Study on corrosion of carbon steel in DEA aqueous solutions

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Abstract: Corrosion of carbon steel in the CO₂ capture process using diethanolamine (DEA) aqueous solutions was investigated. The effects of the mass concentrations of DEA, solution temperature and CO₂ loading on the corrosion rate of carbon steel were demonstrated. The experimental results provided comprehensive information on the appropriate concentration range of DEA aqueous solutions under which low corrosion of carbon steel can be achieved.

1. Introduction

More attention has been paid to the affordable yet technically feasible separation technologies for reducing CO₂ emission. So far, four types of absorption approaches including absorption [1-3], adsorption [4,5], membrane [6,7] and hydration [8] were widely used for CO₂ capture, the chemical absorbents commonly include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and so on, among which DEA has been extensively used in industry and take the advantages of high reaction rate, low cost and thermal stability[9].

Expect the economic and practical considerations of DEA, in the practical application of power plants, there is not only carbon dioxide, but other gases such as SO₂ and NOₓ, dissolved in the absorption liquid, which could also cause the equipment corrosion. According to the existing literatures, the loss caused by corrosion is the most rigorous issue of CO₂ capture pilot. The serious influence of corrosion, such as unplanned downtime, production loss, reduced equipment life, and even injury or death, might result in great damage [10]. Therefore, whether corrosion can be well controlled, directly affects the production capacity and the production efficiency of power plant [11].

On the basis of previous studies, types of alcohol amines influence not only the effect of the absorption amount of CO₂, but also the absorption rate. Among the commonly used amines (MEA, DEA, MDEA, AMP etc.), the best absorption and the highest corrosion rate are respectively MEA (0.23 mol CO₂/mol amine) and AMP (-800mV) [12,13]. With the increase of temperature, the corrosion rate and corrosion density have an obvious upward trend. Besides temperature, the CO₂ loading also has an obvious effect on carbon steel corrosion [12].

So far, many studies are available concerning the influences of temperature and CO₂ loading on carbon steel corrosion. However, more accurate data, variation tendency, comparison of the effects of various factors. In this study, we mainly investigate the influence of various factors on the absorption and corrosion of DEA to obtain the most suitable conditions for industrial production. Moreover, the effect of pH value on corrosion was also investigated, to aid in the identification of alkaline corrosion.

2. Experiment

2.1 Materials
The corrosion test specimen is No. 20 carbon steel. Chemical composition of standard JB/T 6057-92 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 DEA were prepared by adding deionized water (Electrical resistivity >15 MΩ·cm at 298 K) obtained from the Heal Force ROE (Reverse Osmosis Electro deionization)-100 apparatus.

| Chemical name | CAS   | Purity (mole fraction, as stated by the supplier) | source                      |
|---------------|-------|-------------------------------------------------|-----------------------------|
| DEA           | 141-43-5 | \(x \geq 0.99\)                                   | Kermel Chemical Reagent     |
| water         | 7732-18-5 | Electrical resistivity > 15 MΩ·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. CO₂ is imported by the mass flow controller(MFC) into the sealed round-bottomed flask filled with absorption solution. A portion of CO₂ is absorbed in the flask and the unabsorbed gas exported from the flask and move on into the CO₂ analyzer and mass flowmeter(MFM). The remaining CO₂ in the airflow will be detected the amount of absorbed gas in order to determine CO₂ 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 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[3]). This set of data can confirm the reliability of our experiment.

3.2 Corrosion behavior of carbon steel in carbonated DEA aqueous solutions
Figure 1 shows the influence of CO₂ loadings. Under the given temperature, the corrosion voltage is relatively stable, while with the CO₂ loadings increase, the corrosion current increase significantly. At the same temperature, higher CO₂ loading means more CO₂ dissolved in the absorption solution, which bring a decrease in the pH value of the solution, finally cause the aggravation of corrosion.

Figure 2 shows the influence of temperature. Under the given loading, the corrosion voltage is stable as the same, with the temperature increase, the corrosion current increase obviously. Due to the increase in temperature, the enthalpy required for the reaction is reduced. At the same time, the rate of reaction is accelerated by the increase of temperature, accelerate the corrosion.

| $W_{DEA}$ | $\alpha$ | 303.2K | 313.2K | 323.2K |
|----------|----------|--------|--------|--------|
| 0.3000   | 0.1      | 2.452  | 4.433  | 7.743  |
|          | 0.2      | 4.266  | 7.170  | 11.58  |
|          | 0.3      | 6.351  | 10.89  | 19.07  |
|          | 0.4      | 8.685  | 15.29  | 27.02  |
|          | 0.1      | 2.512  | 5.013  | 8.409  |
|          | 0.2      | 4.331  | 7.648  | 12.84  |
| 0.4000   | 0.3      | 6.535  | 11.09  | 21.68  |
|          | 0.4      | 10.58  | 19.03  | 40.46  |

Table 1 shows the result of the experiments in different DEA concentration, CO₂ loadings and temperature. From the Table, it can be confirm of the conclusions drawn in the figure above. Under low temperature conditions used in industry, as the temperature increases, the rate of corrosion increases. As for CO₂ loadings, the increase in CO₂ loadings usually results in accelerated corrosion rates. While other conditions remain unchanged, increase of absorption concentration makes the promotion to the corrosion, and this kind of influence could be more obvious with the increase of the CO₂ loadings.

4. Conclusion
Corrosion of carbon steel in the carbonated DEA aqueous solutions was investigated. The effects of the mass concentrations of DEA, solution temperature and CO₂ loading on the corrosion rate of carbon steel were demonstrated. Our results showed that:

(1) An increase of amine concentration means an advancement of absorption capacity, which
eventually causes the result that more CO\textsubscript{2} dissolved in the solution and proceed to more serious corrosion.

(2) The increase of the temperature of the reaction environment in certain extent could play a promoting role in the reaction as higher temperature reduces the reaction enthalpy.

(3) The increase of CO\textsubscript{2} loadings means that more carbon dioxide dissolved in water, which means a bit of more CO\textsubscript{2} has taken part in the corrosion reaction.

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