CORROSION MITIGATION OF THE FURNACE FEED SATURATOR SYSTEM OF GAIL PATA ETHYLENE PLANT

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ABSTRACT

The petrochemical sector plays a vital role in the functioning of virtually all key sectors of the economy which includes agriculture, infrastructure, healthcare, textiles and consumer durables. Polymers provide critical inputs that enable other sectors to grow. India's petrochemical industry has been one of the fastest growing industries in the Indian economy. In order to ensure smooth and uninterrupted operations of process plants, it is imperative for field operators, control engineers, and designers to be corrosion conscious as lines and component fittings undergo due to corrosion.

This paper gives a comprehensive review of flow accelerated corrosion problems faced in the newly designed furnace feed saturator system and its successful mitigation in the 450000 MT per year ethylene plant-2 of GAIL (India) Limited, Pata, Uttar Pradesh, India. The chemistry of corrosion mechanism has been examined with the various types of corrosion and associated corroding agents in gas cracker unit-2. Factors affecting each of the various forms of corrosion such as furnace feed composition, circulating and make up water quality and blow down rate are also discussed. Ways of mitigating this menace with current technology of low costs have been discussed. This paper brings out the importance of the principles of corrosion that must be understood in order to effectively select materials and to design, fabricate, and utilize metal structures for the optimum economic life and safety of facilities in feed saturator operations.

Key words: Feed Saturator; Corrosion; pH; Neutralizer; Blow down, Iron content.
INTRODUCTION

FURNACE FEED SATURATOR SYSTEM (FIGURE 1)

Furnace feed saturator system is the latest and economic design for the ethylene plant. It is used to saturate the preheated hydrocarbon (ethane/propane) furnace feed to the desired steam to hydrocarbon ratio by means of counter current contact with preheated circulating water. A steam to hydrocarbon balance calculator is provided to adjust the desired steam to hydrocarbon ratio. The feed saturator circulation heaters heat the circulating water to a temperature of 140 °C using low pressure steam. The system receives water from the dispersed oil extraction unit (DOX) via the low pressure water stripper after removal of acid gases (CO₂, SO₂ and H₂S) and styrene to reduce fouling and corrosion of the system. Angle iron decks of 20 rows are utilized in the tower to combat fouling. Around 5-10 wt. % of the process water fed to the feed saturator is removed from the system as blow down to prevent accumulation of non-volatile compounds. Corrosion inhibitor is injected into the LP water stripper bottoms to adjust the pH of the feed to the feed saturator and to prevent corrosion. Anti-foulant is injected into the LP water stripper bottom to prevent fouling of the feed saturator system.
MAJOR ADVANTAGES

- Lower capital and maintenance cost compared to the conventional dilution steam generation system.
- Medium pressure (MP) dilution steam drum and associated exchangers are eliminated and plant MP header system is eliminated.
- Simple operation utilizes LP steam heating of circulating process water, which would otherwise be wasted as mere blow down- contributing a major resource utilisation.

MAJOR CONCERN

- Steam to hydrocarbon ratio for individual furnaces cannot be changed. It will always maintain equal steam to hydrocarbon ratio for each furnace under different operating conditions.

MAJOR CHALLENGE

- Mitigation of corrosion and fouling of the system.
CASE STUDY

PROBLEM DESCRIPTION

New gas cracker unit (GCU-2) was successfully commissioned in January-2016 and the furnace feed saturator system (latest design by M/S. Technip, USA and first ever in India) was commissioned in May-2016. From August-2016 onwards, it had been continuously observed that the average iron content of the feed saturator blow down water was in the higher range (5.0 ppm to 6.0 ppm) against the specification of 0.5 ppm maximum. In spite of maintaining feed water quality, operating conditions etc. as per design, the iron content in the blow down water did not improve.

The increase in the iron content may lead to internal damage, thinning of the metal thickness of the vessels, pipes and heat exchangers, thereby disrupting the entire process operation and also increasing the chances of material failure.

Eventually this would lead to total plant shutdown; hence a proper solution of the problem was mandatory.

INITIAL TROUBLESHOOTING

Sample analysis of the feed saturator blow down water revealed that the pH of the feed saturator blow down water was in the range of only 5.0 - 5.5(low), in spite of maintaining high pH (8.0 – 8.5) of the feed water from the LP water stripper bottom. In case of level deficiency in the feed saturator system, make up is done from the boiler feed water (BFW) system which also has a pH of 8.5 to 9.0. As the system cannot be run for long at this condition, it was initially planned to boost the pH value of circulating water to prevent corrosion.

To fix the problem, from November-2016 onwards, the corrosion inhibitor dosing rate (10 ppm approx.) at the LP water stripper bottom on trial basis. The pH of the feed water improved from 7.5 to 8.5 by this action. But the pH value and iron content of the blow down water did not improve as expected (3.0 – 4.0 ppm), as shown in figure-3.

Figure 3: Feed Water and Blow Down Water (pH vs., iron content)
ROOT CAUSE ANALYSIS

The probable causes contributing corrosion in the feed saturator system are described below:

(i) **Low pH of the circulating water**
- Presence of acidic gases in the feed saturator inlet stream, which when dissolved in water leads to formation of weak acids, thereby reducing the pH levels.
- Presence of gum precursors and unsaturated hydrocarbons like methyl acetylene, propadiene and 1,3 buta-diene leads to fouling which will eventually contribute to corrosion.
- The feed saturator water, in the form of steam mixes with the hydrocarbon feed at around 130°C. As the temperature rises, auto de-protonation of water increases and hence the pH value for the neutral zone decreases.

(ii) **Feed water and make up water poor quality**
- Low pH of feed water and make up water.
- Dissolved oxygen in the feed water and make up water.
- High iron content in the feed water.

(iii) **Low blow down rate**
- This would lead to build up of corrosive components and Iron content.

(iv) **Operating the column inappropriately**

<table>
<thead>
<tr>
<th>Component Name</th>
<th>Inlet Composition (Mol %)</th>
<th>Outlet Composition (Mol %)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>0</td>
<td>35.718</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>0.902</td>
<td>0.580</td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.139</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>75.988</td>
<td>48.846</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>0.622</td>
<td>0.400</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>20.794</td>
<td>13.367</td>
<td></td>
</tr>
<tr>
<td>Methyl acetylene, Propadiene</td>
<td>0.004</td>
<td>0.002</td>
<td>Contribute to fouling (present in recycle feed)</td>
</tr>
<tr>
<td>1,3 buta-diene</td>
<td>0.004</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Butene-1</td>
<td>0.065</td>
<td>0.042</td>
<td></td>
</tr>
<tr>
<td>Other C₄s</td>
<td>0.131</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>1.335</td>
<td>0.858</td>
<td></td>
</tr>
<tr>
<td>1 Pentene</td>
<td>0.005</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Carbon di oxide (CO₂)</td>
<td>0.010</td>
<td>0.006</td>
<td>Contributes to low pH</td>
</tr>
</tbody>
</table>

Total flow rate 116.05 Kg/Hr. 150.87 Kg/Hr.
High flow velocity of the circulating system

IDENTIFICATION OF ROOT CAUSE

Since the feed saturator system operating parameters are strictly maintained as per design values, and the makeup water quality and blow down rates are also closely monitored, the most likely contributing factors of corrosion are envisaged as:

- Low pH of the system
- High flow velocity of the circulating water

(i) Adverse effects of low pH in the feed saturator circulating water
- This water is fed to the hydrocarbon feed in atomised form to maintain steam to feed ratio between 0.3 to 0.35. Low pH in water ultimately results in low pH in the resultant steam + hydrocarbon mixture.
- At low pH, the evolution of hydrogen tends to eliminate the possibility of protective film formation so that steel continues to corrode. However, in alkaline solutions, the formation of protective films greatly reduces the corrosion rate. Corrosion damage can be very severe, including metal loss that is severe enough to cause leakage to the external environment, internal heat exchanger leaks, plugging of trays and other internals that interfere with tower operation and control and impair energy efficiency. This in turn decreases the effective thickness of the line. At this high internal temperature of 650°C and external temperature in the range of 1000°C, the probability of pipe failure due to corrosion is much more. This kind of line failure has been previously observed in the ethylene plant-1.
- Low pH also corrodes the internals of the feed saturator.

(ii) Adverse effects of high flow velocity of the circulating water Flow accelerated corrosion (Figure 4)

Flow accelerated corrosion (FAC) entails a process where a metal's protective oxide film dissolves when exposed to fast-moving water, steam or a combination of the two. For instance, in carbon steels, this phenomenon takes place under well-organized and specific parameters. Some of the major parameters include the following: pH, oxygen content, temperature, water velocity. This corrosion mechanism can take place whenever a metal that is susceptible is exposed to certain environmental conditions involving the parameters mentioned above. This often attacks carbon steel that carries pure wet steam or deoxygenated water. By nature, FAC decreases when pH increases.
FINDING PROPER SOLUTION

Since the flow velocity of the system mostly depends on the system design, it cannot be reduced too much to maintain design operating condition of the system. So controlling the pH levels of circulating water seems technically and economically feasible.

(i) **Solution A: Dosing of caustic solution (NaOH)**
It is the most economic option but discarded due to the deleterious effect of caustic embrittlement of the furnace system.

(ii) **Solution B: Dosing of neutralizing amines (corrosion inhibitor) at the feed saturator system**

Corrosion inhibitors are chemicals that react with the metal's surface or the environmental gasses causing corrosion, thereby, interrupting the chemical reaction that causes corrosion. Neutralizing amines are weak bases that are typically classified in terms of their "neutralizing capacity," "basicity," and "distribution ratio." Neutralizing amines typically applied in petrochemical plants are cyclohexylamine (CHA), methoxypropylamine (MPA), monoethanolamine (ETA), and morpholine.

After getting clearance from the technical service department, in March, 2017, one new pH neutralizer dosing pump (Nalco-5711) was installed at the PA 270 A/B suction (feed saturator recirculation pump), Figure-5. The initial dosing rate was adjusted to 5.0 ppm.
RESULT OF THE EXPERIMENT

Figure 6 shows that after implementation of the above scheme in March-2017, the pH of the water increased considerably (6.5 – 7.0), and the average Iron content of the blow down water reduced to 0.4 ppm. (Ref. 5)

- Corrosion Inhibitor dosing increased in LP water stripper.
- Dedicated FS Neutralizer dosing started at Feed Saturator.

Figure 6: pH data at LP Water Stripper and Feed Saturator after Neutralizer Pump Installation.
CONCLUSIONS

Flow accelerated Corrosion (FAC) is significantly harmful where the velocity of the fluid is more than 5-6 m/s and pH is low, which is the case here. Thus the corrosion awareness needed much more attention, followed by necessary action. Corrosion in the feed saturator might be very crucial and can cause severe damage. Hence, it should not be neglected. The GAIL team from the gas cracker unit successfully solved the above problem. After implementation of the above scheme, the average iron content of blow down water reduced from 6.0 ppm to 0.4 ppm and the feed saturator system has been running stable until today.

RECOMMENDATIONS

(i) The feed saturator system should be thoroughly inspected during the next shut down opportunity to evaluate the effects of corrosion.
(ii) A feed gas inlet online CO₂ analyser needs to be installed to monitor the quality of the feed gas.
(iii) Permanent neutralizing amine dosing system should be implemented.

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