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# Analysis of the tube-sheet cracking in slurry oil steam generators

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1. Introduction

#### ABSTRACT

Tube-sheet cracking is a severe problem in the oil refinery industry with the consequences of shortened service life and increased costs. In this study, the mechanisms of the tube-sheet cracking in slurry oil steam generators have been investigated using optical and scanning electron microscopy with energy dispersive spectrometry. It has been found that the cracks always occurred in the shortest tube-tube ligaments. All the cracks initiated near the expansion joints about 15 mm away from the oil-side surface where stress concentration existed. It was concluded that stress corrosion cracking occurred in the tube sheets due to the high-temperature (200–242 °C) and high-pressure (3.5 MPa) water, rather than the slurry oil containing elemental sulfur and chlorine.

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The slurry oil steam generator is a kind of shell and tube heat exchanger extensively used in the oil refinement. It mainly consists of a shell made of 16MnR, two 16Mn tube sheets and numerous 321 stainless steel tubes, shown in Fig. 1. The thin stainless steel (SS) layers were welded on the oil-side surfaces of the 16Mn tube sheets, and a hydraulic expansion technique was applied to eliminate the 0.4 mm-width gaps between the tubes and the tube sheets, shown in Fig. 2. During the heat exchange process, the temperature of the slurry oil varied from 318 °C (the inlet temperature) to 260 °C (the outlet temperature) in the slurry oil steam generator, while the temperature of the deoxygenated cooling water went up from 200 °C (the inlet temperature) to 242 °C (the outlet temperature). The characteristics of the slurry oil and the cooling water are given in Table 1.

It is well known that the tube-sheet cracking is a severe problem in the oil refinery industry. Previous study has shown that corrosion, such as stress corrosion cracking (SCC), and erosion–corrosion usually occurred in the tubes due to the presence of chlorine, sulfur and/or other impurities in slurry oil or cooling water [1–3]. Recently, a survey conducted by the China National Petroleum Corporation has indicated that cracks almost initiated and propagated in the tube sheets. Finite element analysis performed to simulate the hydraulic expansion process showed that this kind of cracking was related to the residual contact stresses on the interfaces between the expanded tubes and the tube sheets [4]. However, it is presently unknown whether this cracking was SCC or not, and what role the slurry oil and the cooling water played in the cracking process. To our knowledge no systematic studies of the cracking mechanisms in the tube sheets have been performed.

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**Fig. 1.** Schematics of the heat exchange process in the slurry oil steam generator, in the process the temperature of the slurry oil varied from 318 °C to 260 °C, the temperature of the cooling water went up from 200 °C to 242 °C, and the cracking occurred in the tube sheets.



Fig. 2. Schematics of the tube and the tube sheet in the slurry oil steam generator, where the thin stainless steel layers were welded on the oil-side surfaces of the 16Mn tube sheet. A hydraulic expansion technique was applied to eliminate the 0.4 mm-width gap between the tube and the tube sheet, and the oil-side expansion joint was about 15 mm away from the oil-side surface.

#### Table 1

Characteristics of the slurry oil and the cooling water.

| Medium                      | Inlet pressure (MPa) | Outlet pressure (MPa) | Inlet temperature (°C) | Outlet temperature (°C) | Flow (tons/h) | Other parameters   |
|-----------------------------|----------------------|-----------------------|------------------------|-------------------------|---------------|--|
| Slurry oil<br>Cooling water | 1.0<br>• 3.5         | 0.8<br>3.5            | 318<br>200             | 260<br>242              | 280<br>20     | S, 0.44 wt.% Cl, 1.22 mg/kg<br>pH = 9.5, containing K,<br>Ca, Al, Si |

In this work, a detailed analysis, including visual examination, chemical analysis and fractography was carried out to study the mechanisms of the tube-sheet cracking by means of optical microscopy, energy dispersive spectrometry and scanning electron microscopy.

#### 2. Analysis of cracking

#### 2.1. Visual examination

To examine cracks in tubes and tube sheets, non-destructive dye penetrant inspection materials were sprayed on surfaces and sections, shown in Fig. 3. Three types of cracks were observed on the sprayed surfaces. Cracks I and II are located in the upper right corner and the lower right corner in Fig. 3(b) and (d), respectively, and Crack III is located in the lower right corners in Fig. 3(a) and (c). It was found that the Crack I on the oil-side surface in Fig. 3(b) was very small, but the same crack on the section, 5 mm away from the oil-side surface, shown in Fig. 3(d), crossed the whole tube-tube ligament. This macroscopic feature seems to indicate that the Crack I did not initiate on the oil-side surface. As for the Cracks II and III, they did not emerge on the oil-side surface of the tube sheet, shown in Fig. 3(a) and (b). However, the two cracks also crossed the whole tube-tube ligaments in the section, 5 mm away from the oil-side surface, shown in Fig. 3(c) and (d). The visual observation shows that the two cracks' initiation sites were not yet on the oil-side surface. Besides, Fig. 3 also shows that this kind of cracking always occurred in the shortest tube-tube ligaments where stresses concentrated, and the Crack II existed in the tubes as well.

#### 2.2. Initiation and propagation of the cracks

The initiation sites of the cracks were identified according to the directions of the radial stripes on the fracture surfaces, shown in Fig. 4. It has been found that several short radial stripes converged on the left edge of the tube–tube ligament,



**Fig. 3.** Photographs of the surfaces sprayed with dye penetrant inspection materials: (a) view of an oil-side surface, (b) view of another oil-side surface, (c) view of a section at a 5 mm distance from the oil-side surface in (a) and (d) view of another section at a 5 mm distance from the oil-side surface in (b), where I, II and III indicate the Crack I, the Crack II and the Crack III, respectively, and the locations of the three cracks. However, the Crack III did not emerge on the corresponding oil-side surface marked by a circle ring.



**Fig. 4.** Fractographs of (a) the Crack I, (b) the Crack II and (c) the Crack III, where the radial strip, the oblique face, the origin point and the stainless steel are shortened to "RS", "OF", "OF" and "SS", respectively, the crack propagation directions are indicated by the black dotted arrows.

about 21 mm away from the oil-side surface, which indicated that the Crack I initiated at this point, shown in Fig. 4(a). Besides, a few radial strips in the middle of the ligament did not converge at a point. Therefore, the other initiation site of the Crack I was probably on the right edge, about 20 mm away from the oil-side surface, shown in Fig. 4(a). There were also obvious radial stripes on the fracture surface of the Crack II, shown in Fig. 4(b). Most of the radial stripes converged at the boundary between 16Mn and the stainless steel. This shows that the Crack II's initiation site located at this boundary, about 9– 15 mm away from the oil-side surface. As for the Crack III, shown in Fig. 4(c), dozens of radial stripes on the fracture surface indicate that two fracture initiation sites were on the right edge of the tube–tube ligament, 7.5 mm and 13.5 mm away from the oil-side surface, respectively. After the cracks were initiated, they propagated in the tube–tube ligaments. For the Crack I, when materials changed from 16Mn to the stainless steel, the crack propagation direction also changed. An oblique face at the boundary between 16Mn and the stainless steel was observed on the fracture surface of the Crack I in Fig. 4(a). As seen in Fig. 5, the length of the Crack I in the sections 5 mm, 2.5 mm and 1 mm away from the oil-side surface was 8 mm, 7 mm and



Fig. 5. The partial morphology of the Crack I in the sections: (a) 1 mm, (b) 2.5 mm and (c) 5 mm away from the oil-side surface.



Fig. 6. SEM views of the corrosion products on the original fracture surfaces of (a) the Crack I and (b) the Crack III, where the spot-like, needle-like and particle-like corrosion products are in areas marked "1", "2" and "3".

4.5 mm, respectively. This indicates that the Crack I became smaller and propagated from the inside to the oil-side surface when it approached the oil-side surface.

In brief, considering the fact that the oil-side expansion joints are approximately 15 mm away from the oil-side surface in Fig. 2, it is concluded that the three cracks initiated on the edges of the tube–tube ligaments around the oil-side expansion joints. Since the slurry oil was inside the tubes and it did not exist at the crack initiation sites, it is impossible that this kind of cracking was induced by the slurry oil.

#### 2.3. Corrosion products

The corrosion products on the original fracture surfaces of the Crack I and III were observed by a LEICA S440i SEM, shown in Fig. 6. The EDS spectra of the spot-like, needle-like and particle-like corrosion products in areas marked "1", "2" and "3"



Fig. 7. EDS spectra of the corrosion products: (a) spectrum of the area marked "1" in Fig. 6(a) and (b) spectrum of the area marked "2" in Fig. 6(a) and (c) spectrum of the area marked "3" in Fig. 6(b).

are given in Fig. 7(a–c), respectively. It can be seen from Fig. 7 that the corrosion products mainly consisted of iron oxides on the original fracture surfaces of the Cracks I and III. Besides, there was a small amount of elemental sulfur in the spot-like corrosion products on the original fracture surfaces of the Crack I, shown in Fig. 7(a). Elemental chlorine with very low content existed in the needle-like corrosion products on the fracture surface of the Crack I, seen in Fig. 7(b). As a result, the corrosion products on the original fracture surface of the Crack I contained iron oxides and elemental sulfur and chlorine, while there were only iron oxides in the corrosion products on the original fracture surface of the Crack II.

Why did the two elements only exist on the fracture surface of the Crack I rather than the Crack III? It has been found that there were both elemental sulfur and chlorine in the slurry oil, as shown in Table 1. On the other hand, the Crack I appeared on the oil-side surface and the Crack III did not emerge, shown in Fig. 3. This shows that the slurry oil was able to infiltrate into the Crack I and corroded its fracture surface, but the fracture surface of the Crack III was not chemically attacked by the slurry oil. As for the crack initiation sites about 15 mm away from the oil-side surface, and not on the oil-side surface, it is considered that the tube-sheet cracking was not induced by the slurry oil, and should be associated with the high-temperature and high-pressure cooling water, which did not contain elemental sulfur and chlorine.



Fig. 8. SEM fractographs of different materials: (a) the 16Mn tube sheet's fractograph, (b) the 321 stainless steel tube' fractograph and (c) the stainless steel layer's fractograph.

#### 2.4. Fracture mode

The fracture surfaces washed with the solution containing HCl and  $C_6H_{12}N_4$  in an ultrasonic cleaner were studied by LEI-CA S440i SEM. The typical fractographs of the 16Mn tube sheet, the 321 stainless steel tube and the stainless steel layer are shown in Fig. 8(a–c), respectively. The quasi-cleavage brittle fracture occurred in the 16Mn tube sheet, shown in Fig. 8(a). As seen in Fig. 8(b), there were secondary cracks on grain boundaries, and lots of rock-candy-like grains distributed on the fracture surface. These features indicate that the fracture mode of the 321 stainless steel tube was intergranular brittle fracture. As shown in Fig. 8(c), no ductile dimples were observed on the fracture surface, and the brittle fracture also occurred in the stainless steel layer. To sum up, the tube-sheet cracking was the brittle fracture, rather than the ductile fracture.



**Fig. 9.** Variation of the width of the gap between the cracked tube and the cracked tube sheet vs. the distance away from the oil-side surface, it is shown that the minimum gap was 10–20 mm away from the oil-side surface, meaning that there was stress concentration near the oil-side expansion joint in the uncracked tube sheet.

#### 3. Discussion

SCC is a kind of brittle fracture when materials are subjected to stresses in the specific environment [5]. First, for SCC of low alloy steel in water, the fracture mode changed from intergranular to quasi-cleavage as the strength of the steel decreased [6]. The cracking of the 16Mn tube sheet with low strength and low alloying was quasi-cleavage brittle fracture. Second, the cracks always occurred in the shortest tube–tube ligaments where stress concentration existed. Third, iron oxides were observed on the original fracture surfaces. These results explicitly show that the tube-sheet cracking was SCC, induced by the high-temperature and high-pressure cooling water, rather than the slurry oil.

Which stresses cause SCC in the tube sheets? The diameter of the tube sheet hole was about 0.4 mm larger than the external diameter of the unexpanded tube, shown in Fig. 2. After the hydraulic expansion, the inner diameter of the tube increased by about 0.5 mm, shown in Fig. 2. Therefore, the residual contact stresses exist on the interfaces between the expanded tubes and the tube sheets. Finite element analysis results have indicated that the maximum residual contact stresses occurred around the expansion joints [4]. As shown in Fig. 9, on account of stress relaxation of the cracked tube and the cracked tube sheet, the width of the gap between the cracked tube and the cracked tube sheet was about 0.15–0.4 mm, but the minimal gap occurred at a distance of about 10–20 mm away from the oil-side surface, near the oil-side expansion joint. As a consequence, the larger residual contact stresses concentrate near the expansion joints, where cracks are supposed to nucleate. However, the results in this work show that the fracture initiation sites only located around the oil-side expansion joints. Why did not the cracks initiate near the water-side expansion joints? It is noted that there was no stainless steel layer welded on the water-side surface, shown in Fig. 2. It is possible that the peak stresses near the water-side expansion joints relax more easily during the high-temperature operation.

Since the gaps between the tubes and the tube sheets are not sealed completely after the hydraulic expansion, the water molecules near the water-side surfaces are able to diffuse through the gaps and react directly with steel to form iron oxides [7]. The relevant reactions occurring in the tube sheets due to the presence of the deoxygenated water are:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e \tag{1}$$

$$Fe \to Fe^{2+} + 2e \tag{2}$$

$$3Fe(OH)^{+} + H_2O \to Fe_3O_4 + 5H^{+} + 2e$$
(3)

$$\mathbf{H}^{+} + \mathbf{e} \to \mathbf{H} \tag{4}$$

The SCC process can be described as follows, shown in Fig. 10. During operation, the 3.5 MPa, 200–242 °C cooling water permeated through the gap between the tube and the tube sheet. The hole surface of the tube sheet was subjected to corrosion. If the effective stress concentrating near the oil-side expansion joint reached a critical value, the SCC crack would preferentially initiate on the hole surface. Then, the crack propagated from the surface to the interior, and also grew in the axial direction of the tube under the action of the effective stress and the occluded cell at the crack tip. Finally, some cracks, such as the Crack I, emerged on the oil-side surface.



Fig. 10. A schematic plot of the SCC crack in the tube sheet, where the tube-sheet cracking occurred near the oil-side expansion joint, about 15 mm away from the oil-side surface.

#### 4. Conclusions

Analysis of the tube-sheet cracking shows that the cracks always occurred in the shortest tube-tube ligaments. The residual contact stresses concentrated near the oil-side expansion joints where the cracks initiated. Iron oxides distributed on the original fracture surfaces. This kind of brittle fracture was stress corrosion cracking, induced by the high-temperature (200– 242 °C) and high-pressure (3.5 MPa) water, rather than the slurry oil containing elemental sulfur and chlorine.

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