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The Importance of Corrosion Control and Protection Technology in the Refinery

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This paper presents the importance of corrosion control and protection technology with a real case study of heater tube rupture damaged by High temperature H_2S-H_2 corrosion in the refinery. The heater was operated at the Hydrocracking unit and the operation temperature and pressure was 340 ℃ and 18 kg/cm^3 respectively. Top side of the convection tube was thinned by high temperature hydrogen sulfide and hydrogen gas as a uniform corrosion and finally ruptured under operation pressure. Damaged area (Convection tube zone) was blocked by protection wall, so it was impossible to inspect with conventional nondestructive examination. Instead the elbow area which is out of the protection wall was inspected regularly to evaluate the corrosion rate of convection tube indirectly. However the operation temperature and the phase of the process stream was different between inside the chamber and outside the chamber. As a result, it caused severe corrosion to the horizontal convection tube inside the chamber comparing to the elbow outside the chamber. Finally convection tube was corroded more rapidly than the elbow and ruptured after 13 years operation. Because of the rupture, the heater was totally burned and the operation was stopped for 3 months until it has been reconstructed. To prevent this kind of corrosion problem and accident, corrosion control should be strengthened and protection technology should be improved.

Keywords *: corrosion control, protection technology, high temperature H_2S-H_2 corrosion, hydrocracking unit, convection tube, couper-gorman curves*

1. Introduction

Refinery and petrochemical plant consists of a large number of equipments, piping, machinery and instruments. If those facilities would be in trouble an accident that incur great economic loss may happen. A fatal accident also could happen the worst case. Especially a possibility of an accident of fixed equipments is very high because most of them are filled with explosive hydrocarbon that can make a fire or explosion. Fixed equipments in refinery and petrochemical plant are called, according to a use or shape, as tank, reactor, separator, column and piping etc.

Most fixed equipments in refinery plant could be affected by corrodent, temperature and pressure, material and operating mode etc. Impurities contained feedstock or feedstock itself can cause damage in equipments and eventually failure. Various damage mechanisms are possible depending on design and operation conditions. Prediction, mitigation and monitoring of possible damage mechanism are very important to prevent a failure. Even though many activities done to prevent equipment failure still unexpected failures happened occasionally. Good understanding of design/actual operation conditions, damage mechanisms and applying advanced NDT is very important. It will be shown that critical factors should be considered to prevent a catastrophic accident by giving a real failure case study.

Damage mechanism in refinery plant

Possible damage mechanisms (DM) in refinery and petrochemical plant are listed in API 571 'Damage Mechanisms Affecting Fixed Equipment in the Refining Industry'. The number of damage is about 60. Because the damage mechanisms were affected by complicated and various factors, it isn't easy to classify. But damage mechanisms can be classified into 3 groups in accordance with an appearance of damage simply.

The first type is uniform or localized metal loss in thickness.

Most corrosion damages were included in the first group. Typical damage mechanisms in refinery plant are Alkaline Sour water Corrosion, Sulfidic Corrosion (High Temperature Sulfidation and H_2S-H_2 Corrosion), Cooling

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Water Corrosion, CUI (Corrosion under insulation), Dew Pint Corrosion and Metal Dusting etc.

Second type is cracking damage without thinning.

Typical damage mechanisms in refinery plant are Chloride SCC, Caustic SCC, Sulfide SCC, Amine SCC, HIC (Hydrogen Induced Cracking), Mechanical/Thermal Fatigue, Creep Damage etc.

The third type is material degradation which means a change of materials properties without thinning or cracking. Mechanical properties, i.e. tensile strength or/and impact value, decreased gradually with time. HTHA (High Temperature Hydrogen Attack), Softening, Temper Embrittlement is included in this type of damage. Sometimes mixed form of two or three types may happen but it is not common.

Efforts to failure prevention

Many efforts are required to ensure plant reliability by preventing a failure of fixed equipments. The examples are described as follows.

In design and construction stage, Material selection should take into account all predicted cases including as normal and abnormal condition when economical efficiency permit. The purpose of PMI (Positive Material Identification) is checking a material misuse during construction.

Process monitoring is very important to be aware of a changing of feedstock and operation conditions that may cause a critical damage. On-line monitoring for a real time process condition and computerized simulation is used to get more detailed data.

Inspection is an expansive work that monitors condition of equipments and decides a retiring time and takes countermeasure. So it is very important activity to prevent failure. Decision of the possible DM, pointing out week point and applying proper NDT should be done to get reliable inspection data for equipment.

To prevent/mitigate damage, there may be several ways such as control of feedstock quality, using corrosion inhibition chemical and material upgrading. The best way should be chosen as countermeasure that considers a feasibility and economical aspect.

Failure case study

It will be shown that a failure case happened by a rupture of the convection zone tube in hydrocracking unit heater.

Hydrocracking is a kind of hydroprocessing to make low sulfur kerosene and diesel using vacuum distillation residue as feedstock and consumes hydrogen. Also unconverted oil (UCO) is used as feedstock for a lube oil plant.

Hydrocracking unit is consisted of three main sections i.e. Reaction, Separation and Distillation respectively.

The reaction section is also divided into two parts. One

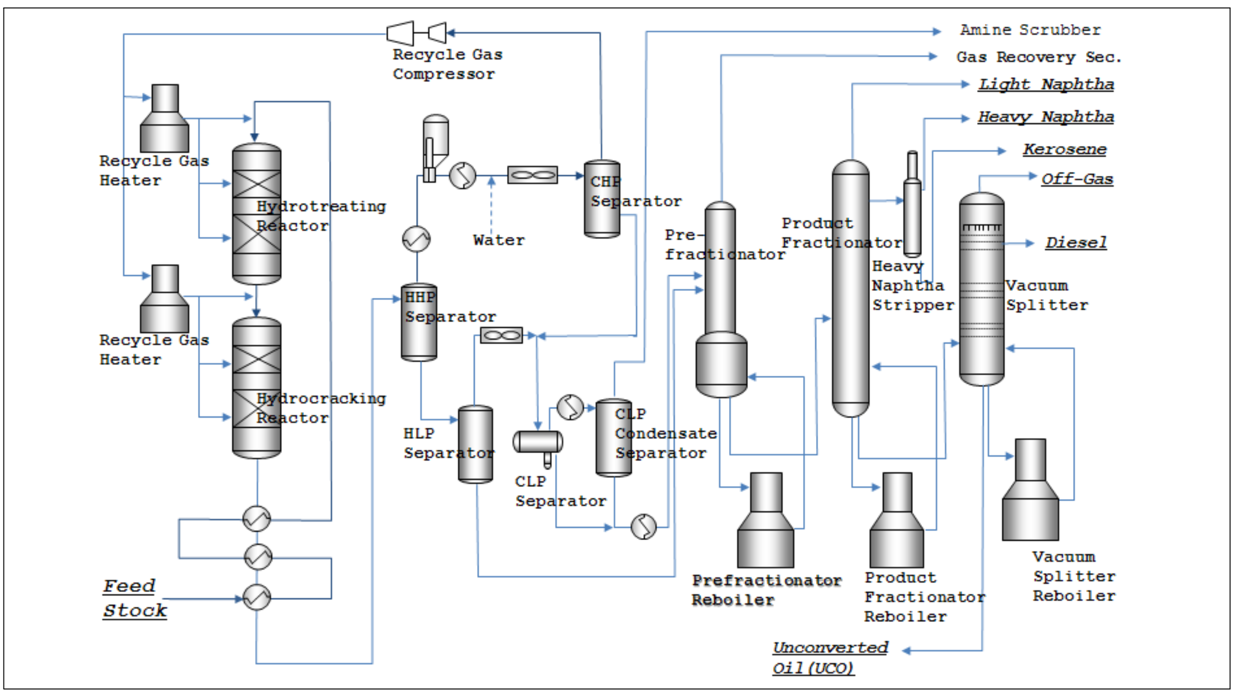

Fig. 1. Simplified PFD of hydrocracking unit

is hydrotreating part designed to remove contaminants such as sulfur, nitrogen, condensed ring aromatics, or metals. Sulfur and nitrogen converted to H_2S and NH_3 by hydrogenation and removed. Another is hydrocracking part heavy hydrocarbon is cracked into light hydrocarbon by cracking reaction using hydrogen.

In separation section, five drums separate gas phase from reactor effluents decreasing temperature and pressure gradually. Components of the gas phase are remained hydrogen and produced light impurities such as H_2S and NH_3. A main portion of the gas phase is hydrogen. And H_2S and NH_3 can exist more than ten% depending on quality of feedstock.

In distillate section, there are three columns to distill the liquid product come from separation section, which are Prefractionator, Fractionator and Vacuum Splitter in sequence. Light gas components removed from the liquid phase at first and distillated into products such as naphtha, kerosene, diesel and unconverted Vacuum Splitter bottoms product (UCO) be fed to the lube oil plant.

The failed heater is prefractionator bottom reboiler fired heater designed for the purpose of reheating a bottom reflux of the prefractionator. Fig. 1 shows a simplified PDF of the hydrocracking unit.

Operation conditions and material specification

The operation temperature and pressure was 340 ℃ and 18 kg/cm^3 respectively and the service was a bottom reflux of the prefractionator column. The failed convection tube material was 5 Cr-0.5 Mo alloy steel with stud fin and O.D was 6inch. Heater uses a process light gas as a burner fuel. Table 1 shows more detailed information about heater. Heater has a vertical radiant tube and horizontal convection tube. Convection zone has 10 row and 6 pass tube arrangement and radiant zone has 6 pass vertical tube arrangements.

Table 1. Operation Conditions

Temperature(℃)	340℃ Convection Tube Inlet: 300 Radiant Tube Out: 357
Pressure(㎏/㎠G)	18
Feedstock	Prefractionator Bottom Reflux

Table 2. Convection Tube Specifications

Tube Material	A335 P5 (5Cr-0.5Mo Steel) with Stud Fin
Tube Size	6inch, Nominal Thickness 7.1㎜
Minimum Allowable Thickness	2.17㎜
Burner Fuel	Process Fuel Gas

Inspection history

Heater was serviced for 13 years and no leakage before this rupture. Radiant tubes and shock tubes were replaced with P9 tubes 4 years ago due to thinning of the wall thickness by corrosion. Shock tubes were bottom rows of the convection zone.

It was impossible to inspect the straight tube of the convection zone because cannot access into flue gas duct, so only a periodic thickness inspection was done for return bends located in convection header chamber. The inspection results indicated insignificant corrosion phenomena. Calculated corrosion rate was less than 0.2 ㎜/year.

Visual examination

A convection module casing of the heater and some connected piping were damaged by flame. Fig. 2 shows appearance of the heater after a fire caused by tube rupturing.

Fig. 3. shows a schematic drawing of side view of the damaged convection module. Rupture occurred at 8th row undermost tube row except two shock tube rows. Shock tube was a bare type tube with no stud fin and replaced with P9 (9Cr-1Mo Steel) from P5 4 years ago.

Fig. 4 shows an appearance of the failed convection module after dissecting. The module casing and upper row tubes were deformed by a rupturing impact and some refractory was broken down. Top of the tube was ruptured along a longitudinal direction of the horizontal tube. There is considerable scale on the inner surface of the ruptured tube and no damage on the outside of the tube. Thickness of the ruptured lip was less than 1 mm and the ruptured

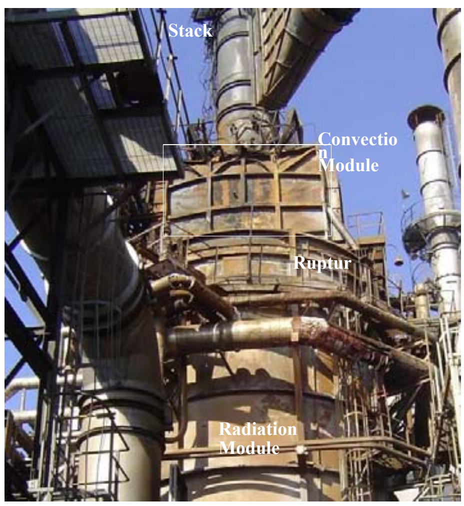

Fig. 2. Appearance of the fired prefractionator reboiler

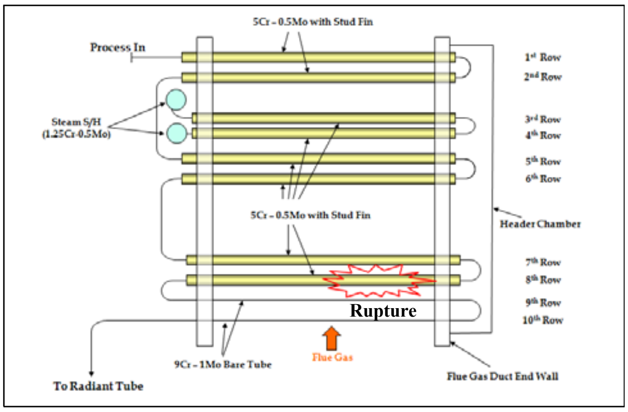

Fig. 3. Side view drawing of convection zone tube configuration

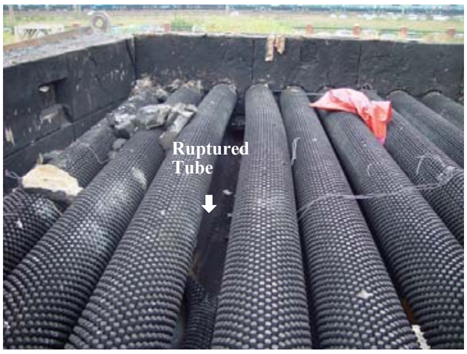

Fig. 4. Appearance of the failed convection module after dissecting

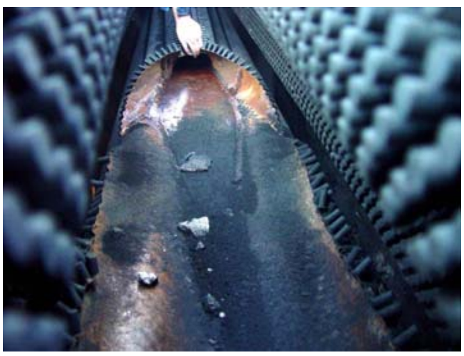

Fig. 5. Appearance of the ruptured tube in situ

Fig. 6. Ruptured tube appearance after dissecting

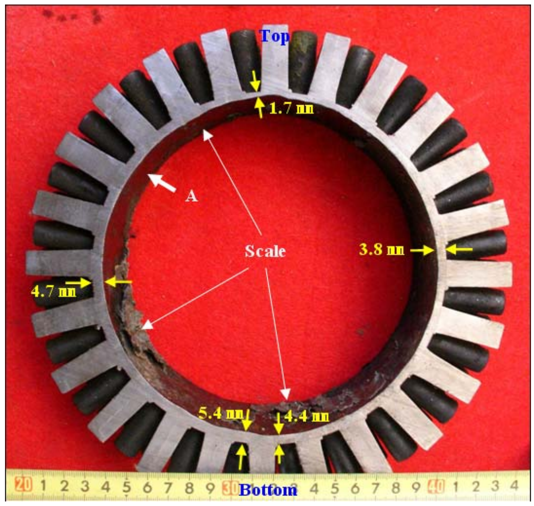

Fig. 7. Sectional view of the corroded tube

Fig. 8. Morphology of the corroded surface ('A' in Fig. 7)

length was about 2.5 m. A detailed appearance on ruptured tube was shown in Fig. 5 and Fig. 6.

Top of the ruptured tube was severely thinned and minimum thickness of top was less than 1.0 mm. But bottom side was 4.3 mm.

A sectional view of adjacent area of the ruptured position was cut for conforming corrosion contour and the sectional view is shown in Fig. 7. The corroded contour is same as that of the ruptured portion, that is, the top of the tube was most corroded such as in Fig. 7.

The corroded area was smooth face covered with black scale and no pit like damage.

Thickness measure

To get more information a thickness measurement was done for all tube. The results are shown in Table 3. A corrosion rate of the ruptured tube was 0.51 mm/yr. And the shock tube, P9, showed maximum corrosion rate 0.33 mm/yr. Thinning happened on all inside surface by uniform corrosion. Remaining thickness of return bend installed in header chamber out of the flue gas duct was

Table 3. Convection Tube Corrosion Rate Calculated from Thickness Data(mm/year)

	Flue Gas Duct				Header Chamber	
	Top	Bottom	90°	180°	Straight Tube	Return Bend
1st Row	0.12	0.12	0.12	0.12	0.10	0.11
2nd Row	0.13	**0.16**	0.12	0.13	0.11	0.15
3rd Row	Steam Coil					
4th Row						
5th Row	0.14	**0.32**	0.22	0.21	0.11	0.22
6th Row	0.16	**0.31**	0.27	0.27	0.10	0.21
7th Row	0.29	**0.41**	0.32	0.33	0.15	0.14
8th Row (Ruptured)	**0.52**	0.34	0.35	0.31	0.24	0.22
9th Row (Shock Tube)	**0.33**	0.28	0.25	0.28	0.23	0.23
10th Row (Shock Tube)	0.20	0.23	0.20	0.23	0.18	0.15

more than 5.7 mm in thickness, relatively mild corrosion occurred. All of radiant tube was thinned along by flame directions.

Upper tubes from 1st to 7th row had minimum thickness at the bottom side but 8th and 9th row tubes had minimum thickness at the top side. There was little difference between P5 and P9 material in corrosion resistance. Vertical radiant tubes were corroded along to flame direction.

Scale EDX analysis

EDX (Energy Dispersive X-ray) analysis was conducted to define corrodent on the scale sampled from corroded surface. Fig. 9 shows appearance of the sampled scale seems typical black flake.

Analyzed EDX spectrum was shown in Fig. 10

When the result of the analysis is considered, the scale was presumed as FeS components formed by corrosion.

Materials tests

Laboratory test was done to verify soundness of the tube material through microstructure examination, hardness test and chemical composition analysis.

Table 4. Result of EDX Analyses

Element	C	S	Fe
Wt %	9.1	20.1	70.8
At %	28.5	23.6	47.9

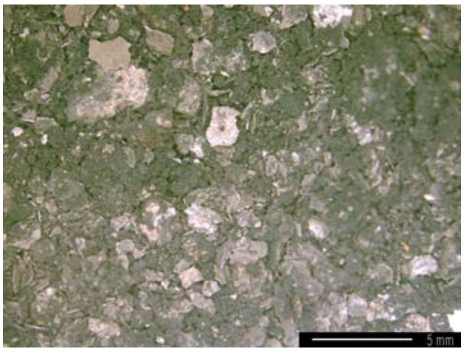

Fig. 9. Tube Inside Scale Sample

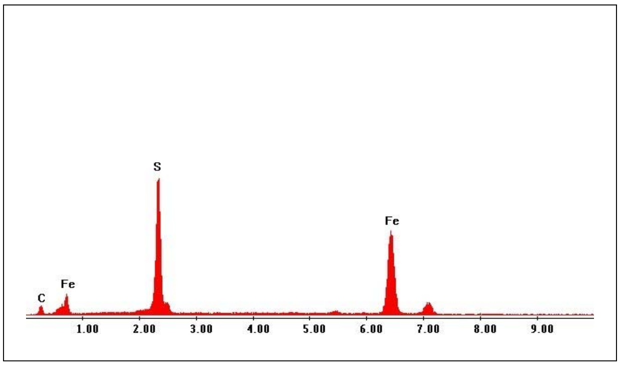

Fig. 10. Scale EDX Spectrum

Microstructure examination

Microstructures examination results using optical microscope were shown in Fig. 1.

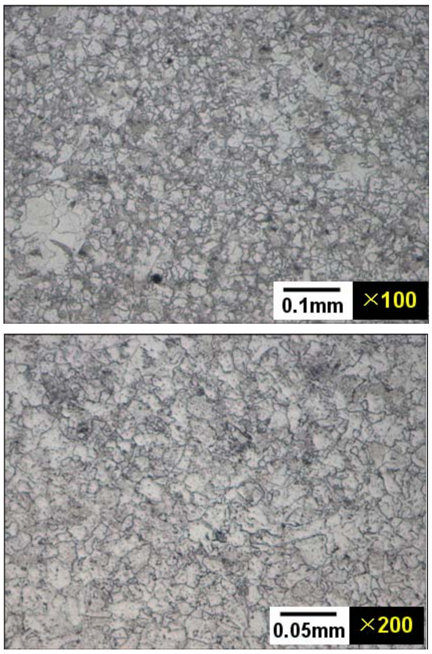

Fig. 11. Tube base metal microstructure

Cr-carbide was scattered in ferrite matrix due to long term operation at high temperature, there was no defect such as crack or creep void.

Hardness test

Hardness test was done for ruptured tube and no damaged 8^{th} row tube. Hardness values were normal range considering operation condition and time in service. There was no difference between the ruptured tube and no-damaged tube.

Table 5. Result of EDX analyses

	Ruptured Tube	No damaged Tube
HBS	138~140	136~145

Hardness value converted from Rockwell B Scale to Brinell Standard Scale.

Chemical composition analysis

Chemical composition analysis was shown in Table 6.

Table 6. The result of composition analysis

	C	Si	Mn	P	S	Cr	Mo
A335 P5 Spec.	0.15 max	0.5 max.	0.30~ 0.60	0.030 max.	0.030 max.	4.00~ 6.00	0.45~ 0.65
Results	0.113	0.439	0.484	0.013	0.007	4.849	0.457

Arc Emission Spectrometer: Model OBLF GS1000

Chemical compositions of the failed tube were satisfied with a requirement of A335 Grade P5 material.

There was no particular finding in tube materials tests.

Investigation of actual operation conditions

To define what corrodent caused rapid corrosion exactly study on actual operation condition was done and found out several important factors.

Only expected corrosive matter according to design conditions was less than several ppm because the most of H_2 and H_2S should be removed by separation drums and small amount of carryover go to Prefractionator column O/H system. So expected corrosion rate was very low.

But it is feasible that in actual operation lots of H_2S can exist during abnormal condition such as start-up or shut-down. It is difficult to verify exact content of H_2S which probably expected more than thousands ppm. It is still difficult to verify exact content of H_2S because that is high temperature and toxic gas phase.

Some other hydrocracking process has H_2S absorber column at upstream of distillation section to remove H_2S gas. Generally higher Prefractionator pressure has higher H_2S and H_2 concentrations of the bottom feed.

Convection tube flow regime simulation

Computerized simulation conducted for understanding flow regime and found out phase change from liquid to gas occurred in 7~8^{th} row tubes in convection zone.

Phase changing occurring in convection zone makes gas phase pocket at the top of the convection tube and H_2S can be concentrated in the gas pocket. In addition the gas pocket obstructs heat transfer from flue gas so tube metal temperature (TMT) was increased. That condition could make severe localized corrosion.

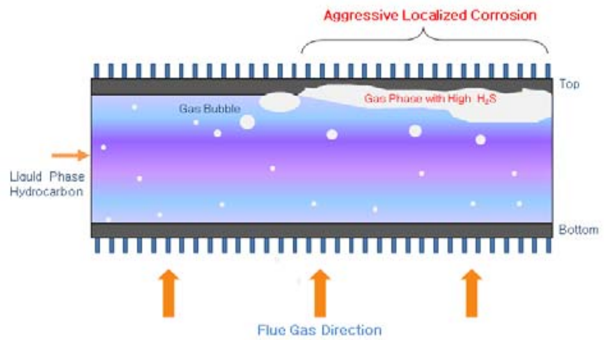

Fig. 12. Rupture Tube

It is accord with the result of thickness measurement that upper row tubes showed minimum thickness at the bottom side but 8^{th} and 9^{th} row tubes had minimum thickness at the top of the tube.

Fig. 12 shows schematic drawing of phase changing effect that make severe corrosive environment

Inspection of other heater tubes

5P Tubes of two heaters located at Fractionation Columns downstream were inspected. It was conformed that slight corrosion was undergoing. The corrosion rate was lower than that of failed heater because most H_2S was removed in Prefractionator Column.

Conclusions

Cause of failure

From the results of operation conditions review, damage morphology and laboratory test,

It was decided that the cause of the tube rupture was H_2S-H_2 Corrosion i.e. high temperature sulfidic corrosion due to H_2S concentrated gas phase.

It was estimated that abnormal operation conditions and phase changing in convection tube made severe corrosion environment. Couper-Gorman curves points out expected

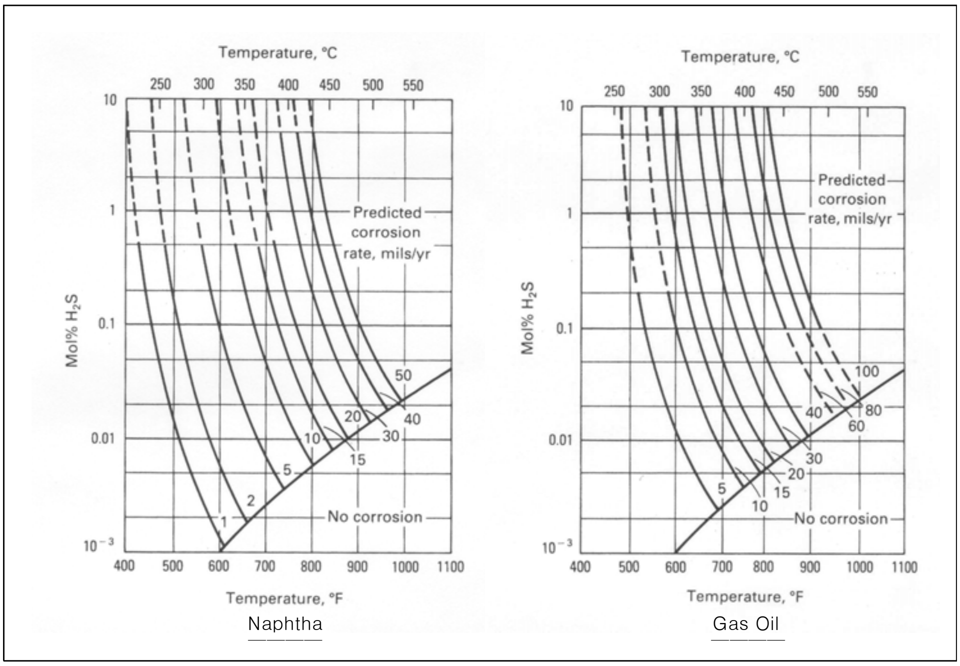

Fig. 13. Couper-Gorman Curves for 5Cr-0.5Mo Steel

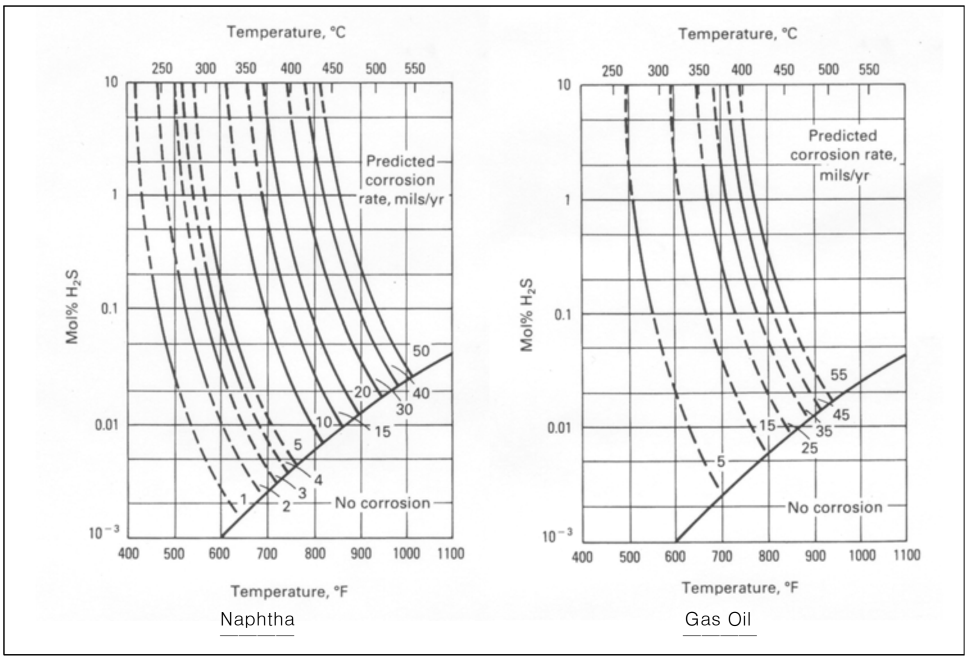

Fig. 14. Couper-Gorman Curves for 9Cr-1Mo Steel

corrosion rate according to H_2S contents and temperature for 5 Cr-0.5 Mo steel and 9 Cr-1 Mo steel in Fig. 13 and Fig. 14 respectively. Estimated H_2S concentration from Couper-Gorman curves was 2,000~3,000 ppm according to operation conditions and corroded rate.

Because the return bends in the header chamber was not direct affected by flue gas flow, a corrosion of the return bend was mild as comparison with that of the stud fin tube located in flue gas duct.

In addition a possibility of accelerated corrosion by mercaptanes or other sulfide compounds was supposed. But it was very difficult to verify that due to limitations of field condition and analysis method.

There was no problem on microstructure, hardness and chemical composition of the ruptured tube material.

Countermeasure

- Convection and Radiant zone tube material was replaced with 347stainless steel because there was little difference between P5 and P9 material in H_2S-H_2 corrosion resistance.
- Access door was installed to inspect tubes that located in flue gas duct casing.
- Periodic Inspection plan was set up and done for connected line piping, columns and heaters. Some pipes thinned by H_2S-H_2 corrosion were found and replaced with stainless steel pipe.
- Applying advanced NDT (Nondestructive Technology) Worldwide survey was done to search advanced NDT that can inspect convection tubes without tube cutting. Several advanced NDT were tested in field.
- Stable operation and impurities control is essential to mitigate damage and get equipment reliability

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