The influence of flow velocity on electrochemical reaction of metal surface

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Abstract. In order to find out the effect of fluid flow velocity on electrochemical reaction, the electrochemical parameters of super 13Cr stainless steel in 3.5% NaCl aqueous solution were measured by a jet flow system at different flow velocities. The electrochemical characters such as open-circuit potential and polarization curve were monitored online using a three-electrode electrochemical system. The results show that the increase of wall shear stress caused by the high flow velocity leads to the rupture of passive films and the exposure of fresh metal in the corrosive media, which causes the increase of corrosion rate. Meanwhile, the corrosion rate shows a significant growth when the flow velocity is less than 0~10.0 m/s. But it gradually decreases after reaching a maximum value.

1. Introduction
Fluid-induced corrosion is defined as an effect of the metal surface damage caused by the electrochemical reaction between metal surface and corrosive media. It is usually influenced by the change in the mass transfer rate of reactants, surface roughness and temperature.

The effect of flow pattern on corrosion character has been investigated by Yabuki[1], Salama[2], Neville [3,4] from many research aspects. The main topic of their study was to find out the change in mass transfer in near wall boundary layer. A new model was explored to predict the detail corrosion rate based on the local flow pattern. At high flow velocity, Yong, et al.[5] pointed out that the increase of wall shear stress caused by the high flow velocity led to oxygen concentration diffusion layer thinning. Beside this, the oxygen quickly transferred to the metal surface and caused the flow corrosion rate to increase.

In this paper, the fluid induced corrosion character of super 13Cr stainless steel is studied by changing the flow velocity, which is of great theoretical significance and useful value for preventing or slowing the occurrence of corrosion failure.

2. Experimental

2.1 Experimental system
The electrochemical reaction of metal surface was studied in a self-made jet system. An image of the experimental system was shown in Fig.1. The experimental system included liquid storage tank, pump,
magnetic flow-meter (8712HR, Rosemount Co, Ltd, America) and electrochemical workstation (CS310, Corrtest, Co, Ltd.).

The three-electrode system consists of a saturated calomel electrode, a platinum electrode and a working electrode that was mounted on the bench. Before testing, samples were weighed using the electronic balance produced by Shanghai Liang Ping Instruments Co., Ltd. The precision of electronic balance is 0.1 mg.

2.2 Experimental conditions

2.2.1 Solution: The concentration of Cl- content was 21239 mg/L, and the solutions used in the preparation were prepared by pure chemical reagent and distilled water.

2.2.2 Selection of materials and preparation of samples: Super 13Cr stainless steel was selected as the research material and the composition was showed in Table 1. The material was processed into rectangular blocks of length × width × height = 12.2 × 6.4 × 19 (in mm). The copper wire was connected and then coated with epoxy resin to seal the other parts, leaving the working surface so that the erosion surface of the area of 0.78 cm² was exposed to the solution. The other surfaces were well packaged and insulated from the solution. Sealing operation should avoid the occurrence of gaps; otherwise it would seriously interfere with the experimental results.

| Steel  | C    | Si  | Mn  | P   | S   | Cr  | Mo  | Ni  | Cu  |
|--------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Super 13Cr | 0.022 | 0.22 | 0.45 | 0.015 | 0.001 | 12.79 | 0.92 | 4.34 | 0.51 |

2.2.3 Test electrode: The test electrode was super 13Cr stainless steel sample, and the material was processed into rectangular blocks. The saturated calomel reference electrode (SCE) which placed in the test chamber was connected to the erosion system by an electrolyte bridge. A long platinum wire was used as the counter electrode (CE).

2.2.4 Fluid flow speed: The liquid flow velocity of this experiment was 0 m/s, 5.6 m/s, 9.6 m/s, 10.0 m/s, 14.8 m/s, 18.1 m/s and 21.4 m/s.
2.3 Experimental procedure

2.3.1 Testing procedure: Firstly, the test material was installed to the sample holder and injection angle was adjusted to 45°. Secondly, started the pump, showing the speed was 2.93m/s, run a few minutes before the temperature of the fluid was measured at room temperature. Thirdly, electrochemical tests were performed. The open-circuit potential monitoring was carried out before the stable value was reached, then the action potential polarization scanning was performed. And the sweep speed was set to 1 mV/s when the polarization curve was measured. The voltage range was set according to the material. The minimum range was -0.8 V ~ +0.8 V relative to the open circuit potential. Finally, the experimental data are collected after the test was completed.

3. Results and discussion

According to the experimental design, the corrosion rate of 13Cr stainless steel at different flow velocities was measured when the injection angle was 45°.

3.1 Electrochemical Polarization Analysis of Super 13Cr stainless steel

The effect of flow velocity on the corrosion rate is obtained by the linear polarization method, and the results are shown in Table 2 and Fig. 2.

| Flow velocity (m/s) | I (A×10⁻⁵) | E (V) | CR (mm/a) |
|---------------------|------------|-------|-----------|
| 0                   | 2.1089     | -0.47529 | 0.2481    |
| 5.6                 | 17.391     | -0.07454 | 1.7662    |
| 9.6                 | 16.26      | -0.20804 | 1.9126    |
| 10                  | 18.895     | 0.06974  | 2.2224    |
| 14.8                | 13.895     | 0.23325  | 1.6343    |
| 18.1                | 13.627     | 0.29482  | 1.6014    |
| 21.4                | 13.351     | 0.32427  | 1.5703    |

Fig. 2. Effect of fluid flow velocity on corrosion rate of super 13Cr stainless steel

The influence of the flow velocity in the range of 0~21.4 m/s on the corrosion rate was considered. It is observed from Fig.2 that the flow velocity has a great influence on the corrosion rate of super 13Cr stainless steel, and the corrosion rate tends to rise first and then decrease with the increase of flow velocity. It is observed from Fig.2 that the corrosion rate gradually increases with the increase of flow velocity from 0~10.0 m/s. Then it gradually decreases after a peak, and the corrosion rate reaches the peak at 10.0 m/s.
Similar conclusions are confirmed by Zhang et al. [6] in previous studies. It was reported that the corrosion rate depended on the steel grade and the critical flow velocity of the corrosion product, higher than this flow velocity, and the corrosion rate was no longer changing. It was believed that it was related to the formation of corrosion products FeCO3 and Fe3O4. High flow velocity affected the dissolution kinetics of Fe and the formation of FeCO3, forming a thin but more protective film, so the flow velocity was increased but the corrosion rate was reduced. Therefore, flow velocity in the range of 0~10.0 m/s, the increase of wall shear stress caused by the high flow velocity leads to the rupture of passive films and the exposure of fresh metal in the corrosive media, which causes the increase of corrosion rate.

In this experiment, it is observed that the corrosion rate of metal surface does not increase but decrease with the increase of flow velocity from 10.0 m/s~21.4 m/s. So 10.0 m/s should be the critical velocity of super 13Cr stainless steel corrosion.

3.2 Analysis of open-circuit potential
The open-circuit potential is one of the most simple and easy to obtain data for all corrosion criteria, which reflects the tendency of metals to dissolve in solution.

As shown in Fig. 3, as the flow velocity increases, the change of the open-circuit potential goes through a process of falling and then rising. The open-circuit potential is -0.32 V at the flow velocity of 5.6 m/s, and the open-circuit potential is -0.23 V when the flow velocity is increased to 9.6 m/s. It is observed from the Fig. 3 that the open-circuit potential of the super 13Cr stainless steel reaches the minimum at 10.0 m/s. When the flow velocity was increased to 18.1 m/s, it was found that the open-circuit potential changed positively to -0.34 V. The open-circuit potential is greater at 21.4 m/s, indicating that the corrosion tendency of metal surface is lower and corrosion is not easy.

In this experiment, it is observed that the corrosion of metal surface is more serious with the increase of flow velocity, and the corrosion is most serious at 10.0 m/s flow velocity. And the direction of the whole change is in the negative direction.

3.3 Polarization curve analysis
The polarization curve usually shows the relationship between the polarization potential and the polarization current. The polarization degree of the electrode can be seen very clearly from the polarization curve [7].

Fig. 3 Variation curves of open-circuit potential with time at different flow velocities
Fig. 4 Polarization curves of super 13Cr at different flow velocities

As shown in Fig. 4 (a), the trend of passivation is not obvious when the flow velocity is low. It is observed from Fig. 4 that the anodic trend of the metal surface is fully activated with the flow velocity continues to increase to 9.6 m/s. In addition, it is also observed that the current density of metal surface reaches the maximum with the flow velocity reaches 10.0 m/s, leading to the most serious corrosion. As shown in Fig. 4 (b), the anodic polarization curve shows an obvious passivation trend when the flow velocity is 21.4 m/s. It shows that the super 13Cr stainless steel can be passivated again, which leads to the decrease of corrosion rate.

In this experiment, at low flow velocities, due to the influence of hydrodynamic factors, the local rupture of the passive film on metal surface results in the dissolution and penetration corrosion of Cl-steel. When the flow velocity is in 10.0 m/s, due to the influence of hydrodynamic factors, the increase of wall shear stress caused by the high flow velocity leads to oxygen concentration diffusion layer thinning, and oxygen achieve a metal surface more and more, so that the flow corrosion rate increases. The flow velocity is in the 10.0 m/s~21.4 m/s range, and the increase in flow velocity makes the shearing stress continue to increase, and the more oxygen is delivered to the electrode surface. The passivation of metal surface is caused by oxygen participating in anodic passivation reaction. The corrosion process is changed from cathode process control to anode control, which results in the decrease of corrosion rate with the increase of flow velocity. The results show that super 13Cr stainless steel has a certain ability of re-passivation.

4. Conclusion
The conclusions derived from the present study can be summarized as follows:

(1) The corrosion rate of super 13Cr stainless steel is very prominently influenced by the variation of the flow velocity. The corrosion rate gradually increases with the increase of flow velocity from 0~10.0 m/s. Then it gradually decreases after a peak, and the corrosion rate reaches the peak at 10.0 m/s.

(2) The change of speed imposes a significant impact on the open circuit potential. The change tendency of the open-circuit potential shows it decrease first and then increase with the increase of the flow velocity of the fluid. The open-circuit potential of the super 13Cr stainless steel reaches the minimum at 10.0 m/s. And the direction of the whole change is in the negative direction.

(3) The current density of metal surface reaches the maximum with the flow velocity reaches 10.0 m/s, leading to the most serious corrosion. But, the decrease of corrosion rate with the increase of flow velocity from 10.0~21.4 m/s. The results show that super 13Cr stainless steel has a certain ability of re-passivation. The passivation of metal surface is caused by oxygen participating in anodic passivation reaction.
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