DEGRADATION OF MONOETHANOLAMINE USED IN CO_2 CAPTURE FROM FLUE GAS OF A COAL-FIRED ELECTRIC POWER GENERATING STATION

Brian R. Strazisar, Richard R. Anderson, and Curt M. White

U. S. Department of Energy, National Energy Technology Laboratory
P. O. Box 10940, Pittsburgh, PA 15236

Introduction

Increasing awareness of the possible influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO_2) emissions.[1,2] One such strategy that has received a great deal of attention involves the capture of CO_2 from large point sources (such as fossil fuel-fired power plants) and the long-term storage underground or in the ocean. The CO_2 capture step is expected to make up the majority (up to 75%) of the expense for a carbon sequestration process.[2]

Although there are several different methods that have been proposed for the capture and separation of CO_2, the only method that has been proven to work on an industrial scale is chemical absorption using monoethanolamine (MEA) as a solvent.[2] In this method, MEA absorbs CO_2 through chemical reaction in an absorber column. Since the reaction is reversible, the CO_2 can be driven off by heating the CO_2 rich amine in a separate stripper column. The MEA may be recycled through the process. For the low CO_2 partial pressure present in flue gas, alternative methods of CO_2 removal are less efficient and more expensive than chemical absorption.[2]

A major problem associated with chemical absorption using MEA is the degradation of the solvent through irreversible side reactions with CO_2 and other flue gas components.[3,4,5] This leads to numerous problems with the process. First, degradation of MEA results in solvent loss, requiring the replacement of up to 8 pounds of MEA per ton of CO_2 captured.[6] It is also known to lead to foaming, fouling, and increased viscosity of the amine. In existing CO_2 capture facilities, the degradation products are separated in an evaporative reclaimer and disposed of as hazardous chemical waste.

In the case of carbon sequestration, the most significant problem presented by MEA degradation is associated with increased corrosion caused by the degradation.[3] In order to keep machinery corrosion rates at an acceptable level, the concentration of MEA must be kept low (typically under 20% for coal boilers and ~30% for natural gas-derived flue gas and then only if corrosion inhibitors are employed). Low MEA concentration reduces the effectiveness of the solvent, necessitating large equipment sizes and faster circulation rates. In addition, more energy is required in the stripping column in order to regenerate the amine.[7] This increased "parasitic load" is of particular concern for carbon sequestration. In addition to being an additional cost, producing this extra energy leads to increased CO_2 emissions, which decreases the overall benefit of sequestration.[2] A sensitivity analysis indicates that increasing the concentration of MEA to 70% will cut the parasitic load on a power plant by more than half.[7]

The current study is aimed at developing an increased chemical understanding of MEA degradation processes. Increased insight into the mechanisms and chemical pathways associated with MEA degradation may result in decreasing or eliminating its negative effects. There have been several previous studies on reactions of alkanolamines with O_2,[5] CO_2,[3] COS,[8] or CS_2.[9] Most of these studies were aimed at understanding natural gas sweetening processes, and all were conducted under laboratory conditions. However, in flue gas from a fossil fuel-fired boiler, the process becomes much more complicated due to the presence of a mixture of CO_2, O_2, CO, SO_x, NO_x, fly ash, and other constituents. The degradation process in this case remains poorly understood, particularly under conditions that are common to power plants.[10]

Experimental

The IMC Chemicals Facility in Trona, California is a plant that has been performing CO_2 capture from flue gas since 1978. CO_2 is separated from flue gas of a coal-fired boiler, which is used to produce electricity. In this case, the captured CO_2 is used for carbonation of brine from Searles Lake, California for the commercial production of sodium carbonate. For the current study, MEA samples were obtained from this plant in order to identify the degradation products from the CO_2 separation process. Three samples were obtained: (1)virgin concentrated MEA, (2)"lean" MEA, taken before the CO_2 absorption step, and (3)reclaimer bottoms, which represents the still bottoms that remain after the amine is distilled to remove the degradation products.

In order to identify the volatile organic compounds in the samples, each mixture was separated and analyzed using combined gas chromatography-mass spectrometry (GC-MS) and combined gas chromatography-Fourier transform infrared absorption spectrophotometry (GC-FTIR). Two separate gas chromatographic columns were used for separation. The first was a 60 m × 0.32 mm i. d. fused silica column coated with a 0.25-µm film of 14%-(cyanopropyl-phenyl)-methylpolysiloxane (DB-1701 from J&W Scientific). This column was temperature programmed from 35 to 280°C at 1 C°/min. The second column, a 60 m × 0.25 mm i. d. column coated with 0.25-µm modified polyethylene glycol (Nukol™ from Supelco), was temperature programmed from 50 to 200°C at 5 C°/min. Helium carrier gas was used with initial linear velocities of 40 and 36 cm/s, respectively. In both cases, samples were introduced via a split injector held at 250°C. GC-MS experiments were performed using an HP 5973 mass selective detector (MSD) and GC-FTIR experiments employed an HP 5965A infrared detector (IRD).

In addition, precise molecular masses of the organic compounds were obtained using low voltage high-resolution mass spectrometry (LVHRMS). Mass spectra were acquired on a Kratos MS-50 high-resolution mass spectrometer. In this experiment, the samples were introduced to the ion source directly without prior separation.

Inorganic ionic species were identified using ion chromatography (IC) as well as combined inductively coupled plasma-atomic emission spectroscopy (ICP-AES). IC experiments were performed for anions using a Dionex DX-100 Ion Chromatograph equipped with a conductivity detector. The analytical column used was an IonPac CS14 (4 mm), and the guard column was an IonPac AG14 (4 mm). The eluent was 3.5 mM sodium carbonate/1 mM sodium bicarbonate, at a flow rate of 1.2 ml/min. A self-regenerating ASRS-Ultra (4 mm) suppressor was used. ICP-AES experiments were performed using a Perkin Elmer Optima 3000 to measure trace metal concentrations.

Also, analyses were performed to determine the total nitrosamine concentration in each sample by a technique described elsewhere.[11]

Results and Discussion

Since the focus of this study was on the MEA degradation products, the reclaimer bottoms sample, where these products were concentrated as a result of distillation provided the most important information. Organic compounds that were identified are listed in Table 1 along with the methods of identification. An "x" in the GC-MS or GC-FTIR column indicates a positive match from an electronic search of either MS or FTIR libraries. MS library searches were performed using the NIST/NIH/EPA Mass Spectral Library. FTIR searches were performed using the FTIRsearch.com service.

The LVHRMS column indicates whether a match within 0.003 amu of the mass of the indicated molecule was present in the mass spectrum of the entire sample. Also included in Table 1 is an indication of the column used for the experiment in which each compound was detected. The % of total area refers to the integrated peak area from the total ion chromatogram as a percentage of the total signal intensity for each chromatogram. Other than the MEA, none of the peaks identified in Table 1 were present in identical experiments performed on the virgin MEA.

Table 1. Identified organic compounds from MEA reclaimer bottoms

		method of identification			GC column		%of total area	
peak	compound	GC-MS	GC-FTIR	LVHRMS	DB-1701	Nukol	DB-1701	Nukol
1	N-acetylethanolamine ($C_4H_9NO_2$)	x		x	x	x	8.86	6.28
2	N-glycylglycine ($C_4H_8N_2O_3$)	x		x	x		<0.01	
3	N-(hydroxyethyl)-succinimide ($C_6H_9NO_3$)	x		x	x	x	0.16	*
4	N-(2-hydroxyethyl)-lactamide ($C_5H_{11}NO_3$)	x	x	x	x		0.07	
5	1-(2-hydroxyethyl)-2-imidazolidinone ($C_5H_{10}N_2O_2$)	x	x		x		0.24	
6	N,N-diacetylethanolamine ($C_6H_{11}NO_3$)		x	x	x		21.83	
7	ammonia (NH_3)	x				x		0.10
8	acetic acid ($C_2H_4O_2$)	x		x		x		2.02
9	propionic acid ($C_3H_6O_2$)	x				x		0.30
10	*n*-butyric acid ($C_4H_8O_2$)	x		x		x		0.01
11	monoethanolamine (C_2H_7NO)	x	x	x	x	x	*	35.18
12	2,6-dimethyl-4-pyridinamine ($C_7H_{10}N_2$)	x		x		x		0.05
13	2-imidazolecarboxaldehyde ($C_4H_4N_2O$)	x		x		x		0.05
14	1-methyl-2-imidazolecarboxaldehyde ($C_5H_6N_2O$)	x		x		x		0.17
15	2-oxazolidone ($C_3H_5NO_2$)	x		x		x		0.80

* Area percentage not calculated due to overlap with other peaks

Peaks 5 and 15 are known degradation products of MEA resulting from reaction with CO_2,[3] but are relatively minor components. Carboxylic acids (peaks 8,9, and 10) have been previously identified as products of oxygen induced MEA degradation.[5] The acetylated MEA components (peaks 1 and 6) are the most abundant degradation products, and are believed to be the result of reaction between acetic acid and MEA.

The results of the ICP-AES and IC analyses are shown in Table 2. ICP-AES measurements were made for 23 different metal cations. Shown are seven metals that were present at no less than 0.2 ppm concentration in either of the two samples. Most prominent is the sodium concentration, mostly due to the sodium carbonate added to the reclaimer in order to regenerate MEA that has been converted to its protonated (acidic) form. Other metals are believed to originate in large part from the coal. In addition, mercury was found to be present in the reclaimer bottoms at 1.0 ppb and was not detectable in the lean MEA (<0.02 ppb).

Anion concentrations are all relatively higher, with chloride being the most significant at 4.9% (wt.). The halogens present in the samples are thought to be present as a result of simple acid/base chemistry between mineral acids (HX where X is any halogen) present in the flue gas with MEA to form "heat stable salts". HX is the combustion product of halogens present in the feed coal. Also, note that, with one exception, the concentration of various anions is greater in the reclaimer bottoms than in the lean MEA. This is what would be expected, since the purpose of the reclaimer is to remove contaminants from MEA and concentrate them in the bottoms. The exception is the sulfate, which is an order of magnitude more concentrated in the lean MEA than in the reclaimer bottoms. It is thought that the concentration of sulfate in the reclaimer bottoms is limited by solubility factors.

Nitrosamines are known carcinogens that are formed by a reaction between an amine with a nitrogen oxide. Nitrosamines were found to be present at a concentration of 580 ppm in the lean MEA. This is believed to be due to reaction between MEA and nitrogen oxides from the flue gas. There was not a detectable amount of Nitrosamines in the reclaimer bottoms, likely due to their low boiling point.

Table 2. Ion Concentrations in ppm

	Lean MEA	Reclaimer Bottoms
Cations		
Sodium	80	821
Potassium	2.2	18
Calcium	1.1	1.3
Iron	1.4	1.1
Copper	0.2	0.1
Zinc	0.3	0.2
Aluminum	not detectable	0.4
Selenium	not detectable	17.4
Arsenic	not detectable	1.7
Anions		
Fluoride	300	1500
Chloride	1600	49000
Bromide	0.9	80
Sulfate	2200	250
Nitrate	290	3100
Nitrite	130	**
Phosphate	7.8	230

** not quantified due to overlap with chloride peak

Acknowledgements

Some work was performed while B.R.S. held a National Research Council Research Associateship Award at the National Energy Technology Laboratory. GC-IR spectra were obtained at the Mass Spectrometry Facility, Department of Chemistry and Chemical Biology, Cornell University. Nitrosamine measurements were performed by Delbert Eatough of Brigham Young University. The authors wish to thank Leroy Williams of IMC Chemicals Inc. for providing the samples and information about the process.

References

1. *Carbon Sequestration Research and Development*, U. S. Dept. of Energy Report, (December 1999).
2. Herzog, H., "An Introduction to CO_2 Separation and Capture Technologies," Energy Laboratory Working Paper, Massachusetts Institute of Technology (August 1999).
3. Polderman, L. D.; Dillon, C. P.; Steele, A. B. *Oil & Gas Journal* **1955**, *54(2)*, 180-183.
4. Chi, S. and Rochelle, G. T., "Oxidative Degradation of Monoethanolamine", Presented at the First National Conference on Carbon Sequestration, Washington, D. C. **2001**.
5. Rooney, P. C.; DuPart, M. S.; Bacon, T. R. *Hydrocarbon Processing*, July **1998**, 109-113.
6. Arnold, D. S.; Barret, D. A.; Isom, R. H. *Oil and Gas Journal* 1982, *80**(47)***, 130-136.
7. Leci, C. L. *Energy Convers. Mgmt*. **1997**, **38**, S45-S50.
8. Dawodu, O. F; Meisen, A. *Ind. Eng. Chem. Res*. **1994,** *33*, 480-487.
9. Dawodu, O. F.; Meisen, A. *Gas. Sep. Purif*. **1996**, *10*, 1-11.
10. Meisen, A.; Shuai, X. *Energy Convers. Mgmt*. **1997**, *38*, S37-S42.
11. Ding, Y.; Lee, M. L.; Eatough, D. J. *Int. J. Envir. Anal. Chem.* **1998**, *69*, 243-255.