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HYDROGEN PERMEATION APPLICATION TO CRUDE UNIT OVERHEAD CORROSION MONITORING

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ABSTRACT

Crude unit overhead corrosion has been a problem for most refineries worldwide. A number of different corrosion mechanisms can result in damage to the crude unit overhead. These mechanisms include low pH corrosion, under deposit corrosion due to salt formation in the overhead, and velocity accelerated corrosion. Hydrogen permeation has been successfully used to monitor crude unit overhead corrosion. A correlation was developed to calculate the corrosion rate based on the hydrogen monitoring technique readings. This paper will discuss the usefulness of the hydrogen permeation correlation in different crude unit overhead troubleshooting scenarios. The correlation corrosion rate showed very good agreement with corrosion rates calculated from ultrasonic thickness measurement (UT) data. In addition, a case history of using the hydrogen permeation monitoring technique to map salt formation areas in one overhead line is discussed.

Keywords: Crude Unit Overhead Corrosion, Hydrogen permeation, amine chloride

INTRODUCTION

Crude unit overhead corrosion has been one of the major concerns for all refineries. Corrosion concerns and problems have continued, despite a good understanding of the corrosion mechanisms and the development of improved corrosion control methodologies. Corrosion in the crude unit overhead can be in the form of acidic corrosion promoted by hydrochloric acid (HCl) and/or under deposit corrosion. Hydrochloric acid attack is primarily caused by the hydrolysis of chloride salts in the crude oil. Gaseous

HCl combines with condensed water in cooler regions of the overhead system. Corrosivity at the dew point is largely a function of the pH of the water. The key to successful control of acid corrosion is to modify (raise) the pH at the aqueous dew point. Proprietary organic amines are commonly injected in an attempt to raise pH, thereby reducing corrosivity of the water.

Under deposit corrosion refers to metal loss that occurs beneath corrosive salts. HCl in crude unit overhead vapors can react with ammonia and amines that are also present in the vapors. This vapor phase reaction takes place above the water dew point[1] and leads to deposition of non-volatile salts. The salts, once deposited, will absorb sufficient water from the surrounding vapors, resulting in severe under deposit corrosion attack. High corrosion rates have been reported in overhead systems at bulk stream temperatures as high as 70 ^{o}F (21 ^{o}C) above the water dew point.[2]

Corrosion on the internal surface of steel equipment results in the evolution of hydrogen. This hydrogen evolution reaction (HER) results in a measured flux of hydrogen which can be detected on the equipment's external steel surface. Hydrogen flux is a direct indication of cathodic activities on the internal surface. This reaction has received a lot of attention from corrosion engineers and scientists because of its crucial role in the corrosion of engineering alloys, especially in acid media. The reaction is also fundamental to the related hydrogen embrittlement mechanism, since it controls the hydrogen entry into metals from the aqueous solution.

The HER proceeds in two steps, with only one reaction intermediate. The first step takes place by transfer of a single electron, and involves discharge of a proton on the surface of metals to form an adsorbed hydrogen atom (see reaction 1).

$$H^+ + e^- + Fe \Rightarrow Fe\text{-}H_{ads} \qquad (1)$$

The adsorbed atomic hydrogen on a metal surface ($Fe\text{-}H_{ads}$) can combine and form molecular hydrogen, which accumulates and bubbles off of the surface. This combination of the adsorbed hydrogen atoms is the second step of the HER. This step can take place through an atom-atom combination as suggested by the chemical recombination mechanism (reaction 2) or through an ion-atom reaction as suggested by the electrochemical recombination mechanism (reaction 3).

$$Fe\text{-}H_{ads} + Fe\text{-}H_{ads} \Rightarrow 2Fe + H_2 \qquad (2)$$

$$Fe\text{-}H_{ads} + H^+ + e^- \Rightarrow Fe + H_2 \qquad (3)$$

Some of the adsorbed hydrogen on the metal surface is absorbed inside the metal (H_{abs}) through the hydrogen absorption reaction (HAR). The HAR is a side reaction that occurs in parallel with reactions (2) and (3) of the HER and is given in reaction 4.

$$Fe\text{-}H_{ads} \Leftrightarrow Fe + H_{abs} \qquad (4)$$

Absorbed hydrogen atoms can permeate to the external (exit) surface of the steel and combine to form molecular hydrogen which then can be measured as hydrogen flux. The measurement of hydrogen flux in the field has been made possible through a commercially available monitoring tool. The tool measures the hydrogen flux by sweeping hydrogen from the steel surface with a stream of ambient air. The increase in the hydrogen concentration in that stream is measured and reported in volume of hydrogen per cross section area of the collection probe per unit time (pL cm^{-2} s^{-1}).

A thorough in-house understanding of this tool has been developed over the years. This tool has been successfully used to identify areas of high hydrogen activity, and thus aids in improving corrosion control strategies. Effective use of this tool requires a high level understanding of the system (e.g. corrosion mechanisms, locations, metallurgy and the process).

For example, it was possible to locate areas of high corrosion activities in one crude unit overhead which was explained by salt formation in that process stream. In another crude unit overhead system, acidic corrosion was detected, and the corrosion rate was determined through an in-house developed correlation. Those findings led to major changes in the corrosion control in both crude unit overhead systems, resulting in measurable decreases in corrosion. These two cases will be discussed in more detail later in this paper.

HYDROGEN FLUX AND CORROSION RATE CORRELATION

Correlating hydrogen flux measured on the outside surface of a metal component to the rate of corrosion occurring on the inside surface is a natural assumption given that the flux is created by the corrosion reaction as a byproduct in the manner described above. The rate of permeation is directly related to temperature, wall thickness, alloy composition, and corrosion rate. Temperature and wall thickness relationships have been discussed in detail most recently[3] by Frank Dean and will not be elaborated here.

Finding the relationship that defines corrosion rate with respect to hydrogen diffusion is confounded by the vast difference in the time lag between the occurrence of a corrosion event and the response of the monitor that is inherent in each monitoring technology. Methods that measure metal loss from the wall of a piece of equipment or a segment of piping only report a time weighted average value and cannot identify individual events. On the other hand, measuring corrosion as a correlation to a byproduct of the reaction, like hydrogen permeation, offers a real time quantitative assessment of the activity during the period of the measurement.

Both the historical and instantaneous methods offer insight into corrosion activity and the impact of the damage on the service life of the component. However, both methods are also limited in the amount of information provided by each technique. While a historical perspective offers no data on individual corrosion events, it does provide a measure of the overall impact of corrosion on equipment reliability. Conversely, the instantaneous measurement method quantifies each event and allows for an analysis of contributing factors at the time of the corrosion.

However; considering the transient nature of most corrosion mechanisms, it is not prudent to assume a particular corrosion rate in a specific location will persist for any amount of time. Still, despite the various differences, the best way to build the correlation is to compare various technologies with each other in the process environment. One needs only to find cases where the corrosion problem is both chronic and consistent to form a basis of comparison. Table 1 represents cases used to construct the correlations used by Baker Petrolite [1]to relate measured hydrogen fluxes to corrosion rate.

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[1] Baker Petrolite Corporation

CASE HISTORIES

Unit #1

The crude unit in this case consists of an atmospheric distillation column followed by a vacuum distillation column. The atmospheric tower has a single stage condensing system. Corrosion inhibitor and neutralizing amine are injected into the overhead line within one meter of the tower top effluent nozzle. Both additives are injected into overhead stream via a carrier media. Control of the injection rates of these streams is known to be poor. The refinery had historical inspection data showing aggressive corrosion immediately downstream of the additive injection point, with diminishing metal loss, moving away from the tower effluent. Figure 1 represents the overhead system immediately downstream of the tower.

Points 1, 2, and 3 denote the areas chosen for hydrogen permeation monitoring based on the inspection history. These locations were surveyed manually with hydrogen permeation measurement to identify the most active areas. Once the most active points of the three areas were located, these were monitored continuously for periods of 2-3 days. The most active points in each area were influenced by the presence of corrosive media, system temperature, and process flow dynamics. During these monitored periods, the refinery made adjustments to various operating parameters, as well as to the additive injection system. The measured corrosion rate did respond predictably, and these adjustments were not successful in reducing the corrosion rate. The refinery elected to continue operating with the active corrosion pending closer inspection of the piping during the upcoming maintenance shutdown. Figure 2 is a graph depicting data representative of each of the monitored points.

Monitoring point 1 shows no evidence of corrosion. This point is located in the overhead system upstream of the additive injection. Point 2 recorded flux levels consistent with 40 mpy (1 mm/y) corrosion rate, while point 3 was always <5 mpy (< 0.l25 mm/y). These measurements were repeated several times, and the calculated metal loss correlated well with ultrasonic thickness measurements. The profile of this data indicates a relationship between the additive chemistries and the corrosion activity since there is no evidence of activity prior to the injection point. Visual inspection during the shutdown confirmed both the location and magnitude of the damage to the piping. The results correlated well with the predicted values calculated from the hydrogen flux measured during operation.

Unit #2

The crude unit in this case consists of an atmospheric distillation column followed by a vacuum distillation column. The atmospheric tower has a two stage condensing system with the first drum designed to remain dry (without an aqueous phase). Corrosion inhibitor and neutralizing amine are injected into the first stage upstream of the first exchangers, and into the second stage upstream of the first exchangers. The refinery was experiencing corrosion in the vapor line from the first stage separator drum at a rate of 50-60 mpy (1.25 – 1.5 mm/y). The estimated remaining life of the equipment was 9 months while the next planned shutdown was 21 months away. An unplanned shutdown would cost an estimated $5+ million. A root cause analysis was performed employing several tools including an ionic model of the process, customer UT data, analyses of various process streams, IR temperature surveys, and hydrogen permeation monitoring. Figure 3 represents the overhead system with the problem area highlighted.

The root cause analysis resulted in the following conclusions:

- Neutralizing amine chloride salt deposition attacked the piping
- Contributing factors
    - Unnecessary chemical treatment of first stage – hot, dry systems do not require neutralizer to control pH
    - Inappropriate neutralizer selection and application – specific amine selected for the neutralizer is known for high salt formation tendency
    - Low operating temperature at the first stage drum – operated over a temperature range that crossed the dew point of water and thus did not remain dry

Figure 4 shows a map of the survey points along the overhead vapor line. Details show the location and relative area of the salt deposits in the inside of the pipe. The sensitivity of the hydrogen permeation monitor permits accurate mapping of the salt deposits including changes in size and shape.

Recommendations included an operating envelope to eliminate the condensation of water in the first drum, and the need for neutralizers in the first stage. These were:

- No chemical treatment of hot, dry first stage
- Injection of neutralizer downstream of hot drum vapor line (also operating hot and dry)
- Set minimum drum temperature target of 127 °C (260°F)
- Monitor the impact of the changes using hydrogen permeation and UT on the vapor line

The results of the changes were dramatic, including:

- Hydrogen flux readings decreased
    - Before new operating envelope > 100 $pL/cm^2/sec$
    - After new operating envelope, < 10 $pL/cm^2/sec$
    - Salt deposits diminished in area to extinction
- Controlled Corrosion of vapor line - UT results show >50% reduction in corrosion during first few months. Subsequent surveys confirmed that the corrosion was under control
- Vapor line remained in service more than 26 months
- Refiner able to defer turnaround
- Savings estimated at more than $ 5 million

SUMMARY OR CONCLUSIONS

Using hydrogen permeation measurements as a means of monitoring corrosion offers insight into the contributing factors of the mechanisms under study not available through more conventional means. The sensitivity and versatility of this technology fit well with the demands of field application. It is possible to correlate the hydrogen flux level to instantaneous corrosion activity. The best application of inspection technology is a combination of instantaneous and historic corrosion measurement. This combination offers the greatest insight and the quickest response to change.

REFERENCES

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3. F.W.H.Dean, *Corrosion 2002*, Paper 02344, NACE Corrosion Conference Series, Houston, Texas.

Table 1: Cases comparing hydrogen flux to other monitoring technologies

Process stream	Corrosion mechanism	Monitoring technology
Atmospheric bottoms piping	High temperature sulfidation	Electrical resistance probe, UT
Atmospheric tower overhead piping	Under salt corrosion	UT
Atmospheric tower overhead piping	Low pH water	UT
Vacuum tower overhead	Low pH water	Electrical resistance probe, UT
LPG separator tower feed	Under salt corrosion	Rate of piping replacement
Atmospheric tower overhead exchanger shell	Under salt corrosion	UT

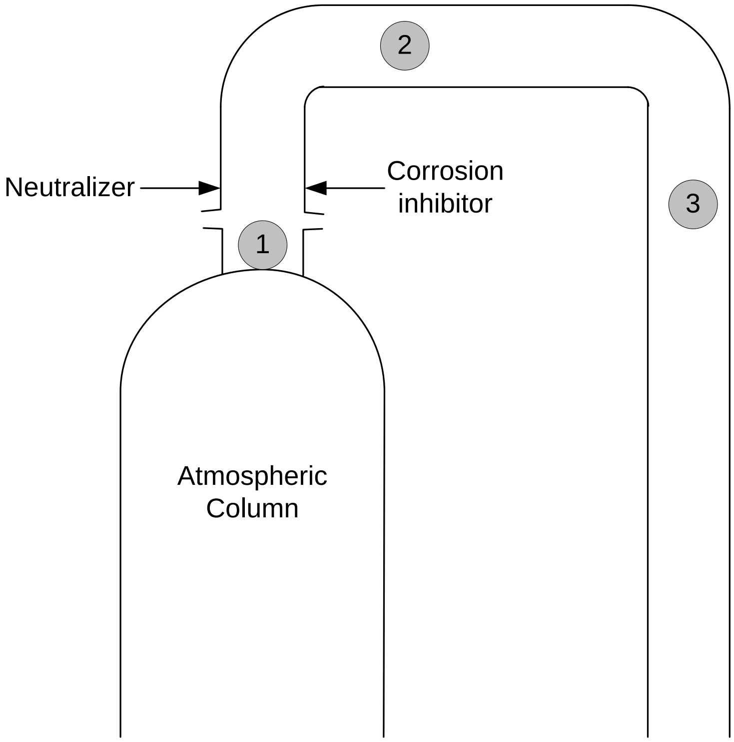

Figure 1: Sketch of unit #1 atmospheric distillation column overhead piping.

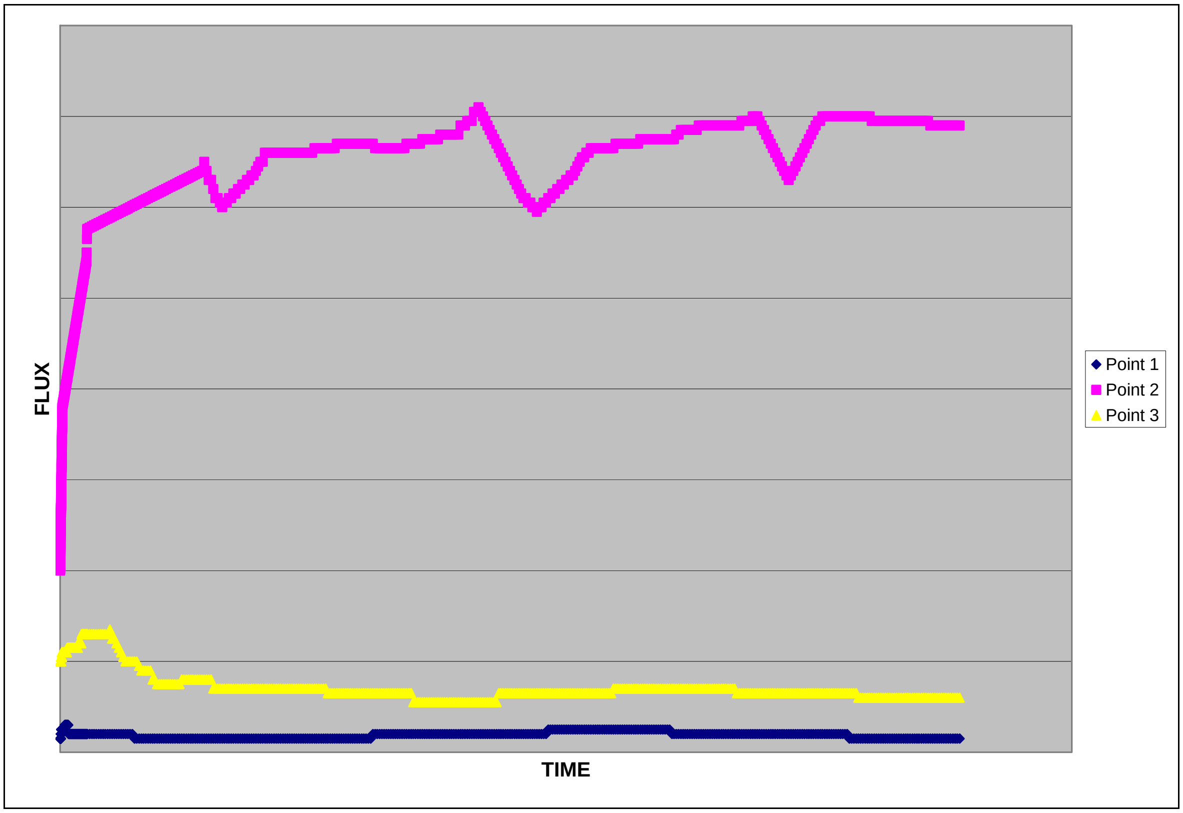

Figure 2: Hydrogen permeation data

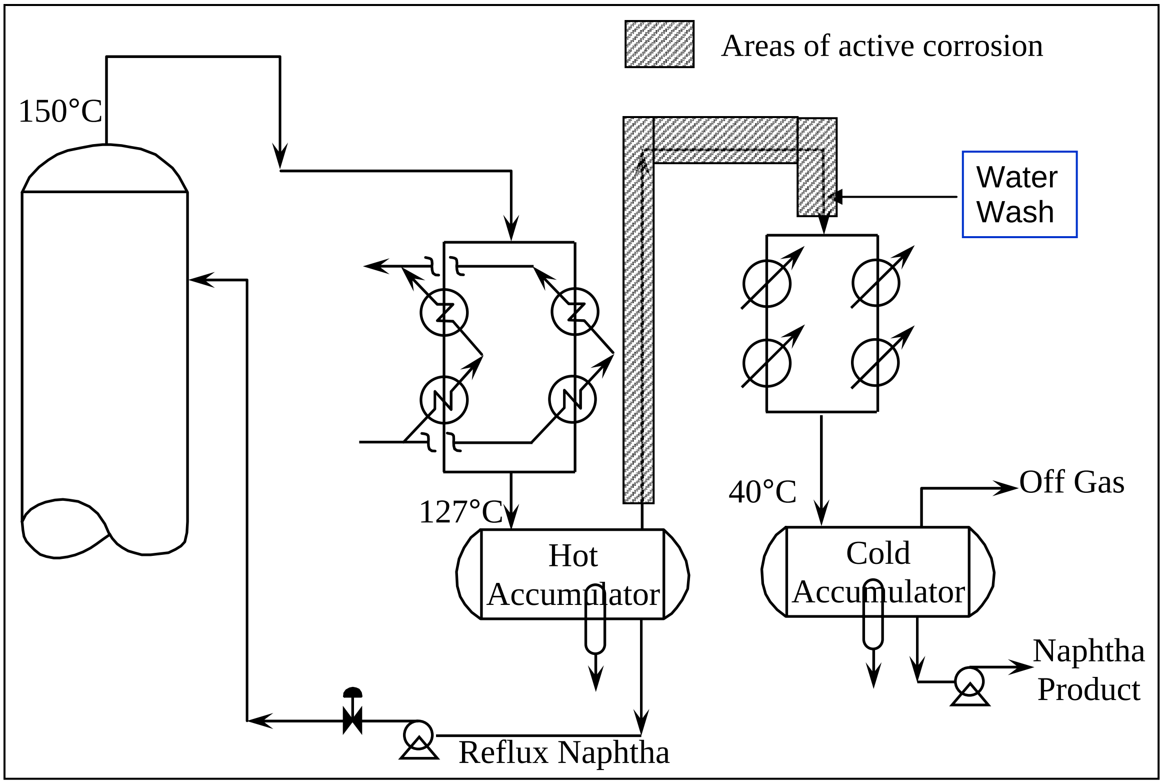

Figure 3: Sketch of unit #2 overhead system

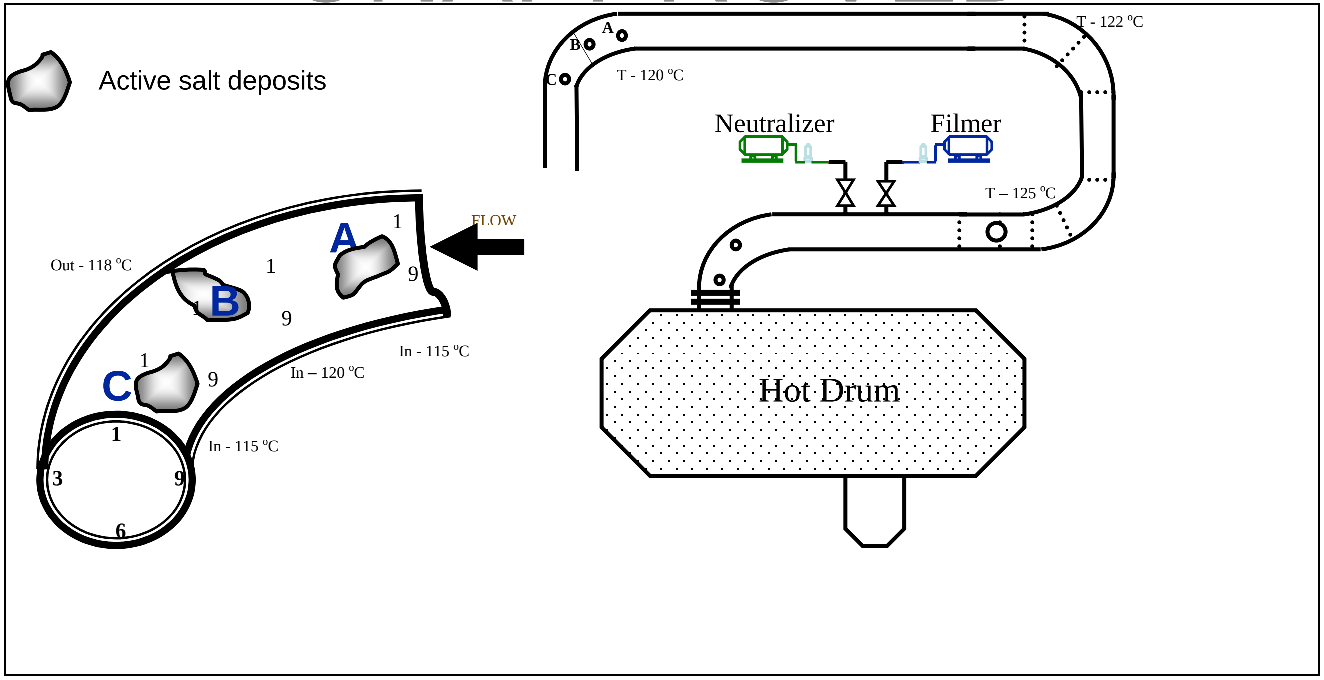

Figure 4: Hot drum vapor line and salt deposit mapping