Journal of University of Science and Technology Beijing
Volume 12, Number 2, April 2005, Page 172

Failure analysis of corrosion cracking and simulated testing for a fluid catalytic cracking unit

Hua Chen[1), Xiaogang Li[1,2) Chaofang Dong[1), Ming Li[1) and Jinwen Yang[3)

1) Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083
2) State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
3) Jiujiang Branch Corp. of SINOPEC, Jiujiang 332000

(Received 2003-12-04)

Abstract: The failure of a fluid catalysis and cracking unit (FCCU) in a Chinese refinery was investigated by using nondestructive detection methods, fracture surface examination, hardness measurement, chemical composition and corrosion products analysis. The results showed that the failure was caused by the dew point nitrate stress corrosion cracking. For a long operation period, the wall temperature of the regenerator in the FCCU was below the fume dew point. As a result, an acid fume NO_x-SO_x-H_2O medium presented on the surface, resulting in stress corrosion cracking of the component with high residual stress. In order to confirm the relative conclusion, simulated testing was conducted in laboratory, and the results showed similar cracking characteristics. Finally, some suggestions have been made to prevent the stress corrosion cracking of an FCCU from re-occurring in the future.

Key words: stress corrosion cracking; fluid catalytic cracking unit; dew point; failure

[This work was financially supported by the Major State Basic Research Development Program of China (973 Program, No.19990970) and Petrochemical Company of China.]

1 Introduction

In recent years, fluid catalytic cracking units (FCCU) in Chinese refineries cracked in succession. Weld cracks of the regenerator, collection tube and flue have been reported occurring in more than 20 FCCUs that are over 50% of the total number of the FCCUs in China. Many cracks penetrated through the wall at the weld cycle of the equipment, and some of them were quite long, around 4-5 m, which caused serious security problem in the operation process.

Most cracking problems of FCCUs occurred after 4 to 7 years of operation, or occurred after 4 to 7 years of refining the oil mixed with heavy oil or paraffin wax [1-2]. Some FCCUs had to be shut down for maintenance, even had to be scheduled for an extended period for cracking examination and reparation. This has caused tremendous economic loss in Chinese refineries [3-4].

The present work analyzed the failure of a FCCU. The facility for corrosion test at a temperature below the dew point was developed for simulated testing in the laboratory. Based on the understanding of nitrate stress corrosion cracking (SCC) and dew point corrosion, and on the experience of industrial failure analysis, the mechanism of dew point SCC of the regenerator was investigated in NO_x-SO_x-H_2O environment by using well-developed SCC technology. The effort was aimed at searching for a mythology to predict SCC for FCCUs in Chinese refineries, providing fundamental basis for the developing of corrosion prevention strategies in industrial application.

2 Failure analysis and simulated testing

2.1 Failure analysis of the cracked component

Many cracks at the outside of the welds were observed on the shell of the regenerator and the pipe of the ascending airflow. The pipe of the ascending airflow with cracks propagating from the inner surface to the outer surface of the wall was replaced **(figure 1).** The area of the pipe with high crack density was cut as samples, and the failure analysis and testing were conducted. The regenerator was made of Q235, and the pipe was 16MnR. The following examinations were performed on the failed pipes.

- Nondestructive detection: A CJE-1 damage de-

Corresponding author: Xiaogang Li, **E-mail:** lixiaogang99@263.net

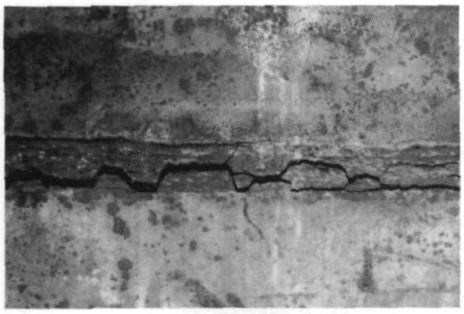

Figure 1 Cracks of FCCU.

tecting instrument was used to detect the magnetic-powder of the inner and outer surface of the failed pipe. A CTS-22 instrument was used to conduct the ultrasonic damage detecting. An HQ2505 instrument was utilized to conduct the X-ray damage detecting.

- Hardness measurement: An HLN-11 instrument was used to test the hardness of the weld material, base material and heat affected zone.

- Chemical composition analysis: The chemical composition of the weld material and the base material was analyzed.

- Dew point measurement: A model 220 acid dew point instrument was used to measure the dew point of the fume.

- Metallography analysis: The metallography analysis of the weld material, base material and heat affected zone was carried out.

- SEM observation: SEM was used to observe the fracture surface.

- X-ray diffraction: The corrosion product was analyzed by using X-ray diffraction technique.

- Chemical composition analysis of corrosion product of the fracture surface: the corrosion product of 0.9 g (powder) was collected from the fracture surface in an area of 500 cm^2 (500 cm×1 cm), and then dissolved in 50 mL distilled water. Ion chromatographic technique was used to analyze the anion composition.

- Stress analysis: The SW 6-98 software package was used to calculate the stress distribution of the regenerator.

2.2 Simulated method and materials

Materials for the simulated testing in laboratory are 20G, 16MnR and Q235-A (including both base metals and welds), which are widely used in FCCUs. Their chemical compositions are listed in **table 1.** Arc welding was conducted with handwork. Based on the residual stress distribution at the weld of regenerator components in a FCCU, U-bending specimens were used in the tests, and they were loaded by using screws. Tensile stress was applied to the outer surface of the specimen, and it reached the maximum value at the top of the bending. It is difficult to quantitatively determine the stress distribution. However this method is sufficient to qualitatively analyze the SCC behavior of metals, and it is widely used in laboratory testing.

Table 1 Compositions of base metals and welding lines for the testing (wt%)

Material		C	Mn	Si	S	P
16MnR	Base	0.150	1.460	0.350	0.0097	0.014
	Weld	0.071	1.240	0.390	0.007	0.009
20G	Base	0.200	0.530	0.270	0.005	0.005
	Weld	0.074	0.940	0.160	0.006	0.012
Q235-A	Base	0.180	0.400	0.240	0.025	0.021
	Weld	0.120	0.440	0.150	0.016	0.016

Four materials, including the base metals of 20G and 16MnR, the weld of 16MnR and Q235-A, were tested. Loaded U-bending specimens were put in the testing equipment **(figure 2).** The equipment mainly consists 4 parts: (1) A constant temperature case, the temperature can be controlled between 70-90°C. (2) A quartz glass tube with gas inlet and outlet, and water inlet and outlet. It is the main part of the facility. (3) A steam heating jacket, it is used to heat the steam that enters the glass tube. (4) The NO_2 injecting component.

SO_3 was produced from concentrated sulfuric acid. During the testing, the specimens were taken out for examination every 4 h.

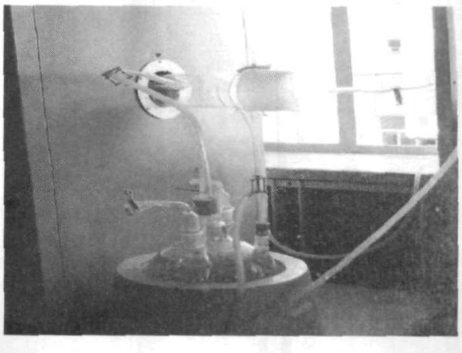

Figure 2 Simulated testing equipment.

3 Failure analysis and simulated testing results

3.1 Failure analysis

The surface of FCCU components was found to be corroded slightly by visual examination and cracks were detected by using a magnetic powder crack detector. Cracks propagated from the inner surface to the outer surface, and some of them penetrated through the wall. There were much more cracks on the inner surface than on the outer surface. Most of them were along the traverse direction, and the maximum crack length was found to be 90 mm. These results were confirmed with ultrasonic detection and X-ray examination. Hardness measurements indicate that the hardness of base metal is normal, but the hardness of the weld and heat affected zone is comparatively higher than the normal value.

The chemical composition of the cracked tube is listed in **table 2.** The contents of C, Mn, Si, S and P are in the right range for 16MnR. The C and Mn in the weld are lower than that in the base metal.

Table 2 Composition of the failure tube wt%

Content	C	Mn	Si	S	P
Weld	0.10	1.22	0.54	0.018	0.014
Base	0.16	1.50	0.43	0.038	0.016

The results of corrosion medium analysis and dew point measurement indicate that the dew point of fume in the pipe is about 143°C, and the pH of the medium is around 2.5. The main composition of the fume is summarized in **table 3. Table 4** is the composition of pole gases in the fume. At that operation period, the fume temperature in the regenerator ranges from 100 to 140°C.

Table 3 Main composition of the fume vol%

Gas	CO_2	O_2	N_2
Content	10.50	9.06	80.44

Table 4 Minim gas contents in the fume vol%

Minim gas	SO_2	SO_2	NO	NO_2	HCl
Content/10^{-4}	<1	2.4	662	<1	<1

The microstructure of the weld is Widmanstätten structure, and the grain size is large. The microstructure gradually changes from Widmanstätten structure at weld to ferrite-pearlite texture at the base metal through the heat affected zone. Cracks were examined under an optical microscope **(figure 3),** and it was found that they were propagated from the inner surface to the outer surface, and then penetrated through the wall. There was no obvious plastic strain at the locations of crack initiation. The cracks appeared narrow at the surface, but deep inside the wall. They mainly grew along grain boundaries with many branches, but some ferrites were found broken. The microstructure near the cracks was normal. SEM observations of the fracture surface **(figure 4)** showed brittle intergranular cracking characteristics, which implied the occurrence of stress corrosion cracking.

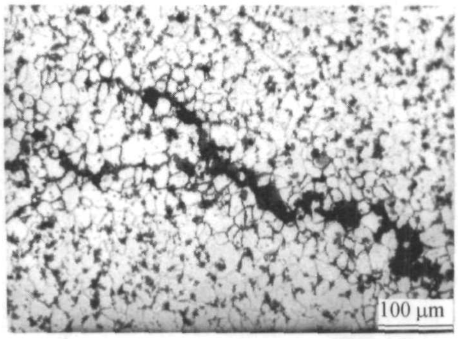

Figure 3 Crack growth path of the FCCU.

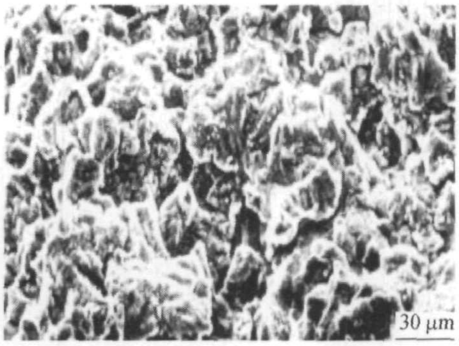

Figure 4 Fractured surface by SEM.

There were many corrosion products formed on the fracture surface. X-ray diffraction shows that they are mainly Fe_3O_4 and Fe_2O_3. The chemical composition analysis of the corrosion products was conducted, and the data are listed in **table 5.**

Table 5 Ion contents on the fractured surface wt%

Ion	NO_3^-	SO_4^{2-}	Cl^-
Content/10^{-4}	3.6	12.3	2.6

The software package SW 6-98 was used to calculate the stress of the regenerator, and the results showed that the tensile stress was 141.2 MPa.

3.2 Simulated testing results

After the specimen was tested for 0.5 h, small amount of discontinuous brown film was observed on the surface. This film grew rapidly; 2 h later, the whole surface was covered with a shell-like film that was full of small bumps and holes. The hot steam was condensed into water on the surface, and the water dropped to the loaded weld area below. The liquid that came out through the water outlet was brown. At the early stage of the test, the pH value of the liquid was ranged from 3.0 to 5.4; after 160 h, it increased to 5.0-7.0.

After 180 h, a crack was observed on the Q235-A weld specimen at the location with the maximum stress. The crack was perpendicular to the tensile stress direction **(figure 5).** After 500 h, no crack was observed on the other specimens. When the testing was finished, the fracture surface and microstructure of the Q235-A weld specimen were examined, and the results are shown in **figures** 6 and 7.

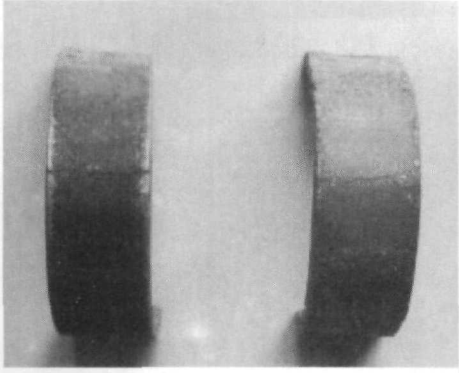

Figure 5 Cracks on the simulated testing samples.

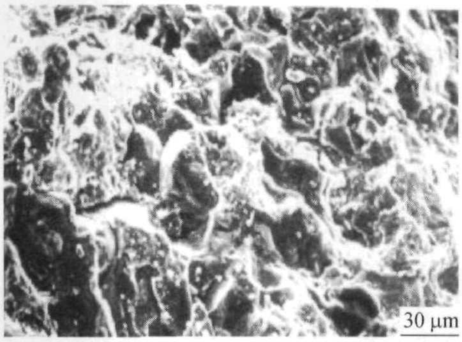

Figure 6 Fractured surface of the simulated testing sample.

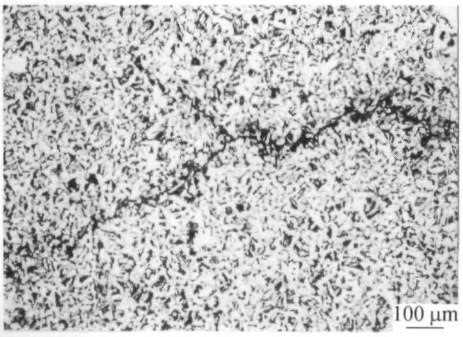

Figure 7 Crack growth path in the simulated testing sample.

4 Discussion

The pipe wall thickness measurement showed that the change of the wall thickness was very small, uniform thinning was not obvious. The cracking was not caused by wall thinning. The magnetic powder crack detection indicated that cracks were along the traverse direction, and propagated from the inner surface to the outer surface, and some of them penetrated through the wall. There were much more cracks on the inner surface than on the outer surface. These results implied that weld cracking was a result of SCC in the fume flowing through the pipe. This conclusion was further confirmed with ultrasonic detection and X-ray examination. Hardness measurements indicated that the hardness of the base metal was normal, but the hardness of the weld and heat affected zone was comparatively higher than the normal value. Generally, if the hardness of a material is high, its yield strength or tensile strength is high. Under the same deformation, the stress corrosion cracking happens quickly when the stress is high. In the weld, the contents of C and Mn were lower than that in the base metal. According to references [5-6], the SCC sensitivity of steels is maximum at a C content of 0.009%-0.05%, and the SCC stress intensity factor threshold, K_{ISCC}, *is* minimum.

The chemical composition analysis showed that the fume mainly contained N_2, SO_x, CO_2 and O_2, and the O_2 concentration was 9.06%; the concentrations of reducing gases, such as CO, were very low. Sulfur in the fume appeared in the form of SO_x; nitrogen was mainly NO_x and its concentration was high (662×10^{-6}). These pole gases were very easily dissolved in water and produced acidic solution. This acidic medium containing nitrogen-oxygen compounds was very corrosive to low carbon steels and low alloy steels, and the SCC sensitivity was high.

The results of X-ray diffraction indicated that oxide films formed on the surface and they were identified as mainly Fe_3O_4 and Fe_2O_3. The results of the chemical composition analysis showed that a certain amount of NO_3^- existed on the fracture surface. The SCC sensitivity of low alloy steels in NO_3^- aqueous solution is much higher than that in SO_4^{2-} aqueous solution; the SCC threshold stress in SO_4^{2-} aqueous solution is higher than that in NO_3^- aqueous solution. Metallography and SEM observations showed typical SCC cracking characteristics: The cracks branched and the cracking was intergranular and brittle. Therefore, a conclusion can be drawn that SCC of the regenerator in the FCCU has occurred in NO_3^- aqueous environment.

The regenerator is a huge and complex structure with heavy weight. In the welding and especially assembling processes, high residual stress was definitely existed in the welding area or heat affected zone. In the area with misalignment, the welding residual stress could be even higher. During the operation, the working stress and thermal stress made additional contribution to the SCC. The calculation indicated that the tensile stress, while resulted from the assembling stress, weld stress, working stress and thermal stress, could be as high as 141 MPa. The metallography analysis indicated that, during the manufacturing, assembling process of the regenerator, the welding process was not well controlled. The current density might be too high, and the cooling is fast. There was Widmanstätten structure formed in the weld line, and the residual stress could be very high. The tensile stress, including the residual stress and some other stresses, might easily exceed the SCC threshold stress.

Chen *et al.* [7] studied the SCC sensitivity of the base metal and weld of 16MnR under the simulated operation conditions of the regenerator. Three-point bending tests and constant tensile loading tests were used to investigate the SCC behavior and determine the SCC threshold stress intensity. The results indicated that the stress in this component during the failure process was higher than the SCC threshold stress intensity. Based on the experiments and stress analysis, the stress at the weld of the regenerator was higher than the SCC threshold stress intensity in acidic nitrate solution. As a result, SCC occurred. The examination of the cracked component showed that most of SCC cracks originated at the weld, fuse line and heat affected zone where the local stress and material strength were higher than other areas. The cracks were perpendicular to the tensile stress direction.

The fume of the regenerator contained 6.4% steam, a large amount of nitrogen compounds and acidic gases, which resulted in low pH in condensed water. The dew point of the fume was as high as 143°C, while during the operation period, the regenerator wall temperature was measured as 100 to 140°C. The equipment was operated below the dew point temperature. The NO_x, SO_x and steam penetrated through the inner liner, and formed acidic aqueous solution. This provided a condition for SCC to occur on the inner surface. The chemical reaction can be decrypted as [8-10]:

$$N_2+1/2O_2 \rightarrow NO_2 \qquad (1)$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \qquad (2)$$

$$2NO_2 + H_2O + 1/2O_2 \rightarrow 2HNO_3 \qquad (3)$$

Nitrate SCC occurred at the weld where high residual stress was present.

Oxygen existed in the fume of the regenerator pipe, a protective passive film formed on the metal surface. However, the passive film on the carbon steel surface was not stable, and its re-passivation was difficult. In a solution containing detrimental anions, the passive film was damaged when defects and tensile stress existed in the base metal or weld. The exposed metal under a damaged film acted as an anode of the micro-electrochemical cell, while a large undamaged area acted as a cathode. The metal atoms on the anode were dissolved into the solution. The anodic current density was very high because the anodic area was much smaller than the cathodic area. As a result, the micro-anode was developed into pits or cracks. After pits/ cracks initiated, corrosion products might block their opening, and the current and diffusion were impeded. Iron ions accumulated inside the pits/cracks. In order to maintain neutral, NO_3^- migrated into the pits/cracks. Inside the pits/cracks, the hydrolysis of iron ions generated proton, resulting in the decrease of pH and formation of nitrate acid. Therefore, the corrosion rate was increased. On the other hand, stress concentration or plastic deformation existed ahead of pits/cracks, enhancing the anodic dissolution of the metal. From the electrochemistry point of view, the small anodic area at pits/crack tips coupled with a large area of metal that covered with a passive film, resulting in continuous crack growth under tensile strength, and finally resulting in the failure of the component.

This corrosion cracking mechanism was proved in the laboratory-simulated test, and the overall reaction can be described as:

$$10Fe + 6NO_3^- + 3H_2O \rightarrow 5Fe_2O_3 + 6OH^- + 3\,N_2 \qquad (4)$$

Because the moisture content in the fume of the regenerator was low (about 6.4%), condensed water penetrated slowly into the wall through turtleback, was slow.

The comparison of the results from laboratory simulated tests and the failed component analysis showed similar characteristics on the fracture surface, corrosion products, microstructure, *etc.* This further confirmed that the failure of the regenerator in the FCCU was caused by nitrate SCC.

5 Conclusions

(1) The failure of a fluid catalytic cracking unit in NO_x-SO_x-H_2O environment was investigated by non-destructive detection methods, fracture surface examination, hardness measurement, chemical composition and corrosion products analysis. The results indicated that the failure was caused by the dew point nitrate

stress corrosion cracking. For a long operation period, the wall temperature of the regenerator in the FCCU was below the fume dew point. As a result, an acidic fume NO_x-SO_x-H_2O medium presented on the surface, resulting in stress corrosion cracking of the component with high residual stress.

(2) The simulated testing results in the laboratory showed similar characteristics with the results of failure analysis, which confirmed that the failure of the regenerator was caused by nitrate stress corrosion cracking.

(3) Based on the present study, the following measures can be used to prevent or inhibit the SCC of a regenerator:

- Increase the temperature of the shell and wall of a regenerator above the fume dew point by improving the inner liner and the out thermal insulation layer.
- Add the transfer catalyst of nitrogen and sulfur.
- Use the material with low strength and high nitrate SCC resistance.
- Reduce the residual stress from assembling and welding by improving the technique of equipment fabrication and installation.
- Protect the components by using coating or some other electrochemical methods.

References

[1] Ellis, *Some Examples of Stress Corrosion Cracking of Metals*, ASTM, 1984, p.421.

[2] L.M. Long and N.A. Locking, The mechanism of stress corrosion cracking in pure Fe-base alloys, *Corrosion*, 27(1971), No.11,p.299.

[3] H. Gong and G.L. Jin, The report of SCC for FCCU, *Petrochem. Corros. Prot.* (in Chinese), 16(1999), No.1, p.17.

[4] G.X. Cheng, J.G. Zhu, W.S. Zhu *et al.*, Characteristics analysis of stress corrosion in catalytic cracking reclaiming equipment, *Petrochem. Equip.*, 31(2002), No.1, p.20.

[5] J. Flis, Action of carbon in stress corrosion cracking of mild steel in nitrate solutions-corrosion, *Corrosion*, 29(1973), No.1,p.37.

[6] D. Cherandi, L. Rivola, and M. Troyli, Inhibition of ammonium nitrate corrosion of mild steel, *Corrosion*, 29(1973), No.1, p.1.

[7] G.X. Cheng, J.G. Zhu, W.S. Zhu, *et al.*, Stress corrosion failure in catalytic reclaiming equipment and experimental investigation of corrosion characteristics for 16MnR steel, *Petrochem. Equip.*, 31(2002), No.2, p.8.

[8] J.R. Galvele and P. Presen, Stress corrosion cracking, *Corrosion*, 55(1999), No.8, p.55.

[9] H. Kajimura and H. Nagano, Stress corrosion cracking of zirconium in hot nitric acid, *Corrosion*, 48(1992), No.1, p.5.

[10] Y.S. Wu, SCC diagram for low alloy steel-nitrate aqueous solution system, *J. Univ. Sci. Technol. Beijing* (in Chinese), 12(1990), p.131.