Degradation Pathways for Monoethanolamine in a CO₂ Capture Facility

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Received November 19, 2002. Revised Manuscript Received May 13, 2003

One of the highest priorities in carbon sequestration science is the development of techniques for CO₂ separation and capture, because it is expected to account for the majority of the total cost (∼75%). The most common currently used method of CO₂ separation is reversible chemical absorption using monoethanolamine (MEA) solvent. In the current study, solvent degradation from this technique was studied using degraded MEA samples from the IMC Chemicals Facility in Trona, California. A major pathway to solvent degradation that had not been previously observed in laboratory experiments has been identified. This pathway, which is initiated by oxidation of the solvent, is a much more significant source of solvent degradation than the previously identified carbamate dimerization mechanism.

Introduction

The combustion of fossil fuels is responsible for ∼85% of the world's energy supply. It is also the most significant source of carbon dioxide (CO₂) emissions worldwide. Because of concern about the effect of CO₂ emissions on the global climate, as well as the world's great dependence on fossil fuels, the development of strategies for the reduction of CO₂ emissions has become increasingly important.[1,2] One such strategy that has received a great deal of attention involves the capture of CO₂ from large point sources (such as fossil fuel-fired power plants) and the long-term storage of CO₂ underground or in the ocean. However, there is great concern in regard to what impact such a plan would have on electricity prices.[3–5] Because CO₂ comprises <15% of flue gas from conventional fossil fuel combustion processes, it would be impractical or too expensive to compress and store the total flue gas output from a boiler. Therefore, it is important to separate the CO₂ from other flue gas constituents prior to storage. This CO₂ separation and capture step is expected to constitute the majority (up to 75%) of the expense for a carbon sequestration process.[3]

Although there are several different methods that have been proposed for the capture and separation of CO₂, the method that has been most widely used on an industrial scale is chemical absorption using an aqueous solution of monoethanolamine (MEA) as a solvent.[3] In this method, MEA absorbs CO₂ through chemical reaction in an absorber column. Because the reaction is reversible, the CO₂ can be driven off by heating the CO₂-rich amine in a separate stripper column. The MEA may then be recycled through the process. For the low CO₂ partial pressure that is present in flue gas, alternative methods of CO₂ removal are less efficient and more expensive than chemical absorption.[3]

There are alternative approaches to electrical power generation, such as integrated coal gasification combined cycle (IGCC), which produce a higher pressure and higher concentration stream of CO₂.[6–8] This allows the use of precombustion CO₂ capture by physical absorption, which is a method for CO₂ separation that is less energy-intensive and less expensive than chemical absorption. However, the great majority (>90%) of new power plants that are projected for construction in the United States by 2020, as well as most existing plants, produce flue gas at 1 atm with a CO₂ concentration of <15%.[9] Clearly, if a significant reduction in CO₂ emissions is to be achieved, chemical absorption will need to play an essential role.

A major problem associated with chemical absorption using MEA is the degradation of the solvent through

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irreversible side reactions with CO_2 and other flue gas components,[10-12] which leads to numerous problems with the process. First, the degradation of MEA results in solvent loss, which requires the replacement of ~2.2 kg of MEA per tonne of CO_2 captured.[13] It is also known to lead to foaming,[14] fouling,[15,16] and increased viscosity[10] of the amine. In existing CO_2 capture facilities that use MEA, the degradation products are separated in an evaporative reclaimer and disposed of as hazardous chemical waste, leading to increased disposal costs.[17]

In the case of carbon sequestration, the most significant problem presented by MEA degradation is associated with increased corrosion that is caused by the degradation products.[10,18] 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 if corrosion inhibitors are employed). Low MEA concentration reduces the effectiveness of the solvent, which necessitates large equipment sizes and faster circulation rates. In addition, more energy is required in the stripping column to raise the temperature and regenerate the amine.[4] This increased "parasitic load" is of particular concern for carbon sequestration. In addition to being an additional cost, production of this extra energy leads to increased CO_2 emissions, which decreases the overall benefit of sequestration.[3] A previously reported sensitivity analysis indicates that increasing the concentration of MEA to 70% will cut the parasitic load on a power plant by more than one-half.[4]

Although CO_2 separation using MEA is a relatively mature technology, the process has not been optimized for the abatement of CO_2 emissions from fossil fuel-fired power plants.[16,19] Its primary uses have been the sweetening of natural gas streams[14] and the commercial production of CO_2 from flue gas.[13,20] Because of the increased concern with efficiency and the parasitic load on a plant, decreasing the role of solvent degradation is a much more important issue to sequestration than to previous applications of the MEA process.

The current study is aimed at developing a fundamental 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,[12] CO_2,[10,21] COS,[22] or CS_2.[23] The results of some of these studies will be further discussed in the Results section of this paper, with comparison to the results of the current study. Most of these previous studies were aimed at understanding natural gas sweetening processes, and all were conducted with pure gases under laboratory-controlled conditions. However, in flue gas from a fossil fuel-fired boiler, the process becomes much more complicated, because of 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.[5]

The IMC Chemicals Facility in Trona, CA, is a plant that has been performing CO_2 capture from flue gas since 1978, longer than any other such plant in the world. 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 the carbonation of brine from Searles Lake, CA, for the commercial production of sodium carbonate.[13]

Experimental Section

For the current study, MEA samples were obtained from this plant to identify the degradation products from the CO_2 separation process. Three samples were obtained: (1) virgin concentrated MEA; (2) "lean" MEA, which was taken before the CO_2 absorption step; and (3) reclaimer bottoms, which represent the still bottoms that remain after the amine is reclaimed by distillation to remove the degradation products.

To identify the volatile organic compounds in the samples, each mixture was separated and analyzed using combined gas chromatography–mass spectrometry (GC–MS), combined gas chromatography–Fourier transform infrared absorption spectrophotometry (GC–FTIR), and combined gas chromatography–atomic emission detection (GC–AED). Two different gas chromatographic columns were used for separation. The first was a 60 m × 0.32 mm (inner diameter) fused silica column that was coated with a 0.25-μm film of 14%-(cyanopropylphenyl)-methylpolysiloxane (DB-1701, from J&W Scientific). Separations with this column were performed using a temperature program from 35 to 280 °C at a rate of 1 °C/min. The second column, which was a 60 m × 0.25 mm (inner diameter) column that was coated with 0.25-μm nitroterephthalic acid-modified poly(ethylene glycol) (Nukol, from Supelco), was temperature-programmed from 50 to 200 °C at a rate of 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 mass selective detection (MSD) (Hewlett–Packard model HP 5973), and GC–FTIR experiments employed infrared detection (IRD) (Hewlett–Packard model HP 5965A). GC–AED experiments were performed using an Agilent model G2350A atomic emission detector. To determine the elemental ratios of carbon, hydrogen, nitrogen, and oxygen in each compound (by GC–AED), three injections were made, each corresponding to a different spectral range of emission detection.

In addition, precise molecular masses of the organic compounds were obtained using low-voltage, high-resolution mass

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Table 1. Identified Compounds from Reclaimer Bottoms Sample

peak number	CAS number	compound	formula	Library Match			authentic standard	% of Total Area	
				GC–MS	GC–FTIR	LVHRMS		DB-1701	Nukol
1		N-formylethanolamine	$C_3H_7NO_2$			×		2.81	0.98
2	142-26-7	N-acetylethanolamine	$C_4H_9NO_2$	×	a	×	×	8.86	6.28
3	497-25-6	2-oxazolidone	$C_3H_5NO_2$	×		×	×	1.28	0.80
4	18190-44-8	N-(hydroxyethyl)-succinimide	$C_6H_9NO_3$	×		×	×	0.16	b
5	5422-34-4	N-(2-hydroxyethyl)-lanthamide	$C_5H_{11}NO_3$	×	×	×	×	0.07	c
6	not available	1-hydroxyethyl-3-homopiperazine	$C_7H_{14}N_2O_2$		a	×		1.16	c
7	3699-54-5	1-(2-hydroxyethyl)-2-imidazolidinone	$C_5H_{10}N_2O_2$	×	×		×	0.24	c
8	59702-23-7	1-hydroxyethyl-2-piperazinone	$C_6H_{12}N_2O_2$			×		1.36	c
9	23936-04-1	4-hydroxyethyl-2-piperizinone	$C_6H_{12}N_2O_2$		a	×	×	12.57	c
10	144236-39-5	3-hydroxyethylamino-N-hydroxy-ethyl propanamide	$C_7H_{16}N_2O_3$		a	×		21.83	c
11	not available	2-hydroxyethylamino-N-hydroxyethyl acetamide	$C_6H_{14}N_2O_3$		a	×		11.69	c
12	7664-41-7	ammonia	NH_3	×		d	×	11.69	c
13	64-19-7	acetic acid	$C_2H_4O_2$	×		×	×	c	2.02
14	79-09-4	propionic acid	$C_3H_6O_2$	×		×	×	c	0.30
15	107-92-6	n-butyric acid	$C_4H_8O_2$	×		×	×	c	0.01
16	141-43-5	monoethanolamine	C_2H_7NO	×	×	×	×	29.99	35.18
17	3512-80-9	2,6-dimethyl-4-pyridinamine	$C_7H_{10}N_2$	×		×		c	0.05
18	10111-08-7	2-imidazolecarboxaldehyde	$C_4H_4N_2O$	×		×	×	c	0.05
19	13750-81-7	1-methyl-2-imidazolecarboxaldehyde	$C_5H_6N_2O$	×		×	×	c	0.17

a Gas-phase IR spectrum not in library but is available as Supporting Information. b Area not calculated, because of overlap with other peaks. c No peak was observed in the chromatogram from this column. d Mass spectrometer was not scanned to a sufficiently low mass to detect ammonia.

spectrometry (LVHRMS).[24] Mass spectra were acquired on a Kratos model MS-50 high-resolution mass spectrometer. The ionizing voltage was set to ~11.5 eV, to minimize fragmentation and, therefore, enhance the detection of molecular ions. 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 model DX-100 ion chromatograph that was 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 model Optima 3000 system to measure trace-metal concentrations.

Also, analyses were performed to determine the total nitrosamine concentration in each sample, using a technique that has been described in detail elsewhere.[25] Briefly, the samples were treated with a mixture of hydrobromic and acetic acids, causing the nitroso compounds to release NO. The released NO was detected by chemiluminescence, using a Thermedics Inc. model 543 thermal energy analyzer.

Results

The focus of this study was on the MEA degradation products; therefore, the reclaimer bottoms sample, where these products were concentrated, as a result of distillation, provided the most-important information. Portions of the total ion chromatograms obtained from GC–MS analysis of this sample on both the DB-1701 and the Nukol columns are shown in Figures 1 and 2, respectively. The numbered peaks are identified in Table 1, along with the methods of identification. A cross symbol (×) in the GC–MS or GC–FTIR column indicates a positive match from an electronic search of either

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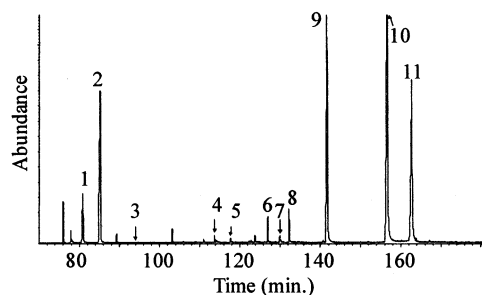(25) Ding, Y.; Lee, M. L.; Eatough, D. J. *Int. J. Environ. Anal. Chem.* **1998**, *69*, 243–255.

Figure 1. Portion of the total ion chromatogram of the reclaimer bottoms sample obtained using the DB-1701 column. Numbered peaks are identified in Table 1. (MEA peak at 9.3 min not shown.)
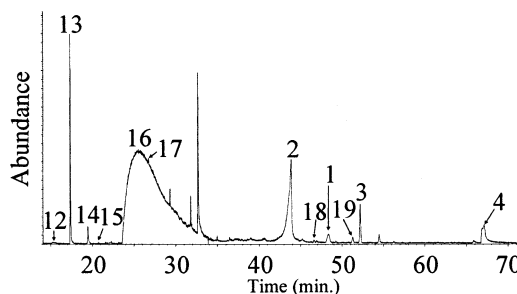

Figure 2. Portion of the total ion chromatogram of the reclaimer bottoms sample obtained using the Nukol column. Numbered peaks are identified in Table 1.

the MS or FTIR libraries. MS library searches were performed using the NIST Mass Spectral Search Program for the NIST/NIH/EPA Mass Spectral Library.[26] FTIR searches were performed using the FTIRsearch.com Internet service.[27] The LVHRMS column indicates whether a match within 0.003 amu of the mass of the

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Table 2. Molecular Formulas Calculated from GC−AED Experiments

retention time (min)	peak number (from Figure 1)	C	H	N	O
76.03	N/A[a]	6	9	1	1
80.77	1	3	7	1	2
85.02	2[b]	4	9	1	2
89.26	3	3	5	1	2
103.23	N/A[a]	5	8	2	1
113.80	4	6	9	1	3
117.93	5	5	11	1	3
123.97	N/A[a]	7	14	2	3
127.09	6	7	14	2	2
130.12	7[b]	5	10	2	2
132.39	8	6	12	2	2
141.50	9	6	12	2	2
156.54	10	7	16	2	3
162.58	11	6	14	2	3

[a] Not applicable. [b] Compounds used as calibration standards for element ratios.

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 percentage 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 shown in Figures 1 and 2 were present in identical experiments that were performed on the virgin MEA.

The use of two separate GC columns (one intermediate and one polar stationary phase) was necessary, because of the large variation in polarity of the degradation products, which is a result of the large number of heteroatoms present in the compounds. This is illustrated by the fact that each chromatogram (Figures 1 and 2) has some major peaks that are not present in the other. This is, in part, due to the fact that the Nukol stationary phase incorporates nitroterephthalic acid functional groups. This allows the column to transmit acidic compounds that might not otherwise be eluted, while adsorbing basic compounds. Thus, the carboxylic acids were observed using the Nukol column, but not the DB-1701 column. For the same reason, the Nukol column does not transmit basic compounds well; some of them are adsorbed and, therefore, do not appear in the chromatogram.

Many of the major organic degradation products do not appear in either the MS or IR libraries; therefore, the identity of some peaks needed to be deduced by interpreting the mass spectra and IR spectra. This interpretation was facilitated by the determination of molecular formulas using GC−AED. For element ratio calibration, two compounds in the sample that had been previously identified and verified by co-chromatography with authentic standards were used: 1-(2-hydroxyethyl)-2-imidazoline and *N*-acetylethanolamine. The calculated empirical formulas for each peak are shown in Table 2. For the majority of the compounds identified, an authentic standard was obtained for verification of the identity. However, in some cases, as noted in Table 1, the standards were not available. For each of these six compounds, identification was based solely on the empirical formula, the mass spectrum, and the gas-phase IR spectrum.

One mechanism of MEA degradation that has been previously studied is carbamate dimerization.[10,21] This

Table 3. Ion Concentrations

	Ion Concentration (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	[a]
phosphate	7.8	230

[a] Not quantified, because of overlap with the chloride peak.

process is a result of reaction between CO_2 and MEA at high temperatures (typically in the stripper column). This process is initiated by the formation of 2-oxazolidone:

(1)
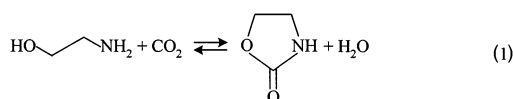
which can, in turn, react with another MEA molecule to form *N*-(2-hydroxyethyl)-ethylenediamine via intermediates of *N,N*-di(hydroxyethyl)urea and 1-(2-hydroxyethyl)-2-imidazolidinone:[21]

(2)
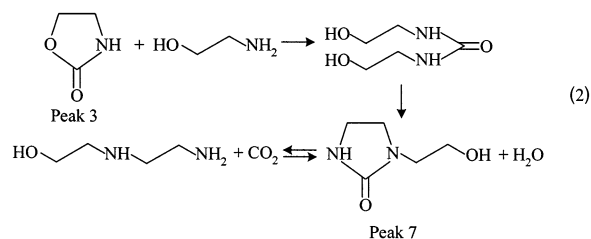
Two of the molecules in this mechanism, 2-oxazolidone and 1-(2-hydroxyethyl)-2-imidazolidinone, were observed in the present study (peaks 3 and 7). However, these are relatively minor components. The carboxylic acids (peaks 13, 14, and 15) and ammonia (peak 12) have been previously identified as products of oxygen-induced MEA degradation.[12] The mechanism for the production of acetic acid and ammonia is as follows:

(3)
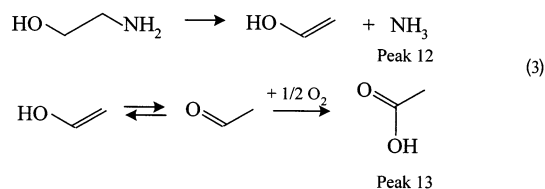
The results of the ICP−AES and IC analyses are shown in Table 3. ICP−AES measurements were made for 23 different metal cations. Shown in the table are seven metals that were present at a concentration of ≥0.2 ppm in either of the two samples. Most prominent is the sodium concentration, mostly because of the

sodium carbonate that is added to the reclaimer 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 a concentration of 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 a result of simple acid/base chemistry between mineral acids (HX, where X is any halogen element) in the flue gas with MEA to form "heat-stable salts". HX is the combustion product of halogens that are present in the feed coal. The amounts of halogen anions observed in the reclaimer bottoms parallel the halogen concentrations that are typically found in 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, because 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. The concentration of sulfate in the reclaimer bottoms is thought to be limited by solubility or volatility factors. In other words, the sulfate may precipitate to form a solid or some volatile substance (such as SO_2) that evaporates from the reclaimer along with the MEA.

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 2.91 μmol/mL in the lean MEA. This is believed to be due to the reaction between MEA and nitrogen oxides, which are known constituents of flue gas. There was not a detectable amount of nitrosamines in the reclaimer bottoms, likely because of their low boiling point. It should be noted that no *specific* nitrosamines were detected in this study. Their quantification was based on a generalized functional group test.[25]

Discussion

Most of the major organic constituents observed in the reclaimer bottoms sample were not identified previously as products of MEA degradation. Therefore, it is clear that not only is there a degradation process taking place in the plant that had not been discovered in laboratory experiments, but this process also plays a major role in the overall degradation of the solvent. The purpose of this study is to understand the major degradation processes; therefore, a possible mechanism is proposed to explain the major peaks in the chromatogram.

The *N*-acetylethanolamine (peak 2) is believed to form as a result of the reaction of MEA with acetic acid that is produced by the reaction shown in reaction (3) as follows:
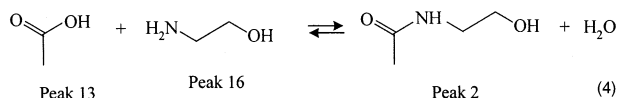

The proposed reaction that follows would necessarily proceed via a radical mechanism, perhaps initiated by

reaction with Fe^{3+} cations. In this reaction, another MEA molecule reacts with the *N*-acetylethanolamine to form 2-hydroxyethylamino-*N*-hydroxyethyl acetamide (peak 11):
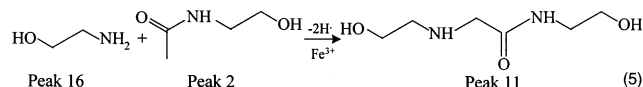
This molecule may then form a six-member ring by internally eliminating water between either alcohol group and the corresponding amine group, forming either 1-hydroxyethyl-2-piperazinone (peak 8) or 4-hydroxyethyl-2-piperizinone (peak 9):
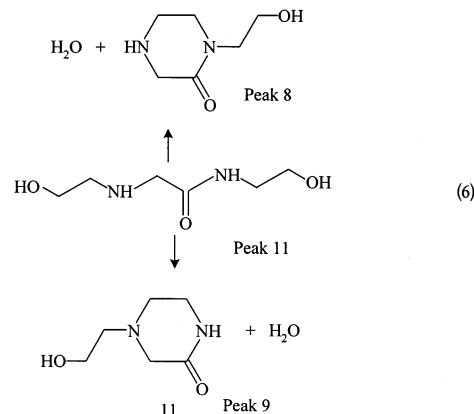
A similar mechanism, starting with the formation of propionic acid (peak 14) rather than acetic acid, could account for the presence of 3-hydroxyethylamino-*N*-hydroxyethyl propanamide (peak 10) and 1-hydroxyethyl-3-homopiperazinone (peak 6).

It is worth noting that one of the compounds identified in the reclaimer bottoms, 4-hydroxyethyl-2-piperazinone, has appeared in multiple patents for its usage as a SO_2 capture solvent and also as a corrosion inhibitor.[28-30] To exclude the possibility that this compound was added to the system, rather than formed in a chemical reaction, a sample of the commercial corrosion inhibitor used by the plant was obtained and analyzed. No compounds that were identified in Table 1 were found to be present at a detectable level in the corrosion inhibitor sample.

Conclusions

Although several of the compounds that have been identified as products of monoethanolamine (MEA) degradation had been seen in previous laboratory studies, there are some major products that had not been previously observed. This clearly indicates that there are chemical degradation reactions that occur under plant conditions that do not occur in laboratory experiments with pure gases. In comparison with the newly

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proposed degradation mechanism, carbamate dimerization is a relatively minor pathway. It is important to note that the samples for this study have been taken from the reclaimer, where degradation products are concentrated and temperatures are higher than anywhere else in the process. It is possible that some of the degradation products identified were formed in the reclaimer itself, rather than in the stripper.

In addition to the neutral degradation products, there are large amounts of "heat-stable" salts produced in the process, as evidenced by the ion chromatographic results. This is not surprising, on the basis of previous literature on the subject.[16]

It is evident from Figure 2 that the reclaimer bottoms contain a substantial amount of MEA. It may be possible to employ a more efficient distillation system to reduce the amount of waste produced and reduce MEA make-up costs.

Supporting Information Available: Gas-phase infrared spectra of selected compounds (PDF). (See Table 1.) This material is available free of charge via the Internet at http://pubs.acs.org.

EF020272I