

Hydrogen Blistering in Stabilizer Overhead LPG Condenser of Naphtha Splitter Facility

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ABSTRACT

Low-strength carbon steels are widely used in refining industries for manufacturing pressurized components such as pipes and pressure vessels. Hydrogen blistering is a common form of hydrogen damage which can occur in components when a wet H₂S environment is present. Equipment operating in sour environment contain H₂S are prone to deterioration by wet H₂S damage mechanisms when particular process variables gets established within the prevailing operating conditions. Blistering and subsequent hydrogen induced cracking damage are strongly affected by the presence of inclusions and laminations that provide sites for the diffusing hydrogen to accumulate. The current study assesses the root causes of hydrogen blistering in a Stabilizer LPG overhead condenser of naphtha splitter facility. The paper discusses in detail the inspection findings, observations, prevailing process conditions for damage and remediation action plans to prevent further accordance and growth of hydrogen blisters.

Keywords: Hydrogen blistering, Wet H₂S, Diffusion, Sour water

INTRODUCTION

Hydrogen damage is a degradation mechanism active in the oil and gas industry where carbon steel is used for pressure vessels and piping that are in contact with wet H₂S environments. Hydrogen blisters may form as internal or external surface bulges, or within the wall thickness of a pipe or pressure vessel. Blistering phenomenon occurs predominantly in low strength alloys when atomic hydrogen diffuses to internal defects such as laminations or nonmetallic inclusions. The hydrogen atoms combine to form hydrogen molecules that are too large to diffuse out and thus the pressure builds up to the point at which local deformation occurs and thereby forms a blister. Hydrogen blisters can form at different depths starting from the surface of the steel, in the middle of the plate thickness or near welds.

This paper discusses in detail the observations of hydrogen blistering that were observed during a shutdown in an IOCL refinery. Observations of hydrogen blistering were noticed on the heat exchanger shell id and external surface of a stabilizer LPG overhead condenser in the naphtha splitter facility. As per design, the stabilizer overhead system is designed with four condensers. The condensed product is taken into the stabilizer reflux drum. The problem of blistering identified in the shut down was due to the high level of H₂S in the feed that was processed for short duration of four months as an operational requirement and to meet the market demand.

When refinery equipment and piping are exposed to wet hydrogen sulfide, hydrogen atoms are produced by surface corrosion of the steel. In the presence of hydrogen sulfide, the recombination reaction of hydrogen atoms to the molecular hydrogen is retarded, consequently allowing, hydrogen atoms to diffuse into the steel. These atoms can move rapidly either by diffusion or by transportation through defects and are trapped at sensitive metallurgical defects such as the interface between non-metallic inclusions and steel matrix. Cracking can occur if the critical amount of hydrogen necessary for crack initiation is exceeded.

Table 1: Design Condition and Material of Construction

Design temperature in °C (Shell)	165 °C
Design pressure kg/cm ² (g)	10.3 kg/cm ²
Material of construction - Shell	SA 515 Gr. 60
Material of Construction – Tube	Admiralty Brass
Process fluid-Shell	LPG
Process fluid-Tube	Cooling water

PROCESS IN BRIEF:

The purpose of the stabilizer column is to stabilize and remove the volatile components like propane, butane and light fraction from naphtha, Figure 1. The feed from pre-topping column is caustic washed before entering the feed surge drum. The feed before entering the stabilizer column is heated to 124° C in feed bottom exchangers. The column overhead vapors are condensed in a condenser and the condensed product is taken into stabilizer reflux drum.

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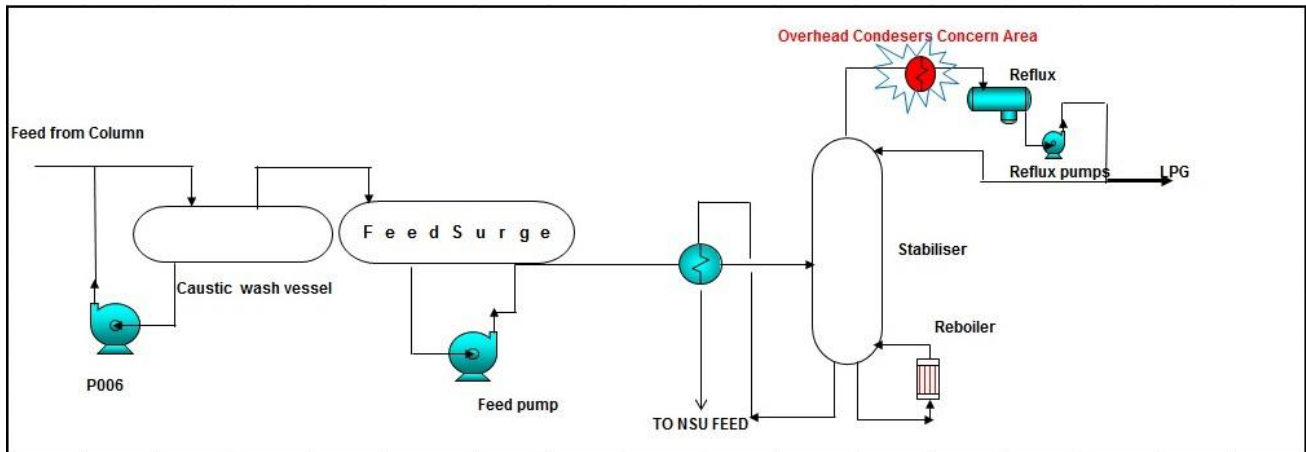


Figure 1: Process Flow Diagram

VISUAL EXAMINATION:

Visual examination revealed hydrogen blisters on the heat exchanger shell id and external surface of all the overhead condensers. The hydrogen blistering was randomly distributed and the quantity of blistering varied in nature for different exchangers. The diameter of the blisters observed varied from 2 mm to 4 mm in diameter. Thickness measurements were done at all the blister locations and shell plate where the surface appeared to be smooth. Thickness measured at the blister location was 3.7 mm where it is suspected to have lamination or internal rolling defects.

PHOTOGRAPHS:

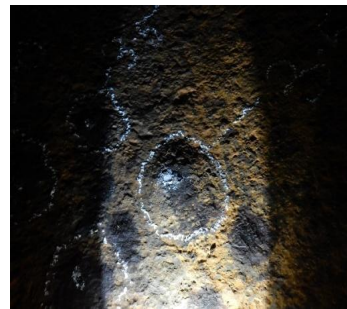
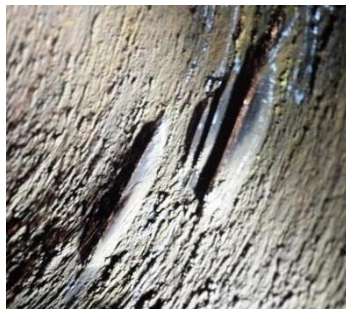


Figure 2 and 3: Blister on shell ID

Figure 4: Blister after puncture

ASSESSMENT:

Thickness scanning for blister mapping and for health assessment of the complete heat exchanger shell was done. The size of the individual blister was measured and recorded for all the exchanger stabilizer condenser shells. Randomly, some blisters were ground smooth and checked with the dye penetrant test (DP) for any initiation of the crack. No surface cracks were observed. No cracking or interconnecting blisters were noticed visually and in the DP test after grinding. Hardness is one of

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the contributing factor for the susceptibility of the cracking. Hence, hardness of the base metal and welds were checked and hardnesses were found between 150-170BHN. As per API 571, carbon steel used in H₂S service hardness is not a critical factor for blister nucleation and growth; nevertheless, hardness tests were conducted for confirmation regarding the material verification and reliability point of view.

THE INFLUENCE OF PROCESS VARIABLES

Process variables exert a strong influence on the occurrence of wet hydrogen damage. Knowledge of these influences can assist in the planning of a survey where greater inspection effort can be concentrated in areas likely to be susceptible to attack. The quality of the material used for manufacturing is also equally important if the process parameters comply with the hydrogen damage requirements.

Generally, wet hydrogen attack does not occur in neutral environments (pH ~ 7.0). Acidic environments are preferred and a common region for this damage is at pH levels below 4.0 with H₂S present. If both H₂S and cyanide are present, hydrogen blistering form of damage can occur if the pH is in the basic range. H₂S levels above 50 ppm are normally required for attack. In the present case, the H₂S levels were in the range of 1000 ppm. Most of the wet-Hydrogen attack classes occur at operational temperatures between ambient and 150 °C.

DISCUSSION:

- As per the past history of the stabilizer overhead condenser no observations of blistering were recorded on the id side of the exchanger shell. Due to operational requirements, high H₂S feed was processed for short duration of 4-6 months which caused blistering in the overhead condensers. The operating temperature range and operating conditions made hydrogen damage phenomenon to be very conducive.
- As per the existing facility and infrastructure, provision of caustic wash is provided for neutralization of the H₂S in the feed. The existing caustic wash facility and strength of the solution used was not sufficient to neutralize the high H₂S in the feed.
- The boot water pH in the reflux vessel was not monitored which could have reflected the carryover of the H₂S stream in the stabilizer downstream.
- The quality of the steel used is an important factor even though the hydrogen is formed due to the corrosion. As the refinery is old there might be chances of material defects like elongated non-metallic inclusions or laminations in the steel that could have aggravated the hydrogen damage.
- As a spare shell was not available immediately, any possible destructive testing for detailed metallographic analysis was not done.

ACTIONS TAKEN AND WAY FORWARD:

- To avoid further damage to shell and as an immediate measure, all blisters were punctured using a 2 mm dia. drill. The release of the gas will not allow the existing blisters to grow further which otherwise could lead to cracking.

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- The existing facility of caustic dosing was reviewed and an increase in caustic strength was recommended when high H₂S feed is processed.
- To take care of corrosion, provision for specialized corrosion inhibitor like polysulfide dosing provision in the existing system is under review.
- All the stabilizer overhead condenser shells are planned for replacement in the near future with carbon steel NACE Material - killed steel normalized condition.

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