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Influence of stainless steel Internals on Corrosion of tower wall materials

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Abstract. In view of the galvanic corrosion of the tower wall material in the tower of a refinery atmospheric vacuum distillation unit, the electrochemical behavior of Q345R steel, stainless steel (201, 304 cold-rolled plate, 304 hot rolled plate and 316L) in 3.5%NaCl solution was studied by electrochemical method. The results show that the corrosion potential of Q345R is much lower than that of stainless steel, and the corrosion rate of Q345R is higher than that of stainless steel. As the anode is etched as the anode corrosion, the anode polarizability of stainless steel shows strong polarization ability, which is anodic polarization control, and Q345R is anode Active polarization control; Q345R / 201 galvanic pair may be the most serious corrosion, and Q345R/316L galvanic couple may be relatively slight. Therefore, in the actual production of tower equipment, material design or tower to upgrade the replacement, it are recommended to use the preferred anode and cathode potential difference with the use of materials.

1. Introduction

Tower equipment was the key equipment in refinery production. Direct contact of various corrosive media in crude oil during operation was one of the most serious corrosion in refineries [1-2].

The corrosion of crude oil medium to refining and refining equipment greatly increased with the trend of crude oil deterioration becoming more and more obvious. In order to protect towers, the method of upgrading inner material is usually used. However, there is a difference in the self-corrosion potential between the carbon steel or alloy steel used as the tower material and the upgraded stainless steel internal material, and the polarization behavior of the material varies. Under the action of environment, medium and other factors, the upgrade of internal material brings the effect of galvanic corrosion on tower wall material. At the same time, other corrosion behavior of galvanic corrosion and corrosion induced by various other forms of synergy, causes pitting corrosion, perforation, greatly reduces the service life of materials, and seriously affect the safety of tower equipment. Therefore, it is important to study the influence of tower internals on galvanic corrosion of tower wall materials for the prevention and protection of tower wall corrosion and the safe operation of tower equipment.

At present, although there are many researches on galvanic corrosion of metal [3-6], however, there are few studies on galvanic corrosion behavior of Internals and wall materials in corrosive media. In this paper, four kinds of stainless steel (201, 304 cold-rolled plates, hot rolled plates, 304 316L) for Q345R tower internals, wall materials were presented. The galvanic corrosion behavior of Q345R steel/stainless steel in 3.5% NaCl solution investigated by means of open circuit potential, potentiodynamic polarization, potential and current measurements. It can provide the basis for the optimization of material selection and the formulation of anti-corrosion scheme in refining and chemical production equipment.

2. Experimental

2.1. Test preparation
The experimental material was Q345R and stainless steel (201, 304 cold rolled plate, 304 hot-rolled plate, 316L), and its chemical composition was shown in Table 1.

The Q345R and stainless steel sample were respectively cut into a cylinder with a base area of $1cm^2$. The wire welding in a cylindrical bottom surface, connecting the specimen and the conductor, with epoxy resin coating, surface by grinding to $800^{\#}$ sandpaper, wash with distilled water, anhydrous ethanol and acetone degreasing, drying dryer into standby. In order to avoid the influence of the oxide film formed in the air on galvanic corrosion [7], the sealed patterns were subjected to electrochemical testing within 1 hour.

The experimental medium was 3.5%NaCl solution with a pH value of 7 and 40℃. Took the NaCl of 35g and distilled water of 965g, mixed and stirred, and took the 500ml solution.

Table 1. Chemical composition of various materials (Mass fraction, %)

Material / Element	304	201	316L	Q345R
C	≤0.07	≤0.15	≤0.03	≤0.20
Si	≤1.00	≤1.00	≤1.00	0.20~0.55
Mn	≤2.00	5.50~7.50	≤2.00	1.20~1.60
P	≤0.035	≤0.060	≤0.035	≤0.035
S	≤0.030	≤0.030	≤0.030	≤0.030
Ni	8.25~10.50	3.50~5.50	16.0~18.0	—
Mo	—	—	2.0~3.0	—
Cr	18.0~20.0	16.0~18.0	12.0~15.0	—

2.2. Test method
In the experiment, it was using the CS300 electrochemical workstation that measured the open circuit potential and potentiodynamic polarization.

The three-electrode system: Q345R and stainless steel as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, platinum net as auxiliary electrode. The working area of $1cm^2$ working electrodes and Q345R stainless steel samples were placed in the test solution respectively. The change of open circuit potential was monitored during the experiment. The polarization curve measured using potentiodynamic polarization. The polarization range was set at -100mV~+180mV (relative open circuit potential), and the scanning rate was 0.4mV/s.

Galvanic corrosion also measured using the CS300 electrochemical workstation. The prepared sample connected by wire, sealed with epoxy resin, and reserved the working area. The area ratio of Q345R/stainless steel pair was 1:1. The influence of different materials on galvanic were studied. In the experiment, the working surface completely exposed to 500mL 3.5%NaCl solution, and the relationship between the electric dipole mixing potential and the galvanic current density measured continuously.

3. Results and analysis

3.1. Open circuit potential and polarization curves

The Q345R and stainless steel were continuously monitored with opening circuit potential in 3.5% NaCl solution. As shown in Fig. 1. Table 1 shows the measured open circuit potential and the corresponding potential difference *ΔE*.

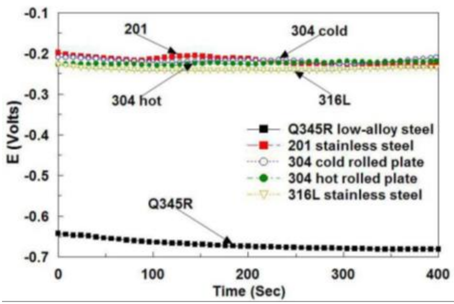

Figure 1. Open circuit potential

Table 2. The open circuit potential and corresponding potential

Open circuit potential *E*(mV)			Δ*E*(mV)
Stainless steel material		Q345R	
201 stainless steel	-204.8	-648.1	443.3
304 cold rolled plate	-213.5		434.6
304 hot rolled plate	-228.1		420.0
316L stainless steel	-233.4		414.7

Figure 1 shows the four kinds of stainless steel open circuit potential changes similar. The whole changes are slightly to the potential positive deviation, which indicts the stainless steel is stable and has certain passivation ability in this medium. However, the opening circuit potential change of Q345R is opposite to opening circuit potential of stainless steel. The potential begins to offset to the negative substantially, which indicates Q345R is more active in the medium and is in the activated state. meanwhile, the open circuit potential of Q345R is much lower than the four kinds of stainless steel, and the potential differenceΔE are more than 400mV, much greater than the threshold of galvanic corrosion potential difference 50mV [8], as shown in Table 2. Therefore, galvanic corrosion is observed in Q345R and four stainless steels, and there is a large difference in driving potential. The greater the potential difference between the two electrode materials, the greater the tendency for galvanic corrosion [9]. It can be predicted that the corrosion tendency of Q345R and four kinds of stainless steel pairs forms is Q345R/201>Q345R/304 cold rolled plate >Q345R/304 hot rolled plate >Q345R/316L.

The Q345R and stainless steel samples were subjected by potentiodynamic sweep, and the polarization curves were obtained as shown in Fig. 2. Table 3 is the fitted Tafel parameter.

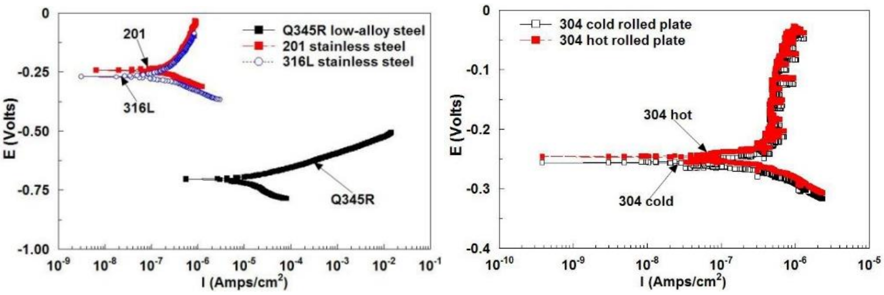

Figure 2. Polarization curves

Table 3. Tafel parameters of Q345R and four kinds of stainless steels

material	E_{corr} mV	i_{corr} μA•cm^{-2}	b_a mV	b_c mV
304 cold rolled plate	-256.3	0.14263	204.74	58.522
304 hot rolled plate	-246.3	0.14765	205.13	58.639
201 stainless steel	-242.9	0.83307	413.26	151.972
316L stainless steel	-270.4	0.34161	371.62	83.541
Q345R	-704.6	47.23681	47.39	64.899

As shown in Fig. 2, 201stainless steel has the largest anode polarizability, followed by 316L stainless steel. The polarization tendency of 304 cold and hot rolled plates is approximately the same, and the polarize-ability is the smallest. The anodic polarize-ability rate shows the different polarization ability of stainless steel, which makes the stainless steel anode polarization control. The anode polarization rate of Q345R is less than the cathodic polarization rate, and it can cause significant changes of potential in the smaller anodic polarization current, and controlled by anodic activation polarization. This is the same as the value of the Tafel slope in table 3.

It is found from Table 2 and Table 3 that the corrosion potentials of the four stainless steels are lower than the open circuit potential. The reason is that the measurement of potential in Table 2 is based on the open circuit potential, and a good passive film was produced on the surface of stainless steel [10], and the corrosion potential is shifted to the positive direction. The potential was controlled by the reduction reaction in the lower section. Meanwhile, the passivation film was removed, resulting in a decrease in the corrosion potential.

3.2. Galvanic corrosion measurement

The galvanic corrosion measurements show that the galvanic potential and galvanic current of the couple w changed with the change of the cathode material after the junction, as shown in Fig. 3 and Fig. 4. Table 4 is the parameter of the galvanic measurement.

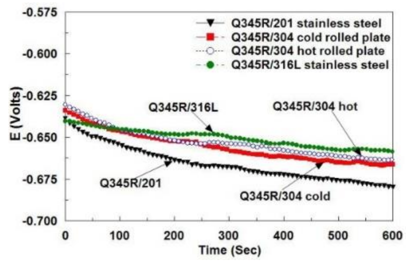

Figure 3. Galvanic mixing potential of Q345R/stainless steel couple

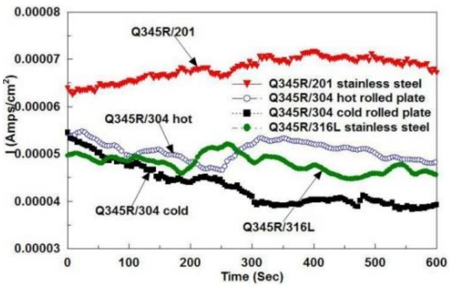

Figure 4. Galvanic current density of Q345R/ stainless steel couple

Table 4. Galvanic measurement parameters of Q345R/ stainless steel couple

Galvanic couple	cathode material	Coupled before the potential E(mV)			Mixed potential E_g(mV)	Galvanic current density i_g (μA•cm-2)
		Anode E_a (mV)	Cathode E_c (mV)	ΔE (mV)		
Q345R/ stainless steel	201	-704.6	-242.9	461.7	-658.2	68.1
	304cold rolled plate	-704.6	-256.3	448.3	-651.7	49.4
	304 hot rolled plate	-704.6	-246.3	458.3	-651.4	51.6
	316L	-704.6	-270.4	434.2	-646.3	48.0

In Fig. 3, the trend of the mixed potential of the Q345R/stainless steel galvanic couple is approximately the same, and the whole offset to the negative direction, and the amplitude of the offset decreases with the extension of time. The Q345R/201 galvanic couple has the largest offset and the Q345R/316L offset is the smallest. It was obvious that the galvanic current of Q345R/201 was much larger than that of other three couples, and the changes were different as well, as shown in Fig. 4. The galvanic current of Q345R/201 is shifted the forward direction, and the amplitude of the offset decreases with the time, and the peak value is about 400s, and the backward direction is slightly shifted and the change process is smooth. Meanwhile, galvanic current of the other galvanic couples are shifted the negative deviation, which fluctuates repeatedly before the 350s, and then gradually stabilized.

Table 4 shows the parameters of the galvanic mixed potential of the order from high to low: Q345R/316L>Q345R/304 cold rolled plate >Q345R/304 hot rolled plate >Q345R/201; the galvanic current density increased in the order: Q345R/316L<Q345R/304 <Q345R/304 hot rolled plate <Q345R/201 cold rolled plate. It can predict that the Q345R/201 galvanic couple is the most serious corrosion, and the Q345R/316L galvanic couple is relatively mild. Therefore, in the tower equipment with the tower wall material as Q345R, the inner material avoid using 201 stainless steel, which can reduce the hazards to the tower wall material galvanic corrosion, save the cost and improve the efficiency.

4. Conclusion

(1) The corrosion potential of stainless steel corrosion potential is higher than Q345R, which can make the galvanic corrosion. There is a large driving potential difference, and Q345R as anode, corrosion intensified, stainless steel is used to cathode protection, corrosion slowed down. Galvanic corrosion tendency: Q345R/201>Q345R/304 cold rolled plate >Q345R/316L>Q345R/304 hot rolled plate;

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(2) The anode of stainless steel shows strong polarization ability, namely strong passivation ability: 201 >316L>304 hot rolled plate >304 cold rolled plate. Under the influence of the passive film, the corrosion potential measured at the open circuit potential is generally greater than that measured with potentiodynamic polarization.

(3) Galvanic corrosion measurement shows that Q345R/201 galvanic couple may be the most serious corrosion, and Q345R/316L galvanic corrosion may be relatively slight, indicating that the selection and collocation of Q345R/316L materials are relatively reasonable and should be given priority.

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