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Corrosion Behavior of Carbon Steel in Carbonated MDEA-MEA Aqueous Solutions

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Corrosion Behavior of Carbon Steel in Carbonated MDEA-MEA Aqueous Solutions

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Abstract: In order to deal with the long-term corrosion problems in the absorption of carbon dioxide (CO_2) using alkylol amines, perfecting the corrosion parameters is necessary. The tafel curves of carbon steel in carbonated N-methyldiethanolamine (MDEA)-monoethanolamine (MEA) aqueous solutions were investigated by using the CHI602E electrochemical analyzer. Then the corresponding corrosion rates were calculated. The temperatures ranged from 303.2K to 323.2K. The mass fractions of MDEA and MEA respectively ranged from 0.30 to 0.40 and 0-0.10. The CO_2 loading ranged from 0.1 to 0.4. The effects of temperatures, mass fractions and CO_2 loadings on the corrosion rates were demonstrated. Results showed that corrosion rates increase with increasing temperatures, mass fractions and CO_2 loadings. Moreover, the corrosion rates of carbon steel in carbonated MDEA-MEA aqueous solutions are obviously less than the corrosion rates in pure MDEA.

1. Introduction

In recent years, the large-scale use of fusil fuel has caused the increase of the carbon dioxide in the atmosphere, resulting in serious global warming[1]. Consequently, the efficient capture of CO_2 in flue gas has attracted worldwide attention.

At present, the main methods of CO_2 capture include: chemical absorption[2,3], physical adsorption and membrane separation. Among these, chemical absorption has been widely applied in industry because of its good absorption effect, high purity and mature technology. The aqueous amine solution method has the advantages in the field of CO_2 capture in low partial pressure flue gas due to its large absorption, fast absorption rate, low cost and good recycling efficiency. Generally speaking，as the simplest primary alcohol amine, MEA has obvious advantage in absorption speed, but disadvantage in small absorption capacity and high energy consumption of regeneration[4]. Besides, the strong corrosion of the equipment limits the industrial application of MEA. By comparison, MDEA and other tertiary amine have the advantages of large absorption capacity, low energy consumption of regeneration and low corrosion rate of equipment, but drawback in absorption rate[5,6]. Therefore, there is a general tendency that capturing CO_2 with MDEA as the absorption basis, add certain amount of MEA as accelerant. Compared with single alcohol amine, the blend absorbent has obvious advantage in absorption performance, regeneration efficiency, and corrosion resistance.

In the process of CO_2 capture with aqueous amine solution, absorption capacity, absorption rate, regeneration efficiency and regeneration rate are the key parameters, which have great significance to absorption and desorption tower design. In addition, the corrosion rate of absorbent to carbon steel is also an important parameter of process design, which is of great significance for equipment operation. In the process of CO_2 capture, due to the formation of a range of compounds such as carbamates and

bicarbonates, the solution alkalinity is reduced, leading to more serious corrosion. The corrosion mechanism of CO_2 absorbed aqueous amine solution to carbon steel is as follow:

Alcohol amine in the solution present basic due to its ammonium, which combine with carbon dioxide in solution to achieve absorption:

$$2RNH_2 + CO_2 \leftrightarrow RNHCOO^- + RNH_3^+ \qquad (1)$$

Next step, combined with water to generate bicarbonate:

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO^{3-} \qquad (2)$$

Typically bicarbonate (HCO_3^-) is the main factor leading to corrosion in carbon dioxide solution, which combined with the iron atoms to release electrons:

$$Fe + HCO^{3-} \leftrightarrow FeCO_3 + H^+ + 2e^- \qquad (3)$$
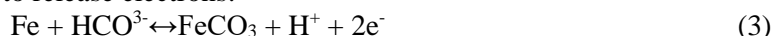
According to (3), the amount of HCO^{3-} is proportional to the amount of iron dissolved, which determines the overall corrosion rate [7].

In recent decades, researches of corrosion of CO_2 absorbed blended amines such as MEA+piperazine（PZ），MDEA+PZ, has been extensively studied[8-11], Louis et al. [12] has studied the corrosion rate of carbon steel in 10 days under the condition of blended amine (7.5%-22.5%，15%-15%，22.5%-7.5%), and analyzed the Fe^{2+} concentration, surface composition and morphology on the surface of carbon steel. On the basis of the study, it can be concluded that the concentration of Fe^{2+} increased with the increase of MEA content in the absorbent, and decreased with the extension of time. Veawab et al. [13] studied the corrosion rate of carbon steel in MDEA (1.5 mol/L) - MEA (1.5 mol/L) absorbing solution loaded with saturated CO_2 at 80°C. The result shows that the corrosion rate of the blended amine is 77.6 mpy, which is much lower than the corrosion rate of 3mol/LMEA under the same conditions (136.4 mpy), and is close to that of MDEA under the same conditions (67.6 mpy).

Up to now, although the corrosion characteristics of MDEA-MEA and other blended amine-loaded CO_2 absorbents have been reported, the research of thermal power plant under the condition of flue gas (40°C) is rarely reported. Based on existing research, high concentration of MDEA-MEA aqueous solution (mass fraction 50%) is conducive to increasing absorption constant and reducing energy consumption. However, the study on the corrosion rate of carbon steel with high concentration MDEA-MEA absorber loaded with CO_2 is rarely reported, the influence of operating temperature, alcohol amine mass fraction and CO_2 loading on corrosion rate are not clear yet.

In this passage, the corrosion behavior of carbon steel in MDEA-MEA aqueous solution loaded with CO_2 at 303.2K-323.2K was investigated. The mass fraction of MDEA and MEA is 0.3-0.4 and 0-0.1, and the CO_2 loading is 0.1-0.4. According to the Tafel curve and corrosion rate, it analyze and clarify the relationship between corrosion rate of carbon steel in alcohol-amine absorbent solution and temperature, alcohol-amine concentration and CO_2 loading.

2. Experiment

2.1 Experimental material

The corrosion test specimen is No. 20 carbon steel. Chemical composition of standard JB/T6057-92 steel is: C(0.17~0.23), Si(0.17~0.37), Mn(0.36~0.65), P(≤0.035), S(≤0.035), Ni(≤0.030),Cr(≤0.025), Cu(≤0.035).

Chemicals used in this work are detailed in Table 1. They were used without further purification. An analytical balance (Jingtian FA1604A) with an accuracy of 0.1 mg was used to weigh all required chemicals. Aqueous solutions of MDEA and MEA were prepared by adding deionized water (Electrical resistivity >15 MΩ·cm at 298 K) obtained from the Heal Force ROE (Reverse Osmosis Electrodeionization)-100 apparatus.

Table.1 Sample description

Chemical name	CAS	Purity (mole fraction, as stated by the supplier)	Source
MEA	111-42-2	$x \geq 0.99$	Kermel Chemical Reagent
MDEA	105-59-9	$x \geq 0.98$	Aladdin Industrial Corporation

Water	7732-18-5	Electrical resistivity > 15MΩ cm at $T = 298$ K	Heal force ROE-100 apparatus

2.2 Apparatus and Procedure
The absorption is carried out in a thermostat water bath. CO_2 is imported by the mass flow controller(MFC) into the sealed round-bottomed flask filled with absorption solution. A portion of CO_2 is absorbed in the flask and the unabsorbed gas exported from the flask and move on into the CO_2 analyzer and mass flow meter(MFM). The remaining CO_2 in the airflow will be detected the amount of absorbed gas in order to determine CO_2 loadings.

The electrolytic cell consists of a working electrode, a reference electrode, and a platinum electrode. Corrosion occurs in an electrolytic bath heated by a thermostatic water-circulator bath. An electrochemical analyzer connected with an electrolytic cell derive the Tafel curve and data of the corrosion process through a computer. The corrosion data is processed into linear graphs and figure out more detailed corrosion rates for further analysis.

3. Result and discussion

3.1 Reliability verification
To determine the feasibility and repeatability, we carried out experiment at the same temperature and concentration with existing literature of 3 kmol/m³, 80°C, MEA. The experimental results show the corrosion rate is 144.6mpy (which is 136.4mpy shown in the comparative literature [13]). This set of data can confirm the reliability of our experiment.

3.2 Corrosion rate of carbon steel in MDEA absorbing solution loaded with CO2
The corrosion rate of carbon steel in MDEA absorption solution is shown in Table 2. The mass fraction of MDEA is 0.3 to 0.4, the temperature is 303.2K to 323.2K, and the CO_2 loading is 0.1 to 0.4. The experimental results in Table 2 show that the corrosion rate increases with the increase of corrosion temperature, CO_2 loading and the concentration of alkanolamine.

Table.2 Corrosion rates of carbon steel in carbonated MDEA aqueous solutions

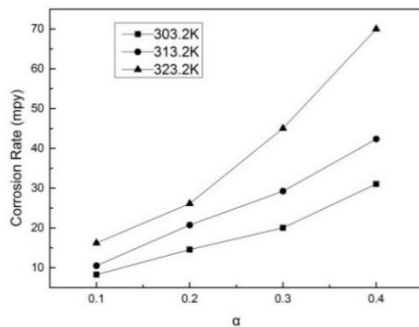| w_{MDEA}	α	Corrosion Rate (mpy)		
		303.2K	313.2K	323.2K
0.3	0.1	8.278	10.5	16.2
	0.2	14.56	20.72	26.14
	0.3	20.04	29.23	45.02
	0.4	31.03	42.32	69.99
0.4	0.1	8.942	15.44	18.02
	0.2	15.63	21.76	27.89
	0.3	21.87	31.55	47.23
	0.4	32.33	44.88	73.54

Figure. 1 Effect of CO_2 loading on the corrosion rate of carbon steel in carbonated MDEA aqueous solutions, w_{MDEA}=0.3. Symbols: experiments, ■T=303.2K; ●T=313.2K; ▲T=323.2K. Lines: trend lines
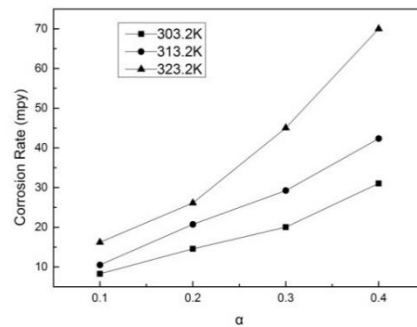

Figure. 2 Effect of CO_2 loading on the corrosion rate of carbon steel in carbonated MDEA aqueous solutions, w_{MDEA}=0.4. Symbols: experiments, ■T=303.2K; ●T=313.2K; ▲T=323.2K. Lines: trend lines

The effect of CO_2 loading on the corrosion rate of carbon steel in MDEA absorption solution is shown in figures 1 and 2. Figures 1 and 2 show that the temperature of the absorption solution and the CO_2 loading have a significant effect on the corrosion rate. For example, α=0.4, w_{MDEA}=0.4, the corrosion rate increases from 31.03 mpy to 69.99 mpy when the temperature increases from 303.2 K to 323.2 K. The influence of temperature can be explained by formula (1) - (3) and two other related reactions.

$$RNH_3^+ \leftrightarrow RNH_2 + H^+ \tag{4}$$
$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{5}$$

Generally speaking, the change of temperature will disturb the balance between different substances. According to the correlation between temperature and equilibrium constants [14], the equilibrium constants of Eq. (2), (4) and (5) will increase as the temperature increase. Thus, a large number of H^+ and HCO_3^- will be generated. Subsequently, metal dissolution equilibrium and oxidant reduction were disturbed. In order to maintain the equilibrium of the reaction, the dissolution of the metal in the solution intensifies, and then more electrons are produced for oxidant reduction, thereby increasing the corrosion rate.

Increasing the CO_2 loading also significantly increases the corrosion rate. For instance, T=323.2K，w_{MDEA}=0.4, α increases from 0.1 to 0.4, the corrosion rate increases from 18.02 mpy to 73.54 mpy. The effect of CO_2 loading on the corrosion rate can be explained simply by equations (1)-(5). Increasing the CO_2 loading produces more HCO_3^- and RNH_3^+, resulting in a significant increase in H^+ concentration, which can exacerbate corrosion.

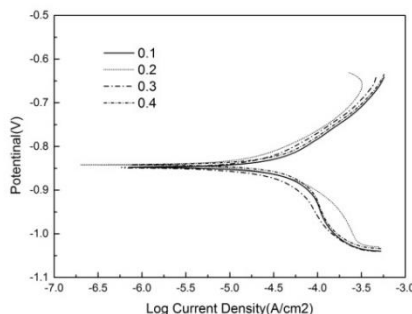Figure. 3 Polarization behaviors of carbon steel in carbonated MDEA aqueous solutions, w_{MDEA}=0.3, T=303.2K. Lines: trend lines, — α=0.1; … α=0.2；··· α=0.3；-.-.α=0.4.
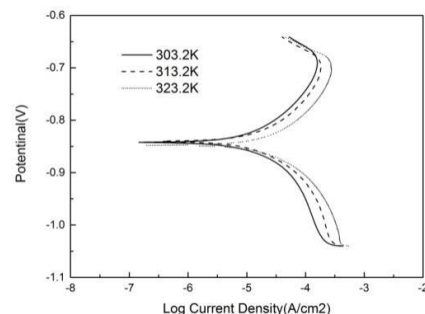

Figure. 4 Polarization behaviors of carbon steel in carbonated MDEA aqueous solutions, wMDEA=0.3, α=0.1. Lines: trend lines, T=303.2K; --- T=313.2K；… T=323.2K.

The polarization behavior of carbon steel in MDEA absorption liquid is shown in Figure 3 when wMDEA = 0.3 and T = 303.2K. It shows that at certain temperature, the Tafel curve of different loadings are densely distributed. As the loading increases, the corrosion current increases slightly, but the corrosion potential does not change significantly. Figure 4 shows the polarization behaviors of carbon steel in carbonated MDEA aqueous solutions, wMDEA=0.3, α=0.1. It shows that under certain loading, the corrosion potential change a little as the temperature rises, and the corrosion current increases significantly.

3.3 Corrosion rate of carbon steel in MDEA-MEA compounded absorbent with CO2 loading
The corrosion rate of carbon steel in the MDEA-MEA absorption liquid is shown in Table 3. The mass fraction of MDEA and MEA is 0.4 and 0.1, the temperature is 303.2K to 323.2K, and the CO_2 loading is 0.1 to 0.4. Similar to single MDEA absorbent, the corrosion rate of carbon steel in the MDEA-MEA absorption liquid increases with the increase of the corrosion temperature and CO_2 loading.
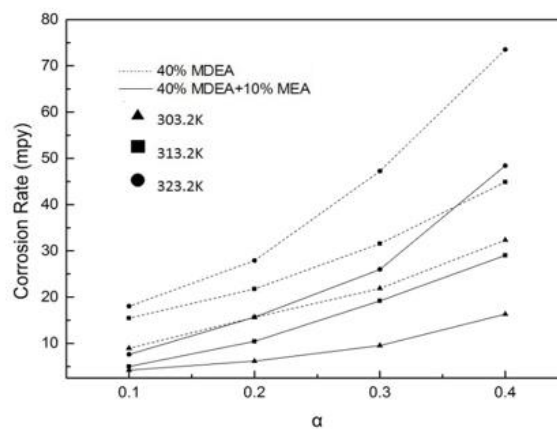

Figure. 5 Effect of CO_2 loading on the corrosion rate of carbon steel in carbonated MDEA+MEA and MDEA aqueous solutions. Symbols: experiments, ▲T=303.2K; ■T=313.2K;●T=323.2K. Lines: trend lines, —— w_{MDEA}=0.4，w_{MEA}=0.1; … w_{MDEA}=0.4.

Table.3 Corrosion rates of carbon steel in carbonated MDEA-MEA aqueous solutions

w_{MDEA}	w_{MEA}	α	Corrosion Rate (mpy)		
			303.2K	313.2K	323.2K
0.4	0.1	0.1	4.219	5.003	7.621
		0.2	6.153	10.43	15.66
		0.3	9.529	19.17	25.99
		0.4	16.32	29.02	48.43

The effect of CO_2 loading on the corrosion rate of carbon steel in MDEA+MEA and MDEA absorbers is shown in Figure 5. Figure 5 shows that with the increase of temperature, the corrosion rate of carbon steel in MDEA absorption solution with MEA increases significantly. Similar to single MDEA, the higher loading of absorbent, the more serious the corrosion. Under the same conditions, the corrosion rate of carbon steel in the mixed MDEA + MEA absorption solution is significantly slower than that in the single MDEA absorption solution.
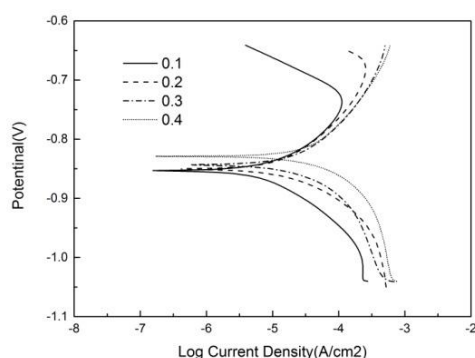
Figure. 6 Polarization behaviors of carbon steel in carbonated MDEA aqueous solutions, w_{MDEA}=0.4, w_{MEA}=0.1, T=313.2K. Lines: trend lines, —— α=0.1; ---α=0.2；-·-·α=0.3；…α=0.4.
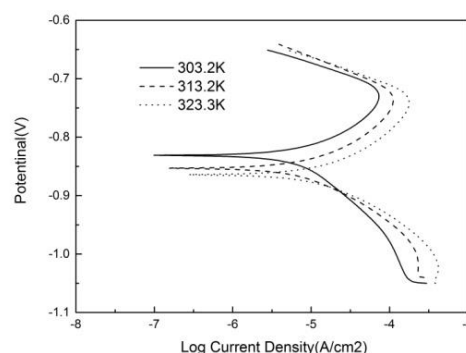
Figure. 7 Polarization behaviors of carbon steel in carbonated MDEA aqueous solutions, w_{MDEA}=0.4, w_{MEA}=0.1,α=0.1. Lines: trend lines, T=303.2K; --- T=313.2K；… T=323.2K.

When wMDEA = 0.4, wMEA = 0.1, T = 313.2K, the polarization behavior of carbon steel in MDEA absorption solution is shown in Figure 6. Combining with Figure 6, 7 and 3, 4, it can be seen that the corrosion effect of carbon steel in the mixed MDEA absorbent solution with MEA is obviously different from that in the single MDEA absorbent solution. Figure 6 shows that the Tafel curve of carbon steel in MDEA+MEA absorption solution moves to the upper right with the increase of loading at certain temperature, and the corrosion current increases. Figure 7 shows that the Tafel curve of carbon steel in MDEA+MEA absorption solution moves downward to the right with the increase of temperature under certain loading, and the corrosion potential and current increase obviously.

4.Conclusion

In this paper, the corrosion characteristics of carbon steel in the aqueous solution of MDEA-MEA loaded with CO_2 were measured by electrochemical analyzer (CHI602E) in the temperature range of 303.2K-323.2K. The mass fractions of MDEA and MEA are 0.3-0.4 and 0-0.1 respectively, and the CO_2 loading is 0.1-0.4. The experimental results show that:

1. For single MDEA absorption liquid, as the rise of temperature, CO_2 loading and alcoholamine concentration, the corrosion rate of carbon steel in the absorption liquid increases, but the corrosion potential does not change significantly.

2. For MDEA+MEA compounded absorption liquid, the corrosion of carbon steel in the absorption liquid aggravates with the increase of temperature and CO_2 loading. At the same time, the corrosion potential changes greatly;

3. After the addition of the promoter MEA, the corrosion rate of the carbon steel in the compounded absorbent is significantly slower than the rate of corrosion in the absorbent without the addition of the promoter.

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