



## CHAPTER II

### LITERATURE REVIEW

This chapter introduces background of CO<sub>2</sub> capture the CO<sub>2</sub> absorption process. The literature related to amine degradation during CO<sub>2</sub> removal process is also reviewed. The types and causes of oxidative degradation of amine as well as the effect of other flue gas components are described as well.

#### 2.1 Carbon Dioxide Capture Process

The removal of CO<sub>2</sub> has been practiced industrially for several decades. In natural gas processing, CO<sub>2</sub> is removed to reduce the costs of compression and transportation. CO<sub>2</sub> is also removed in ammonia manufacture, coal gasification, hydrogen production and power plant flue gases. Due to an increasing awareness of the possible influence of greenhouse gas on global warming has led to recent efforts to develop strategies for the reduction of CO<sub>2</sub> emissions. One such strategy that has received a great deal of attention involves the capture of CO<sub>2</sub> from large point source of emissions such as fossil fuel-fired power plants. A CO<sub>2</sub> removal facility is an expensive plant and the operating cost could be high. For a power plant, the removal of 90% of the CO<sub>2</sub> from the flue gas can use up to 30% of the energy produced by the plant (IEA Greenhouse Gas R&D Programme). This represents a heavy parasitic loss, and thus, the focus of research in this field is to reduce the costs of removal, in particular, reducing its parasitic energy requirements.

The CO<sub>2</sub> capture technology was first developed as early as 1930 for natural gas treatment with its application having been found attractive also for coal derived flue gas purification (Kohl and Riesenfeld, 1985). There are several different methods that have been proposed for the capture and separation of CO<sub>2</sub>, the only method that has been proven to work on an industrial scale is chemical absorption using monoethanolamine (MEA) as a solvent.

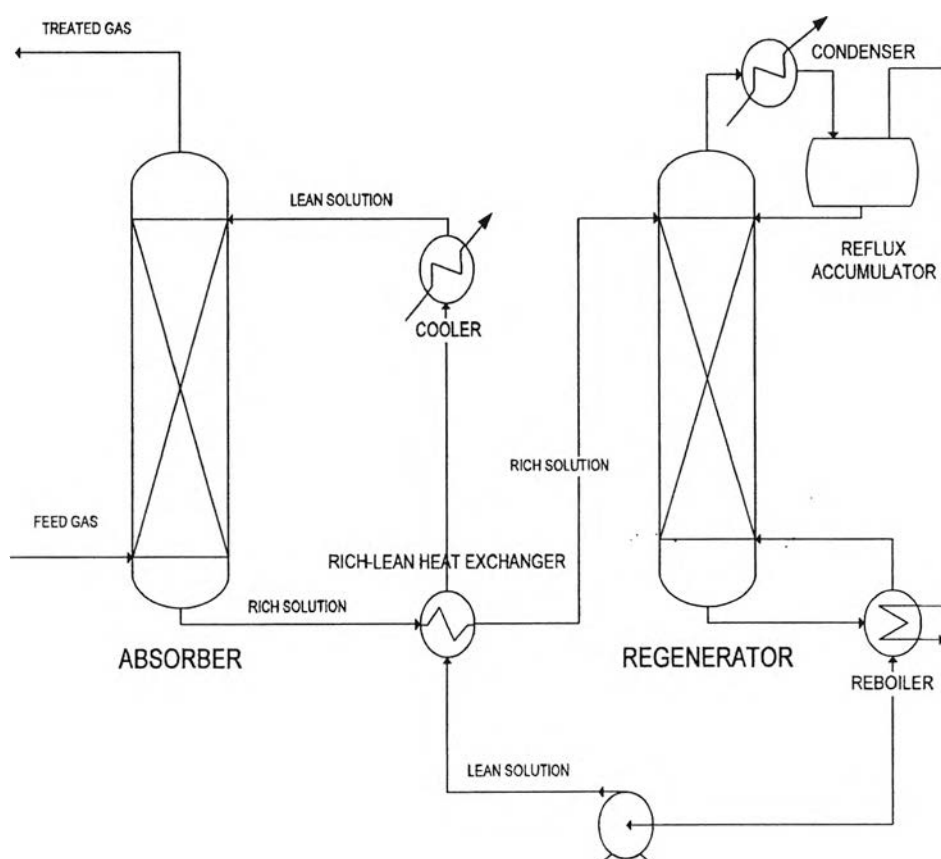
MEA is chosen as the current solvent of choice for flue gas treating because of its high capacity for CO<sub>2</sub>, fast reaction kinetics, and high removal efficiencies (Kohl and Nielsen, 1997). Figure 2.1 shows a simplified flow schematic of a typical process for CO<sub>2</sub> capture which employs MEA in absorption-regeneration region.

In this process, a flue gas containing CO<sub>2</sub> is introduced at the bottom of the absorber where it contacts counter currently with an aqueous solution of alkanolamine that is introduced at the top of the absorber. As the alkanolamine solution travels down the column, it becomes loaded with CO<sub>2</sub> and leaves the bottom of the absorber as rich alkanolamine. The alkanolamine solution rich in absorbed CO<sub>2</sub> is pumped from the bottom of the absorber through heat exchanger where the temperature is raised. The amine solution is introduced at the top of a stripper where it counter currently contacts steam at a reduced pressure and at a high temperature. The steam produced in a reboiler, provides the energy necessary to reverse the reactions of the CO<sub>2</sub> with alkanolamine, increasing the CO<sub>2</sub> partial pressure and, simultaneously, stripping the CO<sub>2</sub> from the solution. The lean alkanolamine solution is pumped through a heat exchanger, where it is cooled and reintroduced at the top of the absorber. The stripped CO<sub>2</sub> is sent for further processing.

Due to the closed loop nature of alkanolamine-based CO<sub>2</sub> capture processes, non-regenerable contaminants tend to accumulate resulting in products from which the amines are not easily recovered. This phenomenon is called degradation. One of the serious causes of MEA loss is degradation (Kohl and Nielsen, 1997). The formation of degradation compounds is undesirable not only because it represents a loss of valuable products, but also because generation of degradation compounds may result in plant operating problems (Chakma and Meisen, 1986). Also, degradation and corrosivity have forced the use of low concentrations of MEA leading to larger overall equipment size, higher solvent circulation rate and increased in energy requirement for CO<sub>2</sub> regeneration.

Alkanolamines are susceptible to several types of degradation; thermal degradation, CO<sub>2</sub> induced degradation, degradation caused by COS and CS<sub>2</sub>, amine loss through the formation of heat stable salts and the reaction of amines with strong acids, carbamate polymerization and oxidative degradation. There are only three

types of degradation that occur with MEA and a flue gas stream that contains 7-15% CO<sub>2</sub> and 2-12% O<sub>2</sub> (Rochelle et al., 2002; Rooney et al., 1998; Chakma et al., 1995).



**Figure 2.1** Simplified alkanolamine-based CO<sub>2</sub> capture process.

Since most gas treating processes that use amines for CO<sub>2</sub> removal are applications without oxygen, oxidative degradation is an additional source of solvent degradation in flue gas treating applications that has not been properly quantified. There are three main reasons the oxidative degradation of MEA must be quantified: potential adverse environmental impact of degradation products, process economics, and process performance.

Oxidative degradation requires the presence of dissolved O<sub>2</sub>; therefore, it would only occur in the absorber section affecting the performance of the system, as

indicated in Figure 2.1.  $O_2$  induce alkanolamine degradation results in reduction of  $CO_2$  removal capacity of alkanolamines and introduce unwanted degradation products into the solution. Also, the negative corrosive effects towards plant equipment of these degradation products have been periodically reported in the literature (Howard and Sargent, 2001; Rooney et al., 1996; Rooney et al., 1997). A more serious degradation could potentially be obtained with  $SO_2$  since its high solubility makes it easy to be carried over to the regeneration-reboiler section where the high temperature speeds up the rate of degradation of the alkanolamines. Not only does this  $O_2$ - $SO_2$  induced degradation reduce the  $CO_2$  absorption capacity, they also introduce various corrosive and stable degradation products to the  $CO_2$  capture system as well. The existence of these problems means there is an urgent need in finding ways to prevent degradation, a degradation prevention strategy needs to be formulated, and this requires knowledge of the products, stoichiometry, mechanism as well as kinetics of the degradation process (Straizisar et al., 2003 and Supap el al., 2001). Degradation prevention is required in order to maintain the capture performance and minimize the plant's operating cost.

Most of the unwanted degradation products are removed from the process through solvent reclaiming. The liquid and solid waste from this process must be disposed of, and currently the composition, toxicity, and volume of this waste are not well known, and are potentially considered hazardous wastes.

Previous studies has provided useful information on various aspects of oxidative degradation of alkanolamines, in which the most attention has been given to the identification of degradation products (Blanc et al., 1982; Hofmeyer et al., 1965; Strazisar et al., 2003) and formation of heat stable salts (Rooney and Dupart., 2000; Veldman, 2000). Some works have been focused only on identifying the liquid phase degradation products (Bello and Idem, 2005; Strazisar et al., 2003), while other studies have attempted to quantify degradation rates by measuring the rate of formation of these products (Lawal et al., 2005; Rooney et al., 1998). A kinetic evaluation also helps in the formulation of a degradation prevention strategy which is considered to be the overall goal of degradation studies (Rochelle et al., 2002). However, its formulation is so far limited to measurement of either the concentration decline of alkanolamine reactant or production rate of a gaseous product (Chi and

Rochelle, 2002; Goff and Rochelle, 2004; Lawal and Idem, 2006; Supap et al., 2001).

There are several options as to how to control amine degradation such as using solvents that oxidize slower than MEA, minimizing contact time with O<sub>2</sub> and SO<sub>2</sub> with MEA, removing O<sub>2</sub> and SO<sub>2</sub> from flue gas streams, and adding degradation inhibitors to the system. There is difficulty to completely remove O<sub>2</sub> and SO<sub>2</sub> from flue gas streams in order to prevent amine degradation. Especially, the detection and removal of O<sub>2</sub> is known to be time consuming and also labor-intensive (McKnight, 1988) and it requires process modification. This has made the addition of an effective degradation inhibitor a more attractive method of choice as recommended in the literature (Rooney et al., 1998) in order to decrease the degradation rate. The lack of appropriate inhibitors has urged a need in searching and evaluating the performance of potential additives for reducing or even eliminating severity of O<sub>2</sub>-SO<sub>2</sub> induced amine degradation.

The research objective of this study is to develop a degradation prevention technique using degradation inhibitors and evaluate the performance of degradation inhibitors in minimizing O<sub>2</sub>-SO<sub>2</sub> induced degradation of MEA based CO<sub>2</sub> absorption from coal-fired power plant flue gases (i.e. MEA-H<sub>2</sub>O-O<sub>2</sub>-SO<sub>2</sub> and MEA-H<sub>2</sub>O-O<sub>2</sub>-SO<sub>2</sub>-CO<sub>2</sub> system). The ranges of experimental conditions were selected to simulate the extremes normally encountered in CO<sub>2</sub> capture process in a coal fired power plant flue gas streams. MEA concentration, O<sub>2</sub> concentration, SO<sub>2</sub> concentration, CO<sub>2</sub> loading (mol of CO<sub>2</sub>/mol of MEA), and degradation temperature were respectively used in the range of 5 kmol/m<sup>3</sup>, 6 – 100%, 0 – 196 ppm, 0.33 CO<sub>2</sub> loading and degradation temperature was chosen as 120°C.

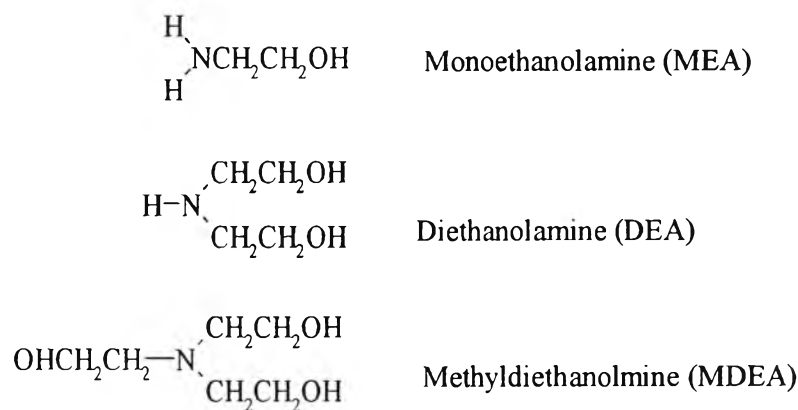
## **2.2 Amines and Their Reaction with CO<sub>2</sub>**

Traditionally, absorption-regeneration via circulated aqueous amines have been the most favored technology for removing CO<sub>2</sub> from process and waste gas streams. This technology has played a major role in acid gas removal for petroleum refining, natural gas treating, coal gasification, hydrogen production, synthesis gas

production, ammonia manufacturing and ethylene manufacturing. The commercially available absorbents that are sufficiently active for recovery of CO<sub>2</sub> from flue gas at atmospheric pressure are aqueous solutions of amines.

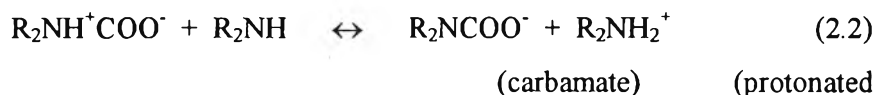
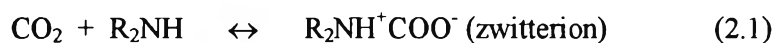
The amines are bases, and they react with the acid species such as CO<sub>2</sub> to form different reaction products. They contain the hydroxyl group (OH) which contributes by reducing the vapor pressure of amines thereby increasing the solubility of CO<sub>2</sub> in water, while the amino group provides the alkalinity in aqueous solution which is responsible for the absorption of the acid gas. This leads to accelerated absorption of CO<sub>2</sub> from gas streams with low partial pressure (Kohl and Riesenfeld, 1985).

The amines are distinguished as primary, secondary and tertiary, according to the number of organic groups attached to the alkaline nitrogen. Monoethanolamine (MEA) is a primary amine, diethanolamine (DEA) is a secondary amine, and methyldiethanolamine (MDEA) and triethanolamine (TEA) are tertiary amines. Structural formulas for several commercially alkanolamines are presented in Figure 2.2.



**Figure 2.2** Chemical structures of conventional alkanolamines used in gas sweetening.

Typically, primary and secondary amines react to form a carbamate species, and the reaction may or may not proceed through an intermediate called the zwitterion.



amine)

Tertiary amines cannot form a carbamate species, because they do not have hydrogen attached to the nitrogen atom. Typically the tertiary amines react according to equation 2.3.



According to Kohl and Nielsen (1997), primary and secondary amines usually react faster than tertiary amines, and  $\text{CO}_2$  has higher heats of absorption in these amines. Heats of reaction at  $25^\circ\text{C}$  and unloaded conditions are approximately 20.3 and 14.8 kcal/mole for MEA and MDEA respectively. Among many amines, MEA is the most widely used because MEA has the highest alkalinity; hence it reacts most rapidly with  $\text{CO}_2$ . As well, it can be reclaimed with ease from contaminated solution. Mechanism of  $\text{CO}_2$  absorption into alkanolamine solution is complex and not totally understood (Astarita et al., 1983). However, a generic mechanism proposed several decades ago could represent the absorption process (Danckwerts et al., 1967).

In general, MEA has the highest  $\text{CO}_2$  separation rate which should lead to relatively low overall costs. However, MEA requires a large amount of high grade energy for regeneration, degrades most rapidly in the presence of oxygen ( $\text{O}_2$ ), has the highest corrosivity among commercially available amines, and has a substantially higher vapor pressure than other alkanolamines resulting in significant vaporization and solvent losses.

### 2.3 Amine Degradation and Types

Studies made over the years have shown that amines degrade in service. Degradation is an irreversible chemical transformation of alkanolamine into undesirable compounds such as heat stable salts resulting in its diminished ability to absorb acid gas. The heat stable salts are formed when the amine and an acid react to form a salt that cannot be generated in the regenerator (McCullough et al., 1996). Degradation is undesirable and leads to valuable amine loss, impaired process efficiency and corrosion. The direct and indirect costs resulting from amine degradation are considerable thus mandating a clear and comprehensive understanding of the fundamentals regarding degradation chemistry, mechanism and kinetic.

Flue gas typically contains 3-15% of CO<sub>2</sub>. Flue gas from a natural gas turbine contains 4% CO<sub>2</sub>, 15% O<sub>2</sub>, and 81% N<sub>2</sub>. Flue gas from a coal-fired power plant typically contains about 7-15% CO<sub>2</sub>, 2-12% O<sub>2</sub>, 65-75% N<sub>2</sub>, 2-400 ppm SO<sub>2</sub>, and 1-400 ppm NO<sub>x</sub> (Rochelle et al., 2002; Rooney et al., 1998; Chakma et al., 1995). They contain trace contaminants and their levels vary widely depending on fuel composition, combustion system, and operating conditions.

Flue gases from power plants, especially in coal-fired power plants, not only contain considerable volumes of N<sub>2</sub>, but also contain other gases such as NO<sub>x</sub>, O<sub>2</sub>, SO<sub>2</sub> and SO<sub>3</sub>. Table 2.1 shows typical flue gas composition after SO<sub>2</sub> scrubbing for coal-fired power plants.

**Table 2.1** Typical composition of coal-fired power plant flue gases after SO<sub>2</sub> scrubbing (Chakma et al., 1995).

COMPOSITION	CONCENTRATION (mole %)
CO <sub>2</sub>	7-15
O <sub>2</sub>	2-12
N <sub>2</sub>	65-75



COMPOSITION	CONCENTRATION (mole %)
H <sub>2</sub> O	5-15
SO <sub>2</sub>	2-400 ppm
SO <sub>3</sub>	1-10 ppm
NO <sub>x</sub>	1-400 ppm
Particulates	0.1 – 0.5 grains/SCF

Degradation of MEA in a flue gas stream can be classified into three different types depending on its products, mechanisms and conditions. There are

- Carbamate polymerization; this is the most common degradation mechanism. It requires CO<sub>2</sub> and high temperature. Since only primary and secondary alkanolamines form carbamates with CO<sub>2</sub>, tertiary amines do not undergo this type of degradation reaction. The degradation products resulting from carbamates polymerization are usually of high molecular weight.
- Oxidative degradation requires O<sub>2</sub>. It produces oxidized fragments of the solvent, such as organic acids and ammonia, and is expected to occur in the presence of dissolved O<sub>2</sub> in the liquid holdup at the bottom of the absorber. Since flue gas contains 5% O<sub>2</sub>, oxidative degradation can be significant. Neither CO<sub>2</sub> nor high temperature is required in this case.
- Thermal degradation is not commonly encountered since it involves high temperatures than 205°C; therefore, it is the least well studied.

#### 2.4 Effect of Other Components of Flue Gases on Amine Degradation

As stated earlier, apart from O<sub>2</sub> and CO<sub>2</sub>, other components of flue gas include N<sub>2</sub>, fly ash, and trace contaminants such as SO<sub>x</sub> (primarily SO<sub>2</sub>) and NO<sub>x</sub> (primarily NO<sub>2</sub>). Most of these contaminants are undesirable in amine treating unit (Goff et al., 2003). Fly ash is the fine solid component in flue gas typically consisting

of inorganic oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{P}_2\text{O}_5$  (Goff et al., 2003). The presence of fly ash in flue gas stream can lead to a number of operational problems.

$\text{SO}_2$  and  $\text{NO}_2$  are the combustion products of sulphur and nitrogen compounds in the coal. If these gases enter to the  $\text{CO}_2$  absorption process, they will degrade the amine solvent, forming heat stable salts and depleting the absorption capacity of the solvent and it can, also, increase the consumption of amine (Goff et al., 2003).

## 2.5 Oxygen Induced Degradation of Alkanolamines

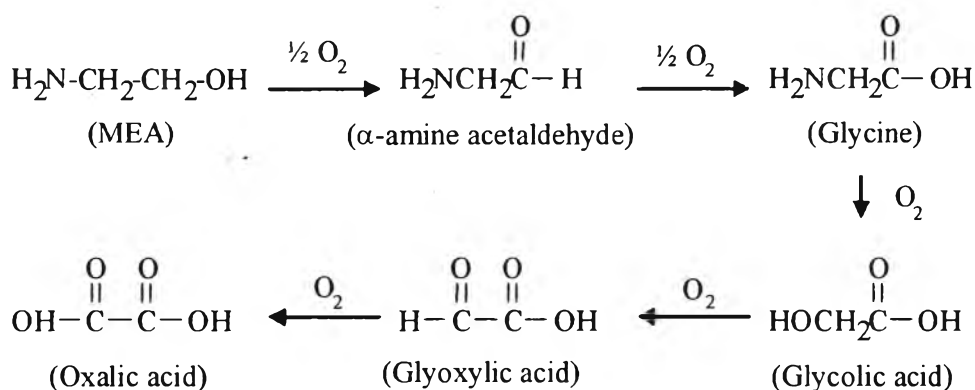
Most of the degradation studies were long-term experiments. The experiments were performed by sparging a gas containing  $\text{CO}_2$  and  $\text{O}_2$  through a loaded amine solution, or using high pressure-temperature reactor and partial pressure of  $\text{O}_2$ . Most of these studies were performed at low gas rates, and subsequently low mass transfer conditions. Degradation rates were low and required long experimental times to accumulate enough degradation products for accurate detection.

MEA are subject to oxidative degradation by contact with free  $\text{O}_2$ . Products of the oxidative degradation of MEA have been identified that the primary degradation product is ammonia, followed by various aldehydes. It has been well established that aldehydes are very susceptible to autoxidation in the presence of oxygen. Oxygen has two unpaired electrons in its ground state and is therefore considered a diradical, often represented as  $\cdot\text{O}\cdot$ . The oxygen will react with aldehydes to form carboxylic acids via a peroxy acid intermediate. Since the MEA solutions have high pH (9-12), the carboxylic acids would dissociate in solution to form heat stable salts with MEA, partially neutralizing the amine and reducing the capacity for  $\text{CO}_2$  absorption (Fessenden et al., 1994)

Products of the oxidative degradation of MEA have been identified to include carboxylic acids (i.e. formic acid, oxalic acid, and glycolic acid), glycine, ammonia, water, substituted amides (i.e. n-(2-hydroxyethyl) acetamide and n-(2-hydroxyethyl) lactamide), pyridines, substituted alkanols (i.e. 2-(methylamino)

ethanol), amines (i.e. ethylamine and 1-propylamine), substituted alkanones (i.e. 4-amino-2 (1H) pyridinone and di-homoserine lactone), substituted azetidines (i.e. 2 methyl azetidine) , 5-hydrazinocarbonyl imidazole, uracil, and 5-ethyl uracil, substituted aldehydes (i.e. 1-piperidinecarboxaldehyde), and high molecular weight polymers (Polderman et al., 1950; Hofmeyer et al., 1965; Rooney et al., 1998; Straizisar et al., 2003; Goff et al., 2003). Several oxidative degradation mechanisms have been identified to account for some of these products.

A mechanism attributed to Jefferson Chemicals to account for the reaction between MEA and O<sub>2</sub> alone is shown in Figure 2.3. Pathway of MEA oxidation has been identified that reaction of MEA with O<sub>2</sub> initially producing α-amine acetaldehyde. The acetaldehyde was further oxidized to glycine and glycolic acid, respectively. The acid reacted more with O<sub>2</sub> giving glyoxylic acid which was finally oxidize to oxalic acid. It only proposed for oxalic acid as a final product. Not only did this mechanism not include other degradation products, kinetic data was not provided to support the mechanism.

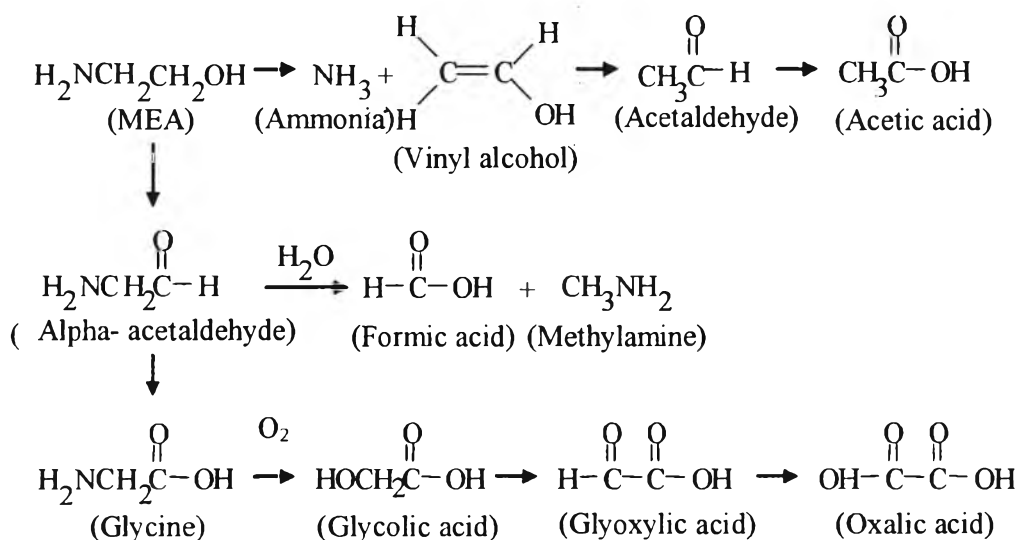


**Figure 2.3** One of the first mechanisms of oxidation degradation of MEA attributed to Jefferson Chemicals.

In 1998, Rooney et al. studied the oxygen's role in alkanolamine degradation. A scheme, Figure 2.4, was proposed to account for the presence of all the observed anions and those reported from past studies. It was concluded that the

acetic, formic, glycolic, glyoxalic and oxalic acids were shown as ions. Each of these anions was completely ionized to amine heat stable salt such as oxalates and glyoxalates in strong base solutions. In a comparative study, Kohl and Nielsen (1997) indicated that primary amines such as MEA are more vulnerable to oxidation than secondary and tertiary amines, the result of which was confirmed by Hofmeyer et al. (1965) and Rooney et al. (1998).

A study of the aqueous degradation products of MEA performed by Rooney et al., 1998 involved measurement of the rate of degradation of various alkanolamine mixtures in 0.25 CO<sub>2</sub> loaded and unloaded solutions. The experiments were conducted by bubbling O<sub>2</sub> into the various alkanolamine solutions using 20 wt% MEA, 30 wt% diethanolamine (DEA), 50% di-glycol amine (DGA) as well as 30 and 50wt% MDEA at 82°C over a 28 day period was quantified by liquid analysis with ion chromatography. It was observed that oxidation resistance increased in the order of 30% DEA > 50% MDEA > 30% MDEA > 50% DGA > 20% MEA in the absence of CO<sub>2</sub>, whereas the resistance order changed to 30% DEA > 50% DGA > 20% MEA > 50% MDEA > 30% MDEA when CO<sub>2</sub> was present.



**Figure 2.4** Mechanism of the oxidative degradation of MEA (Rooney et al., 1998).

It is implying that MEA degraded the fastest and both of the MDEA solutions degraded faster than the MEA solutions for the loaded solutions. There was a larger total moles of acetate, formate, glycolate, and oxalate as compared with the case with CO<sub>2</sub>, by which they concluded that the presence of CO<sub>2</sub> lowered the O<sub>2</sub> solubility. This work did not identify all the possible degradation products formed with the result that no overall mechanism was proposed to account for these degradation products both CO<sub>2</sub> alone and O<sub>2</sub>-CO<sub>2</sub>. Only a modification of the mechanism proposed by Jefferson Chemicals (Figure 2.3) to show the formation of some of the oxidative degradation products not observed by Jefferson Chemicals was put forward (Figure 2.4). This implies that products included in the modified mechanism are only part of the products that could be formed in the presence of O<sub>2</sub>. There was no indication of products resulting from the reaction of MEA with CO<sub>2</sub>.

Strazisar et al. (2003) performed various analytical techniques to identify the degradation products from industrial samples. The IMC Chemicals Facility in Trona, CA removes CO<sub>2</sub> from a coal-fired power plant using an aqueous MEA solvent, and uses the purified CO<sub>2</sub> to carbonate brine for the sale of commercial sodium carbonate. This facility has been removing CO<sub>2</sub> from flue gas since 1978, which is longer than any other facility. Solution analysis was performed on make-up lean MEA (inlet to the absorber), and the liquid waste from the reclaimers. Volatile compounds were identified using gas chromatography combined with mass spectrometry (GC-MS), FTIR, or atomic emission detection. Ionic species in the liquid were quantified using ion chromatography and inductively coupled plasma-atomic emission spectroscopy. Pathways of some of those degraded products were proposed including 2-oxazolidone, N-acetyethanolamine, and 1-hydroxyethyl-2-piperazinone. This is the first published study to attempt a quantitative analysis of degraded solutions from industrial. In addition to the known carboxylic acid degradation products, several new degradation compounds were detected in this experiment, but using this data to extract kinetics or mechanisms for oxidative degradation is problematic. First, since this analysis was done using an actual flue gas, many of the degradation products are attributable to reactions with impurities in the flue gas such as SO<sub>x</sub> and NO<sub>x</sub>. Sulfate was found in the liquid solution, as well as nitrosamines. No solution analysis was performed on the rich MEA solution. This

makes it impossible to determine whether the “new” degradation products are being formed in the absorber-regenerator process or in the solvent reclaimer. Additionally, the solid precipitate in the reclaimer was not analyzed so a complete material balance around the reclaimer is impossible. No analysis was done on the treated flue gas or the purified CO<sub>2</sub> stream to analyze for volatile degradation products like NH<sub>3</sub>. Many of the degradation products identified in this study are likely the result of carbamate polymerization, CO<sub>2</sub> side reactions, or from thermal degradation in the reclaimer. While quantitative data on rates of oxidative degradation of MEA cannot be determined from this study.

Early studies on the oxidative degradation of alkanolamines were primarily driven by the U.S. Department of the Navy starting in the early 1950's. This study performed by the Girdler Corporation was intended to screen a wide range of potential amine absorbents based on several properties including resistance to oxidative degradation. In this case alkanolamine was being used to remove CO<sub>2</sub> from the air supply of nuclear submarines. Oxidative degradation in these types of systems is particularly important since ammonia, which is a known toxic air pollutant, is volatile and can be released into the closed atmosphere of the submarine. Oxidative degradation tests were performed on 39 amines and 11 blends of amines. Experiments were performed by sparging a 50:50 blend of CO<sub>2</sub>:O<sub>2</sub> through amine solutions for seven days. Degradation was quantified by measuring free amine concentration, primary amine concentration, total organic nitrogen content, and NH<sub>3</sub> evolution. Results from the experiments showed significant degradation of MEA when studied alone and in blends with other amines. MEA was not recommended for further study as a CO<sub>2</sub> capture solvent in nuclear submarines due to the high degradation rates.

Despite the findings of this study, MEA was selected as a solvent for air purification in nuclear submarines. Degradation of MEA solutions in nuclear powered submarines was noticed by the smell of ammonia in the atmosphere, as well as a darkening of the solution color, decreased CO<sub>2</sub> capture efficiencies, and an increase in amine make-up rates (Blachly and Ravner, 1964). A series of studies was conducted to quantify and inhibit the oxidative degradation of MEA (Blachly and Ravner, 1963; 1964; 1965; 1966; Lockhart and Piatt, 1965). Studies were performed

by sparging gas (with various O<sub>2</sub> and CO<sub>2</sub> concentration) through MEA solutions. Degradation was quantified by measuring the rate of NH<sub>3</sub> evolution over several days. These studies are important because they are the first to quantify the presence of peroxide production during the degradation mechanism, although the structure of the peroxide was not identified. An inhibitor package was developed based on two additives, the tetra-sodium salt of ethylene-diamine-tetra-acetic acid (EDTA), and the monosodium salt of N,N-diethanol glycine (VFS, or bicine). The EDTA was used as a chelating agent to bind the Cu and other dissolved metals to prevent them from acting as catalysts, and VFS functioned as a peroxide scavenger to inhibit the degradation mechanism. These inhibitors were both found to be effective at inhibiting Cu catalyzed degradation. Specifications were developed for an additive package consisting of both EDTA and VFS, which was subsequently employed in nuclear submarines to minimize oxidative degradation of MEA.

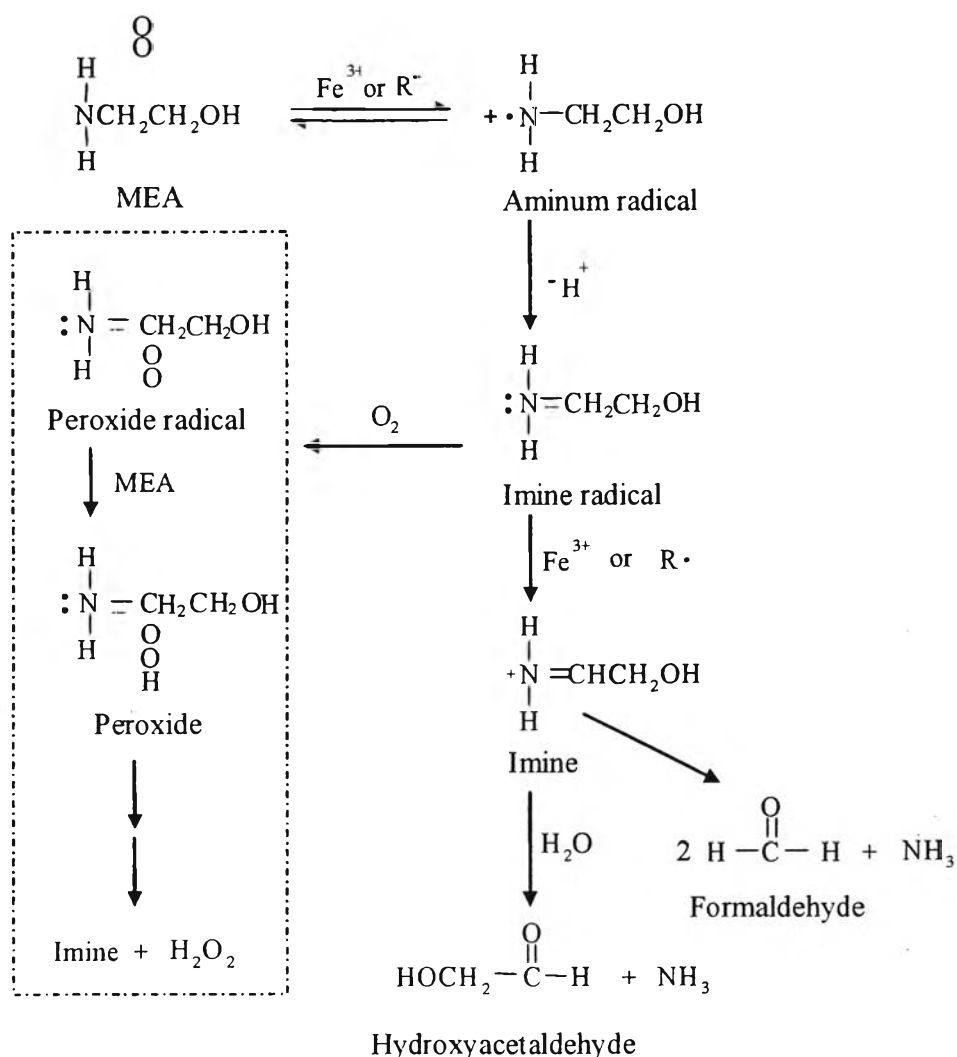
Chi and Rochelle (2002) measured the concentration of evolved ammonia by Fourier-Transform Infra-Red (FTIR) analysis. The benefit of this method is that it allows instantaneous measurements of gas-phase products (NH<sub>3</sub>), without having to run experiments for long periods of time. Data points were obtained in a matter of hours as opposed to weeks. Since these experiments were run at conditions with much higher mass transfer conditions, volatile compounds were stripped from the MEA solutions so that the concentration of dissolved NH<sub>3</sub> is negligible. This method allows amine degradation rates to be quantified only by gas analysis, and eliminates the messy and complex liquid analysis. Only primary amines that form NH<sub>3</sub> as the primary degradation product can use this analysis method.

The MEA degradation mechanism proposed by Chi and Rochelle (2002) shown in Figure 2.5. It was showed that products included in the mechanism are only part of the products that could be formed in the presence of O<sub>2</sub>. There was no indication of products resulting from the reaction of MEA and CO<sub>2</sub>. Although, this study did not propose a mechanism to account for degradation products obtained in the presence of CO<sub>2</sub> alone, as well as for the presence of both CO<sub>2</sub> and O<sub>2</sub>.

Chi and Rochelle (2002) also studied the effect of dissolved Fe on the oxidative degradation of MEA, and found that dissolved iron, over a concentration range of 0.0001 to 3.2 mM, catalyzed the degradation rates from 0.12 to 1.10 mmoles

$\text{NH}_3$  evolved / liter of solution-hr. This degradation rate is significantly higher than the rates encountered in the other reported studies. The effect of EDTA and VFS were also studied to confirm the inhibiting potential in MEA solutions under conditions found in flue gas applications. These studies showed that a ratio of bicine to total dissolved iron of 100 to 1 cut the degradation rate by half. EDTA studies by these investigators contradicted the findings of Blachly and Ravner (1963). Moreover, Chi and Rochelle (2000) also found that in solutions with a  $\text{CO}_2$  loading of 0.40, a ratio of EDTA to total dissolved iron of 22.5 to 1 cut the degradation rate by 40%. A second experiment at a lower total iron concentration showed that at a ratio of EDTA to iron of 130 to 1, the rate was also decreased by 40%. This data shows that further study on the effectiveness of EDTA as a degradation inhibitor is needed, since it appears that EDTA is potentially as strong an inhibitor as VFS for Fe catalyzed degradation.





**Figure 2.5** Mechanism of MEA oxidation (Chi and Rochelle, 2002).

Goff and Rochelle (2004) investigated kinetics and mechanism of oxidative degradation of MEA. The mechanism for the oxidative degradation of MEA was reported unclearly. It might involve two different mechanisms of electron abstraction and hydrogen abstraction that give the same degradation products. Electron abstraction mechanism was set off by free radical such as  $Fe^{3+}$  removing an electron from the nitrogen atom of MEA to form an amine radical. The amine radical then deprotonates further to form an imine radical and reacts with a second free radical to form an imine and then reacts with water to form an aldehyde and ammonia.

According to Chi and Rochelle (2002) propose that the imine radical can react with oxygen to form an amino-peroxide radical. The peroxide radical could then react with another molecule of MEA to form an amino-peroxide and another aminium radical. The peroxide could then decompose to form hydrogen peroxide and an imine, which would in turn react with water to form an aldehyde and ammonia. The latter mechanism involves the radiation-induced radical which removed a hydrogen for the nitrogen, the  $\alpha$ -carbon, or the  $\beta$ -carbon of MEA molecule. Kinetics of MEA degradation was indirectly analyzed by measuring evolution rate of  $\text{NH}_3$ . The rate of  $\text{NH}_3$  formation was concluded to be dependent of agitation speed, thus, controlled by  $\text{O}_2$  mass transfer. This study concluded that the rate-limiting step is the electron abstraction, rather than the hydrogen abstraction. The degradation rate of MEA in actual  $\text{CO}_2$  capture unit was also thought to be mass transfer limited.

Bello and Idem (2005) more recently performed MEA degradation studies and analyzed the liquid solution to determine the degradation products and mechanism of degradation. MEA Experiments were performed in an autoclave reactor at temperatures of 55, 100 and  $120^\circ\text{C}$  and  $\text{O}_2$  pressures of 250 or 350 kPa over several days. Degradation experiments were performed with and without  $\text{O}_2$  and  $\text{CO}_2$  to quantify the effect of  $\text{CO}_2$  loading and degradation in the absence of  $\text{O}_2$ . A significant number of degradation products were identified using a GC-MS, most of which had not been identified and reported in the literature, with methods developed by the same research group (Supap, 1999). The effects of  $\text{O}_2$  pressure, presence of  $\text{CO}_2$ , MEA concentration, and degradation temperature were all taken into account upon building the degradation mechanisms. Change in temperature or addition of  $\text{CO}_2$  to the degradation system were both found to alter MEA degradation mechanisms. The extent of degradation was found to decrease in the order of MEA- $\text{H}_2\text{O}$ - $\text{O}_2$  followed by MEA- $\text{H}_2\text{O}$ - $\text{O}_2$ - $\text{CO}_2$  and MEA- $\text{H}_2\text{O}$ - $\text{CO}_2$ . A comprehensive study of kinetics of MEA oxidative degradation was proposed by the same research group (Bello and Idem, 2006). General mechanisms were also proposed for the systems with and without  $\text{CO}_2$ . Kinetic equations were then derived based on those mechanisms so that it could predict the oxidation of MEA in various environments including with and without a corrosion inhibitor-sodium metavanadate.

Lawal et al. (2005) studied the mechanistic role of MDEA in mixtures of MEA-MDEA system. The presence of MEA in the blended system was found to change the degradation mechanism of the MEA alone system. In addition, at temperature higher than 120°C, the addition of MDEA to the MEA solutions was found to be more prone to oxidation than MEA. The degradation rate of blended system with and without CO<sub>2</sub> was studied under various conditions including different total amine concentration, temperature, and MEA/MDEA ratios. Total amine concentration was found to increase the degradation rate. While, increasing CO<sub>2</sub> concentration (CO<sub>2</sub> loading) gave an opposite effect.

## 2.6 Sulfur Induced Degradation of Alkanolamines

When capturing CO<sub>2</sub> from coal-fired power plants flue gas, containing other acid gas components such as SO<sub>2</sub>, the amine process requires that SO<sub>2</sub> be removed first from the flue gas stream. These acid gas components also have a chemical reaction with the amine solution. This is undesirable as the irreversible nature of this reaction also leads to the formation of degradation products such as heat stable salts, and hence, a loss in CO<sub>2</sub> absorption capacity and the risk of formation of solids in the solution. In addition, SO<sub>2</sub> reacts quickly with O<sub>2</sub> in the amine solution to form sulfate (SO<sub>4</sub><sup>2-</sup>), forming a heat stable salts with amine (Kohl and Nielsen, 1997). SO<sub>2</sub> concentrations in the flue gas are typically around 300-500 ppm, and 2-400 ppm in coal-fired power plant flue gases (Table 2.1). Commercially available SO<sub>2</sub> removal plants will remove up to 98-99%. Therefore, prior to flue gases being introduced to the CO<sub>2</sub> removal process, SO<sub>2</sub> is usually removed to very low values in flue gas desulfurization processes known as FGD units using a number of existing techniques. FGD may be divided into wet and dry process. In wet scrubbing, for example, slurries of limestone (CaCO<sub>3</sub>) or lime (Ca(OH)<sub>2</sub>) (Speight et al., 1994) is brought into contact with flue gases and SO<sub>2</sub> is removed as a wet sludge of CaSO<sub>3</sub>/CaSO<sub>4</sub> or CaSO<sub>3</sub>. On the other hand, in a dry process, dry limestone known as dolomite (CaCO<sub>3</sub>.MgCO<sub>3</sub>) is used within the combustor removing SO<sub>2</sub> as calcined products along with sulfite and sulfate salts. Even after subjecting to one of these FGD processes, flue gas streams from coal-fired often contains SO<sub>2</sub> and is carried

over to contact with the amine solution in CO<sub>2</sub> removal process. This can potentially induce amine degradation. At the present time, only a few SO<sub>2</sub>-related amine degradation studies have been reported. In addition, amine decomposition by other sulfur species such as carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>) usually present in natural gas is available, although limited.

Uyanga and Idem, (2007) investigated the kinetic of MEA degradation in the presence of both O<sub>2</sub> and SO<sub>2</sub>. Experiments were again carried out in a stirred batch reactor using varied MEA concentrations, O<sub>2</sub> and SO<sub>2</sub> concentrations in the simulated gas mixture and temperature. A corrosion inhibitor, NaVO<sub>3</sub>, was also evaluated and found to increase the rate of MEA degradation.