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Corrosion control strategies for hydrotreaters and fluidized catalytic cracking unit

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ABSTRACT

Hydrotreaters and Fluidized catalytic cracker (FCC) units play a major role in modern refiners for meeting the stringent fuel specification and upgrading the bottom of barrel respectively. Corrosion in a refinery is not only restricted to primary crude units but also prevalent in these secondary units. Instances of severe corrosion have caused unnecessary unit shutdown and at times leakage/fire.

Overhead aqueous phase and under deposit corrosion has always been a concern in secondary units. Factors like feedstock quality, corrosive species and operational severity govern the intensity and location of corrosion in hydrotreaters and FCC. The corrosion is aggravated by ammonia and Hydrogen sulfide which is being abundantly generated in these units.

This paper will discuss on the type of corrosive species, corrosion prone location, mechanism, monitoring practices and corrosion mitigation strategies along with case studies.

Keywords: Contaminants, under deposit corrosion, water washing, corrosion inhibitor.

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INTRODUCTION

The significance of hydrotreaters and Fluidized Catalytic Cracking Units (FCCU) is ever growing in refinery complex to meet the desired objectives. Hydrotreaters purify the refinery products by reacting hydrocarbon containing heteroatoms with hydrogen. FCC is the most effective unit for heavy gas oil conversion to lighter components. Owing to the major role of these two units in a refinery complex, the downtime should be as short as possible.

The reliability of hydrotreaters and FCC is often challenged by potential corrosion issues owing to change in feedstock quality and operational philosophy. In the context of corrosion, the financial impact of loss of production is a significant factor in the risk management of corrosion in refineries. A case study published by the Joint research Centre[1] indicates that out of the corrosion related accident which were recorded; almost 20% occurred in Hydro-treatment units and 5% in FCC units (Figure 1). 5% instances of corrosion related accidents in FCC should not be neglected since downtime of the unit eventually reduces the primary unit feed rates.

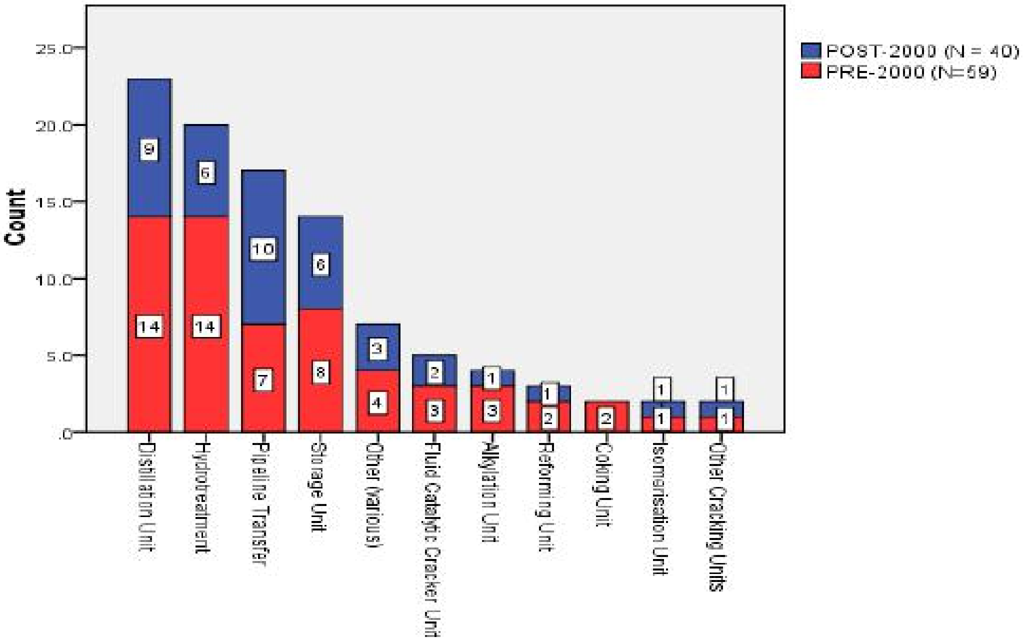

Figure 1: Corrosion related accidents

Aqueous phase corrosion is the most common type of corrosion experienced in secondary units. This paper will address the dew point and under-deposit corrosion related issues in the hydrotreater and FCC. This paper will also discuss the key corrosive species, mechanism, contributing factors and mitigation plans. Through the discussion, the significance of chemical solutions has also been emphasized with necessary supporting case studies.

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CORROSIVE SPECIES

The major corrosive species which can cause potential corrosion in secondary units are Hydrogen Sulfide (H_2S), Hydrogen Chloride (HCl), Ammonium Bi-sulfide (NH_4HS), Ammonium Chloride (NH_4Cl) and Hydrogen Cyanide (HCN). The corrosive species are distinct to each other with respect to source, characteristics, reaction with metal surface etc.; hence the location of attack may vary from unit to unit. The most common contaminants present in the secondary unit feedstock are Sulfur, Nitrogen and Chloride which are the key sources for the above mentioned corrosive species. Depending on the amount of these contaminants coupled with severity of the unit operation, the corrosion problem aggravates in the secondary units. Hence it is better to understand the corrosive species and its significance in Hydrotreaters and FCC.

- *Hydrogen Sulfide (H_2S):*

Abundant H_2S is generated in Hydrotreaters and FCC from Sulphur present in the feedstock. Wet H_2S corrosion or Hydrogen Sulfide corrosive attack refers to the corrosion of carbon steel in the presence of aqueous hydrogen sulfide (H_2S).The wet H_2S corrosion is a function of the concentration of the acid found in the aqueous phase in a system. The higher the concentration of H2S in the water, the more corrosive it becomes. Hydrogen sulfide solubility in water increases with increase in pH and decrease in temperature. The corrosion product formed from the corrosion of hydrogen sulfide and a metal is a metal sulfide, such as iron sulfide (Equation 1)

$$\mathbf{H_2S + Fe\,(H_2O) \rightarrow FeS + H_2\uparrow} \qquad \text{------------ 1}$$

Hydrogen sulfide attack is characterized by a generalized or uniform type of corrosion attack which produces large volumes of corrosion products. Hydrogen sulfide attack is generally most severe at temperatures below 170°F (75°C) which can typically prevail in Stripper/Stabilizer/fractionator overhead system of Hydrotreaters and FCC.

- *Hydrogen Chloride (HCl):*

Hydrogen chloride finds its source from hydrolysis of magnesium, calcium and sodium chloride present in the crude oil. Being a lighter gas, HCl distills to the overhead and tends to solubilize in water at higher temperature causing lower pH environment in the dew point region favorable for corrosion. Hydrochloric acid (HCl) cause both general and localized corrosion. The reaction with metal surface is shown below (Equation-2, 3, 4) and at elevated pH, hydrogen sulfide further comes into play forming Iron Sulfide (FeS);

$$\mathbf{2HCl\,(H_2O) \rightarrow 2H^+ + 2Cl^-} \qquad \text{------------- 2}$$

$$\mathbf{2HCl + Fe\,(H_2O) \rightarrow FeCl_2 + H_2\uparrow} \qquad \text{------------- 3}$$

$$\mathbf{FeCl_2 + H_2S\,(H_2O) \leftrightarrow FeS\downarrow + 2HCl} \qquad \text{------------- 4}$$

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Unlike crude unit overhead, secondary unit typically has less concentration of hydrogen chloride and following are possible routes for chlorides to hydrotreaters and FCC.

1. Inorganic Chlorides from Crude: HCl generated from the hydrolysis of salt slipped from the desalters not only land in overhead but also land in the side cuts varying from Naphtha to Diesel which eventually impacts the respective hydrotreaters. Heavier streams like gasoil and atmospheric residue tend to have higher amounts of sodium chloride which hydrolyze at FCC operating temperature. This is further aggravated by addition of caustic.

2. Organic chlorides from Crude: These chlorides find its source from the organic solvents added in the crude and hydrolyze in the crude temperatures eventually landing in different cuts of the distillation column. There can also be organic chlorides in the gasoil & residue streams feeding the FCC and hydrolyze at unit operating conditions.

3. Chlorides from other source: HCl injected for restoring the activity of CCR unit catalyst can cause chloride contamination in hydrotreater unit if recycle hydrogen gas is used from the same source. Improper HCl guard design and inadequate guard bed are the key reasons for HCl contamination from these sources[2]. In FCCU, chlorides can also source from Zeolite catalyst which is used as binders and depending on operating conditions; these chlorides can land in the fractionator section[3].

➢ *Ammonium Chloride (NH_4Cl):*

The source for ammonia is nitrogen present in the feedstock of hydrotreaters and FCC. The hydrogen chloride source has been explained in the above section. Ammonium chloride is a salt which is formed by the reaction of hydrogen chloride gas and ammonia gas (Equation 5 and 6). The salt is formed between a strong acid and a moderately weak base. The salt has the ability to absorb water (hygroscopic nature) from steam at temperatures above the dew point of water. Eventually the under deposit promotes electrochemical cell and reactions continue to happen as per Equation 3 and 4.

$$\mathbf{NH_{3\,(VAPOR)} + HCl_{\,(VAPOR)} \rightarrow NH_4Cl_{\,(SOLID)}} \qquad \text{------------- 5}$$

$$\mathbf{NH_4Cl\ (H_2O) \rightarrow NH_3\uparrow + HCl} \qquad \text{------------- 6}$$

The damage can be general or localized corrosion, often pitting, normally occurring under ammonium chloride deposits, in absence of a free water phase.

➢ *Ammonium Bi-sulfide (NH_4HS):*

Ammonium Bi-sulfide is a product formed due to gaseous phase reaction of ammonia and Hydrogen sulfide which are abundantly generated in hydrotreaters and FCC. Ammonium bisulfide attack is very similar to simple sulfide corrosion attack. This is shown by Equation 7. At lower temperatures the presence of bisulfide ion accelerates generalized sulfide attack. Eventually the under deposit promotes electrochemical cell and reactions continue to happen as per Equation 1.

$$\mathbf{NH_{3\,(VAPOR)} + H_2S_{\,(VAPOR)} \rightarrow NH_4HS_{\,(SOLID)}} \qquad \text{------------- 7}$$

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$$2\ NH_4HS\ (H_2O) \rightarrow 2NH_4^{+} + 2HS^{-} \qquad \text{------------ } 8$$

NH4HS salt deposits lead to under deposit corrosion and fouling. The salts are not corrosive unless they get hydrated.

- *Hydrogen Cyanide (HCN):*

Hydrogen cyanide forms due to cracking of nitrogen compounds in FCC operating conditions. Hydrogen Cyanide corrosion leads to hydrogen blistering. The basic corrosion process starts with Ammonium bisulfide formation (Equation 7) and dissociation into Ammonium and bisulfide ion (Equation 8). These ions react with Fe to form Iron sulfide layer (Equation 1) and in this process molecular Hydrogen is liberated. With presence of cyanides, the brittle FeS layer is destroyed there by forming an Ammonium Ferro-Cyanide complex (Equation 9) which is accomplished by hydrogen blistering.

$$FeS + 6NH_4+ + 6CN^{-} \rightarrow (NH_4)_4Fe\ (CN)_6 + (NH_4)_2S \qquad \text{----------- } 9$$

CORROSION PRONE LOCATION

Depending on the corrosive species, operating conditions and availability of water, corrosion takes places in different locations of secondary units and below is the mapping of corrosion locations in hydrotreaters and FCC (Figure 2, 3 & 4):

Corrosive Species	Type of Corrosion	Unit and Location
Hydrogen Sulfide	Wet H2S attack	Hydrotreater and FCC strippers/Splitters/Stabilisers/Fractionators overhead system
Hydrogen Chloride	Dew Point Acidic	Hydrotreater and FCC strippers/Splitters/Stabilisers/Fractionators overhead system
Ammonium Chloride	Under-Deposit	Hydrotreater REAC and High pressure separators. FCC Main fractionator overhead system and heavy gasoline section.
Ammonium Bi-Sulfide	Under-Deposit and Wet H2S attack	Hydrotreater REAC and High pressure separators. FCC Gas plant overhead receivers
Hydrogen Cyanide	Hydrogen Blistering	FCC Main fractionator overhead and Wet gas compressor inter-stage coolers

Figure 2: Corrosion location mapping in Hydrotreaters and FCC

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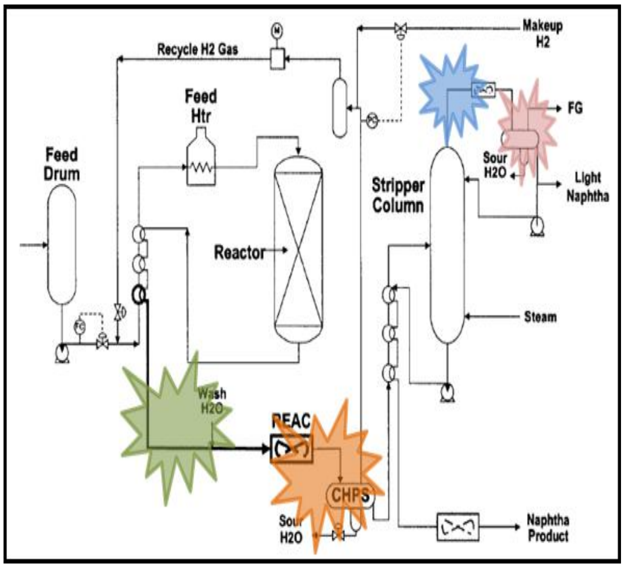

Figure 3: Schematic of hydrotreater with corrosion prone location[4]

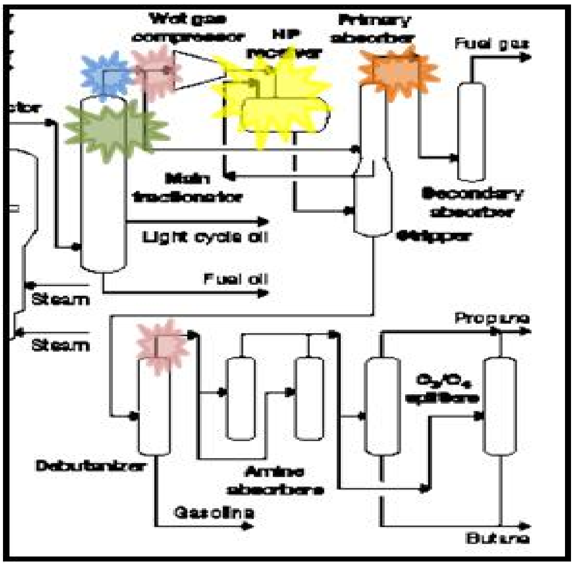

Figure 4: Schematic of FCC gas plant with corrosion prone location

CORROSION CONTROL STRATEGIES

Corrosion control strategies can be a combination of change in operating conditions, dilution of acidic species or use of chemicals. Below are some of the corrosion control strategies with respect each corrosive species:

- Minimizing sources of HCl:

  As indicated earlier the key source for corrosive species in secondary unit are Sulfur, Nitrogen and chloride present in respective unit feedstock, however sources like Sulfur and nitrogen cannot be mitigated. But there is scope for reduction in chloride source in hydrotreaters/FCC and below is couple of the mitigation plans to reduce the HCl sources.

  1. Effective desalting helps reduce salt slippage and hence reduction in HCl to crude column overhead and side cuts feeding the respective secondary unit. Use of “Multi-functional Emulsion breaker” can help alleviate desalter issues while processing challenging crude. By this plan, one can reduce the overall HCl concentration in the feedstock to contain dew point acid and ammonium chloride under deposit corrosion.

  2. Depending on the hydrolysis pattern of Organic chlorides, HCl can also distill in the atmospheric and vacuum side cuts like Diesel and gasoil. This aggravates when specific crude containing organic chlorides are processed and experience indicates chloride loading in Diesel and Gasoil hydrotreaters. Some refiners were able to manage such phenomena by provision of effective water washing of the Diesel and gasoil side cut rundown so as to reduce the fouling and corrosion in respective hydrotreater REAC.

  3. Coupled with effective desalting, reduction in caustic addition will also reduce Sodium chloride (NaCl) loading in the atmospheric residue feeding the Resid FCC (RFCCU).

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Depending on the temperatures, the ammonium chloride not only deposits in the overhead system but potentially deposits in the heavy gasoline section of main fractionator posing corrosion and fouling threats.

4. Reduction of chlorides from other sources is also key in mitigating corrosion caused by HCl. Monitoring the efficacy of HCl guard in CCR and limiting the use of recycle hydrogen gas can put a check on this contamination. Similarly in FCC, optimizing the reactor-regenerator operations to ensure minimal catalyst carry over to fractionator is critical in limiting the chloride contamination from Zeolite catalyst.

- Water washing:

Following are the best practices of water washing in hydrotreaters and FCC with respect to potential corrosive species:

1. Wash water can be injected in the overhead system of splitters, strippers, stabilizers and fractionator to dilute the acidic species present in hydrotreaters and FCC. Water washing is necessary to prevent fouling and corrosion of effluent heat exchangers by removing ammonium chloride and ammonium bi-sulfide salt deposits. Injection point and frequency of water washing is critical for such hydrotreater loops. To be effective, the water wash should be located upstream from the point where wet ammonium chloride deposits are expected to form. Figure 5 & 6 show the typical wash water scheme in hydrotreater and FCC.

2. Wash water quality: It is always preferred to have a fresh wash water source for REAC washing purpose. For main fractionator one can adopt a co-current or counter-current washing technique with provision of fresh water addition in main fractionator overhead. Based on industry best practices, following should be the quality of the wash water; (pH: <8, Oxygen content: <25 ppb, Chlorides: <50 ppm, Total Dissolved solids: <100 ppm, Free cyanides: 0 ppm).

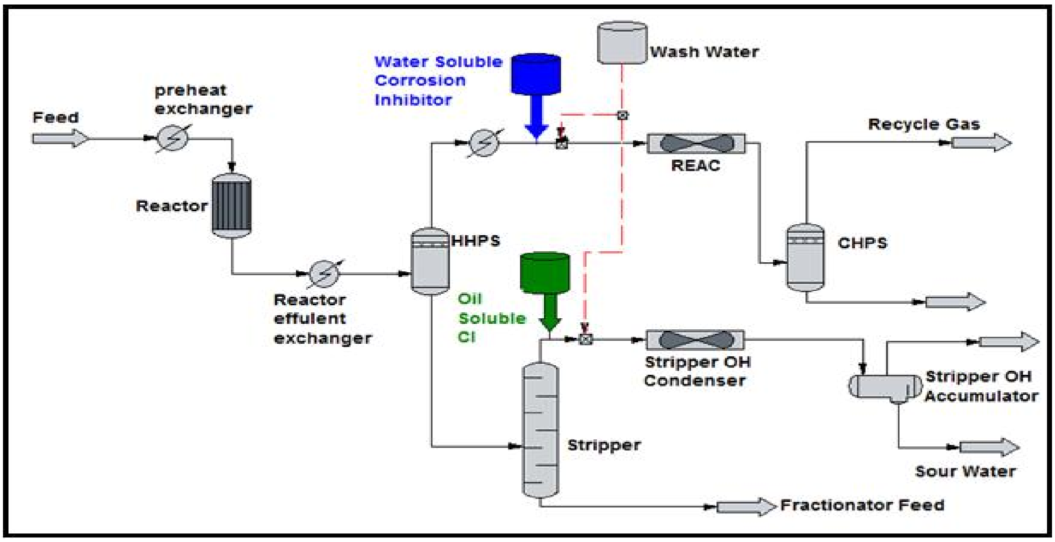

Figure 5: Wash water and chemical injection scheme for Hydrotreater

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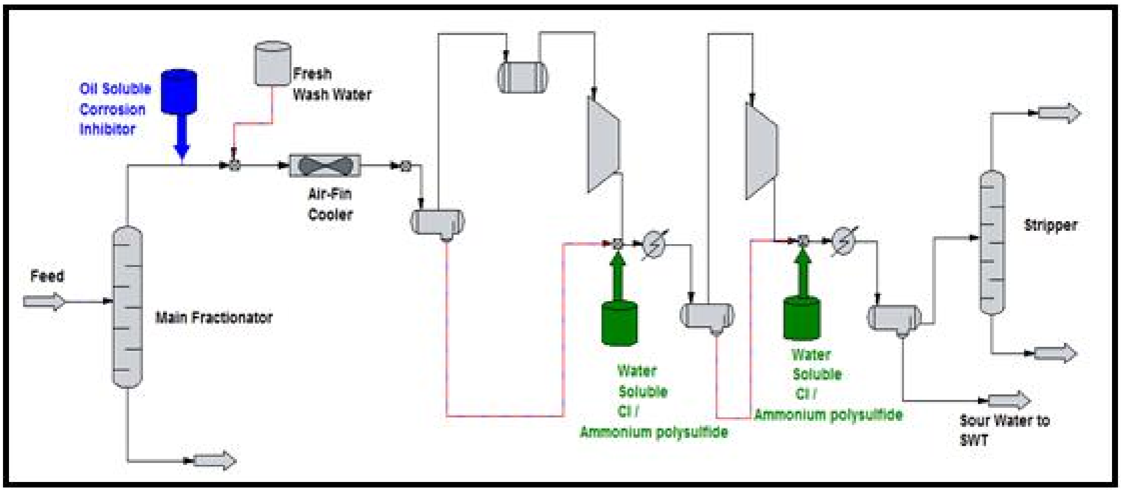

Figure 6: Wash water and chemical injection scheme for FCC

- Chemical Solution:

For many years, chemical solutions have been the preferred technique for corrosion control. Chemicals include use of corrosion inhibitors and Neutralizing amines.

1. *Oil soluble Corrosion inhibitors*: Filming amine or corrosion inhibitors are injected in the desired location to form a tenacious film on the metal surface. Oil soluble inhibitors are used in location where the bulk condensed phase is hydrocarbon. Oil soluble inhibitors have polar head which sticks itself to the metal surface and hydrocarbon soluble tail which typically repel the water containing corrosive species. Such a mitigation plan will be effective in locations which is more prone to wet H2S attack like strippers, stabilizers, splitters and fractionators overhead of hydrotreaters and FCC. For effective performance provision of injection quill and slipstream is recommended. Figure 5 & 6 show the injection location of oil soluble corrosion inhibitors.

2. *Water soluble corrosion inhibitors*: Water soluble based chemistry is preferred in location where bulk condensed phase is water. These are more effective in protecting the metal surface from electrochemical cell formed under the deposits of ammonium chloride and ammonium bi-sulfide salts. Water soluble inhibitors are typically added along with wash water in locations like REAC (hydrotreater) and wet gas compressor discharge (FCC). Figure 5 & 6 show the injection location of oil soluble corrosion inhibitors.

3. *Ammonium poly-sulfide (APS):* It is a cyanide scavenger which reduces cyanide ion concentration by formation of thiocyanate (as shown by Equation 10). The complex formed has minimal interaction with FeS layer there by reducing the hydrogen blistering phenomena. It is recommended to inject APS in the wash water added in the wet gas compressor inter-sage and discharge coolers. APS has its own limitation and requires some precaution for continuous addition.

$$\mathbf{CN^- + S_x^{2-} \rightarrow SCN^- + S_{(x-1)}^{2-} + 2e^-} \qquad \text{------------ 10}$$

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- Other strategies:

Other stratergies include use of suitable metallurgy with respect to the corrosive species and the design. As per the API standards 571 alloys like 300 series, SS duplex, Inconel and titanium are recommended for better corrosion resistance from the corrosive species. Monitoring plays a key role in sustaining the reliability of an unit from corrosion point of view. Based on industry standards monitoring practices like periodical thickness survey, analysing boot water for corrosive species, pressure survey across REAC and estimation of salting points will help to keep a check on the corrosion.

CASE STUDY[5]

A Vacuum gasoil hydrotreater in Asia Pacific was experiencing corrosion and fouling issue in the Reactor Effluent Air Coolers (REAC). The issue was severe to an extent that plant throughput was forced to reduce and desired temperature was not achieved in the air fin cooler outlet. High iron content in the boot water analysis indicated severe under-deposit corrosion causing reliability issues for the plant. Detailed investigation concluded that fouling and corrosion was majorly due ammonium bi-sulfide under deposition (Graph1). Moreover, it was observed that lower wash water (<2% BFW) added in the upstream of REAC aggravated the problem.

Eventually based on detailed investigation, wash water was increased to 4% and "*water soluble corrosion inhibitor*" was injected in the wash water line going to upstream of REAC (Figure 7). Post injection of the corrosion inhibitor significant improvement was observed in terms of corrosion rates (as indicated by boot water iron, Graph 2) and fouling severity (as indicated by the AFC outlet temperature, Graph 3). There was a significant improvement in the run length and the hence the treatment continued for a longer period.

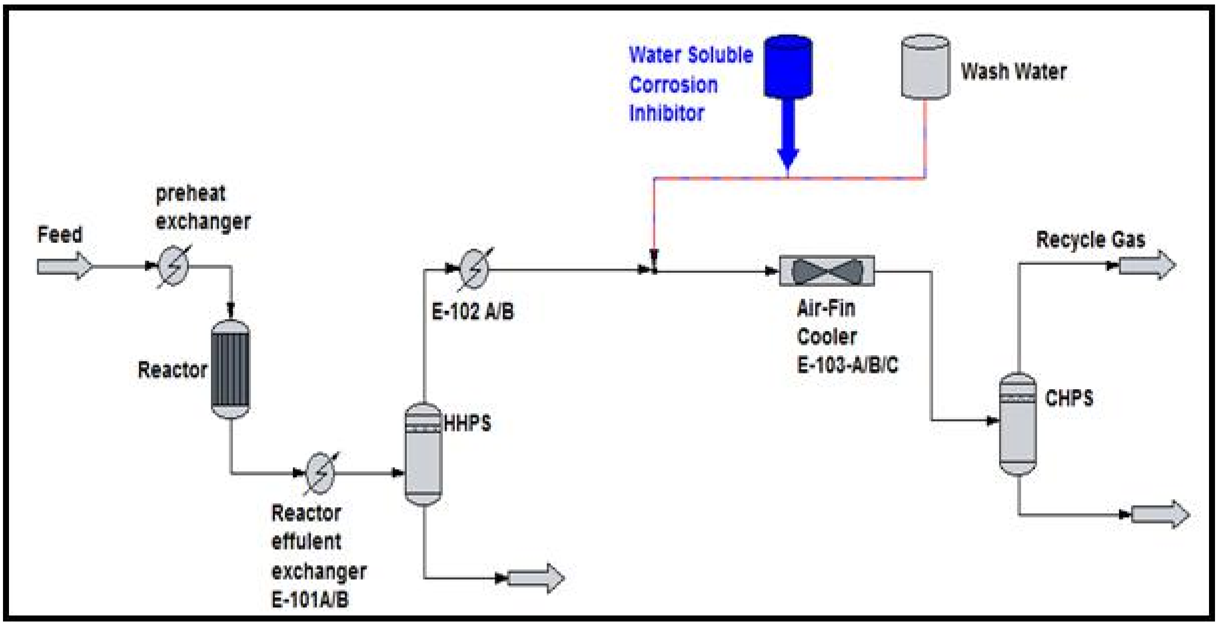

Figure 7: Injection of water soluble corrosion inhibitor in VGO HT REAC

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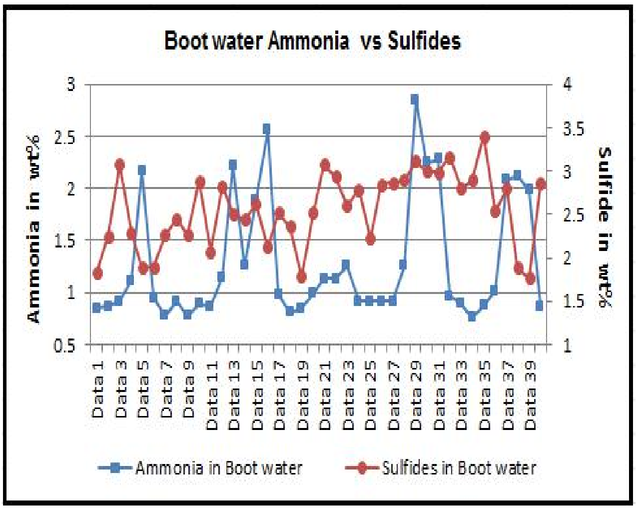
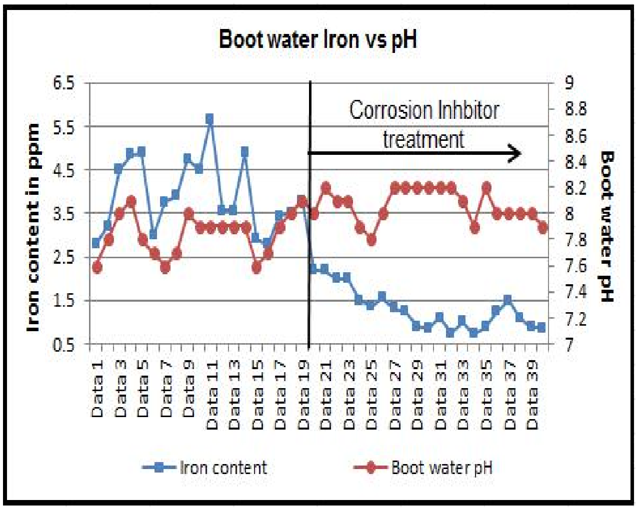
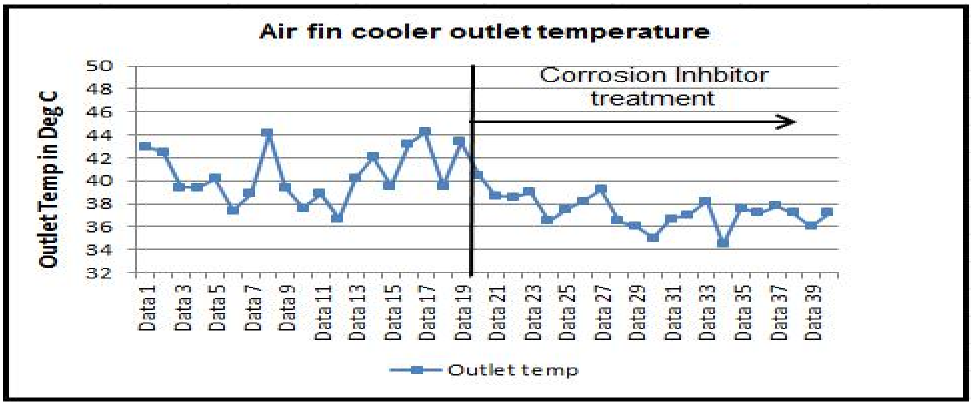


Graph 1: HP separator Boot water Ammonia and sulfides



Graph 2: HP separator Boot water Iron vs pH



Graph 3: Reactor effluent air coolers outlet temperature

CONCLUSION:

Corrosion will remain a challenge to refiners and the important step towards mitigating corrosion is to have a good risk assessment plan in place. Combination of different mitigation strategies along with use of appropriate chemical technology will help sustain unit reliability in Hydrotreaters and FCC unit.

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4 Hydrotreater schematic retrieved from “Design Considerations to Minimize Ammonium Chloride Corrosion in Hydrotreater REAC’s”, Paper 01543, NACE corrosion 2001

5 Data shown in case study is actual treatment conducted by Dorf Ketal in VGO hydrotreater REAC section

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