CHAPTER VI

PRELIMINARY STUDIES ON DEGRADATION PREVENTION TECHNIQUES USING DEGRADATION INHIBITORS FOR MEA BASED CO_2 ABSORPTION FROM POWER PLANT FLUE GASES

6.1 Research Objectives

Obviously, CO_2 must be removed from coal-derived flue gases to minimize CO_2 emissions and its effect on climate change. Although the use of the chemical absorption technique with aqueous alkanolamine is found to be appropriate for CO_2 removal from such low pressure flue gas streams, the capture process still suffers from degradation of the alkanolamines caused by flue gas contaminants such as O_2 and SO_2. A more serious degradation could be obtained with SO_2 since its high solubility makes it easy to be carried over to the regeneration-rebolier section where the high temperature speeds up the rate of degradation of the amine. 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. The existence of these problems means there is an urgent need in finding ways to prevent degradation in order to maintain the capture performance and minimize the plant's operating cost.

The complete removal of O_2 and SO_2 from gas streams to prevent degradation of alkanolamine seems to be highly complicated and practically difficult. Especially, the detection and removal of O_2 is known to be time consuming and also labor-intensive (McKnight, 1988). This has made the addition of an effective degradation inhibitor a more attractive method of choice as recommended in the literature (Rooney et., 1998). Although, information on the use of degradation inhibitors in alkanolamine system is limited, useful guidelines for selection of appropriate inhibitors are available as given in detail in Chapter II. In brief, for inhibitors to work effectively, they must scavenge O_2 at ambient temperature and should have more favourable kinetics than the partial oxidation reactions involved in degradation (Veldman, 2000). Various compounds including EDTA and Na_2SO_3

were evaluated in copper and iron catalyzed degradation of MEA in the O_2 alone system (Goff and Rochelle, 2006). To the present knowledge, efforts in inhibitor search for prevention of alkanolamine degradation has been really limited and only given to O_2-induced degradation systems. For a more realistic case such as coal-fired flue gas purification, none of the inhibitor studies has included SO_2 in the degradation system. In addition, SO_2 has been shown to also trigger additional degradation to alkanolamine as demonstrated in details in Chapter 5. 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_2-SO_2 induced degradation of alkanolamine.

This preliminary study investigated the effect of Inhibitor UR-A as a potential degradation inhibitor for the systems of MEA-O_2-SO_2. The extreme degradation conditions normally found in the regenerator-reboiler region was selected to show the most severe effect of the degradation. The MEA concentration used was in the range of 5 – 7 kmol/m^3. MEA solution was spiked with Inhibitor UR-A having a concentration between 0 – 0.3 kmol/m^3. The simulated flue gas used was composed of 6 – 100% O_2, N_2, and 0 -196 ppm SO_2. All experiments were carried out at 393 K degradation temperature. The degraded samples were analyzed by the HPLC technique. The rate information was then used to compare the effect of Inhibitor A in minimizing degradation.

In addition, it has been previously found that CO_2 inhibits O_2-induced degradation of MEA (shown in Figure 5.6). This implies that CO_2 can also act as an inhibitor to minimize the degradation rate of MEA during CO_2 capture process. Therefore, it was decided to study inhibition effect of CO_2 also for the system of MEA-O_2-SO_2 which could possibly be used as one of the degradation prevention approaches. The CO_2 results were also compared with that of Inhibitor UR-A.

6.2 Results and Discussion

6.2.1 Determination of Optimum Concentration of Inhibitor UR-A using MEA-O_2 Degradation System

The oxidative degradation of MEA without SO_2 was initially used to determine the optimum concentration of Inhibitor UR-A necessary for minimizing the degradation rate. MEA-O_2-H_2O degradation system was first used containing 5 kmol/m^3 MEA solution and 6%O_2 simulated flue gas stream. Degradation temperature was chosen as 393 K to mimic the extreme condition in the stripper column. Figure 6.1 shows the effect of Inhibitor UR-A concentration on the MEA degradation rate. Inhibitor UR-A of 0.05 kmol/m^3 was first added to the MEA solution. At this concentration, the initial rate of MEA degradation was measured at 7.98×10^{-5} kmol/m^3.h which was approximately 5 times lower than that of the run carried out in the absence of Inhibitor UR-A (e.g., 4.5×10^{-4} kmol/m^3.h degradation rate). Inhibition efficiency of Inhibitor A was calculated using Equation (6.1). Percent inhibition of Inhibitor A in MEA-O_2 degradation system was found to be 82%.

$$\%\text{Inhibition} = \frac{\left|r_{w/o} - r_w\right|}{r_{w/o}} \times 100 \qquad (6.1)$$

Where $r_{w/o}$ and r_w are respective rate of MEA degradation without and with inhibitor (kmol/m^3.h)

A further experiment was conducted using a higher Inhibitor UR-A concentration of 0.1 kmol/m^3. This served to determine the optimum concentration needed for best preventing the oxidative degradation of MEA. An opposite trend was obtained as also shown in Figure 6.1. Its rate of oxidative degradation was calculated as 6.6×10^{-4} kmol/m^3.h which was 1.5 times higher than that of the run without Inhibitor UR-A. A higher degradation rate of 1.3×10^{-3} kmol/m^3.h was even observed when Inhibitor A concentration was increased to 0.3 kmol/m^3. The rate was 3 times as fast as that for the run conducted in the absence of Inhibitor UR-A.

It is clear that not only did an increase in inhibitor concentration speed up the degradation rate, it also added up the cost of the chemical. To confirm the negative effect in using excess concentration of Inhibitor UR-A (concentration of 0.1 kmol/m^3 or higher), different degradation runs were used. Figure 6.2 shows the adverse effect of excess Inhibitor UR-A (e.g. 0.1 kmol/m^3) to the system consisting of 7 kmol/m^3 MEA, 100% O_2 and 393 K.

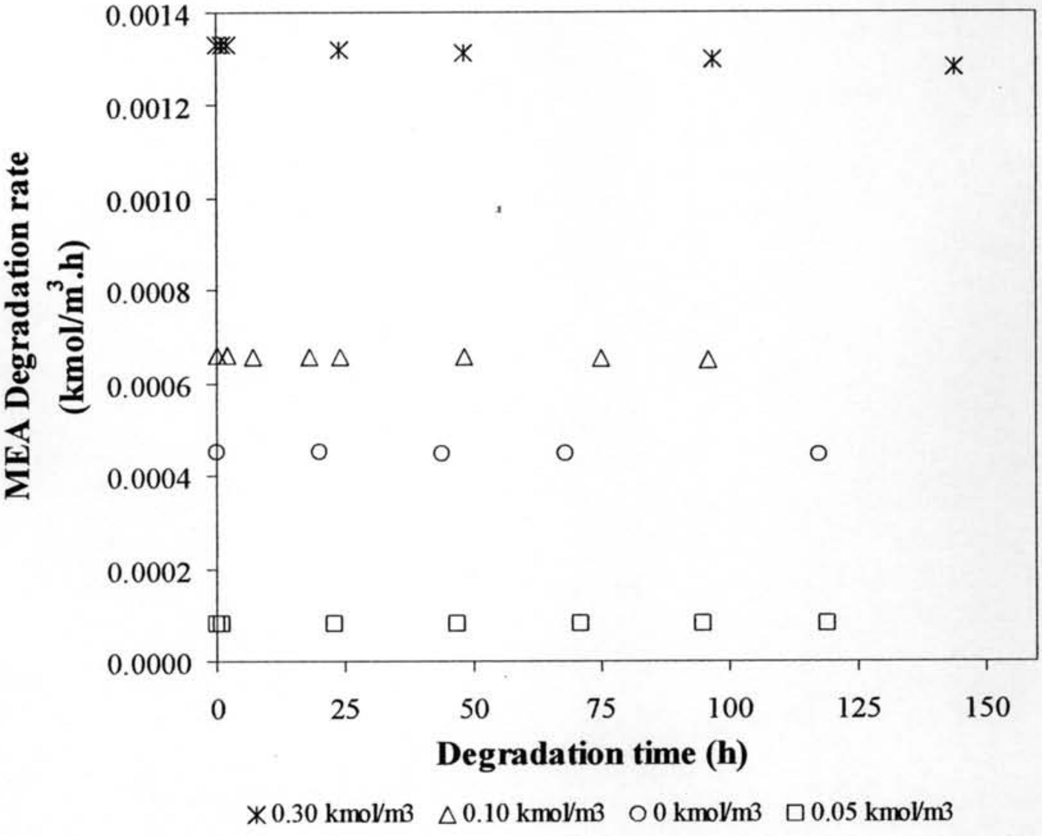

Figure 6.1 Effect of concentration of Inhibitor UR-A on MEA-6%O_2 degradation system (5 kmol/m^3 MEA, 6% O_2, 393 K).

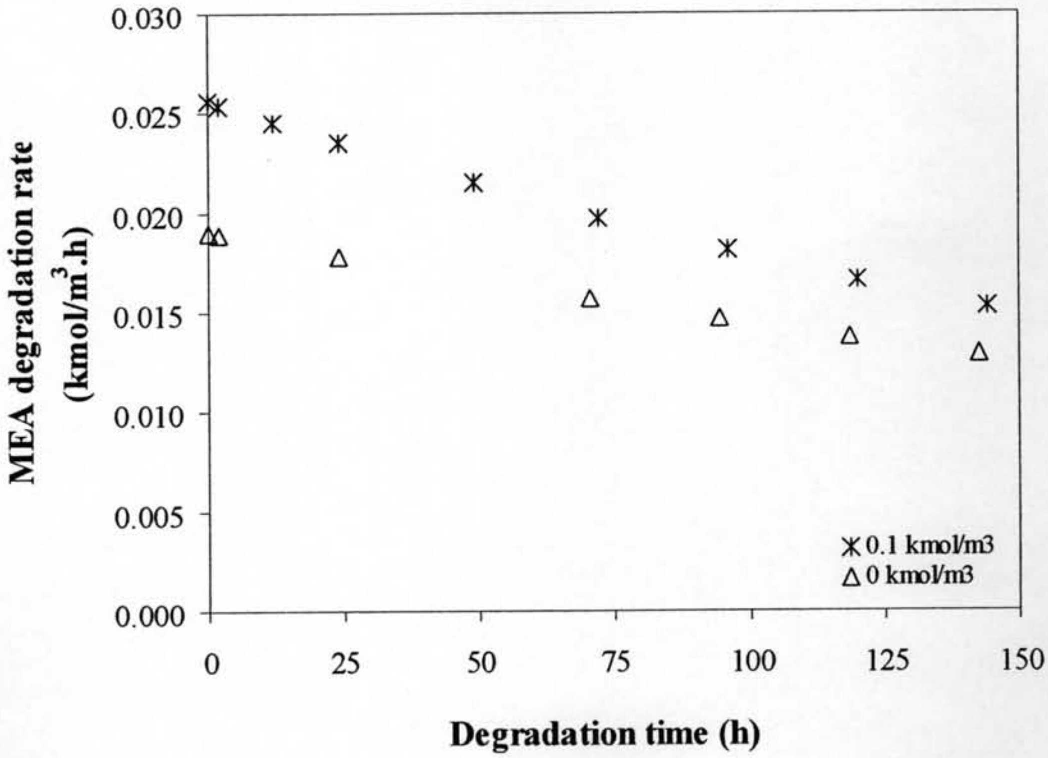

Figure 6.2 Adverse effect of excess Inhibitor UR-A on MEA-100% O_2 degradation system (7 kmol/m^3 MEA, 100% O_2, 393 K).

The presence of Inhibitor UR-A at 0.1 kmol/m^3 again increased the degradation rate by a similar factor of 1.5 as previously observed in the 6% O_2 system. It was possible that excess amount of Inhibitor UR-A could possibly trigger additional degradation itself either by breaking down molecules of MEA or catalyzing the reaction between O_2 and MEA resulting in a faster rate of degradation. More research work (beyond the scope of this work) is however needed to prove this hypothesis. It was now certain that Inhibitor A concentration of 0.05 kmol/m^3 was the best in minimizing the degradation rate of MEA in the presence of O_2. This concentration was therefore selected for further evaluation using a more realistic system consisting of MEA-O_2-SO_2.

6.2.2 Effect of Inhibitor UR-A in MEA-O_2-SO_2 Degradation System

Not only does flue gas contain O_2, SO_2 is often present. Previously, it has been confirmed that an increase of SO_2 concentration also increases the MEA oxidative degradation rate. Hence, it was essential to determine the effect of Inhibitor UR-A in the system containing both O_2 and SO_2. A run using 5 kmol/m^3 MEA, 6% O_2, and 6 ppm SO_2 was initially conducted for comparison. Two additional runs with 6 and 196 ppm SO_2, both with 6% O_2 and an addition of 0.05 kmol/m^3 Inhibitor UR-A (the optimum concentration determined earlier) were subsequently done to evaluate the effect of the inhibitor. All the experiments were carried out at 393 K (stripper condition). The degradation rate-time plots are shown in Figure 6.3.

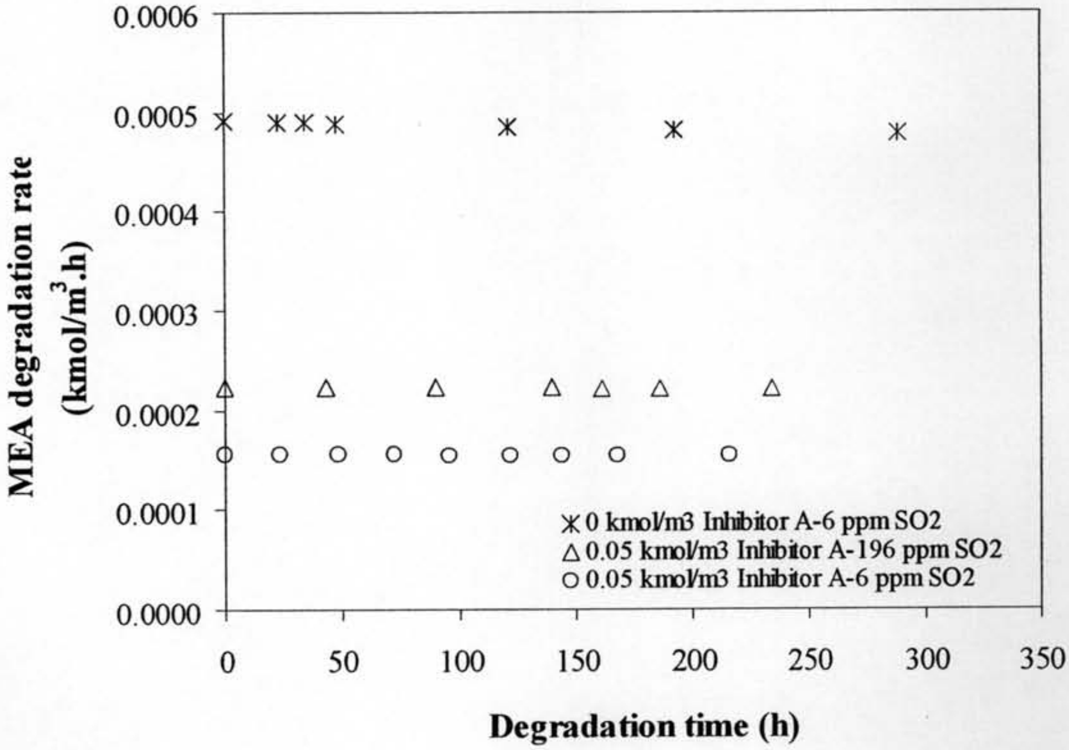

Figure 6.3 Degradation rate-time plots of MEA-O_2-SO_2-H_2O system with 0.05 kmol/m^3 Inhibitor UR-A (5 kmol/m^3 MEA, 6% O_2, 393 K).

The rate of degradation for the run without Inhibitor UR-A (6 ppm SO_2) was found to be 4.9×10^{-4} kmol/m^3.h. The rate decreased drastically to 1.6×10^{-4} kmol/m^3.h when 0.05 Inhibitor UR-A was used in this system. The 196 ppm SO_2 system with the addition of Inhibitor UR-A at the same concentration also resulted in a low degradation rate of 2.2×10^{-4} kmol/m^3.h. This rate was even much lower than that of 6 ppm SO_2 run without the inhibitor indicating a strong inhibition effect of Inhibitor UR-A in reducing the degradation rate. Percent inhibition of Inhibitor UR-A in 6 ppm and 196 ppm SO_2 systems calculated using Equation (6.1) were 67% and 55%, respectively.

6.2.3 Inhibition Effect of CO_2 in MEA-O_2-SO_2 Degradation System

The rates of MEA degradation were calculated for runs conducted with 5 kmol/m^3 MEA, 6 ppm SO_2, and 393 K with 0.33 CO_2 loading/without CO_2. Their degradation rates were plotted against times as shown in Figure 6.4. The initial rate of run without CO_2 was found to be 4.91×10^{-4} kmol/m^3.h. When 0.33 loading of CO_2 was added to the same run, the degradation rate of MEA reduced to 4.37×10^{-4} kmol/m^3.h. This accounted for 1.1 times of rate reduction. With the use of Equation (6.1), % inhibition of CO_2 was calculated as 11%. Runs of 7 kmol/m^3 MEA, 11 ppm SO_2, 393 K with/without CO_2 were also used, also plotted in Figure 6.4, to confirm the inhibition effect of CO_2 to MEA degradation rate. CO_2 loading of 0.24 was found to inhibit the MEA degradation by approximately 15%. This confirms that CO_2 could already act as an inhibitor for O_2-SO_2 induced degradation.

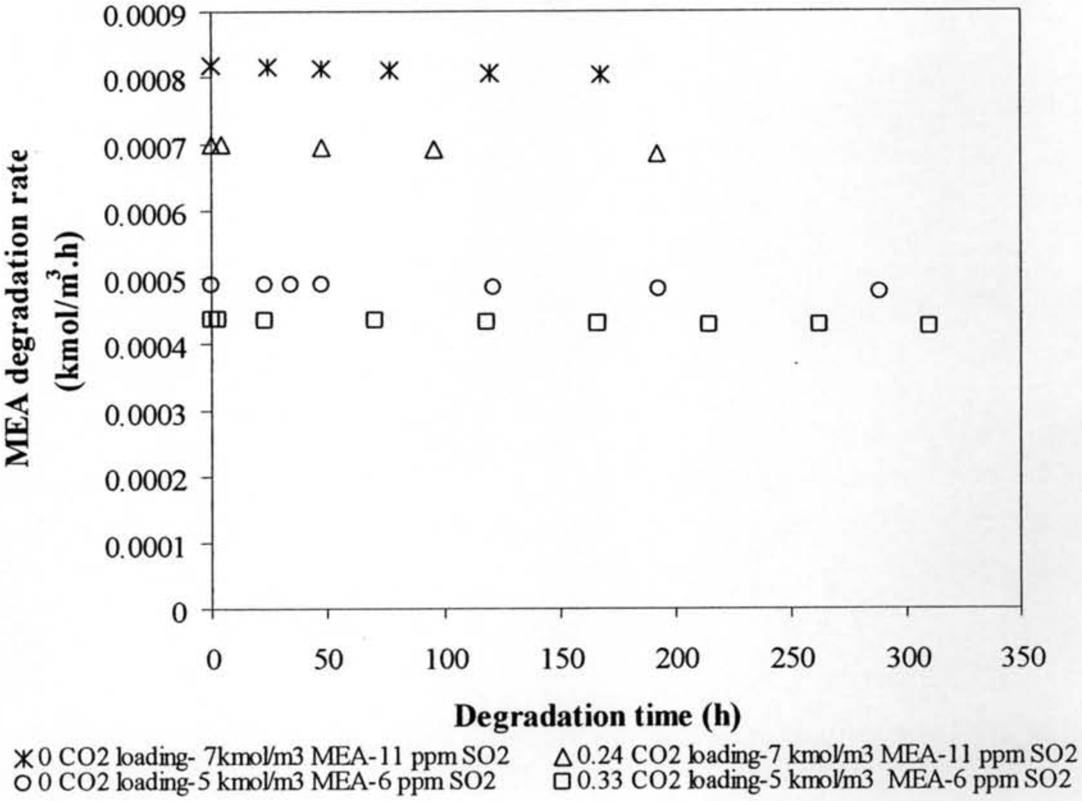

Figure 6.4 Inhibition effect of CO_2 in Degradation of MEA-O_2-SO_2 system (6% O_2, 393 K).

Although, under the same degradation conditions, the effect of CO_2 in retarding the O_2-SO_2 induced MEA degradation was not as strong as the effect obtained from Inhibitor UR-A as shown by their % inhibition. Its presence in MEA solution actually provided a positive effect in reducing the degradation rate of MEA. This information suggested that if Inhibitor UR-A is added in a lean CO_2 MEA solution, O_2-SO_2 induced degradation in CO_2 capture unit might be further reduced. However, it will need to be thoroughly investigated to confirm this combined effect of CO_2 and Inhibitor UR-A.

6.3 Conclusions

The following conclusions could be drawn from this study;

1. Inhibitor UR-A at the optimum concentration of 0.05 kmol/m^3 was found to be the best in minimizing the oxidative degradation in both MEA-O_2-H_2O and MEA-O_2-SO_2 degradation systems.

2. Outside this optimum concentration (e.g. 0.1 and 0.3 kmol.m^3) resulted in an adverse effect of speeding up the MEA degradation rate.

3. The presence of CO_2 decreased the O_2-SO_2 induced MEA degradation rate, although this inhibition effect was not as strong as that of Inhibitor UR-A.