Numerical simulation of galvanic corrosion and sacrificial anode protection of U-tube Material of kettle reboiler in N-Methyldiethanolamine solution

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As a common heat exchanger in the field of petroleum industry, the structure of reboiler is extremely complex, in which U-tube bundle is the key part. The N-Methyldiethanolamine medium contains hydrogen sulfide, carbon dioxide and other acidic gases, which is highly corrosive. In addition, due to the contact with a variety of materials, there is the risk of galvanic corrosion. Firstly, the galvanic corrosion behavior of reboiler materials in solution was studied by numerical simulation, and it was found that the corrosion of U-tube bundle was serious. Then, the combined protection design of coating and sacrificial anode is used to protect the reboiler U-tube bundle from corrosion. The numerical simulation results show that the combined protection of coating and sacrificial anode has a good effect. This numerical simulation method also provides an effective idea and method for the corrosion research of super complex structures such as reboiler.

Keywords: Reboiler; Galvanic corrosion; Sacrificial anode cathodic protection; Numerical simulation

1. INTRODUCTION

The natural gas produced by oil and gas wells is usually accompanied by a large amount of natural gas, including CO₂, H₂S and other acidic components [1-3]. It will not only reduce their calorific value, but also lead to serious corrosion of metal equipment in downstream section, resulting in huge economic losses and serious social consequences. Therefore, desulfurization and decarbonization treatment is generally required before further processing natural gas. Ethanolamine process is a mature,
stable and efficient natural gas desulfurization and decarbonization process. N-Methyldiethanolamine (MDEA) is one of the most used solvents for natural gas purification, the solution itself has no corrosive effect on metals. After the regeneration process, although most of H₂S and CO₂ are resolved into acid gas, a small number of acidic components still remained in the water. The media makes that metal tends to corrode [4-5].

Kettle reboiler, a widely used shell and tube heat exchanger in natural gas purification system, is a kind of horizontal heat exchanger with evaporation space in shell side. The shell side usually needs to be equipped with inclined conical shell to connect the big and small end cylinders. The function of kettle reboiler is to heat the semi-lean solution to a certain temperature through tube bundle heat exchange, so that the acid components absorbed in the solution can be desorbed and separated. In recent years, unplanned shutdown of the unit caused by corrosion of heat exchange tube of reboiler at the bottom of regeneration tower occurred many times in a petrochemical company [6]. For one side, MDEA solution containing acid residual acid gas is highly corrosive for metals; for another side, reboiler consists of many metals with different electrode potential in MDEA solution, it undergoes galvanic corrosion, and corrosion rate of metal of lowest electrode potential is accelerated. Both of them makes reboiler galvanic corrosion of multi-metals more serious.

For reboiler galvanic corrosion of multi-metals, experiment study is difficult. For laboratory experiments the single factor control method is usually used, which is not consistent with the complex environment; for the complex couple of reboiler, the geometry is complex and the experiment is impossible. For the field test many factors affect corrosion, time cost and financial cost is very high, making it difficult to carry out. Fortunately, the development of computer technology has brought about the change of traditional experimental technology, which breaks through its limitation, solves the correlation between the corrosion problems of small samples and complex parts in practical engineering, and greatly shortens the research cycle and cost [7-9].

Currently, the numerical simulation method is usually used to calculate small and medium-sized structure. For U-tube kettle reboiler, the galvanic simulation is hard to handle. In this paper, geometric model of the large-scale U-tube kettle reboiler (a kind of horizontal heat exchanger with evaporation space on the shell side) with multi-metals in an oil field is built according to the real object 1:1. Then reboiler complex galvanic corrosion simulation is carried out by finite element method software Comsol Multiphysics. According to simulation results, the reasonable layout of sacrificial anode is determined to protect galvanic corrosion. In other word, results from numerical simulation provide a basis for corrosion prevention of reboiler U-tube bundle.

2. MATHEMATICAL MODELING

2.1 Reboiler structure

The reboiler structure schematic is shown in Figure 1. It can be regarded as a shell and tube exchanger. In tube side, high temperature heat transfer oil with more heat flows along the U-tube region. In pipe box, from the view on the left, it contains a vertical separator plate, and a right half-horizontal
separator plate (Figure 1 A-A section). First, heat transfer oil enters to the inlet in the upper right corner of the pipe box, then it goes to the tubes in the upper right corner. The U-tube bundle is arranged in regular triangle. Going through the U-tube bundle, the oil flows to the upper left pipe box, going to lower left region. Then oil flows into the lower left tubes, and flows out of lower right tubes into pipe box, last it left pipe box. The oil flowing path, orange region in Figure 1(a) is the tube side. MDEA flows in to the shell from lower left MDEA inlet, then part of it evaporates and leaves from the upper steam outlet, and other part flows out from MDEA outlet. MDEA flowing paths, orange region (Figure 1(a)), calls shell side. In shell side, it has four baffle plates (Figure 1(a) B-B section), changing the flow direction of MDEA. The baffle plate is an incomplete circle, and many U-tube bundles are inserted. When MDEA reaches a certain amount, it passes over the overflow plate and flows out from MDEA condensate outlet. The temperature of MDEA increases through the heat transfer of U-tube bundle.

Figure 1. Schematic of U-tube kettle reboiler structure
The reboiler metals don’t corrode in the heat transfer oil, but metal corrosion is serious in shell side MDEA solution. In shell side, baffle plate and U-tube bundle are made of 20# steel. The shell and overflow plates materials are Q245R steel, and tube sheet material is Q345 steel. All of these metals have different corrosion potentials in MDEA solution, there is a risk of galvanic corrosion for the complex galvanic structure. From the numerical simulation result of galvanic corrosion of the reboiler, current density and potential distribution of the whole surface can be calculated. We can directly judge where the corrosion is serious and where the corrosion is light, which is useful to evaluate the corrosion risk and corrosion protection. Cathodic protection is one of the most common corrosion protection methods, and its basic principle is galvanic corrosion. So galvanic corrosion and cathodic protection simulation modeling processes are described together as section 2.2.

### 2.2 The numerical model based on Laplace equation

Not only the electron potential and electrolyte potential can change with time and space, but also the composition of electrolyte can change with time and space. A high precise corrosion and protection model must be able to describe the composition of electrolyte and the potential distribution of metal and electrolyte. The charged ion flux in the electrolyte, the mass conservation of all substances and the condition of electronegativity are taken as the model equations, and the relationship between potential and current density of electrochemical reaction are taken as the boundary conditions of metal surface. The equation (1) describing the transport of charged ions in electrolyte is called Nernst-Planck equation [10-11]. The charged ion flux $N_i$ includes diffusion, migration and convection. In mass conservation, flux changes in different directions are balanced by time accumulation, which is the transient term in the equation described below, where $c_i$ is the concentration of substance $i$.

$$N_i = -D_i \nabla c_i - z_i F u_i c_i \nabla \varphi + c_i V$$

(1)

where $D$ denotes the diffusion coefficient of species $i$, $z$ the charge of an ion $i$, $u$ the mobility, and $V$ the velocity vector that describes the flow of the electrolyte. On the right side of the equation (1), the three terms from left to right represent the fluxes caused by diffusion, electromigration and convection.
respectively. Taking the derivative of both sides of this equation with respect to time, it can be written as [10-11],

$$\frac{\partial c}{\partial t} = - \nabla \cdot N_i = D_i \nabla^2 c_i - z_i F u_i \nabla \cdot (c_i \nabla \phi) + \nabla \cdot (c_i V)$$  \hspace{1cm} (2)

Assuming well mixed, incompressible and electro-neutral electrolyte solution, the governing equation takes the form of Laplace equation for potential and is represented by equation (3) as,

$$\nabla^2 \phi = 0$$  \hspace{1cm} (3)

Equation (3) is solved over the electrolyte domain subject to boundary conditions. It is assumed that dissolution reaction takes place at the anode surface and that hydrogen evolution or oxygen evolution occurs on the cathode surface. Boundary conditions are relationship between current density and electrode potential of materials, which is as shown in equation (4).

$$i_M (\phi) = - \sigma \nabla_n \phi$$  \hspace{1cm} (4)

where $i_M (\phi) = i_a (\phi) - i_c (\phi)$ is net surface current density of material, and $i_a (\phi)$ and $i_c (\phi)$ are surface current density of anode and cathode current density respectively, M represents different materials, $\sigma$ is solution conductivity, $\nabla_n \phi = 0$ indicates that no reactions occur at insulation boundary [12].

2.3 Materials and experiment

The reboiler is mainly composed of shell, U-tube bundle, baffle plate and tube sheet. The reboiler structure and main chemical elements are displayed in Table 1, in accordance with the corresponding China material standards. All samples are processed to 1cm×1cm×1cm, and the treated specimens were embedded in the epoxy resin, exposing 1cm×1cm surface for testing. All specimens were wet ground to a 1000 grit-finish, cleansed with distilled water and dried in a compressed hot air. The test solution is a MDEA solution collected under field condition.

| Table 1. Reboiler structure and main chemical elements of three materials |
|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Reboiler structure          | Material grade | C   | Si  | Mn  | P   | S   | Ni  | Cr  | Cu  | Fe  |
| U-tube bundle, baffle plate | 20#         | 0.21 | 0.32 | 0.5 | 0.03 | 0.031 | 0.28 | 0.14 | 0.2 | Bal. |
| Shell                      | Q245R       | 0.2  | 0.3  | 0.72 | 0.021 | 0.001 | 0.3  | 0.28 | 0.3 | Bal. |
| Tube sheet                 | Q345        | 0.18 | 0.35 | 1.4  | 0.027 | 0.029 | 0.27 | 0.29 | 0.23 | Bal. |
Figure 3. Polarization curves of 20#, Q245R and Q345 in MDEA solution

The polarization tests were performed in a three-electrode cell, using a piece of platinum as counter electrode and a saturated calomel electrode $\text{Hg/Hg}_2\text{Cl}_2$ (SCE, 0.242 V$_{\text{SHE}}$) electrode as reference electrode, using Zahner Zennium electrochemical workstation. The open circuit potential was measured for 15 min prior to polarization test in order to establish an approximately stable potential. Polarization measurements were carried out at a scan rate 0.333 mV/s and tests were performed in triplicate. In order to determine boundary condition for galvanic corrosion, polarization curves are obtained in Figure 3.

3. RESULTS AND DISCUSSION

3.1 Galvanic corrosion numerical simulation of the reboiler

Figure 4(a) shows potential distribution of the whole reboiler shell surface. The potential is from -0.61V$_{\text{SCE}}$ to -0.34V$_{\text{SCE}}$. In general, along the length of the shell, the closer to the left side of the shell, the smaller the potential. It has the largest value -0.34 V$_{\text{SCE}}$, which is on the right side of the overflow plate of the reboiler. The lowest potential on the left side of the shell is -0.61V$_{\text{SCE}}$. In Figure 4(b) it displays the potential of U-tube bundle external surface, and the potential is between -0.71V$_{\text{SCE}}$ and -0.58 V$_{\text{SCE}}$. On the U-tube bundle right side potential is higher, which is close to the overflow plate and the shell right side. On the left side, between the sheet plate and the leftmost baffle, potential is lower. It can be seen from the left cross section of the U-tube bundle, the potential gradually decreased from the outside (light red color) to the center (blue color). From Figure 4(c) potential of one sheet plate and four baffle plates is between -0.68V$_{\text{SCE}}$ to -0.43V$_{\text{SCE}}$, and the potential difference of each baffle is small. All the baffle plates potential ranges from -0.69V$_{\text{SCE}}$ to -0.58V$_{\text{SCE}}$, and along the radial direction, the potential gradually decreases from outside to inside. For overflow plate, the potential distribution is uniform, and the difference between the maximum and minimum potential is less than 30 mV.
Figure 4. Potential distribution of the reboiler structure (V) (a) Shell; (b) U-tube bundle; (c) tube sheet; (d1-d4) four baffle plates; (e) overflow plate.
Figure 5 displays the current density distribution of the reboiler, including shell, U-tube bundle and so on. When the oxidation reaction occurs on the surface of the material, the specified current is positive and the material is used as the anode; when the reduction reaction occurs on the surface, the current is negative and the material act as the cathode. The shell, tube sheet and overflow plate act as galvanic cathodic metals. U-tube bundle and baffle plates act as anodes. From the current density distribution of the whole reboiler, the maximum reduction current on the cathode surface is \(-31.5\) A/m\(^2\), the region is near tube sheet and the shell. The maximum surface current density of anode can reach \(4.87\) A/m\(^2\). The minimum surface current density even can keep \(0.59\) A/m\(^2\). From the current density distribution of the U-tube bundle, current density is largest on the left side, on the right side it is smaller, and in the middle region it is smallest. From the left side region, the current density decreases from outside to inside along the radial direction. From the current density results, it can be referred that U-tube bundle nearby the tube sheet undertook seriously corrosion because of galvanic corrosion. Although there are no relevant simulation results to compare, fortunately, there are many service results under actual working conditions, which confirms the serious corrosion of the U-tube bundle near the tube sheet [13-15]. Only a few studies directly related to corrosion failure analysis of complex heat exchangers are discussed from the perspective of heat field and flow field. In order to reduce the difficulty of calculation, the geometric model of reboiler is simplified by using the similarity principle, so the number of U-tube bundles is reduced and the diameter of U-tube bundle is increased [13-16]. The results also show that corrosion is easy to occur at the contact between tube sheet and U-tube bundle or at the junction between baffles and U-tube bundle. As for the corrosion at the contact between U-tube bundle and tube sheet, our results are similar to these simulation results.

3.2 Cathodic protection of the reboiler

Electrochemical protection is one of the most common electrochemical corrosion protection methods, including anodic protection and cathodic protection. Anode protection requires that the material should be passivated in corrosive medium and have a wide passivation range [1]. According to the polarization behavior of three materials of reboiler in MDEA, the condition of anode protection is not satisfied. Cathodic protection is to apply negative current to the protected metal and make its electrode potential move to the metal oxidation-reduction equilibrium potential through cathodic polarization, so as to inhibit metal corrosion. In the cell made up of cathodic protection system, the
oxidation reaction concentrated on the anode, which hindered the corrosion of the protected metal as the cathode [1]. If the negative current is applied directly through the external power supply, it is called forced current cathodic protection; If a galvanic cell is formed by connecting a metal with more negative potential as anode to provide cathodic current to the protected metal, it is sacrificial anode cathodic protection. Due to the complex structure and heavy workload of management and maintenance, forced current cathodic protection is easy to lead to hydrogen embrittlement of steel, so it is not suitable to be arranged and implemented in the reboiler. The sacrificial anode cathodic protection method has the advantages of no external power supply, simple construction and management, self-regulation of output current and uniform distribution of protection current, which is suitable for corrosion protection of the reboiler materials [17–19].

3.2.1 Parameter selection of sacrificial anode cathodic protection

According to the field service condition of reboiler, the U-tube bundle inside the reboiler is seriously corroded and there are many stabs and leaks. This is because the U-tube bundle is made of 20# steel, which is not corrosion-resistant. After contacting with tube sheet, shell, etc., the U-tube bundle is used as anode with corrosion rate further accelerated. Therefore, the protection of the U-tube bundle is mainly considered.

From the results of galvanic corrosion simulation, the corrosion of the tube bundle near the contact with the tube sheet is the most serious, and its protection should be considered. Therefore, the sacrificial anode protection scheme is designed for the tube bundles between the tube sheet and baffle plates. The area of protected heat exchange tube is \( S = 520 \text{ m}^2 \). If only sacrificial anode is used to protect bare steel, the minimum protection current density should be at least \( I_{pro} = 120 \text{ mA/m}^2 \), and the total current \( I_{tot} = I_{pro} \cdot S = 62.4 \text{ A} \). Considering the internal structure and installation of reboiler, it is better to assume that the sacrificial anode is between the baffles just like the U-tube bundle. However, because there are too many U-tube bundles, which occupy most of the area of the baffles, the remaining sacrificial anodes can’t meet the requirements even if all the sacrificial anodes are arranged. Moreover, it is unrealistic to arrange all the sacrificial anodes in the remaining area. According to the actual situation, the combination of sacrificial anode and coating is considered. The use of the coating reduces the minimum protection current density to \( I_{pro} = 35 \text{ mA/m}^2 \), and the total current is 18.2 A. The generating current \( I_0 \) of a single anode is calculated according to the equation (5) [20].

\[
I_0 = \frac{\Delta V \sqrt{S_0}}{0.315 \rho} \tag{5}
\]

Where \( \Delta V \) is the anode driving potential, 250mV; \( S_0 \) is the exposed area of single anode, its value equals to 85% of the surface area \( S_a \), cm²; \( \rho \) is the dielectric resistivity, 72.0 Ω·cm.

Considering the U-tube bundle structure inside the reboiler, a circular sacrificial anode is used and erected on the baffle plate. Aluminum sacrificial anode has the advantages of light weight, large specific capacity, low consumption rate, low price and simple construction, so it is selected as sacrificial anode material. The total length of sacrificial anode is 4600 mm and the radius is 35 mm from the tube sheet to the far right; The surface area of a single sacrificial anode is calculated as \( S_a = 10188 \text{ cm}^2 \), and
the output current of a single anode is calculated as $I_0 = 1.03$ A, so the total anode number $N = I_{tot}/I_0 = 17.7 \approx 18$. Therefore, five anodes are arranged along the left circumferential direction of the baffle, five anodes along the right circumferential direction, five anodes on the upper side and three anodes on the lower side. Its diagram of layout of sacrificial anode is displayed in Figure 6.

![Diagram of layout of sacrificial anode: (a) Front view; (b) left view.](image)

**Figure 6.** Diagram of layout of sacrificial anode: (a) Front view; (b) left view.

### 3.2.2 Numerical simulation results of sacrificial anode cathodic protection

Sacrificial anode cathodic protection is to connect the sacrificial anode with more negative potential to the protected structure to form a galvanic couple. As the anode, the sacrificial anode provides cathodic current for the protected structure, so that the potential of the protected part is reduced to the equilibrium potential and the corrosion rate is reduced. In other words, the principle of sacrificial anode cathodic protection is the principle of galvanic corrosion. Therefore, the process and steps of numerical simulation of galvanic sacrificial anode protection are consistent, and the potential control equation is consistent. However, the boundary conditions may change with the coating damage during long-term service. According to Det Norske Veritas [21], the coating damage can be modelled as a coating factor $f_c$, which is a percentage of the total immersion area. The value of the factor $f_c$ is between 0 and 1. For a perfect coating, $f_c$ equals to 0, while for a no effective coating, which is actually a bare metal, it is 1. The smaller the coating factor $f_c$, the better the coating effect. The factor $f_c$ is used to obtain the polarization curve of a coated surface from the corresponding bare surface, reducing the current density proportionally or the same potential by factor $f_c$ [22-23]. So, the cathodic protection simulation boundary condition of the coated metal is obtained. In this paper, three different value of factor $f_c$ ($f_c = 1, 0.01$) representing different coating damages are chosen to simulate and discuss.

Figure 7 shows the potential distribution of reboiler and its parts under sacrificial anode cathodic protection. From Figure 7(a) the shell’s potential very high, and it acts as cathode. The farther away it is
from the U-tube bundle, the higher the potential is. The potential of the shell near the tube sheet decreases to -0.7 V_SCE. From all U-tube bundle (Figure 7(b)), the potential is about -0.99 ~ -0.62 V_SCE. The potential distribution of sacrificial anodes is shown in Figure 7(c), it ranges from -1.1 to -0.998 V_SCE, the potential of the anode near the baffle plates is higher.

Figure 7. Potential distribution for $f_c = 1$ under sacrificial anode cathodic protection of the reboiler (a) Reboiler protected by sacrificial anode; (b) U-tube bundle; (c) Sacrificial anode

The net current density of U-tube bundle is shown in Figure 8(a), and the U-tube bundle is as cathode. The maximum reduction current density reaches -6.9 A/m². In Figure 8(b), anodic current density distribution of U-tube bundle is nearly from $1 \times 10^{-4}$ to $9 \times 10^{-4}$ A/m². At this time, the current density of sacrificial anode is as shown in Figure 8(c), and the current density ranges from about 3.0 to 24.0 A/m².
From the numerical simulation results of the reboiler galvanic corrosion in Figure 4 and Figure 5, U-tube bundle act as anode, and corrosion rate reaches maximum value near the tube sheet, which is cathode in contact with U-tube bundle directly without electrolyte solution resistance. In addition, the corrosion rate of the bending part of the U-tube bundle is relatively high, because it is close to the overflow plate, which plays a cathodic role. The electrolyte distance between the bending part of the U-tube bundle and the overflow plate is short, so galvanic corrosion rate is high, which is in consistent with basic galvanic corrosion theory.

From Figure 4 and Figure 7, the overall potential range of the U-tube bundle changes from -0.71~ -0.58 V_{SCE} without sacrificial anodes to -0.99~ -0.62 V_{SCE} with sacrificial anodes. Because of the cathodic polarization of sacrificial anode, the potential of U-tube bundle become negative. From the result of Figure 5 and Figure 8, corrosion rate of U-tube bundle decreases because of the role of sacrificial anodes. Without cathodic protection, U-tube bundle act anode, nevertheless, U-tube bundle play a cathodic role with sacrificial anodes cathodic protection. The maximum corrosion rate decreases from 4.87 to 9×10^{-4} A/m^2, indicating that sacrificial anodes cathodic protection has a good effect. But from the U-tube bundle potential distribution, the potential in some region is positive than the commonly used cathodic protection criteria, -780 mV_{SCE} (or -850 mV_{CSE}), that is to say, the total U-tube bundles cathodic protection effect of metal is not good. This may be due to the complex structure and the shielding effect.
of current density distribution.

For \( f_c = 0.01 \) potential and current density distribution of U-tube bundle under sacrificial anode cathodic protection of reboiler is shown in Figure 9. The current density decrease, and the potential is below the cathodic protection criteria \(-780 \text{ mV}_{\text{SCE}}\), indicating that cathodic protection for coating damage factor \( f_c = 1 \) takes effect.

![Figure 9. Potential (V) and current density distribution (A/m²) for \( f_c = 0.01 \) under sacrificial anode cathodic protection of U-tube bundle](image)

According to the international standards such NACE (RP0169), ARAMCO (SAES-X-400), and BSI (BS 7361-1), the overprotection range ranges from \(-2.5 \text{ V}_{\text{SCE}} \) to \(-5 \text{ V}_{\text{SCE}} \) [24-26]. So, hydrogen embrittlement of U-tube bundle can be omitted.

4. CONCLUSIONS

In this paper, the galvanic corrosion of the reboiler in solution is studied by numerical simulation. It is found that the corrosion of U-tube bundle is serious, especially at the contact part with tube sheet. The design of coating and sacrificial anode cathodic protection is used to protect the U-tube bundle of the reboiler from corrosion. The numerical simulation results show that the coating with low damage factor and sacrificial anode cathodic protection has a good effect. This numerical simulation method also provides an effective idea and method for the corrosion research of super complex structures such as the reboiler.

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