, AMP, PZ, DIPA, DEA, DGA™, MDEA	Thermal	Cylinder	-	5-10	100-150	-
6	MEA, MDEA	Oxidative/ Thermal	Autoclave	0-500	20-450	55-170	0.2-2.17 MPa
1	MDEA	Oxidative/ Thermal	Cylinder	-	1-30	140	-
1	MEA	Oxidative/ Impurities	Autoclave	500	450	55-120	250 kPa
1	MDEA/PZ	Oxidative/ Thermal	ISDA	1440	750	55-120	14.7-58 psig

Table 4: Summary of Pilot Plant Degradation Analyses

Amine	Pilot Plant	Data Type	Flue Gas Type	Flue Gas Capacity	CO ₂ Capacity
Toshiba	Tsinghua	Liquid-Phase Degradation	Synthetic	73,000 SCFD	N/A
MEA	Esbjergvaerket	Liquid-Phase Degradation	Actual	4,230,000 SCFD	24 tpd
MEA, XYZ	Niederaussem	Emissions	Actual	1,300,000 SCFD	7.2 tpd
MEA, MDEA/PZ	EERC	Liquid-Phase Degradation	Actual	187,000 SCFD	N/A
MEA, CASTOR	Esbjergvaerket	Emissions	Actual	4,230,000 SCFD	24 tpd
MEA, MEA/MDEA	Boundary Dam, Regina	Liquid-Phase Degradation	Actual	169,000-500,000 SCFD	1-4 tpd
MEA	SINTEF	Emissions	Synthetic	127,000 SCFD	0.24 tpd

While pilot plant analyses are limited to date, current efforts are focused to increase available pilot plant emissions data. One particular example is data collected at the Niederaussem pilot plant in Germany; this research effort provided concentrations of volatile degradation products and amine from an MEA solution subjected to oxygen (O₂), nitrogen dioxide (NO₂) and sulfur dioxide (SO₂)². These concentrations are shown in Table 5. Results from the purified CO₂ stream provide an indication of the concentration of volatile components that could be emitted from the regenerator.

Table 5: Niederaussem Pilot Plant Volatile Emissions

<u>Compound</u>	<u>Lean Flue Gas</u>	<u>Purified CO₂ Stream</u>
	Concentration Range (ppmv)	Concentration Range (ppmv)
Ammonia	35.5 – 62.1	0 – 1.5
Acetaldehyde	0 – 0.1	6.0 – 6.7
Acetone	0.2 – 0.4	0.1 – 0.4
MEA	0.008 – 0.012	3.2 – 4.6

4.0 Future Work

A search of physical property data for common MEA degradation products revealed that a large amount of physical property data for suspected degradation products is not available. Of the compounds listed, vapor pressure data were found for only 30 of those compounds. For those 30 chemical constituents, CO₂ and water solubility data in terms of vapor-liquid equilibrium (VLE) or liquid-liquid equilibrium (LLE) data was found for only 12 compounds. In other words, physical property data necessary for the determination of the fate of chemical constituents in the downhole CO₂ stream has been published for 16% of a group of representative compounds.

Prior to investing the time and effort into performing bench-scale experiments and conducting analyses to gather more information regarding degradation products and their physical properties, a reasonable next step would be to prioritize the list of compounds. This prioritization could be based on the best estimates of the fate of each compound along with health and environmental risks.

After identifying the group of highest priority compounds, the next step would be to develop a work plan for gathering experimental data. Experimental work is expected to be needed in two areas: measuring the time-dependent rates at which the constituents are formed, and acquiring the physical property data needed for predicting the fate of these compounds once they are generated.

5.0 Acknowledgements

This paper summarizes work sponsored by the Electric Power Research Institute in 2010³.

6.0 References

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