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Preventing corrosion and tube failure in sulfur condenser during normal operation, startup, and shutdown of the south pars gas processing plant (case study)

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ABSTRACT

In each sour gas processing plant, the sulfur recovery unit is one of the most important processes regarding environmental aspects, since improper performance of this unit can impose critical problems on the environment. Gas containing H_2S is sent to a sulfur recovery unit to recover the sulfur and avoid venting H_2S to the atmosphere. Corrosion is a major concern in the sulfur recovery process due to the presence of a high percentage of hydrogen sulfide, as well as high temperatures in most of the unit's equipment. The leaking tubes were found in the bottom of the low-pressure steam condenser. A set of operational parameters such as H_2S, CO_2, and hydrocarbon concentration, reaction furnace temperature, process configuration, cold or hot bypass need to demonstrate the cause of the corrosion issues encountered in the sulfur recovery condenser. The main objective of this paper is to thoroughly investigation about root cause analysis of corrosion problem that is occur in sulfur recovery from a gas processing plant located in south of Iran. Moreover, it will propose protective actions to avoid reoccurrence of corrosion problems. This paper will review potential corrosion mechanisms and operational data which illustrate the importance of warm up and cool down during startup and shutdown procedure and also bad operation.

1. Introduction

Sulfur, one of the principle by-products of natural gas production, is of a much more substantial nature. Sulfur is recovered in its elemental form from the hydrogen sulfide content in natural gas. The yellow product is kept in liquid form by maintaining it at about 150 °C. At this temperature, sulfur is about 80% denser than water, and has a low viscosity. The feed to the Sulfur recovery plant, which applies the Claus process, consists of H_2S, CO_2 moisture, and trace of miscellaneous light hydrocarbons. These have been dissolved or entrained in the rich amine used to scrub the sour natural gas. The sulfur recovery process is used for recovering elemental sulfur from acid gas. The modified Claus process basically consists of burning one third of the H_2S to produce sulfur according to the following reactions:

$$H_2S + \frac{1}{2}O_2 \leftrightarrow \frac{1}{3}SO_2 + \frac{2}{3}H_2S + \frac{1}{3}H_2O \quad (1)$$

$$SO_2 + 2H_2S \leftrightarrow \frac{2}{3}S_2 + 2H_2O \quad (2)$$

Reaction (1) takes place in the reaction furnace by burning one third of the total acid gas with air. Reaction (2) is between H_2S and SO_2 to form sulfur, and begins immediately in the combustion zone of the reaction furnace. This requires further contact between the processed gas and the Claus Catalyst at controlled temperatures in converters following each other in series, carrying the reaction towards completion. The sulfur vapor formed by the reaction (2) is condensed and recovered as liquid. Corrosion is the main concern in each sulfur recovery plant. The compounds that cause corrosion in the sulfur recovery process equipment are SO_2, SO_3, H_2S, CO_2, and elemental sulfur. H_2S, and CO_2 are the main corrosive agents in the petroleum industry (Garcia et al., 2001).

Lins and Guimara (2007) investigated the corrosion of carbon steel heat exchangers in constant contact with H_2S, CO_2, SO_2, and SO_3 compounds present in the acid gas of the Sulfur Recovery Unit

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(Lins and Guimara, 2007). The air and gas ratio is an important parameter in the Claus Process. If an excess of air occurs, more than 1/3 of H_2S will react, creating an excess of SO_2. This compound can react with water, producing corrosive acids such as H_2SO_4. Lobo (1982) reported that the corrosion in boilers is caused by sulfuric acid that is a product of the oxidation of SO_2–SO_3, which mixes with water vapor and produces gaseous acid (Lobo, 1982). The acid in a gaseous state condenses in the colder parts of boilers. Corrosion caused by sulfuric acid occurs by an electrochemical mechanism, and is usually localized corrosion. Another probable reaction is the oxidation of the SO_2 to produce SO_3. The SO_3 is a reactive substance, and a strong oxidant that reacts with metallic oxides to form sulfate (Craig and Anderson, 1995). Steel corrosion due to SO_2 usually occurs in a form of pitting (Roberge, 1999).

If a lack of air occurs, less than 1/3 of H_2S will react and H_2S will then be in excess in reaction (1). The most familiar forms of carbon steel corrosion when in contact with a H_2S environment are: sulfide stress cracking, hydrogen stress cracking, hydrogen blistering, localized corrosion (pitting) (Ramos et al., 1982), and cracking in the welded region (Salles, 1990).

The stress corrosion cracking caused by H_2S depends on its concentration, temperature, and the pH of the solution (Chen et al., 2005).

Another corrosive threat is H_2CO_3. CO_2 dissolves in water to produce H_2CO_3, which reduces the pH of water and is very aggressive to steels (Craig and Anderson, 1995). The presence of H_2S in the environment with CO_2 intensifies the corrosion of carbon steel. The corrosivity of CO_2 depends on its water solubility. CO_2 produces localized corrosion (pitting) on steels. Water content control is necessary owing to the severe corrosion of the steel caused by sulfur in the presence of water at room temperature. This corrosion process is due to the production of SO_2 and H_2S.

Sulfur, in the presence of water, causes localized corrosion on steels due to the production of SO_2 and H_2S. Dutra and Nunes (1999) reported that the corrosion caused by sulfur on steels occurs in the colder part of equipment due to the condensation of gases (Dutra and Nunes, 1999). Sulfidation is a mechanism of corrosion related to the presence of impurities in sulfur compounds.

2. Case study

South pars gas processing plant, phase 5, is equipped with 3 bed Claus sulfur recovery unit with hot gas bypass system as a reheater (Fig. 1). As it noted in Introduction, Acid gas consist of H_2S, SO_2, H_2O and etc. the last laboratory result for acid gas composition is presented in Table 1.

To eliminate produced sulfur in converter catalyst beds, three condensers are provided that work at 169, 129 and 128 °C in order to their location (Fig. 2). The purpose of the sulfur condenser is to remove energy from the process gas, condense the sulfur product to the liquid phase, and remove the sulfur product from the processed gas stream at each intermediate point. Phase 5 is equipped with a 6 barg steam generator for the first and second condenser. The final condenser is a boiler feed water heater with which the temperature can be controlled (Fig. 2). Table 2 summarizes the performance of the exchangers.

Sulfur condensers serve the primary function of cooling and condensing sulfur formed in the upstream reaction step. Sulfur condensers are horizontal, kettle type shell and tube boilers. In addition to condensing product sulfur from the process gases, the liquid sulfur must also be separated from the process gases before they flow to the next processing step. This is normally done in an oversized outlet channel. Ideally, sulfur is condensed from the processed gas at the cool condenser tube wall, flowing from the tube into the outlet channel. It is then separated from the processed gas, and is drained from the condenser. Sulfur seals, look boxes, and rundown lines can have an impact on the sulfur condensers. The ability to observe the sulfur production from each condenser is a very valuable process evaluation and troubleshooting tool. The sulfur rate, consistency of rate, color, temperature, and presence of bubbles are all important information items that can only be obtained from individual seals and look boxes. Each sulfur condenser drain line, sulfur seal, look box, and rundown line to the sulfur pit is fully steam jacketed. The drain line between the condenser and seal should have a steam jacketed plug valve located as close as practical to the condenser to allow on-line rodding of the drain line and sulfur seal. Clear access must be provided for rodding the drain line, and overhead access must be provided to rod the seal.

In May 2013, during cold start up (just after an annual overhaul in April 2013), a sever fluctuation in the shell side water level of the last condenser was observed and the startup procedure stopped immediately (Figs. 3, 4). The First and the most possible cause of fluctuation is tube rapture in the last condenser. An inspection team exposed the sulfur dome in the right terminal of the condenser (separation section) just after they opened condenser man-way (Fig. 5). Inspection of the condenser tubes and also hydro-test were done for both 2nd and last condenser (Fig. 6). Unfortunately 4 tubes in last condenser, and 7 tubes in 2nd condenser were plugged. Also 117 seal welds in the last condenser, and 34 seal welds in 2nd condenser needed relieving.

Before investigation on any possible corrosion mechanisms, it was necessary to review what happened inters. The SRU passed 4 stages until May 2013; Normal operation (until 8-April-2013), Planned shutdown (between 8and 13 April 2013), Overhaul (13 April to 12 May) and an Unsuccessful startup (13 and 14 May). Each stage and also faults that occurred during these periods are investigated separately.

2.1. Normal operation

It's necessary to note, this stage, and all other stage studies are only focused on corrosion. Other faults such as high temperature in the 2nd and 3rd reactors, much fuel gas co-firing, low reaction furnace temperature, and etc. were neglected and NOT discussed here.

During normal operation, level and pressure of shell side, and also outlet temperature of 2nd and last condenser are pored to find any possibility of leakage before other stages:

As shown in Fig. 4, sever fluctuation was occurring in the last condenser, especially between 12th March and the 8th April, but continuous steam venting and intermitted blow down guided operators to wrong way. They thought fluctuation just occurred by venting so they started make up 2 or 3 times per week until annual overhaul.

Continuous steam venting can cause level drop but its effect is too small to make sever fluctuations. In other hand, the 2nd condenser had steam venting but fluctuation isn't mentioned in the Distributed Control System (DCS) trend.

So the first sign of corrosion and rupturing in tubes is identified: level fluctuation in water level. No attention to inspection and maintenance team to check the condenser is the first and biggest fault and reason of unwanted shutdown.

But what happened for 2nd condenser? And what reason magnified corrosion phenomenon?

The other fault in the operation is that no consideration on sulfur condensation in last condenser. The source of accumulated sulfur in last condenser is plugging of seal-pots and the sign of it, is lower/no sulfur production from the condenser during normal operation.