

Failure Analysis of Air Cooler Tubes in a Gas Refinery

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Abstract-Corrosion-erosion phenomena are the common cause the failures of the air cooler tubes in gas refineries. This paper studies such failures experienced in gas dehydration unit of Parsian Gas Refinery, Iran. Surface analysis of the failed sections through Scanning Electron Microscopy (SEM), X-Ray Diffraction, Energy dispersive spectroscopy (EDS) were performed. During gas dehydration process, all parts of fin fan coolers suffer from different types of corrosion such as sweet (CO₂) corrosion, dew-point corrosion, high temperature corrosion, and erosion. In the operational condition of the air cooler, temperature drops dramatically from 250 to 50 °C at a pressure of 78 bar and as a result a considerable amount of water condensate inside tubes. Presence of water and corrosive components of the gas stream combined with high temperature, accelerate corrosion processes. XRD analysis of the scales, formed inside the heat exchanger tubes, revealed presence of aluminum oxide particles. This indicated that particles have detached form the molecular sieve bed and entered the gas phase. Corrosion-erosion processes are accelerated with presence of solid particles in the gas stream. CO_2 is the only acid gas present in the feeding gas stream. Therefore, CO2 corrosion is expected to be responsible for the occurred corrosion attacks on the tube surfaces. Moreover, XRD data confirmed presence $FeCO_3$ in the scale. This indicated that CO_2 corrosion is dominant in the studied system.

Keywords-Corrosion, Erosion, Gas Processing, Heat Exchanger, Air Cooler

I. INTRODUCTION

Corrosion–erosion processes are very common in upstream section of oil industry due to the high pressure and temperature [1]–[4]. Moreover, such phenomena have been experienced in tubular equipment of gas treatments and petrochemical plants. Synergic effect of corrosion and erosion and the damage mechanisms are very complicated. The magnitude of metal destruction caused by corrosion-erosion is much greater than summation of individual damages by corrosion and erosion [5].

Natural gas demand is rising since it is a cleaner energy than other fossil fuels [6]. Generally, the main duties of natural gas refineries are the dehydration and sweeting of the gas phase. Sweeting means the removal of acid gases such as CO_2 and H_2S . One of the main stages of gas dehydration is water

removal process. Water removal can be achieved by several methods. Parsian Gas Refinery (PGR) employs molecular sieves as the absorbent of water [7]. Molecular sieves undergo a regeneration cycle through heating and cooling processes. The heating process is brought about by the gas stream; hence, we have to cool the hot gas in order to separate absorbed water from them and prepare it for the next processes. In the course of operation, all components of the heat exchangers suffer corrosion in different ways, the corrosion rate and its type depending on the materials from which the parts are made.

Air cooler has many finned tubes and is utilized to lower the gas temperature and to fit the other process conditions and to be economically advantageous. Environment air is forced upward through tube bundle by fans located under them. Despite the low corrosion resistance, carbon steel tubes are employed for air cooler due to economic reasons [8].

During the dehydration process, solid particles can enter the gas phase detached form the surface of molecular sieves due to high velocity of the gas phase. It is self-evident that erosion damage resulting from such solid particles is much higher than the erosion occurred by homogenous flow stream [9].

Sour gas is the natural gas which is, due to consisting a significant amount of hydrogen sulfide (H₂S), corrosive. Just when there are more than 5.7 milligrams of H₂S per cubic meter (4 ppm H₂S by volume) of natural gas, our gas is reckoned as sour gas. On the other hand, when the gas consists of less amount of hydrogen sulfide, it is considered as 'sweet gas'. Sweet gas consists of water, carbon dioxide and various types of hydrocarbon gases with methane is the dominant component. Water and carbon dioxide and the small amount of hydrogen sulfide in sweet gas are among the important factors of corrosion. Among the many different kinds of corrosion in gas and oil industries, one is sweet corrosion, which is caused by carbon dioxide solution in water [10].

The overall chemical and electrochemical reactions behind sweet corrosion are as follows:

$$H2O+CO2=H2CO3 \tag{1}$$

$$H2CO3 + Fe = FeCO3 + H2$$
(2)

 H_2S solution in water causes sour corrosion and H_2S forms a corrosive weak acid. Its overall reaction is given as follows:

$$Fe+H_2S=FeS+H_2$$
(3)

Because of the temperature drop in gas and dew formation in tubes, the dew-point corrosion decreases tube thickness and steel corrosion resistance [11]. Hence, the sweet corrosion is increased by acid carbonic solution, and as a result, corrosion occurs faster on the bottom wall of tube where water drops fall. In addition to the chemical mechanisms of dew point in causing corrosion, the physical mechanisms also play an important role in triggering erosion due to the high flow velocity and the turbulent current of the developed inside the tubes. During cooling stage, the formed drops, due to the high speed of the wet hot gas, hit the tube walls very hard. Due to not being smooth, tube walls cause turbulent currents. This deflects liquid drops towards the tube walls.

Many studies have been conducted on carbon steel corrosion in oil and gas industries [12], [13]. However, there is not many investigations of high temperature corrosion by sweet gas in air cooler tubes, which makes the current study worthwhile.

II. EXPERIMENTAL PROCEDURE

A. Background

Air coolers work to cool the hot gas at 90 bar and input temperature of 50 to 250° C (depending on the stage), and reduces outlet temperature about $45-20^{\circ}$ C (depending on environmental temperature). The two pass air cooler employs four fans (2*2). Each pass includes 84 tubes which are divided into two rows.

B. Tube material and properties

Tubes are made of A-214 carbon steel. Each tube is 9140 mm long, 2.64 mm thick and 25.4 mm in external diameter, that is fin installed by using 1060 grid aluminum.

C. Metallography

Some pieces of internal walls of the tubes were chosen as samples and scanned through SEM, analyzed through EDS, and the corrosion products on the internal walls of the tubes were shaved to for performing XRD analysis.

D. Salts measuring

The amount of salt in condensed water at unit outlet was measured to analyze the corrosion caused by salt roles.

III. RESULTS AND DISCUSSION

The EDS and XRD patterns of corrosion products are shown in figure 1 and 2 respectively. The existence of Al(OH)₃ in XRD and Al in EDS shows that particles from the surface of molecular sieve have entered the gas phase, cause fluid inhomogeneity, and as a result, increase the rate of corrosion and erosion inside the tube. Molecular sieve particles impinge the tube walls with a high velocity, which is equal to the speed of gas current, and damage the tube walls gradually. Molecular sieve particles or 4A artificial Zeolite (crystalline metal alumino silicates) consists of 0.20 Na₂O, 0.80 CaO, x H₂O, 2.0 \pm 0.1 SiO₂ and Al₂O₃ which are observable on the tube walls in EDS analyses.

Siderite (FeCO₃) is the main corrosion product in CO₂ corrosion environments. XRD pattern shown in Figure 2, confirmed the presence of siderite in the scale formed on the inner wall of the heat exchanger tubes. This indicates the occurrence of sweet (CO₂) corrosion. Sweet corrosion is a common type of corrosion in gas industries. The highest amount of carbon dioxide in gas was recorded to be 4.6 mole percent, which will increase through time as more gas is extracted from the upstream reservoir [14].

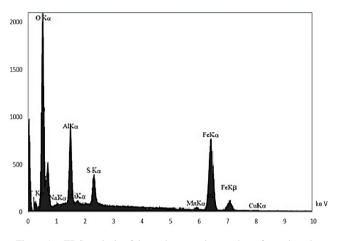


Figure 1. EDS analysis of the to the corrosion products formed on the internal walls of the tubes

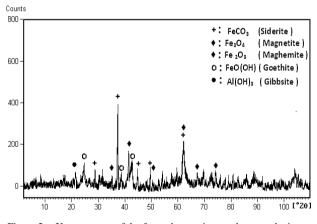


Figure 2. X-ray pattern of the formed corrosion products on the internal walls of the tubes.

Figure 3 shows the EDS analysis of the topside of the tube walls. It shows that corrosion on this part is less than on the bottom of tube. The amount of Al (30 mg) and other components are observable on EDS patterns. On the contrary, on the bottom tube walls (Fig 4), these amounts are less because the sediment is swept by condensed water in wet gas flow on the bottom tube walls.

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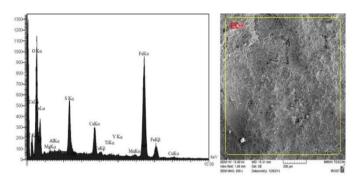


Figure 3. EDS elemental analysis of the scales formed on the topside of the tube wall.

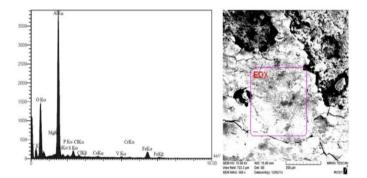
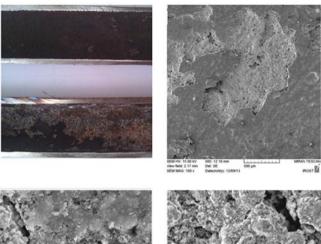


Figure 4. EDS analysis of the scales formed on the bottom of the tube wall.

The EDS elemental analysis of the bottom and top side of tube walls are shown in Figures 3 and 4 to compare the corrosion on these two parts. Regarding the amount of Fe in precipitated scale, the corrosion on the bottom wall is much higher than the top side of the wall. Main reason for this observation is that water phase is in contact with the bottom of the tube more efficient than the top side. Furthermore, presence of dissolved carbon dioxide in the water solution accelerates corrosion rate in bottom of the tube. Sediments, which can be unsettled easily, are observed on the top walls of the tubes. These sediments include the corrosion products and the detached particles from molecular sieve during dehydration. Figures also indicate a high amount of S:Absorption and regeneration sequence of molecular sieves include 8 hours of absorption, 1.40 hours heating and 1 hour cooling. Feed gas consists of only 0.2% H_2S . Water and H_2S existing in 2,200,000 m3 gas are absorbed by molecular sieve. In the next step, H2S is separated from molecular sieves by 45,000 m³ hot feed gas, which rises the amount of H₂S to 22% at the peak value.

Figure 5 shows SEM patterns of the top walls of tube. Scaling and internal attack, which are the well-known signs of high temperature corrosion, are observable on the walls [15]. According to XRD data of the main component of the scales formed inside tubes are the particles detached from molecular sieve. This is another reason why molecular sieve particles escape from the bed and influence the process of corrosionerosion.



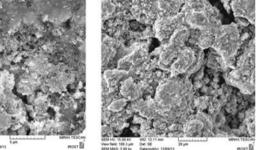


Figure 5. SEM images show morphology of the scale and/or corrosion products on the top tube's wall

Figures 5 and 6 show the difference in corrosion morphology on top and bottom of the tubes. Washing sediments and rusts by condensed water on the bottom wall has been the major cause of difference. The condensed water, due to high density and viscosity, separates more particles from bottom wall, and hence, the corrosion attacks is more obvious on these areas. Since the measured mount of salt was low (15mg/L). Therefore, it could not play a major role in the corrosion processes. Since the input gas temperature reaches 160 °C at the time of arrival, another type of corrosion shows up which is called 'high temperature corrosion'.

Natural gas normally consists of sulfides which can bring about corrosion at high temperatures. This process is called "sulfidation". It is a common type of corrosion in various units of gas refineries.

Even though the fundamental information such as the information on chemical composition, temperature, fluid velocity and intensity must be specified, more detailed information should not be neglected. Hydrogen attack and decarburization are important factors leading to the destruction of steel at high temperature. The firmness and strength of the carbon steels depend on the amount of carbon. Decarburization, on the other hand, decreases both the strength and flexibility of them. Steel decarburization by Hydrogen and water vapor are given below:

$$C(Fe) + 2H_2 = CH_4 \tag{4}$$

$$C(Fe) + H_2O = H_2 + CO$$
(5)

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In addition to the mentioned reactions, when water vapor touches the iron at high temperature, the iron reacts directly as in the following formula:

$$Fe+H_2O=FeO+H_2$$
(6)

Therefore, decarburization and oxidation are the possible reactions in the areas where water vapor and hydrogen exist.

The velocity of gas is an important factor in erosion. When a number of tubes become blinded, the flow of gas increases in the remaining non-blinded tubes; and as a result, the tension on the walls increases. The formula is as the following:

$$U = \frac{Q}{A} \tag{7}$$

If:
$$A_1 = \frac{1}{2}A_2$$
, $Q_1 = Q_2 = Constant$
Then: $U_2 = 2U_1$
 $E = K.V^n. f(\theta)$ (8)

$$U = \frac{Q}{4}E = K.V^{n}.f(\theta)$$
⁽⁹⁾

There is a direct relation between erosion and velocity; in other word, when the velocity increases, erosion on the tube walls increases too.

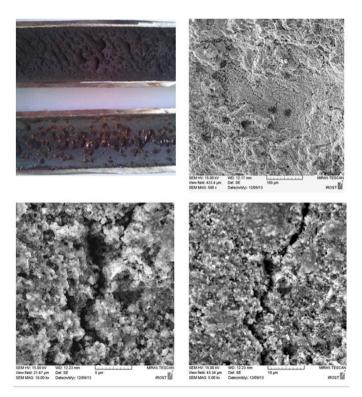


Figure 6. SEM images show morphology of the scale and/or corrosion products on the bottom of tube's wall

A. Measures Taken

According to analyses results, in order to limit erosion rate in fin fan cooler tubes by molecular sieve particles, a filter with 10 elements (1 micron nominal) has been installed. After 6 month, deferential pressure between inlet and outlet of filter reached 0.3 Bar. In addition, corrosion coupons analyses show 20 percent decrease in corrosion rate during the same period. More process corrections, such as establishing a gas sweetening unit for striping CO_2 , are being studied to decrease corrosion rate.

IV. CONCLUSIONS

1. Sweet corrosion mechanisms are the dominant cause of corrosion attacks as XRD data detected the formation of $FeCO_3$ in corrosion product scales.

2. Since condensation happens in the presence of carbon dioxide, dew point corrosion is inevitable.

3. Molecular sieve particles detached form the bed and enter the gas phase. This phenomenon accelerates corrosionerosion processes.

4. Clogging of some of the tubes causes the more tension in the clogged tubes, generated a higher gas velocity in the other tubes

5. During the heating stage, H_2S and water get separated from molecular sieve; hence, the concentration of H_2S in hot wet gas increases and causes corrosion. This is one of the most important mechanisms leading to tube failures, and further research is being conducted on constructing a gas sweetening unit prior to the arrival of gas to this stage. Consequently, the corrosion rate will decrease dramatically after the construction of this unit and as a result of which the amount of H_2S in the gas decreases prior to getting to the tubes.

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