Improve the Reliability of High Flux Reboilers

A Treatment Approach for Dilution Steam Generator (DSG) Reboilers in Ethylene Plants

Karl Kolmetz[1] **Charles D. Nolidin**[2] **Zainudin Mustaffa**[3]

[1]*KLM Technology Group. P O Box 963, Sulphur LA 70664, USA*
kkolmetz@yahoo.com

[2]*Titan Petrochemicals. PLO 312, Jalan Tembaga 4, 81700 Pasir Gudang, Johor. Malaysia.*
charles@titangroup.com

[3]*GE Betz. 13 Jalan SS 26/8, Taman Mayang Jaya, 47301 Petaling Jaya, Selangor. Malaysia.*
zainudin.mustaffa@gesm.ge.com

Abstract

The reliability of high heat flux reboilers can be a challenge. The tube life can be at times as low as three months between average mean failures. The proper operation and chemical treatment program can extend this average mean failure to greater than a 400% improvement.

Corrosion is an operating challenge encountered in the DSG reboilers for a typical liquid cracker ethylene unit. Low or high pH and / or presence of dissolved oxygen typically cause corrosion. With medium pressure steam as the heat source, DSG reboilers operating at high heat flux or high percentage of water evaporation rate with respect to circulation flow, can experience departure from nucleate boiling and formation of steam / water interface. These phenomena promote organic / inorganic fouling and can lead to under-deposit localized low pH acidic corrosion.

Corrosion can also occur in the dilution steam itself if the steam is wet, although this is not a common problem. Tube leaks are the most common cause for shutdown of DSG reboilers. If the reboilers are heated by quench oil, tube leaks could result in massive organic fouling on waterside from quench oil contamination.

A novel operation and chemical treatment approach has proven the present reboilers treatment program at the DSG generation system can be revised to provide a more robust treatment approach. This is due to the fact that the incoming water into the system is pure and hence does not have a buffering capacity. Any change in the feed water chemistry will lead to pH variations and cause problems.

The benefits of the new approach, while combining with the organic dispersant for hydrocarbon dispersion and amines for neutralization treatment can be summarized as follows:

- *Water in the reboiler has higher buffering capacity, which enables it to accept feed water variations and not cause the pH to vary.*
- *Addition of pH booster will neutralize organic acid and prevents under-deposit corrosion through concentration effect.*
- *Additional polymeric dispersant add another defensive measure which prevents iron deposition.*

The correct analysis of a high heat flux duty reboiler combined with proper operation and treatment approach has greatly improved the reliability of an Ethylene Unit's Dilution Steam Reboilers.

Keywords:

Low pH, Corrosion, Under-deposit, Heat flux, pH/PO_4 coordinated.

Introduction

In the pyrolisis cracking of Naphtha, steam is added to reduce the partial pressure of the hydrogen and shift the equilibrium to produce more ethylene. DSG adds this steam to the feed.

Figure 1 shows the simplified flow diagram for quench water treatment for the DSG system. A DSG receives water from the Quench Water Tower. The Quench Water Tower has mainly four functions:

- Provides further cooling of the cracked gases.
- Condenses most of the dilution steam in the cracked gases.
- Maintains proper temperature of the gases prior to compression.
- Separates light hydrocarbon (pyrolysis gasoline) in the cracked gases.

Some of the condensed dilution steam at the bottom of the tower (82 ^{o}C) is circulated as a heating medium through various process heaters and reboilers before returning to

Quench Water Tower; while, the rest of the condensed dilution steam will be used as a feed to the 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.

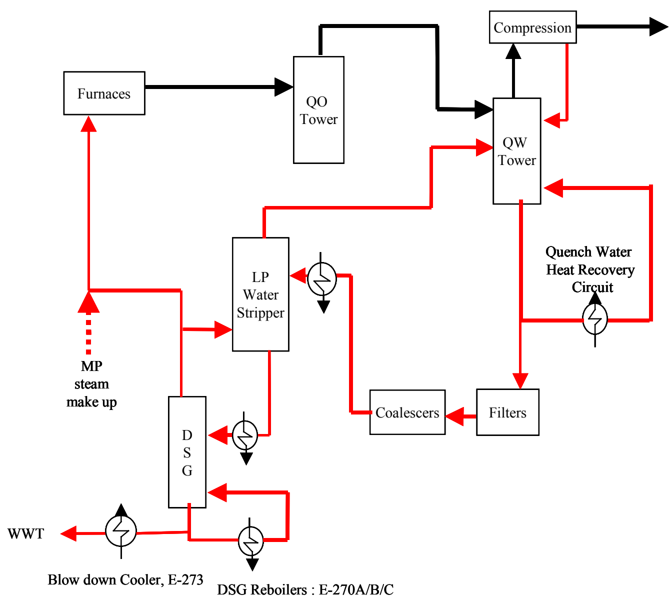


Figure 1: Simplified Flow Diagram for Quench Water Treatment for Dilution Steam Generator (DSG) System.

The dilution steam feed water is then heated up against the quench oil before entering the Low-Pressure (LP) Water Stripper, which is 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 (MP) Steam at 14 kg/cm^2G and 260 ^oC is used to raise dilution steam temperature to slightly above superheated, preventing condensation along the dilution steam piping.

Corrosion, erosion and fouling in the DSG are not uncommon problems. Thus, most systems are designed with a spare for cleaning and repair. An Ethylene unit example has also faced corrosion and erosion challenges in the DSG system particularly at the DSG reboilers, LP Water Stripper tower, DSG feed pumps and dilution steam condensate lines.

The type of corrosion observed in the Ethylene unit example's DSG reboilers is of low pH under-deposit form, normally at the waterline area where two phases exist. So far maximum fouling has been detected. Frequent cleaning and retubing of the reboilers has been required. Water losses via the blowdown cooler, E-273, to the wastewater treatment due to leaking tubes have also increased the 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.

MP steam is used in Dilution Steam Generator reboilers 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 blowdown to the wastewater treatment.

This paper will only discuss the water chemical treatment of the DSG reboilers system.

Chemical Treatment Program in DSG System

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

- An Amine is injected at Quench Water Tower bottom and Dilution Steam Generator bottom to control pH.
- An O_2 scavenger is injected at DSG feed water to eliminate dissolved O_2 in DSG system.
- An emulsion breaker is injected at the re-circulating quench water return to the quench tower to prevent emulsification of oil and water.
- pH/PO_4 coordinated program for the DSG reboilers' chemical treatment.

Short DSG Reboiler Tubes Life

The Ethylene unit example has three reboilers for the DSG; namely E-270A, E-270B and E-270S. Two reboilers are on line at the same time, while one reboiler is on standby.

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 three years in operation and two years later an entire new tube bundle was installed. E-270B and E-270S were retubed once.

Chronology or history of tubes leak will be discussed in the later part of this paper.

Under-deposit Corrosion at Reboiler Water 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.

The deposit sample above the water line was found to be mostly (98.8%) of hydrocarbon polymers and iron oxide, with trace amounts of silicon, aluminum, phosphorous and sulfur species. The iron oxide was either coming from the tubes themselves due to corrosion or a carryover from the upstream equipment and process. The sulfur was derived from DMDS (Di-methyl Disulfide) injection into the dilution steam before admixing with the naphtha feed for pyrolisis cracking.

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

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

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 deposit 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.

Treatment Approaches: Review of Reboilers' Water Chemistry and Heat flux.

Increase pH and Control in the Required Range

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 leaking continued to be a challenge.

A Chemical Treatment Specialist has recommended that the present reboiler treatment program at the dilution steam generation system be revised to provide a more robust treatment approach than the present system. This is due to the fact that the incoming water into the system is pure, and hence does not have a buffering capacity. Any change in the feed water chemistry will lead to pH variations and cause problems.

The new approach treats the reboiler system as a normal boiler – where the system buffering capacity is added through a pH booster. The strategy is to add a base amount of a pH booster and trim the pH to target range with amines. There is also additional polymer formulation to further prevent deposition in the system.

The benefits of the new approach, while retaining the previous benefits (organic dispersant for hydrocarbon dispersion and amines for neutralization) to the DSG are summarized as follows:

- Water in the reboiler has higher buffering capacity, which enables it to accept feed water variations and not cause the pH to vary.
- Addition of pH booster will neutralize organic acid and prevents under-deposit corrosion through concentration effect.
- Additional polymeric dispersant add another defensive measure which prevents iron deposition.

Reboilers' Heat Flux Review

A review of the process design of the reboilers is conducted to determine if the percentage (%) evaporization rate plays a role in the corrosion failures. The % evaporation is defined as the % steam produced over the circulation water flow rate between the DSG and steam separator. Comparison of results was made for the Ethylene unit example's DSG design % evaporation rate to a case study involving two DSG systems in another Ethylene units.

Case Study - Systems Information:

- Two Ethylene units (Plant A and B) in the same site.
- Plant B is of older design.
- Horizontal DSG reboilers in both plants.
- Both plants have eight Quench Oil Reboilers and two MP steam reboilers.
- Both DSG systems were treated with the same amine program.
- Plant A experienced no corrosion/tube leak problem in all reboilers.
- Plant B experienced severe corrosion, fouling and tube failures in MP steam reboilers.

A review of the process design of the reboilers had noted significantly higher % evaporization rate in Plant B with MP steam reboilers as shown in the following table.

Plant	Reboiler Type	% Evap	Remark
A	Quench Oil	7.6	No corrosion
A	MP Steam	5.8	No corrosion
B	Quench Oil	8.2	No corrosion
B	MP Steam	35	Severe corrosion and fouling

The following table shows the Ethylene unit example's DSG design % evaporization rate as compared to the case study.

Plant	Reboiler Type	Water Circulation	Steam Generation	% Evap
B	MP steam	277 T/hr	97 T/hr	35
Ethylene unit example	MP steam	128 T/hr	40 T/hr	31

In standard industrial boiler design, the % evaporation rate over water circulation rate is typically about 10% to ensure proper water circulation. Figure 2 shows the schematic of the Ethylene unit example's DSG system, water circulation and steam generation rates.

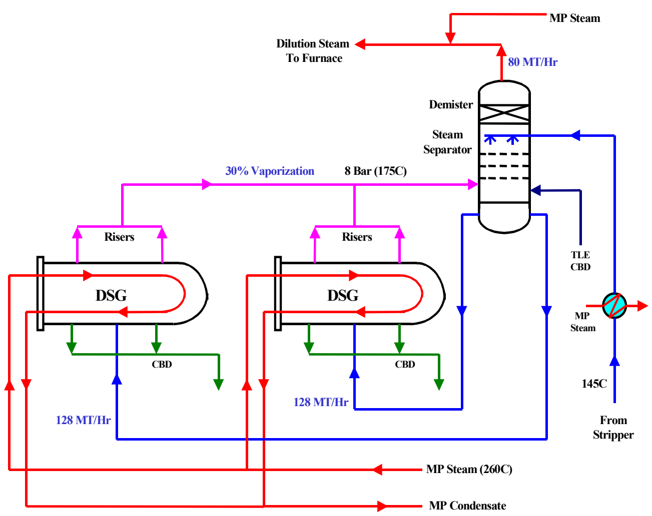


Figure 2: The Ethylene Unit Example's DSG Reboiler % Evaporation and Circulation Flow Rates.

From the above review, it can be concluded that the previous amine treatment program apparently unable to provide satisfactory corrosion protection in DSG reboiler designed with high % evaporation rate. When operating under high % evaporation rate, the even water circulation in the entire horizontal reboiler can be compromised. As a result, pockets of steam/water separation will develop in the upper section of the reboiler. The existence of water line at certain areas in the upper section of the reboiler during inspection at the Ethylene unit example is a testimony to steam/water pockets formation. In addition, high evaporation rate in combination with steam/water separation promote iron and hydrocarbon deposition. This creates potential for localized under-deposit organic acids concentration, which leads to low pH corrosion effect.

At the Ethylene unit example, currently two reboilers are in service with one on standby. With all three reboilers in service the % evaporation would be lower (theoretically 20% lower), and consequently will help to reduce the propensity to develop high heat fluxes on the reboilers' tubes.

Water Chemistry

Chart 1 shows the pH control trend for DSG reboilers blowdown at E-273 cooler before the new treatment program was implemented. The target pH control range was 8.0–9.0. The DSG blowdown reactive iron trend is shown in Chart 2. The average blowdown iron was 1.6 ppm.

About 10–40% of the time (6 pH data points per day), the reboiler water pH controls were less than 8.0. At pH below 8.0, the passive magnetite film, which protected the carbon steel, would be destroyed; and as such, significantly increased the general corrosion rate.

Chart 1: pH Trend at DSG Blowdown Before New Treatment Program at the Ethylene Unit Example.

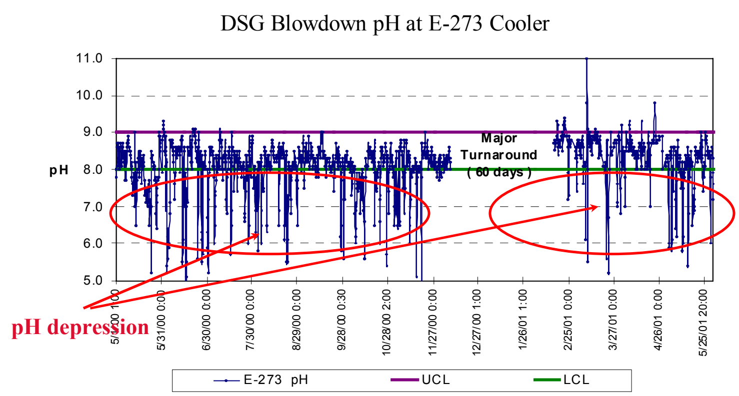
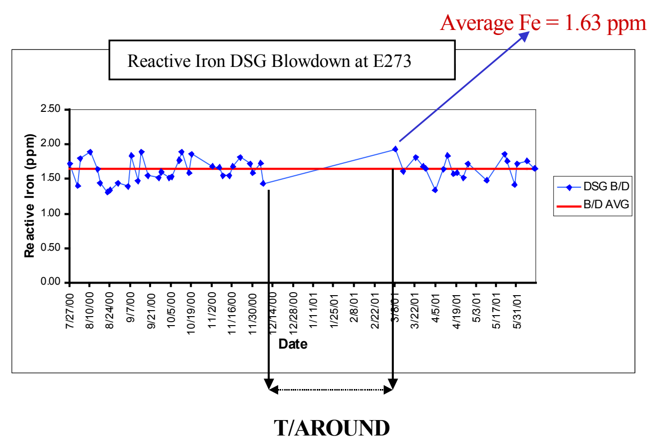


Chart 2: Reactive Iron Trend at DSG Blowdown Before the New Treatment Program at the Ethylene Unit Example.



However, visual inspection revealed that the tube leaks were not related to tube wall thinning as a result of general low pH corrosion. The failures were related to the localized under-deposit corrosion, and all the leaks were located at the upper section of the reboiler where bulk of the evaporation was expected to take place. The under-deposit corrosion developed as a result of the concentrated organic acids (mostly acetic) underneath the porous deposit as illustrate in Figure 3.

The contaminants in DSG water include organic acids (majority acetic, some propionic & butyric), ammonia and some carbonates. Typical acetic acid level in blowdown is 300 – 600 ppm. Ammonia in the DSG incoming water is about 20 – 50 ppm. The corrosion protection rendered by the previous chemical treatment program used a low volatility neutralizing amine to neutralize all the acid species and elevate the water pH to 8.0 – 9.0. Ammonia, an alkaline compound has the same effect as the amine. It is however, much more volatile.

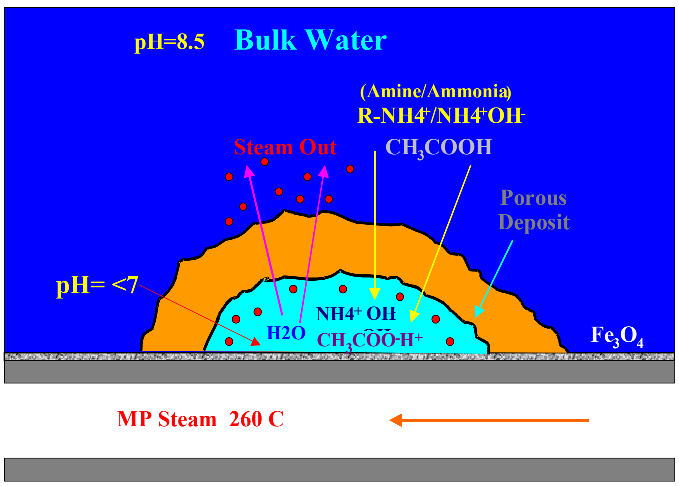


Figure 3: Under-deposit Concentration Cell–Low pH Corrosion.

When bulk water at alkaline pH enters the porous deposit, compounded with the high % of evaporation rate taking places at the upper section of the bundle, the condition for setting up concentrated cells under the deposits (like a miniature boiler) prevails. The highly volatile ammonia will vaporize and travel with the steam, upsetting the base/acid ratio in the water phase. This can result in a localized low pH environment, which is highly corrosive towards magnetite and carbon steel; thus ultimately leads to tube leak.

The conditions favorable for under-deposit concentration effect to take place are as follows:

- Bulk water temperature is approaching boiling point, and
- High heat flux (heat absorbed per unit area) on the tubes surfaces.

Both of these conditions prevail when the % evaporation rate in the bulk water is high. This explains why the tube leaks are found only at the upper section of U-tubes bundle. In the case study discussed previously, the MP steam reboilers in Plant A with lower % evaporation rate did not have any tube leak with the same amine treatment program.

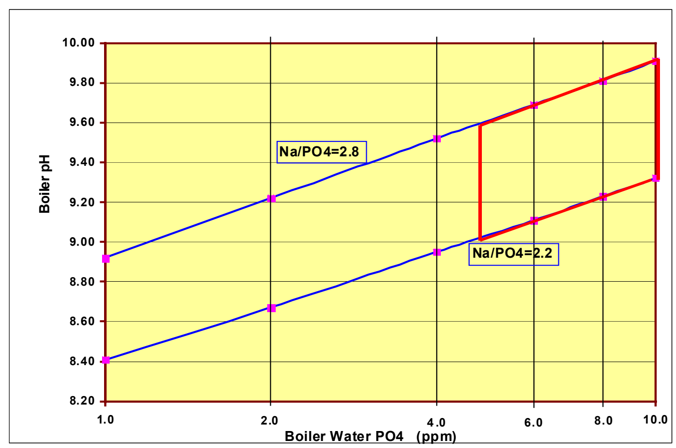
Treatment Method: pH Buffering

The Na and Ortho-PO_4 chemistries are controlled based on coordinated pH/ PO_4 coordinated as shown in Chart 3. The recommended control limits are 5–10 ppm Ortho-PO_4 and pH at 9.0-9.8. This involves two-dimensional control to keep the data points in the control box. Conformance to the coordinated pH/ PO_4 control range (Na/PO_4 molar ration between 2.2 –2.8) ensures no free caustic the DSG blowdown.

Phosphate, PO_4 provides corrosion protection by buffering and neutralizing excess alkalinity or acidity, and precipitation of hardness intrusion into the reboilers system.

Chart 3: Phosphate /pH Coordinate – Chemical Treatment for DSG Reboilers.

Recommended Coordinated pH/PO_4 Control Box



At pH below 8.0, the passive magnetite film, which protects the carbon steel, will be destroyed and as such, significantly increases the general corrosion rate.

The formation of the protective layer of black iron oxide, magnetite is as follow:

$$3Fe + 2H_2O \implies Fe_3O_4 + 4H_2$$

Magnetite will act as a barrier between the steel surface and water to inhibit further corrosion. The stability of the magnetite layer formed is highly dependent on the pH of the boiler water. Both high acid and high caustic levels lead to corrosion. Highest stability and protection are maintained in the 8.5 to 11 pH range. This is the primary reason for maintaining alkaline boiler water conditions.

The basis for the pH/PO_4 control is the ability of different forms of phosphate to consume or add caustic as the phosphate shifts to proper form.

Results

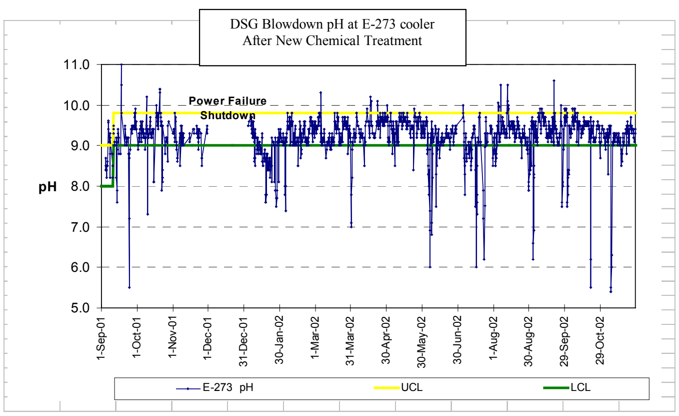
pH/PO_4 Coordinated: Improvement and Benefits

- The stronger buffer (pH control 9.0 –9.8) in DSG blowdown means that the water chemistries are less sensitive to any pH swing due to changing organic acids load in the feed water. This will provide overall improvement in corrosion protection.
- Eliminates under-deposit localized low pH corrosion with the use of non-volatile high Na/PO_4 molar ratio base products. It is far more cost-effective than amine at the same DSG blowdown pH control.
- Incorporates synthetic polymeric dispersant to reduce iron deposition by improving iron rejection via blowdown.

These benefits ultimately translate not only to extended DSG reboiler run length between cleaning, but also a reduction in equipment maintenance cost.

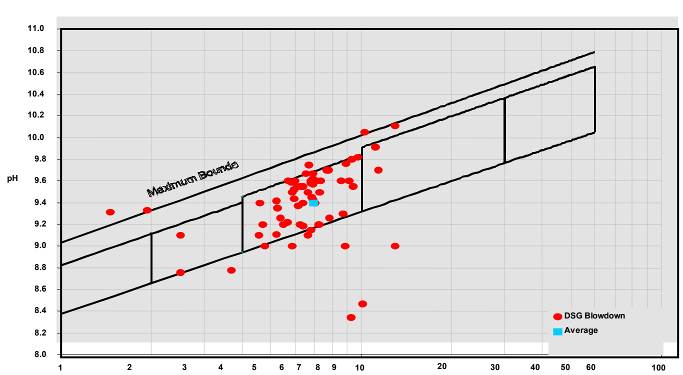
As shown in Chart 4, the pH control is more stable in the range of 9.0 – 9.8. The pH depression below the target limit has been reduced.

Chart 4: pH Trend at DSG Blowdown after the New Treatment Program at the Ethylene Unit Example.



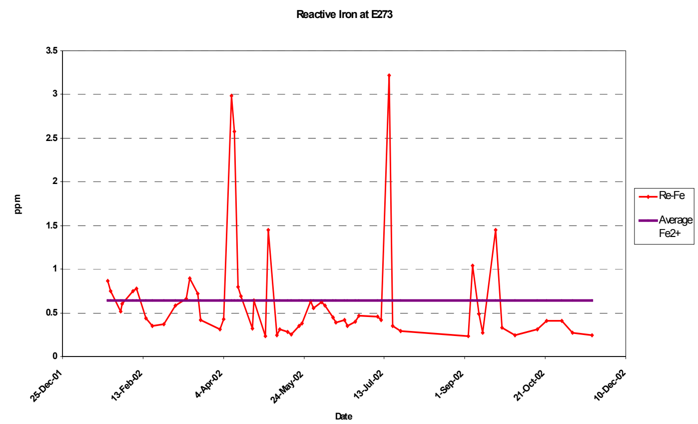
Since the new DSG program is using the coordinated pH/PO4 approach, the control of pH within 9.0 – 9.8 and PO4 within 5 – 10 ppm is very essential. Chart 5 shows the Coordinated pH/PO4 control for the new DSG chemical treatment program.

Chart 5: Coordinated pH/PO4 Control in DSG Blowdown After New Treatment Program at the Ethylene Unit Example



The most important key performance indicator of the new program is the reduce corrosion and iron fouling rates by monitoring iron loading at the blowdown cooler, E-273, and the tubes failures history. As shown in Chart 6, the iron loading in DSG dropped from 1.6 ppm to below 0.6 ppm. This is more than 60% of iron reduction.

Chart 6: Iron loading of pH/PO_4 coordinated program.



The following two tables show the historical tubes leakage before and after the implementation of pH/PO_4 coordinated chemical treatment.

Table 1: DSG Reboilers Tubes Leakages History Before the pH/PO_4 Coordinated Chemical Treatment.

Date	E-270A	E-270B	E-270C
Feb 94	Under Brand-X Treatment Program.	Under Brand-X Treatment Program.	Under Brand-X Treatment Program.
Dec 94	Brand-B Amine Program Start.	Brand-B Amine Program Start.	Brand-B Amine Program Start.
1st Mar 95	46 tubes leak within 390 days. Mostly top section leaks.		
19th Oct 95		133 tubes leak within 600 days. Mostly middle section leaks.	
7th Feb 96		Retubed E-270B bundle.	
24th May 96	82 tubes leak within 300 days.		
24th July 96			61 tubes leak 480 days. Mostly middle section leaks.
1st Dec 96		10 tubes leak within 190 days.	
9th Dec 96	9 tubes leak within 162 days. About 14% plugged. Exceeded 13%.		
19th Jun 97		16 tubes leak within 192 days.	
17th Mar 98	116 days tubes leak within 414 days. Total tubes leak was 245 (26%).		
26th Jun 98	Retubed E-270A.		
6th July 98		30 tubes leak within 111 days.	

17th July 98			9 tubes leak within 393 days.
24th Dec 98	247 tubes leak within 179 days.	22 tubes leak within 160 days.	
16th Feb 99	60 tubes leak within 45 days. 32% tubes plugged.		8 tubes leak within 54 days.
21st Oct 99	12 tubes leak within 247 days.		
30th Oct 99		29 tubes leak within 256 days.	
9th Feb 00	Retubed E-270A.		
22nd Feb 00			3 tubes leak within 124 days.
31st May 00		7 tubes leak within 98 days.	
28th Oct 00	40 tubes leak within 256 days.		
15th Nov 00			121 tubes leak within 168 days.
29th Jan 01	45 tubes leak within 90 days.	110 tubes leak in total. 12 tubes leak within 53 days.	
3rd May 01	27 tubes leak within 80 days.		
8th Sept 01		9 tubes leak within 210 days.	
15th Sept 01	10 tubes leak within 130 days.		

Table 2: DSG Reboilers Tubes Leakages History After the pH/PO_4 Coordinated Chemical Treatment.

Date	E-270A	E-270B	E-270C
20th Sept 01	Start Brand-B pH/PO_4 coordinated program.	Start Brand-B pH/PO_4 coordinated program.	Start Brand-B pH/PO_4 coordinated program.
1st Nov 01			Retubed E-270C.
27th Jan 02		1 tube leak within 120 days.	
5th Feb 02	8 tubes leak within 110 days.		
20th Mar 02			Open. No leak after 140 days.
10th Jun 02		Open. No leak after 150 days.	
25th July 02	3 tubes leak within 180 days.		
28th Nov 02			Open. No leak after 380 days.

From Table 1 and Table 2, it can be observed that before the implementation pH/PO_4 coordinated chemical treatment, the average tubes leaked between 1995 to 2001 was 158 tubes per year. A new bundle would leak within six months period.

After the implementation of the pH/PO_4 coordinated chemical treatment, the average tubes leaked between 2001to 2002 was only 12 tubes per year. A new bundle is free of any leak after running for more than one year.

Conclusions

In summary, the following factors have contributed the frequent DSG reboilers' tubes failures at the Ethylene unit example:

- High % of low pH control in the blowdown.
- High % of water evaporation rate occurring at the upper section of the tubes bundle promotes under-deposit concentration effect. This in turn leads to the formation of localized low pH, and ultimately tubes leak.
- Heavy iron and hydrocarbon deposits offer sites for under-deposit low pH corrosion.

The more robust pH/PO_4 coordinated treatment has managed to tackle the above three main operating challenges; thus, prolonging the reboilers' tubes life span.

References

[1] Mustaffa, Z; Woo, P.Y; Siong, W.H; Lee, C. 2002. *Summary of Dilution Steam Improvement*, Chemcials Treatment Specialist Malaysia.

[2] Lee, S.H; Cheah, P.S.; Kolmetz, K.K. 2000. *Challenges in a Dilution Steam Generator System.* The 5th Regional (ASEAN) Olefins Conference, Johor Bahru, Malaysia.

[3] Nolidin, C.D. 2002. *Ethylene Unit Dilution Steam Generator System: Challenges and Strategic Improvements.* Training Presentation, Titan Petrochemical Technical Department, Malaysia.