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Research on Corrosion Mechanisms of Carbon Steel in Natural Gas Field Methanol Recovery Towers

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Abstract

Regarding the problems caused by the strong corrosiveness of alcohol-containing wastewater in natural gas exploitation and its direct discharge or reinjection, this paper studies the corrosion behavior of carbon steel materials in the methanol distillation column, and comparatively analyzes the corrosion resistance of Q345R and 20# carbon steels in the alcohol-containing wastewater environment. Through water quality analysis, corrosion coupon experiments, SEM and EDS characterization, it is found that the produced water is weakly acidic and contains high concentrations of Cl-, SO42-and high salinity, with a serious risk trend of electrochemical corrosion coupled with scaling. The results show that the corrosion rates of both carbon steels exceed 0.25 mm/a, which belong to severe corrosion. Affected by high temperature and high chloride ions, Q345R is more seriously corroded, while 20# shows more excellent corrosion resistance.

Keywords

Alcohol-containing wastewater; Methanol distillation column; Corrosion mechanism; Q345R steel; 20# steel.

1. Introduction

In natural gas production, methanol is injected into gas gathering pipelines to suppress hydrate formation and ensure safe transportation [1]. However, the methanol mixes with formation water, generating alcohol-containing wastewater. Direct discharge of this effluent leads to substantial methanol loss and serious environmental pollution. If reinjected without treatment, it may cause corrosion and reservoir impairment. Therefore, the recovery and recycling of alcohol-containing wastewater are of great importance in petroleum and gas extraction.

The methanol distillation column, as the core unit of the methanol recovery system, employs distillation technology to separate and purify methanol from the wastewater [2]. Since the wastewater contains multiple acidic components and is highly corrosive, the materials selected for the distillation column must exhibit high corrosion resistance to such environments [3].

This paper investigates the corrosion behavior of common carbon steels used in methanol distillation columns, evaluating the corrosion resistance of different types of carbon steels. The findings aim to provide a theoretical basis for the material selection of tray internals, thereby supporting the efficient and sustainable recycling and reuse of alcohol-containing wastewater.

2. Experimental Materials

The chemical compositions of the Q345R and 20# steel carbon specimens required for the experiment are shown in Table 1.

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Table 1 Chemical composition of carbon steel (wt%)

carbon steel	Q345R	20#钢
C	0.168	0.2
Si	0.289	0.21
Mn	1.397	0.41
P	0.006	0.014
S	0.003	0.005
Mo	0.025	-
Cr	0.045	0.06
Cu	0.011	0.165
Ni	0.035	0.05
Fe	Residual Amount	Residual Amount

3. Experimental Methods

3.1. Water Quality Analysis of Gas Field Produced Water

Water quality analysis of the produced water was conducted in accordance with SY/T 5523-2016 "Analysis Method for Oilfield Water" and SY/T 5329-2022 "Water Quality Index and Analysis Methods for Injection Water in Clastic Rock Reservoirs".

3.2. Corrosion Rate Calculation Method

The weight-loss corrosion method is a commonly used technique for evaluating the corrosion performance of materials, which involves measuring the mass loss of a material after exposure to a specific corrosive environment.

The assessment of corrosion extent in metallic materials was performed based on SY/T 0026-2024 "Determination of Corrosion Rate of Metallic Materials in Oilfield Media", as summarized in Table 2.

Table 2 SY/T 0026-2024 Corrosivity Classification Criteria for Oil and Gas Field Media

Grade	Average Corrosion Rate (mm/a)
Low Corrosion	<0.025
Moderate Corrosion	0.025~0.12
High Corrosion	0.13~0.25
Severe Corrosion	>0.25

3.3. Analysis Method for Corrosion Coupon Morphology

SEM and EDS analyses were performed on the surface of the corroded coupons to investigate the corrosion mechanisms through imaging and elemental composition characterization.

4. Results and Discussion

4.1. Water Quality Analysis

The composition of the water samples was analyzed to investigate their characteristics and provide a basis for subsequent research. The analysis results are presented in Table 3.

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Table 3 Analysis Results of Water Quality Composition of Produced Water

Testing Indicator	Raw Water 1	Raw Water 2
pH	4.75	6.78
SS (mg/L)	214.21	373.4
Cl^- (mg/L)	15030.96	21587.32
HCO_3^- (mg/L)	53.68	340.20
SO_4^{2-} (mg/L)	5.35	93.98
Total Iron (mg/L)	51.80	120.26
Ca^{2+} (mg/L)	3807.30	7877.09
Mg^{2+} (mg/L)	241.26	378.65
Ba^{2+} (mg/L)	439.70	-
Sr^{2+} (mg/L)	351.45	-
ΣNa^++K^+ (mg/L)	4614.83	4420.03
Total Mineralization (mg/L)	24596.33	34716.00
Oil (mg/L)	542.28	2020.74
Alcohol Content (%)	18.35	30.69
Water Type	$CaCl_2$	$CaCl_2$

The produced water exhibits overall acidity and high corrosivity. The excessively high concentration of Cl^- induces corrosion, while the strong electrolyte environment formed by Cl^-, SO_4^{2-}, and high salinity accelerates electrochemical corrosion. Oil and total iron content promote microbial corrosion and oil-deposit corrosion. Additionally, the high salinity and variable content of scaling cations indicate a high tendency for scaling, potentially leading to carbonate and strontium-barium sulfate deposition. Overall, the methanol recovery tower is in a state of extremely high corrosion-scaling coupling risk.

4.2. Corrosion Rate Monitoring in the Distillation Tower

Coupons made of 20# and Q345R steel were selected as test specimens. These coupons were secured with tooling at the bend of the 10th and 38th trays inside the distillation tower. After operating for a period, the coupons were retrieved for corrosion inspection, as shown in Figure 1. The corroded coupons are presented in Figure 2, and the pickled coupons in Figure 3. The corrosion test results are shown in Figure 4.

As shown in Figure 4, the average corrosion rates of both materials exceed 0.25 mm/a, indicating a state of severe corrosion. For 20# steel, the corrosion rate increases with rising temperature. In contrast, for Q345R steel, the corrosion rate increases as temperature decreases. In summary, the bottom section of the tower experiences stronger corrosion, while scaling is more severe at the top section. Among the two materials, Q345R steel exhibits more severe corrosion compared to 20# steel.

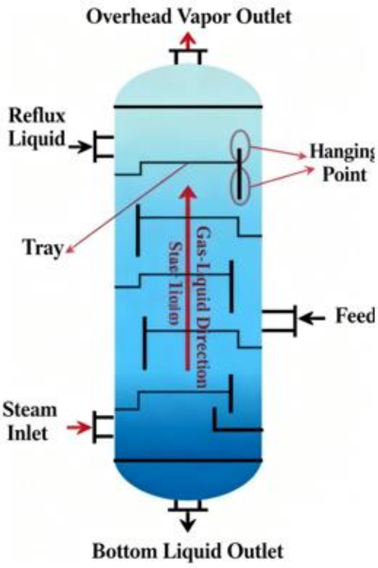

Figure 1 Structure of the Plate Tower and Hanging Location

(a) Tray 10 (b) Tray38

Figure 2 Appearance of Corroded Coupons

(a) Tray 10 (b) Tray 38

Figure 3 Appearance of Pickled Coupons

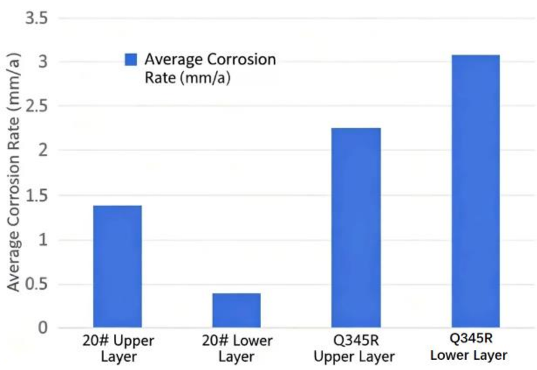

Figure 4 Corrosion Rate Measurement Results in the Distillation Tower

4.3. SEM and EDS Analysis of Surface Morphology

SEM and EDS analyses were conducted on the surface of the corroded coupons to examine the morphological and compositional characteristics. The results are presented in the following figures and tables.

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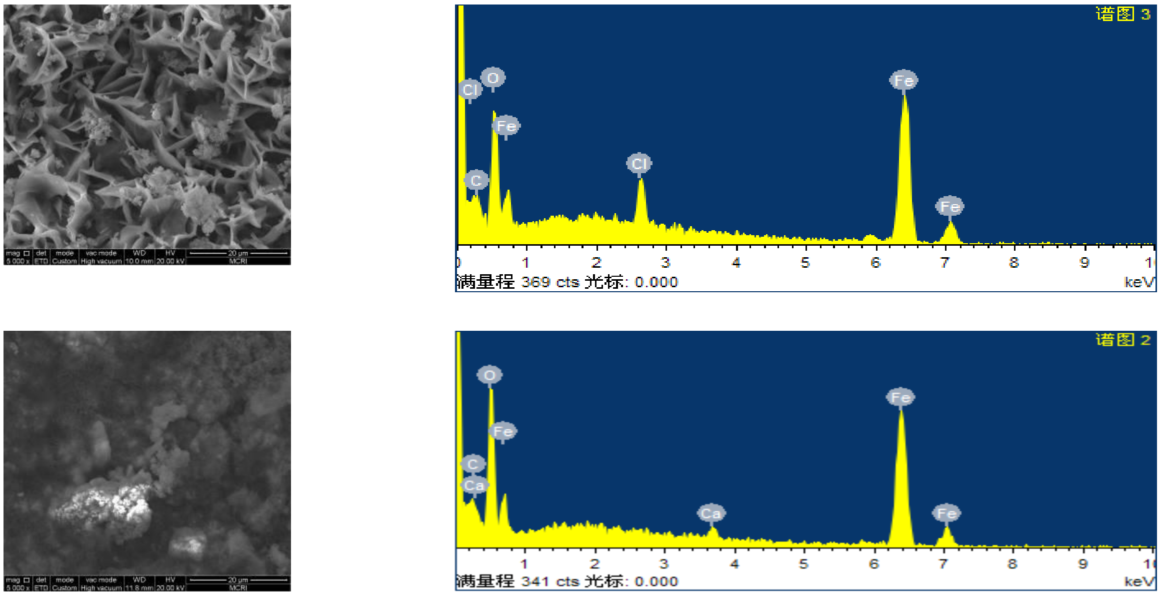

Figure5 SEM images and EDS analysis diagrams of Q345R steel before pickling from the upper (top) and lower (bottom) layers of the distillation column.

Table 4 EDS Analysis Results of Q345R Steel Before and After Pickling in Upper and Lower Layers

Element (wt%)	Upper Layer (wt%)	Lower Layer (wt%)
C K	6.78	5.73
O K	19.82	23.95
Cl K	3.56	-
Ca K	-	0.98
Fe K	69.84	69.34
Total	100	100

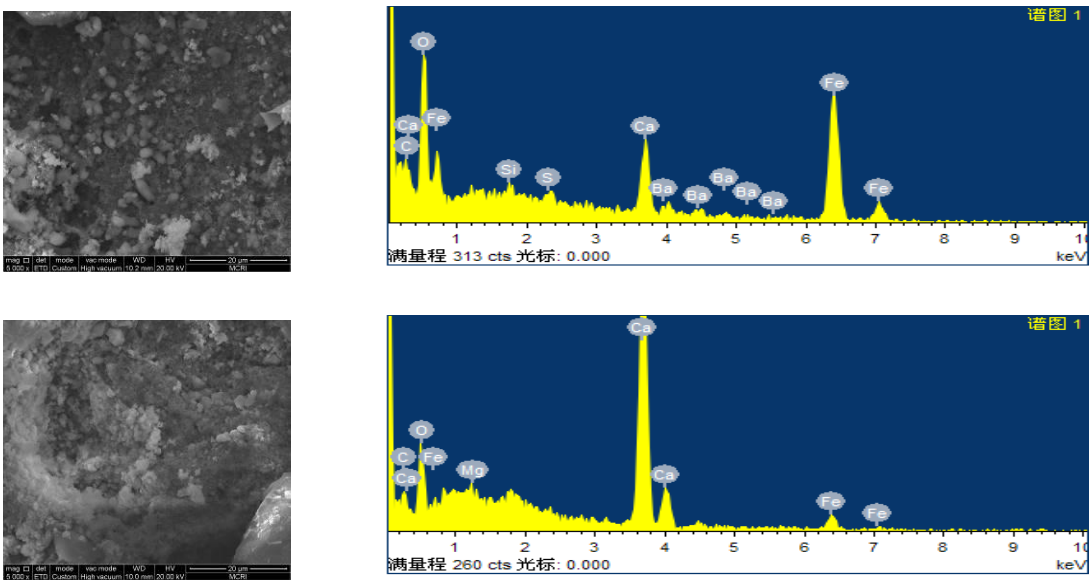

Figure7 SEM images and EDS analysis diagrams of 20# steel before pickling from the upper (top) and lower (bottom) layers of the distillation column.

Table 5 EDS Analysis Results of 20# Steel Before and After Pickling in Upper and Lower Layers

Element (wt%)	Upper Layer (wt%)	Lower Layer (wt%)
C K	7.62	4.45
O K	47.83	27.27
Mg K	0.26	-
Ca K	36.41	5.97
Fe K	7.88	57.86
Ba L	-	2.28
S K	-	0.80
Si K	-	1.37
Total	100	100

Observations from SEM images reveal severe corrosion on the steel coupons, characterized by uneven surfaces with porous crystalline structures exhibiting spherical and flocculent overlapping morphologies. In some cases, large corrosion products have detached, and the surface is covered by a layer of flocculent film.

EDS analysis indicates that the coupon surfaces are extensively covered by deposits, with consistent elemental composition dominated by C, O, Ca, and Fe. For Q345R steel, the iron content in the deposits is approximately 70% in both upper and lower layers, indicating severe corrosion. In contrast, for 20# steel, the iron content in the upper layer deposits is only 7.88%, while it reaches 57.86% in the lower layer. Nevertheless, the corrosion degree of 20# steel remains lower than that of Q345R under the same conditions.

In summary, the surface composition of the coupons is similar, primarily consisting of C, O, Ca, and Fe, largely due to the coverage by deposits. Corrosion is more severe at the bottom of the tower, while scaling is more prominent at the top. Overall, 20# steel exhibits comparatively lighter corrosion, whereas Q345R steel suffers more significant corrosion damage.

4.4. Analysis of Corrosion Mechanisms

The corrosion mechanisms of 20# and Q345R steels in the methanol recovery tower can be attributed to the following factors:

(1) The produced water is acidic, with high Cl^- content and high salinity, forming a strong electrolyte environment with severe corrosive tendency. The complex composition of the produced water, including high concentrations of Cl^-, SO_4^{2-}, and scaling ions (Ca^{2+}, Mg^{2+}, etc.), leads to a corrosion-scaling coupling risk, exacerbating material degradation [4].

(2) The iron and carbon within both materials form numerous microscopic galvanic cells in the electrolyte solution. Under acidic conditions, the cathode undergoes hydrogen evolution reaction, resulting in continuous corrosion of iron[5]. Additionally, when the fluid flow is uneven or gas-liquid interfaces exist inside the tower, oxygen concentration differences between regions create oxygen concentration cells, which also contribute to material corrosion [6].

(3) High Cl^- concentration damages passive films, inhibits the formation of protective oxide layers, and initiates pitting and uniform corrosion. The temperature gradient and fluid dynamics within the distillation tower accelerate corrosion kinetics and promote under-deposit corrosion [7].

5. Conclusion

(1) The produced water exhibits overall acidity and high corrosivity. Excessively high Cl^- content induces corrosion, while the strong electrolyte environment formed by Cl^-, SO_4^{2-}, and high salinity accelerates electrochemical corrosion. Additionally, high salinity and variable scaling cation concentrations indicate a strong tendency for scaling, leading to the formation of

carbonate and strontium-barium sulfate deposits. Overall, the methanol recovery tower operates under extremely high corrosion-scaling coupling risks.

(2) The average corrosion rates of both materials exceed 0.25 mm/a, indicating severe corrosion. Among them, Q345R steel suffers more significant corrosion damage compared to 20# steel.

(3) The surface composition of the coupons is similar, primarily consisting of C, O, Ca, and Fe, largely due to deposit coverage. SEM images reveal porous crystalline structures and flocculent corrosion products on both steels, with localized exfoliation, indicating that corrosion is accompanied by scaling and deposition. EDS analysis confirms that corrosion products are dominated by Fe, O, and C. Scaling at the upper trays is more influenced by Ca and Ba, while the lower trays are dominated by iron oxidation and corrosion.

(4) High temperature and high Cl^- concentration are the primary factors driving coupon corrosion. The temperature gradient and fluid dynamics within the distillation tower intensify corrosion kinetics and promote under-deposit corrosion. The high-Cl^- environment also inhibits the formation of protective oxide films, further contributing to material degradation.

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