

Failure analysis for tube bundle of methanol condensation recovery heat exchanger

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Abstract: The S30408 tube bundle of methanol condensation recovery heat exchanger in a chemical company was found leaked during use. The cause of tube bundle leakage was analyzed by means of macroscopic inspection, chemical composition analysis, metallographic analysis, hardness test and leakage fracture analysis. The results show that formic acid and chloride condensate are formed by the exhaust gas in the shell side near the outlet of the shell side, which results in the spot corrosion and stress corrosion cracking of the tubes. Surface coating or replaced material is recommended to prevent such failure.

1 Introduction

Abnormal temperature signals were found in the operation of methanol condensation recovery heat exchanger in a chemical company in Zhejiang province. Then this vertical heat exchanger was shut down for inspection. The tube bundle near the upper tubesheet in the tube side was found leaked, and there were 32 leakage position in the 168 tubes of the heat exchanger. When some of the severely leaked tubes were extracted, the medium sediments were found covering the tubes and the baffle plate near the upper tubesheet. There was corrosion phenomenon in the tubes near the outlet of the shell side, which was near the upper tubesheet. No cracks were found on the weld joints of the upper and lower tube-to-tubesheet by dye penetrant inspection. Also there were no leakage points found in the tube bundles near the lower tubesheet.

The heat exchanger was a vertical fixed tube-sheet heat exchanger designed and manufactured according to GB/T 150-2011 "Pressure Vessels" and GB/T 151-2014 "Heat Exchangers". The working pressure of the tube side in the heat exchanger was 0.1MPa, and the working temperature was 180°C~200°C. The working pressure of the shell side was 0.025MPa, and the working temperature was 95°C~115°C. The specification of the tube bundle was OD19×1.5mm. The material of the tube bundle was S30408. The tubes and tubesheets were connected by strength welding and sticking expansion. The heat exchanger was put into use in 2014 and the expected life of the tube bundle was 10 years. There was no condensing system in front of the heat exchanger, and the exhaust gas entered from the lower part of the shell side. After cooling, the exhaust gas coming to the outlet was discharged to the environment from the upper part of the shell side. Schematic diagram for the medium flow structure of the shell side and pipe side was shown in

Fig.1. The methanol recovery device cannot be used due to leakage of the tube bundle. In order to confirm the failure process of the tube bundle and prevent the recurrence of similar problems, a comprehensive analysis was made on the leakage causes of the tube bundle.

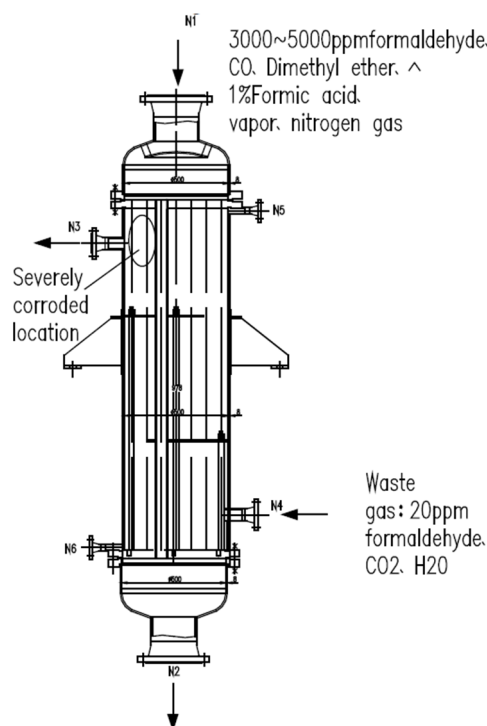


Fig.1 Schematic diagram for the medium flow structure of heat exchanger

2 Failure analysis test

2.1. Macro examination

The corrosion position was close to the lower side of the

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upper tubesheet after the leaked pipe section was cut down. The closer the tubes were to the tubesheet, the more serious the corrosion of the tubes were, as shown in Fig.2. There was basically no corrosion at the tubesheet position. The leaked tubes had no obvious plastic deformation and no thinning of wall thickness. The surface of the tubes was partially covered by corrosion products. The leakage points were rough and black with local yellow-brown and a little of dark red. After grinding the position of corrosion products covering, many corrosion holes were found in the tubes, as shown in Fig.3. Part of corrosion holes only occurred on the outer wall and did not penetrate to the inner wall of the tubes. In addition, a total of 32 corrosion holes penetrated the tubes by macroscopic inspection. Therefore, it can be confirmed that the corrosion leakage started from the outer wall of the pipe. In other words, the leakage started from the corrosion of the outer wall by the medium of shell side^[1].

2.2. Chemical composition analysis

A 20mm tube segment was cut from a leaked tube and polished into a spectral analysis sample. The chemical composition of the sample was analyzed by a Spectro Lab.M7 direct reading spectrometer according to GB/T 11170-2008 "Stainless steel - Determination of multi-element contents - Spark discharge atomic emission spectrometric method (Routine method)". The results were shown in Tab.1. The results showed that the chemical composition of the leaked tube satisfied the material standard requirements of GB 13296-2013.

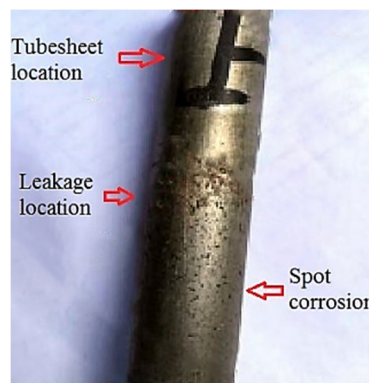


Fig.2.Morphology of a leaked tube



Fig.3 Spot corrosion after grinding

Tab.1 Chemical composition of a leaked tube (%)

Elements of S30408	C	Si	Mn	Cr	Ni	S	P
Specified values by Standard	≤0.08	≤1.0	≤2.0	18.0~20.0	8.0~11.0	≤0.03	≤0.035
Measured values	0.048	0.44	0.74	18.51	8.19	0.009	0.014

2.3. Metallographic examination

The cross-section metallographic sample were taken from the position shown in Fig.3. The metallographic examination was conducted in accordance with GB/T 13298-2015 "Methods for Examination of Metal Microstructure". The metallographic microstructure of the leaked tube was normal single-phase austenite. There were some spot corrosion pits on the outer wall of the tube, and there are cracks under the spot corrosion pits^[2].

One of the spot corrosion pits penetrated the tube selected as 1# specimen and the other did not penetrated the tube selected as 2# specimen. No accumulation and growth of carbide was observed, as shown in Fig.4. A small range of plastic deformation could be seen at the edge of the leakage hole on the outer surface of the tube. The dislocation line of the slip step plug was found in the deformation area. All the main cracks and the secondary cracks showed the characteristics of transgranular propagation.

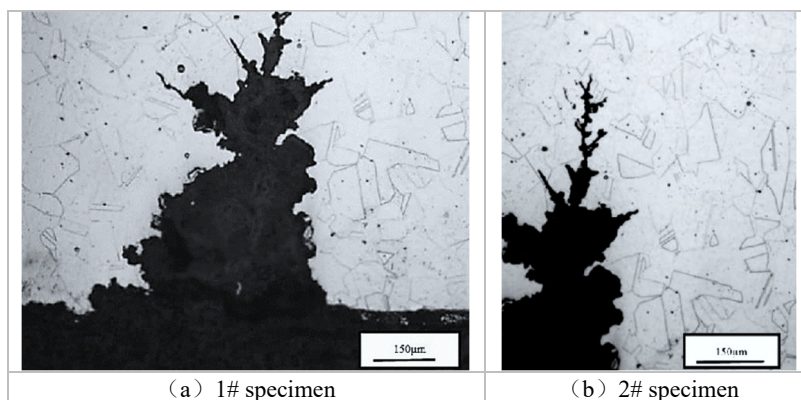


Fig.4 Metallographic structure of the leaked tube

2.4 Hardness test

According to GB/T4340.1-2009 "Vickers hardness test for metallic materials - Part 1: Test methods", the Vickers hardness was tested on the surface of the cross-section sample after metallographic examination and on the surface of an uncorroded tube. The test results showed that hardness values near 1# and 2# specimens were similar to those at the uncorroded tubes. All hardness of the inner and outer surface were less than 200HV, which was satisfied the hardness requirement of not more than 200HV specified in the design document. The hardness test results are shown in Tab.2.

Tab.2 Hardness test results

Location	Hardness values (HV ₅)	
	Outside surface	Internal surface
Near 1# specimen	178.3, 180.8, 179.5	185.4, 187.8, 184.3
Near 2# specimen	186.6, 179.4, 183.3	177.4, 179.2, 177.8
Uncorroded tube	179.7, 172.1, 174.5	184.4, 188.1, 185.8

2.5. Leakage fracture analysis

The specimens were processed, polished and cleaned with acetone. The microscopic morphologies of the samples were observed by Scanning Electron Microscopy (SEM). The river pattern and a small amount of fan pattern were found in the microscopic morphology of 1# specimen, which was a typical characteristic of cleavage fracture^[3], as shown in Fig.5(a) and (b). The surface of the leakage fracture was covered by corrosion products. The main leakage crack appeared at the leakage section, which was characterized by transgranular propagation. The secondary cracks and dislocation slip lines were visible on the leakage fracture. The river pattern and a small amount of fan pattern were also observed in the microscopic morphology of 2# specimen, as shown in Fig.5(c) and (d). The surface of the leakage fracture was also covered by corrosion products, but no cracks and dislocation slips were obviously found.

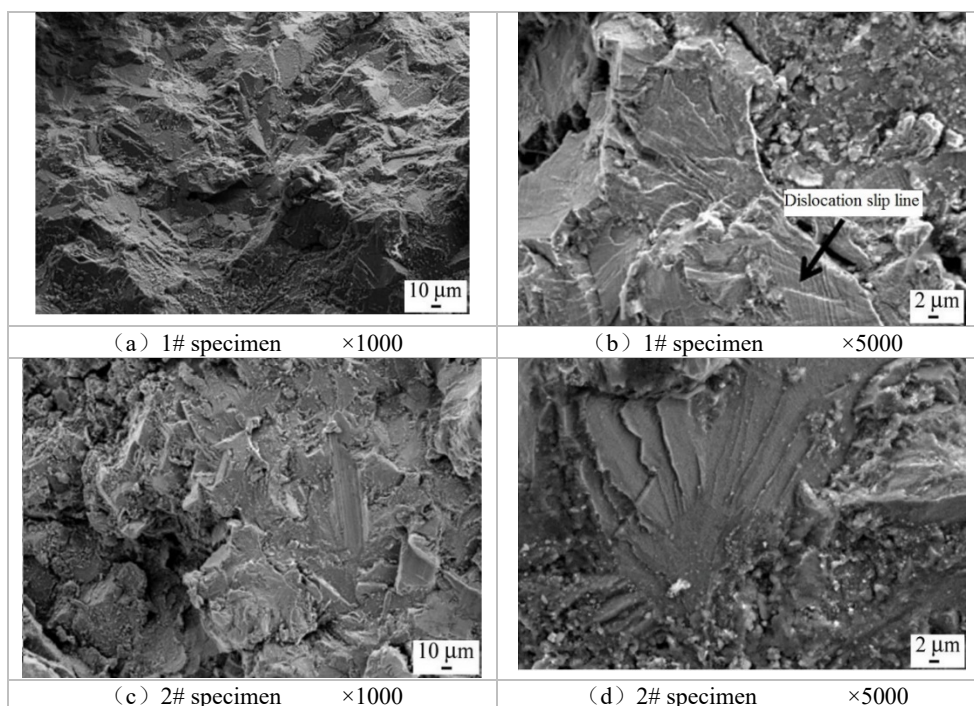


Fig.5 Microstructure of leakage fracture By SEM

The corrosion products covered on the surface of 1# and 2# specimen were analyzed by Energy Disperse Spectroscopy. The analysis results were shown in Tab.3. The element content of Carbon and Oxygen in the corrosion products on the surface of 1# leakage specimen was very high, and the mass fraction of harmful element Chlorine was 2.25%. The content of Carbon and Oxygen on the surface of 2# specimen were also very high, and the mass fraction of Chlorine was 0.91%. The content of harmful element Sulfur on the surface of 1# or 2# specimens was very small and basically equal to Sulfur content of the tube. The high levels of Carbon and Oxygen were inferred to come from the medium. The Chlorine content in corrosion products on the surface of 1# specimen was 2.473 times that of 2# specimen. This was because the cracking time of the 1# leakage was long and the media infiltrated into the leakage surface and affected the covered corrosion products.

Tab.3 Energy spectrum analysis results

Elements	1# leakage fracture	2# leakage fracture
C	17.69	18.62
O	19.99	20.36
Mn	0.22	0.20
Si	0.46	0.39
P	0.016	0.016
S	0.015	0.013
Cl	2.25	0.91
K	0.30	0.03
Ti	0.15	0.13
Cr	16.69	16.64
Fe	33.73	33.84
Ni	8.29	8.31

A large number of corrosion products were covered near the upper tubesheet on the heat exchanger, where Chloride ions were concentrated. The corrosion by Chloride ions will be accelerated in the presence of dissolved oxygen. Stress corrosion cracking of austenitic steel generally occurs above 60°C^[4]. The working temperature of tube side and shell side of heat exchanger is 180°C~200°C and 95°C~115°C, which are at the temperature range of this corrosion.

3 Leakage failure analysis

According to the design documents and process flow, the medium in shell side contained formaldehyde. Formaldehyde and Oxygen would react as follows: $2\text{HCHO} + \text{O}_2 = 2\text{HCOOH}$.

The condensing system was not installed in front of the gas outlet in the heat exchanger. The pressure at the outlet of the shell side was 0.025MPa, the operating temperature fluctuated between 95°C and 115°C. The saturated steam temperature is 106°C when the water is 0.025MPa. Therefore, under the operating conditions, a condensate containing formic acid at the outer wall of the tubes was formed near the gas outlet due to the temperature decrease. With local increase on the concentration of formic acid, the high concentration of formic acid solution will corrode the outside of tubes,

which were made of S30408. Therefore, the corrosion area was concentrated in the tubes near the upper outlet of the shell side.

When the medium sediment was gathered on the surface of tubes, the spot corrosion of formic acid was easily occurred under the sediment. S30408 was prone to stress concentration under pits^[5]. According to the results of energy spectrum analysis, there was a large content of chloride ion in the corrosion position of the leakage fracture. According to GB/T 30579-2014 "Damage modes identification for pressure equipments", when chloride ion is contained in the medium and the tubes was in the dry-wet, water-vapor alternated environment, the chloride is locally concentrated, and the sensitivity of stress corrosion cracking is significantly increased. The microstructure pattern of river and a small amount of fan in the leakage fracture indicates the stress corrosion cracking of the tubes^[6].

In summary, the main reason for the leakage of the tube bundle was the reaction of formaldehyde contained in the exhaust gas medium and Oxygen to produce formic acid, which formed formic acid condensate near the outlet of the heat exchanger. With the increase of local sediment concentration, spot corrosion was occurred on the surface of the tube bundle. Meanwhile, the stress concentration was occurred in the etched pit. The chloride ion in the medium concentrated locally near the outlet of the water-gas alternating shell side, which leads to stress corrosion cracking and finally leads to the leakage of the tube bundle.

4 Suggestions and repair measures

Through the above analysis, the following suggestions and repair measures are recommended:

(1) There are many leakage positions in the tube bundle, so it is not feasible to block all the leaked tubes by welding which will directly affect the heat transfer efficiency. Therefore, the shell side with the tube-to-tubesheet part is recommended to be replaced.

(2) Chloride ion was found in the corrosion products by energy spectrum analysis, so the current tubes material of S30408 is suggested to change into a material with strong resistance to stress corrosion cracking by Chloride ions, such as S32205 (the brand is 022Cr23Ni5Mo3N). Another method is to apply a coating on the surface of the tube bundle to avoid direct contact with Chloride ions.

(3) Sampling and analysis of the media in the process should be strengthened. The specific content of Chlorine ions in the medium and the pH value of the liquid phase should be analyzed, so as to clarify and reduce the source of chloride ions. This will provide data support for analyzing the mechanism and process of corrosion and preventing the recurrence of corrosion.

When the new replaced part are manufactured, reasonable technology should be adopted to reduce the stress produced in the manufacture process. The content of Chlorine and Oxygen in the medium should be strictly controlled in use, and the content of Chloride ions in water should be controlled during the hydraulic test. In the daily examination, it is recommended to strengthen

monitoring and detailed records of the operating parameters. The eddy current test can be added to timely find the defects of the tube bundle during periodic inspection.

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