An Exploration of Corrosion in the HF Neutralization Section at Linear Alkyl Benzene Production Plant

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ABSTRACT: *The Hydrofluoric acid (HF) is a catalyst for the production of linear alkyl benzene (LAB). In this research the corrosion and perforation in the overhead line of HF neutralization section in Bistoun Petrochemical Company (BPC), at Iran was investigated. The accumulation of sediment and under deposit corrosion has resulted in the perforation of the mentioned line. The main causes of failure were explored by visual checking, chemical characterizations, scanning electron microscopy (SEM), and X–ray fluorescence (XRF). The effects of process conditions, pipeline design, water content and oxygen amounts were studied. Corrosion and perforation in the line is based on the composition of the liquid or gases passing through the line and operating conditions. The reverse return of water vapors contaminated with KOH from relief gas scrubber to overhead line can accelerate the corrosion. Lastly, the suggestions have been proposed for trouble shooting, prevention from failure in the line and HF leakage.*

KEYWORDS: *Hydrofluoric acid (HF); HF neutralization section; Under deposit corrosion; Perforation; Trouble shooting.*

INTRODUCTION

Linear alkyl benzene plant produces LAB from the raw material of benzene and 1–dodecene with production capacity of 50,000 tons per year. The alkylation reaction is catalyzed by HF through Fridel–Crafts mechanism. Prior entering to the reaction section, the Olefin and benzene feed are treated to remove water and other impurities [1].

The HF is an enormously corrosive acid; therefore, polymer materials are generally used in industries with HF, and less consideration has been focused on the corrosion of metallic materials by HF. Still, in some industries such as LAB plants, the contact between HF and the metal is inevitable. Due to the corrosiveness, toxicity and hazards of HF, it should be neutralized in the unit. The acid containing vessels in the unit is made from carbon steel, but the locations that had water are made from Monel alloy because of resistance again corrosion. The influence of fluoride ion on the passivation of 316L –steel in acidic environment was considered by Li et al., and they found that a passivation film composed of fluorine is formed on the surface of steel [2]. The effect of F^- on passivation of –steel was not clear. But, some researchers found that fluoride ions can accelerate local corrosion in –steel by adsorbing at the grain boundary edge, and subsequently causing intergranular corrosion [3]. Therefore using resistant and appropriate materials such as Monel alloy is needed. Monel is an alloy of Iron, Nickel, and Copper.

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Pawel et al. established that nickel–based alloys showed a wonderful corrosion resistance in HF [4]. So Nickel can be important for corrosion resistance of 904L in HF environment. Mild steel is a comparatively low–cost material that is often successfully used for the storage and equipment containing hydrofluoric acid (70% HF). Uniform corrosion of HF equipment's is inevitable and normally ranges 0.5 mm per year [5]. There has been significant interest over the past several years in decreasing the hazard of operating HF alkylation Units, but little information has been published on the influences of operating circumstances [6].

The corrosion products were deposited on the inner wall line by continuous corrosion. Deposits can immerse the vapor or liquid fluid under sediment or limitation of the fluid flow in the line, which cause the line to be damaged. The gradual accumulation of sediments is likely to occur in dead zones and, in regions with low slope locations [7]. In pitting corrosion, the corrosion process begins in a localized and in areas in the line and gradually advances until it decreases the thickness of the line locally, finally the perforation and leakage of fluid from the line was happened [8–9].

The HF is a catalyst for alkylation reaction. All Vents' pumps, the outlets of pressure safety valves, acid vapors, and insoluble acidic gases from reaction section were released to the Acidic Flare Line. The output of the Acid Flare Line enters to the Liquid Knockout Drum (Fig. 1). The mixture of hydrocarbons specially benzene, water and acidic fluids in the flare line are gathered in the bottom of the drum and sampled on weekly. If the amount of water and impurities in the drain is high, its contents are sent to neutralization basin, otherwise the liquid contents of the knockout drum will be sent to the acid drain storage and after filling, its contents will be sent to spent acid storage drum. The vapors and acid gases from the top of the Liquid Knockout Drum are sent through the overhead line to the relief gas scrubber. The relief gas scrubber, has 5 trays that the acid vapors were enters from the beneath of the bottom tray into the tower, while the potassium hydroxide solution is poured from the top of the trays and reacted with acid and neutralized by the following reaction(Eq.(1)).

$$HF + KOH \rightarrow KF + H_2O + Heat \quad (1)$$

The Overhead line is made of carbon steel divided into two separate lines before entering the tower, these lines are near the tower and exposed to water vapors produced heat due to the above reaction (Eq.(1)). Therefore, based on the severe corrosion condition, the tube of this part is made of Monel.

The Overhead line of Liquid Knock out Drum experienced a major corrosion failure. After this happening, checkup investigation was increased on all of the process lines in acidic zone. In addition, more attention was given for the prediction of corrosion and the effect of process variables on such corrosion rates.

This paper describes the scale analysis; process condition, visual checking and water content to determine the effect of chemical corrosion and deposition. Lastly, with an exact checkup of the gradual leakage and corrosion in the overhead line, the solutions were suggested: that the maintenance and repair of equipment would be easier without contaminations and hazards. Employing the outcome of this investigation can be useful in related industries through the world.

EXPERIMENTAL SECTION

Analysis of the tube line materials

The chemical composition of the tube was quantified to approve that the tube adapt with the standards of ASME SA–106–grade B –steel. The chemical composition of the tubes was quantified by Thermo ARL, ARL 3460 Optical Emission Spectrometer (Thermo Scientific). According to the quantum analysis (Table 1) on the tubes, and the comparison with the standard ASME SA–106–grade B (Table 2), it was obvious that the tubes, is in agreement with the standard. As it can be seen from Tables 1 and 2, the standard does not straight refer to the amount of impurities in the steel.

Scale analysis

The corrosion is started from internal face and prolonged to the external surface of the overhead line, the chemical analysis of the porous scale in the internal surface is necessary. The ARL PERFORM'X model of XRF was used. A powdery deposition was extracted from the internal content of overhead line. The sediments were washed with warm water and the acid and some impurities were removed then the treated deposits were tested by XRF for characterization of the chemical composition of compounds. The main element of the scale was iron; other elements can be seen in the structure of scales as presented in Table 3.

Table 1: Chemical compositions of the studied overhead line (wt %).

Fe	Si	Mn	S	P	Cr	Ni	Mo	Cu
Base	0.17	0.45	0.009	0.015	0.28	0.22	0.09	0.33
Ti	Co	Al	Sn	Pb	As	Sb	C	V
0.024	0.0	0.018	0.011	0.003	0.007	0.08	0.27	0.003

Table 2: The chemical composition of the line based on the standard ASME SA–106–grade B.

	C	Si	P	S	Mn
Min	0.06	*	*	*	0.29
Max	0.3	0.1	0.048	0.058	1.06

Table 3: The XRF analysis of pretreated scale in the line (after removing impurities).

Component Formula	Fe_3O_4	CuO	K_2CO_3	Fe_2O_3	NiO	K_2O	FeF_2	$FeCO_3$	P_2O_5	SiO_2
%W/W	16.10	0.24	5.10	51.2	0.87	4.24	8.22	12.10	0.85	1.08

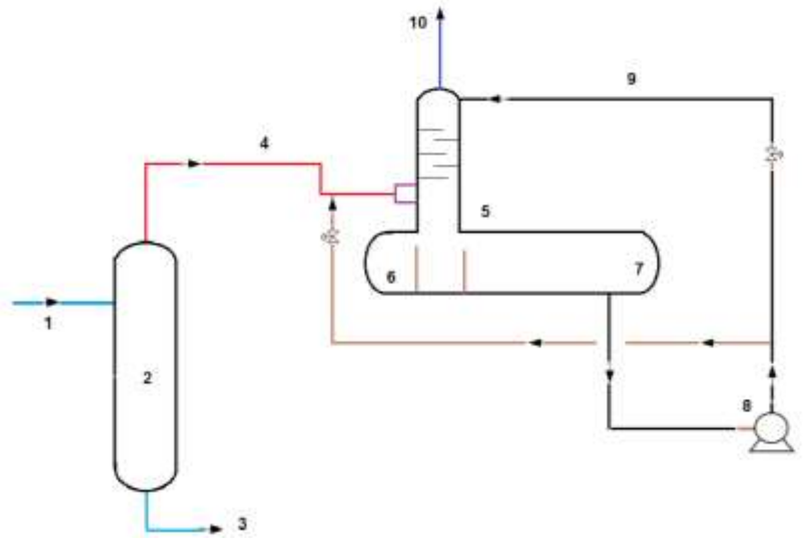

Fig. 1: The schematic diagram of neutralization section in BPC Company; 1) Acidic flaring line, 2) Acid Knockout Drum, 3) Liquid Drain, 4) Over head line, 5) Relief gas scrubber Tower, 6) Hydro carbonic side, 7) KOH compartment, 8) KOH circulation pump, 9) KOH solution,10) Exhaust gases to non–Acidic Flaring line.

The SEM images of scale

The surface topology and imaging corrosion products on the inner surface of the overhead line were studied by SEM images (Fig. 2 A, B, C). After removing the huge amounts of fouling accumulated in the tube, the analysis of the surface of the tubes displayed that these sediments are frequently based on iron oxides. It was found that the thickness of the oxide layer in different parts was until 234.18 microns (Fig. 2 A). The thick and porous corrosion products are coated on the internal subsurface of carbon steel.

Case study of the Liquid Knock out Drum

The overhead line of the Liquid Knock out Drum was composed of carbon steel. The corrosion thinning of the line was tested, and it was found that the localized corrosion failure had happened. The pictures of the damaged line were presented in Fig. 3A, B, C.

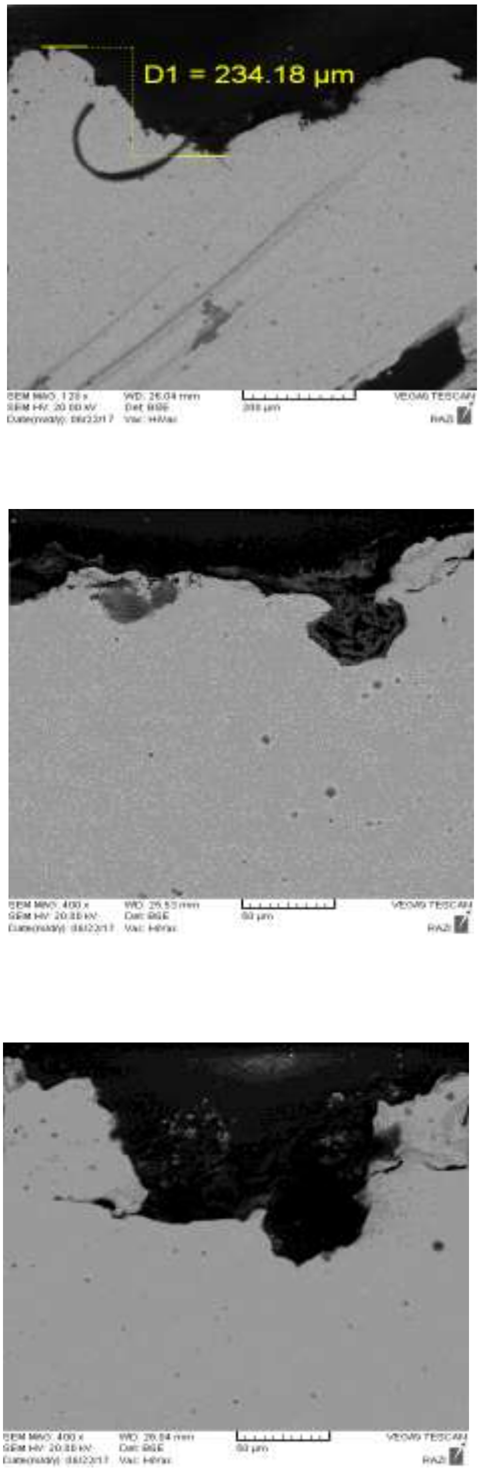

Fig. 2: A) The depth of the cavities observed in different areas of the inner surfaces of the line. B) The thickness of the deposited oxide layer on the inner surfaces of the tube. C) The SEM images of corrosion products.

As it can be seen from Fig. 3A, the main part of the wearied line was the middle of the line near the flange. From Fig. 3A& C, it is obvious that the main part of brown deposits is Iron compounds.

RESUTLS AND DISCUSSION

Mechanism of corrosion

As can be seen from Fig. 3 A&C, the inner surface of the line is covered with brownish and white deposits. The presence of such sediments can be originated from under deposit corrosion [10].

The corrosion of the line was happened by contacting the carbon steel with HF. The following reaction (Eq. (2)) had happened when the corrosion of the line started. Therefore, at first the scale was formed in the line that reduces the attack of the line by HF, and the lifetime of the line was extended. But the iron fluoride scale in the overhead line was developed by continuous corrosion reactions, resulting in the corrosion of the line and subsequently the first leak from the overhead line was detected [11].

$$2H^{+} + 2F^{-} + Fe \rightarrow H_2 + FeF_2 \quad (2)$$

When facing the carbon steel with water vapors and oxygen the following reaction can be happened [12]:

$2Fe + H_2O + O_2 \rightarrow Fe_2O_3 + H_2$

$$2Fe + H_2O + O_2 \rightarrow Fe_2O_3 + H_2 \quad (3)$$

The oxygen concentration is sharply reduced under the sediments compared to outer spaces with areas where no scale is produced. The presence of sediment in the line together with the formation of a concentration cell of oxygen can increase the corrosion in the system.

The metal oxides can increase the corrosion of overhead line in the existence of trace amounts of HF acid. Upon exposure to HF acid, these oxides can become a source of water beneath the passive film and lead to the creation of an obstructed corrosion cell.

It is clear that oxides can increase corrosion through the formation of water. An oxide will react with HF to form water and fluoride based on the following equation (Eq.(4)):

$$Me_xO_y + 2y\,HF \rightarrow xMeF_{2y} + yH_2O$$
(4)

The newly formed metal fluoride could bind the water as hydrate, depending on the metal. If not, the water

Fig. 3: A) The internal corrosion and fouling of the overhead line. B) The outside view of perforated overhead line. C) The cutted view of the overhead line with internal scales and sediments.

remains free to produce a dilute fluoridic electrolyte that is potentially corrosive. The produced water absorbs HF vapors exhausted from the liquid knockout Drum in overhead line to form a corrosive pocket of HF–acid on the interface of metal and Fe–fluoride film. It should be noted that the following reactions (Eqs. (5) & (6)) was happened in the presence of HF:

$$\text{Metal interface: } Fe \rightarrow Fe^{2+} + 2e^{-} \tag{5}$$

$$\text{Int the scale: } Fe^{2+} + HF \rightarrow FeF_2 + 2H^{+} \tag{6}$$

When Fe^{2+} is exposed to water and oxygen, it was changed to porous compounds such as FeO(OH), Fe_3O_4, and H^+ Cations, this closes the reaction loop(Eqs. (7) & (8)):

$$3Fe^{2+} + 2H_2O + O_2 \rightarrow Fe_3O_4 + 4H^{+} \tag{7}$$

$$Fe^{3+} + 2H_2O \rightarrow FeO(OH) + 3H^{+} \tag{8}$$

Without water and oxygen present, the Fe^{2+} Cations cannot react and stay in the iron–fluoride film.

The visual check result

Through the visual check in leakage period, it can be seen that the variation in the corrosion flow pattern is not constant with the known performance, (Fig. 3, B). The total weight–loss discovered in the overhead line through visual check was significant. The visual check from internal and external surfaces presented that perforation is due to pitting corrosion (Fig. 3, B and Fig. 5, B). The study showed that the perforation was started from internal surface and expanded to the external surface.

Most equipment in acidic zone is made from carbon steel. Upon contact with highly concentrated acid, a stable iron fluoride layer is formed inside the equipment that provides suitable protection for the carbon steel over more corrosion by HF acid. However, an unstable and porous hydrate scale is shaped in contact with a mixture of acid and water, which swells and can be removed from the overhead line. The pictures were taken from the inner surface of the line by a digital camera, it displayed that the line had a severe cramp, which was choked to some extent in several areas (Fig. 5A).

The deposited layer shaped on the line surface is not dense, and there are many gaps inside it. With increase in the released HF from Acidic equipment through the flaring line and subsequently to overhead line, the amount

Fig. 5: A) Cross–section of the overhead line with huge amounts of sediments and impurities. B) The cross sectional of the overhead line without deposits after welding.

of corrosion products on the internal surface of the line was increases and the deposited layer becomes thicker.

The black deposit was Magnetite but the red deposit has been often Hematite (Fig. 3C and Fig. 5 A).The ferric hydroxide ($FeF_3.3H_2O$) has a yellow–brown color whereas Iron fluoride (FeF_2) has a grey color. The black color is characteristic of oxidation (iron II/III oxide) of the steel [13]. A blend of all these colored substances made the scales in the line and supported to the distinctive colors visible when the flange of the line was opened for inspection and maintenance.

The deposited layer is formed by accumulation of solid products; therefore, its density is not as high as that of the passivation film. It is clear from Fig. 5A that a large volume of sediments and nets have been filled the overhead line. Some of these impurities are products of corrosion, but the major part of those compounds is backed from the tower side(T-508) to the overhead line, which is probably due to design or process problems which increases the volume of sediments and Corrosion intensification is subjected to sedimentation. Yellow deposits are probably potassium oxide, and potassium carbonate is also colorless sediment and the XRF results from Table 3 confirmed this subject. Hydrocarbons fumes may also be blocked between sediments and eventually condensed as a result of ambient temperature.

The corrosion products are first deposited on the internal surface of the overhead line in the form of scales. Firstly, these products act as a defensive wall to prevent the corrosion of the tube surface [14]. But most of the corrosion products are porous and can arrest corrosive agents such as water molecules, fluoride ions, and oxygen in it and accelerate the pitting corrosion. The concentration gradient of the corrosive agents inside and surrounds the pores were increased. The concentration of corrosive agent under deposits can form pitting corrosion and the consequent creation of perforation in the line.

After perforation and welding, the line itself is susceptible to corrosion and the carbon steel resistance decreases because the percentage of key elements such as Cu, Ni and Cr in the welded points is reduced. When carbon steel pipe components with high and low content of residual elements are welded together, severe corrosion can happen.

Effect of Process conditions on Corrosion

Corrosion and fouling in the overhead line are originated from the absence of care in operational parameters and equipment control. Therefore, the characteristics and composition of the fluid in the line is important. Thus the content of oxygen, water and other impurities are important. The corrosion in HF alkylation units depends strongly on process conditions and operational parameters such as temperature, phase change, HF concentration, the content of oxygen, water and other impurities. Upon phase change: if a 98% of HF and 2% water vapor mixture is condensed, the first droplet will hold about 30% water. A higher operating temperature quickens the corrosion of carbon steel. Therefore, Monel is usually used above 70°C.

Table 4: Operating parameters in neutralization section [15].

	Relief gas scrubber (T–508)	Liquid Knockout Drum (D–511)
Bottom pressure (barg)	0.35	0.4
Top pressure (barg)	0.30	0.4
Bottom Temperature (°C)	40	Ambient
Top Temperature (°C)	30–50	Ambient

The neutralization reaction (Eq .1) produces heat and the corrosion rate was increased at high temperatures. The operating condition of the neutralization section in BPC plant is presented in Table 4. The residence time of vapors in overhead line was decreased with increase in the pressure differences between Liquid Knockout Drum and Relief gas scrubber. The corrosion rate was improved with an increase in the amounts of released acidic gases to Acid Knockout Drum.

Effect of pipe line design on corrosion

The corrosion was occurred in the overhead line and deposits were formed in it from corrosion products and impurities. The thickness of the line was reduced progressively by forming the deposits. The velocity of the acid vapors in the overhead line was decreased by an increase in the cross sectional area of the line, according to the following equation (Eq. 9) and this phenomenon can accelerate corrosion by an increase in the residence time of acid vapors in the line.

$$Q = A \times V \tag{9}$$

Where Q is the volumetric flow rate of vapor phase passing through the line, A is the cross section area of the overhead line and V is the velocity of the acid vapors. The slope of the line is an important parameters, it should not be horizontal because in dead zones the formation of sediments is high.

The diameter of overhead line was 20–inch; the use of paraffin flush for washing the line can waste paraffin, which cannot be extracted. The periodic openings of the liquid knockout drum should be done to inspect it for corrosion and other affected problems. It is better to isolate the drum and overhead lines from the equipment's and upgrade them every six months and, if necessary, clean up and repair. It should be noted that in the unit documentation, the type of fluid entering the drum and its composition is not known.

Effect of water content on Corrosion

Water is a main impurity that increases corrosion [16]. The concentration of HF acid and temperature are affected on the corrosion and the high rates of corrosion can happen at low concentrations of HF [17]. Therefore a conductivity meter or moisture analyzer should be employed to continuously monitor water. Oxygen can increase the corrosion rate of overhead line because it has a tendency to stay with HF and can dissolved and accelerates corrosion of carbon steel. The Oxygen can enter the process through perforation of acid flare line and related equipment, the input feedstock; or loading fresh acid incorrectly especially if oxygen–contaminated nitrogen is employed for draining acid from iso containers to Acid storage drum. The monitoring of the present Oxygen in the acidic zone is difficult and only it can be removed through the venting of non–condensable into the flare header. The input acidic and non–condensable gases to liquid knockout drum can be swept away with the injection of nitrogen at the beginning of the acidic flare line.

The carbon steel corrodes faster in lower concentration of HF. Regardless the foundation of the defensive fluoride (FeF_2) scale layer at the pre–passivation stage. The FeF_2 is soluble in water and in the low–concentration of acids that there was higher water content the scale dissolved freely and the wall of the line was attacked by HF. The Particles of iron fluoride scale become displaced and resulting in the fouling and choking of the overhead line.

Therefore, it was obvious that, the lower HF concentrations resulted in considerably higher corrosion rates but higher HF concentrations corroded carbon steel pointedly slower [18–19], therefore water content can dilute HF and accelerate corrosion.

Offering remedial actions to prevent from failures

The following solutions are recommended to resolve the corrosion problem of the Overhead line. The use of these solutions with a little change can be applied to similar industries around the world. 1– During the neutralization of acidic vapors with potassium hydroxide in relief gas scrubber, heat and water vapor can also be produced.

A suitable pressure difference between the liquid knockout drum and the relief gas scrubber is necessary to prevent from water vapors returned back from the tower towards the overhead line. 2– One of the effective factors is the oxygen problems. By reducing or eliminating oxygen, the corrosion rate is significantly reduced, for this purpose, a continuous injection of a small amount of nitrogen can be used as N_2 sweeper, and in addition the diffusion of oxygen to the equipment should be avoided by holding positive pressure of nitrogen on the liquid knockout drum and taking care while draining it. 3– Changes in design factors such as the slope and cross section of the overhead line can also prevent corrosion that costs the organization. 4– Continually checking the contents of the liquid in the liquid knockout drum and draining immediately if water is present. 5– Controlling the process conditions so that it has the lowest vent of vapors, especially acidic fluids. 6– Due to the fact that replacing the material with Monel cost to the company, it is suggested that the inner wall of the pipe is covered with a layer of Monel sheet (3–5 mm) to prevent corrosion and this is the last solution.

CONCLUSIONS

The present study investigates the high corrosion in the overhead line Acid Neutralization section in the Linear Alkyl Benzene Production plant in BPC Company. The main reasons for the failures of the line were investigated by visual checking, chemical analysis characterizations, SEM, and XRF analysis of the scale.

The effect of process condition such as water and oxygen content, the slope of overhead line, pipe line design, the pressure difference between the beginning and the end of the line, and composition of deposits and scales on the failures of the overhead line was considered. The corrosion and perforation of the line is based on the composition of the liquid or gases in the line and operating conditions.The reverse return of water vapors contaminated with KOH from relief gas scrubber to overhead line can accelerate the corrosion. Finally, the recommendations have been proposed for trouble shooting, prevention from failure in the line and leakage of HF.

This study is certainly a shortcut, as many other parameters might affect corrosion and perforation in the Liquid Knock out Drum Overhead line. Therefore a complete examination is out of the scope of this project; therefore further research on this subject is essential in the future.

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