CHALLENGES IN A DILUTION STEAM GENERATOR SYSTEM

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Introduction

In the thermal cracking of Naphtha, steam is added to reduce the partial pressure of the hydrogen and shift the equilibrium to produce more ethylene. A Dilution Steam Generator (DSG) or a Saturator adds this steam to the feed.

A Dilution Steam Generator receives water from the Quench Tower after pretreatment and vaporizes this water. A Saturator receives water from the Quench Tower after pretreatment and using a trayed or packed column saturates the feed utilizing counter current flow with the re-circulating heated water.

Corrosion, erosion and fouling in the DSG and Saturators are not an uncommon problem. Thus, most systems are designed with a spare for cleaning and repair. Titan has also faced corrosion and erosion challenges in the DSG system in Cracker One particularly at the DSG reboilers, LP water stripper tower, DSG feed pumps and dilution steam condensate lines.

The DSG reboilers in the Cracker Two are beginning to show signs of similar challenges. The type of corrosion observed in Titan is of low pH under-deposit form, normally at the waterline area where two phases exist. So far minimal fouling has been detected. Frequent cleaning and retubing of the reboilers has been required. Water losses via blowdown to the wastewater due to leaking tubes have also increased operating cost.

The LP water stripper has seen acid corrosion and steam erosion resulting in reduction of the overall thickness of the shell and conical section of the tower.

DSG feed pumps casing and impeller have experienced coke erosion and corrosion problems. Sections of the condensate lines have experienced weak acid corrosion and erosion due to water hammering and condensate flashing.

1.1 Current Design of DSG System

Water for the dilution steam system is withdrawn from the circulating quench water loop of the Quench Water Tower and fed to filters and coalescer to remove most of the entrained hydrocarbons and coke fines.

The dilution steam feed water is then heated against quench oil before entering the low-pressure water stripper, upstream of the dilution steam generator. The LP water stripper uses dilution steam to strip-off the volatile hydrocarbons in the dilution steam feed water back to the Quench Water Tower. Medium Pressure Steam at 14 kg/cm^{2}G is used to raise dilution steam temperature to slightly above superheat, preventing condensation along the dilution steam piping.

MP steam is also used in dilution steam generator reboiler as the heating medium. Blowdowns from furnace steam drums and boilers are also fed to the DSG tower. Dual flow trays are used throughout the tower to reduce tower size and cost while providing resistance to fouling. Heavy compounds leave the dilution steam system in the tower bottom blow down to the wastewater treatment.

1.2 Chemical treatment Program in DSG System

Titan currently is utilizing chemical treatments to help mitigate the corrosion in the DSG System. Below is a synopsis of the chemical treatment program.

1. An Amine is injected at Quench Water Tower bottoms and dilution steam generator bottoms to control pH.

2. An O2 scavenger is injected at DSG feed water to eliminate dissolved O2 in DSG system.

3. An emulsion breaker is injected at the re-circulating quench water return to the quench tower to prevent emulsification of oil and water.

2.1 Corrosion/erosion at LP water stripper

2.1.1 Inspection

Titan Cracker One was commissioned in 1994. In 1996, the LP water stripper T-260 was found to have internal pitting corrosion on the cone and shell below the conical section. The nature of the pitting is patch, smooth, cluster, isolated and singular with minimum depth 2.0 mm. Monitoring the defected area was continued.

In 1997, the shell below conical section minimum thickness was 5.6 mm. In January 1998, overall thickness at the shell below conical section was 4.7 mm to 6.5 mm, and overall thickness at the conical section was at 6.9 mm to 6.0 mm. In August 1998, overall thickness at the shell below conical section was at 3.7 mm to 6.0 mm, while conical section overall thickness is 5.6 mm to 9.0 mm. Yearly average wall thinning at shell below conical section is 1.075 mm and for conical section is 0.85 mm.

2.1.2 Action Taken

Since the minimum required thickness for the shell below conical section is 3.42 mm excluding corrosion allowance at 3 mm, the detected area was cut and replaced by new portion an additional with stainless steel lining early in 1999.

2.1.3 Monitoring after repair

One year after the replacement of the defected section, Ultrasonic Corrosion Scan (UCS) was conducted on the same section. The result shows maximum wall loss at 1.56 mm at conical section and 1.01 mm below conical section. The localized thinning rate has not declined compared to original material before stainless steel lining. More significant internal corrosion/erosion was detected in the shell wall (conical and below).

2.1.4 Possible Causes and Recommendations

1. Acidic Corrosion – raise pH

"Examination of the plate section from T-260, revealed evidence of general acidic attack. The pattern of attack suggested that condensate is present/form in the conical and below section and acid gases (e.g., H2S, CO2) cause the formation of acid in the aqueous phase." 1

Based on analysis result on defected metal, the corrosion is suspected to be caused by low pH at T-260. Most possible source is from the dilution steam from dilution steam generator, T-270 because the defected portion is near to the dilution steam inlet nozzle.

Dilution steam pH had been increased from 6~7.5 to 7~8 since August 1998. Average pH in year 1999 is more than 8.0. However, the latest Ultrasonic Corrosion Scan on T-260 still detected wall thinning at the repaired portion. This is somehow in contradiction to the assumption made earlier.

2. Steam erosion – raise dilution steam temperature from 177 to 180°C

Second possible cause is dilution steam temperature. The assumption is where the dilution steam appeared in saturated form when entering LP water stripper. The droplets of condensation will act as 'bullet' and eroded the shell wall. Temperature had been raised and maintained 5°C superheated without much improvement on the latest scanning. Furthermore, the inspection did on the metal surface indicated the corrosion defect on metal surface and not erosion.

3. Initial dew point pH corrosion

Technical Service mentioned the 'initial dew point pH' in dilution steam. This is referring to the condensate pH when steam starts to condense after entering T-260. The water dew point is lower than neutralizing chemical. Thus when water condenses, the amine still appeared in gas phase causing low pH in the condensate. The low pH droplet will cause corrosion on the metal surface. No measuring device is presently for the initial dew point pH.

2.1.5 Conclusions

Several adjustments had been done on LP water stripper, however the problems still exist. The root cause for this problem still under investigation.

2.2 DSG feed pump casing and impeller corrosion/erosion.

2.2.1 Inspection

Dilution steam generator feed pump in Cracker-1 has seen severe erosion problems.

In 1997, the pump casing and pump head was badly eroded and repairs were initiated. In 1998, the pump bearing housing was badly corroded and repairs were completed.

2.2.2 Possible causes

1. Coke erosion

Suspected coke fines from furnace during decoking passes through quench water filters and enters to dilution steam generator system. These coke fines eroded the pump impeller and casing. This problem is unlikely after furnace decoking line modification in early 1999.

The modification on furnace decoking line is to shorten the piping between MOV (motorized operating valve) to quench system and block valve to the firebox. Before modification, coke fines accumulated at the dead leg between these two valves during decoking. The coke accumulated was then purged back to quench towers and some passed into DSG system. After modification, less coke was in quench oil and quench water. To date, no new erosion defects have been found.

2. Acidic corrosion

An additional safeguard is that the pH of the water in T-260 had been raised to 7~8 from initially 6~7 since August 1998. This helps to eliminate possibility of acidic corrosion on DSG feed pumps, P-260A/S internal.

2.2.3 Conclusion

The amount of coke in the system has been reduced and the pH raised to reduce erosion challenges.

2.3 DSG reboiler tube life problems

2.3.1 Inspection

The initial detection of leaking tubes was 14 months after the reboilers were put into operation in 1994. Subsequently, the reboilers were periodically cleaned and plugged in the time frame of 1 to 10 months depending on the severity of the tube failure. One of the three reboilers, E-270A was retubed after 3 years in operation and 2 years later an entire new tube bundle was installed. E-270B was retubed only once. E-270S has never been retubed and to date, both reboiler tubes are approximately only 10% plugged.

2.3.2 Possible causes

1. Under deposit corrosion at reboiler interface

A clear water line marking was present at the top portion of the tube bundles indicating that the reboiler tubes were not fully immersed in water during operation. Most of the leaked tubes were located at and within the water line where the tubes were covered with deposits. Meanwhile, the number of tubes leaking is at a minimum in the area under the water line where the tubes are totally submerged in water.

Waterline formation was also different between reboilers. This may suggest that the flow velocities were more turbulent in reboilers E-270B and S than E-270A. The less turbulent or lower velocity could be a result of the different piping arrangement of the inlet and outlet of the reboiler. At lower velocity, the potential of deposit accumulation is higher for E-270A as the piping have slightly more bends than B or S. Moreover, both E-270 B and S are further away from the blowdown point than A, hence, the unremoved solids tend to settle at the nearest reboiler.

The deposit sample above the water line was found to be mostly of iron oxide (98.8%), with trace amounts of silicon, aluminum, phosphorous and sulfur species. The iron oxide is either coming from the tube itself due to corrosion or a carryover from the upstream equipment and process. The sulfur is derived from DMDS injection.

Visual examination of the ruptured reboiler tube revealed that the propagation of the attack was from external surface inwards. Metallurgical failure analysis report concluded that the tube corrosion was due to acidic under deposit crevice corrosion.

The condition of low pH exists when deposits or crevices are present, a concentration of acid producing species may induce hydrolysis to produce localized low pH environments, while the bulk water pH remain alkaline.

Example: $M^{2+}SO_4^{2-}$ + H_2O ----→ $M(OH)_2$ + $H_2^{+}SO_4^{2-}$

In order for this to happen, two most basic mechanisms should exist here.

a. Deposition

It occurs when the solids are concentrated up in the reboiler, especially, when the reboiler is not fully flooded. The particles agglomerate, thus forming deposit. The deposits itself provides the right environment for the gouging process to take place underneath it.

b. Evaporation at water line

Heat applied to the tube causes the water to evaporate, leaving an acidic solution underneath the deposits. Concentration of acid can occur either as a result of steam blanketing which allows salts to concentrate on reboiler metal surface above or at the water line or by localized boiling beneath porous deposits on the metal surfaces.

C. Low pH due to presulfiding

During the addition of furnace effluent to the quench towers and following DMDS injection, the quench water pH will drop significantly. Water pH is even lower at the DSG. Once this occurs it can take period of time to bring the pH back to acceptable levels.

2.3.3 <u>Action Plan</u>

1. <u>Increase pH and control in the required range</u>

In order to prevent low pH during presulfiding, the quench water pH is first increased higher to approximately 8.0 to 8.5. pH will start to drop to at least 7.0 after starting DMDS injection.

In August 1998, DSG water pH control range was revised higher from 7.0 - 8.0 to 8.0 – 9.0.

However, despite the stricter pH control, the reboiler tubes continue to be a challenge.

2.3.4 Future plans

i. Redesign of blowdown system

It is clear that the present blowdown design is not effective, thus accumulation of corrosion products and other solids in the reboilers are inevitable. One of the solution is to redesign the blowdown system to allow more of the suspended solids be removed to the wastewater. The options are:

a. re-orientate the blowdown pipe configuration downwards

b. blowdown directly from the tower bottom itself instead of from upstream of the reboilers.

c. blow down from individual reboilers – this is risky as it may have diverse effect on thermosyphon reboilers if not properly administered

ii. Injection of filming agent and dispersant

The filmer is to provide corrosion protection when the pH falls below the 7.0 minimum target. The dispersant properties is to reduce organic fouling due to small amounts of entrained oils getting into the DSG and preventing corrosion products from adhering to the exchanger tubes. This chemical injection was tried and halted because it caused high turbidity in the quench water and oil appeared at the LP water stripper bottom. Study to resume back the injection at a lower dose than initially is in progress.

iii. Retubing the reboilers with corrosion resistant alloy

A different material, less susceptible to corrosion to replace the current carbon steel (A179) tube construction. This is an expensive option recommended by a maintenance consultant. The material recommended was initially SUS444 but due to its difficulty to procure in this region as well as the special welding method required, another material SUS316L was recommended.

2.3.5 Conclusion

Since the pH is within the required control range, the most likely cause of frequent reboiler tube leaking is the deposits accumulated which, will eventually lead to under deposit corrosion.

2.4 Dilution steam condensate piping corrosion/erosion

2.4.1 Inspection

In 1997, a section of the pipe from the condensate steam to the quench water tower failed due to thinning. The internal of the pipe was covered with a thin, grayish-brown deposit. The wall thickness ranged from 1.3 to 4.0 mm.

In 1999, a tee-joint of the steam condensate line failed due to thinning. The minimum thickness detected was 3.8 mm as compared with 7.6 mm (original). The surrounding pipes were also thinning with thickness ranging from 2.8 to 4.8 mm.

2.4.2 Possible causes

1. Weak acid corrosion

A smoothly contoured metal wastage indicated that the thinning was characteristic of weak acid corrosion. The pipe has been exposed to low pH condition, likely from the formation of organic acid species in the steam condensate. No indication of erosion or erosion corrosion was observed. The deposit consisted mostly of iron oxide (85.4%) with significant quantity of sulfur (12.5%) compound and trace amount of other species.

2. Erosion

The tee-joint suffered from erosion. This section of the line was experiencing water hammering, high vibration as well as flashing of condensate. This pipe was previously upgraded from schedule 40 to schedule 80 in 1996. The erosion rate at the tee is about 1.1mm/yr and the surrounding piping at 0.9mm/yr.

2.4.3 Action plan

In order to reduce the water hammering water hammering and two-phase flow, the entire steam trap along this line is replaced to new models with lower leakage rate.

2.4.4 Conclusion

With the increase in system pH, new steam traps and continued monitoring no additional failures have been identified.

Summary

Corrosion, erosion and fouling in the DSG and Saturators are not an uncommon problem. Titan has also faced corrosion and erosion challenges in the DSG system. A systematic approach has been undertaken to determine the cause of the challenges and to remove or mitigate the effects of the root causes.

Footnotes

1. BetzDearborn metallurgical report by Mr. David J. Kotwica, P.E., Metallurgist)