The Effects of High HCl and Changes in pH Levels in CDU Overhead Corrosion

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Abstract— Many corrosion management methods for Alfulla treatment had been investigated. Corrosion inhibitors and neutralizer in addition to high efficient desalting have been proposed as the superior corrosion treatment technique for Alfulla crude processing equipment. Generally the overhead of a crude unit can be subjected to a multitude of corrosives species. Hydrochloric acid, formed from the hydrolysis of calcium and magnesium chlorides, is the principal strong acid responsible for corrosion in crude unit overhead. Mitigation of this type of corrosion is performed by process changes, materials upgrading, design changes, and injection of chemicals such as neutralizers and corrosion inhibitors. Process changes include any action to remove or at least reduce the amount of acid gas present and to prevent accumulation of water on the tower trays. Material upgrading includes lining of distillation tower tops with alloys resistant to hydrochloric acid. Design changes are used to prevent the accumulation of water. They include coalesces and water draws. The applications of chemicals include the injection of a neutralizer to increase the pH and a corrosion inhibitor. This investigation proved that maintaining a low chloride level and stable pH levels were the most effective ways to control equipment damage from corrosion. Also, the study found that several inspection techniques were particularly useful in estimating service life for pipes and other crude-unit equipment. Applying better pH control and improved monitoring and inspection programs can reduce equipment damage from corrosion. In this study, some field results are presented, including chemical analysis, pH and corrosion rate for a CDU tower overhead in Viscosity Breaking Unit.

Index Terms — Corrosion rate, pH, Neutralizer, HCl.

I. INTRODUCTION

Significant corrosion problems have been reported in crude unit overhead operations, including those due to chloride and sulfur species in the crude [1]. Most of these problems, such as those due to NH4Cl or HCl have been dealt with after the damage has occurred, and continue to be a source of significant material degradation in CDU overhead operations [2]. Chloride salts are found in most production wells, either dissolved in water emulsified in the crude oil or as suspended solids. Salts also originate from salt water injected for secondary recovery or from seawater ballast in marine tankers [3]. The amount of salt contained in the emulsified water may range from 10 pounds to 250 pounds per thousand barrels of crude oil. The salt typically contains 75% sodium chloride, 15% magnesium chloride, and 10% calcium chloride. Hydrogen chloride corrosion is caused by the presence of hydrogen chloride. Hydrogen chloride evolves from heating magnesium chloride and calcium chloride to above 300°F (149°C). Sodium chloride is essentially stable up to about 800°F (426°C) [4]. Hydrogen chloride evolution occurs primarily in the crude preheat furnace. Dry hydrogen chloride is not corrosive to carbon or low alloy steel, especially when large amounts of hydrocarbon vapor or liquid are present. However, when steam is added to the bottom of the crude tower to facilitate the distillation process, dilute hydrochloric acid is produced [3]. The hydrochloric acid can cause severe corrosion in carbon steel equipment at temperatures below the initial water dew point [5]. The corrosion rate increases with a decrease in water pH [6].

Alfulla Crude Oil properties

Alfulla crude from South Kurdufan area wells has such properties: High calcium content, high acid value, high water content, high density and viscosity [7]. These properties need to be reduced to a minimum; to improve the product quality [8]. Alfulla has quite different characteristics, depending on the time of sampling and analytical lab performing [7]. It is especially related to TAN, viscosity, Fe, Ca and specific gravity. High quality corrosion monitoring and control must be celebrated and adjusted to give optimum units performance with the ever-changing properties of crude [8]. For crude-unit overhead systems, pH is the main process parameter that impacts corrosion rates [9]. To control corrosion conditions, many operators use various neutralizers at optimum ranges determined by site-specific conditions [10]. A three-year study (2011–2014) was conducted at a VBU using amine-blend solutions to control pH. Over this period, corrosion rates were measured through ultrasonic inspections and weight-loss coupons [7].

II. MATERIALS AND METHODS

LABORATORY METHODS

The laboratory test methods should be carried out under conditions that simulate operational conditions in the field, including composition of material and environment, temperature, flow, pressure, and the method by which the inhibitor is added, continuous or batch. The simplest, and longest-established, method of estimating corrosion losses in
plant and equipment is weight loss analysis [11]. A weighed
introduced into the process, and later removed after a
reasonable time interval. The coupon is then cleaned of all
corrosion products and is reweighed. The weight loss is
converted to a corrosion rate (CR) or a metal loss [8].

Field data
First year, the observed corrosion rates in pipes, were obtained
from thickness measuring via ultrasonic testing. Corrosion
rates reached values of 0.25 mm/yr. Some thickness loss and
stress-corrosion cracking were also reported on the safety vents
of the CDU, which can be attributed to H₂S levels (2,553 ppm)
in the neutralizing solution used. Second year, high chloride
levels, caused by inefficiencies in the crude preparation and
desalting processes, generated high corrosion rates, the average
corrosion rate observed by the coupon weight loss over two
years was 0.29 mm/yr. The pipes connecting the top of the
atmospheric tower and condensers have flaws from previous
campaigns. Localized under-deposit corrosion in the lower
blank of the condenser shell was observed. Third year, monitoring results for coupons installed in the overhead, had
average corrosion losses of 0.16 mm/yr. This reflects a uniform
thickness loss expected in equipment and pipes. But there were
failures in reflux pipes caused by localized under-deposit
corrosion. The average service life was five years, and failures
were reported immediately after the flow entrance, where condensation begins.

Thickness measuring
For this study, two regions of the overhead pipe were selected
at train A to conduct thickness measurement via ultrasonic
testing [11]. Initially, the testing was separated into two areas:
• Overhead atmospheric tower and condenser
• Between the condenser and accumulator drum.
Different behaviors are expected from the pipes carrying the
fluid before the condenser in the vapor phase (by design), then
after, where the water is already in liquid phase. Thus, the
observed corrosion rates were different, as shown in Fig. 1.

The locations for thickness measurement are always chosen
based on the experience of the inspection team supervising the
unit and the measurements usually apply these aspects:
• In the curves, the corrosion rates may be higher due to an
increased propensity for the occurrence of corrosion associated
with erosion.

III. RESULTS AND DISCUSSION
In the overhead atmospheric system, pH, chloride, iron and
corrosion rates were monitored by weight-loss coupons. Fig. 2
shows data of pH values measured in the accumulator drum
since 2008. The figure shows the mean values and standard
deviations for measurements over each month, except May and
September, when there were no analysis reports.

It is observed that the average pH over the years has always
been very close to or within the recommended range. But the
high standard deviations showed a lack of control during some
periods. There were some incidents in January in which a pH
reaching 1.5 was observed and adjusted to 3 on the same day
and recovered to a pH = 6.6 on the next day. On two days, the
pH reached 4. The higher standard deviation observed in this
month contributed significantly to increased corrosion rates.
Fig. 3 shows the measured chlorine values in the same drum.
The target is 40 ppm as the maximum, which can only be

Figure 1. CDU showing locations identified for thickness
monitoring by ultrasonic testing

Figure 2. Data of pH values in the overhead accumulator drum
of the tower for train A
guaranteed with efficient control in crude preparation at the storage tanks and desalter.

**Figure 3.** Data of chloride values in the overhead accumulator drum of the tower for Train A.

It is observed that the values remained above the recommended targets throughout the year, showing deficiency in the early stages of crude processing. As an immediate consequence, we can expect greater usage of neutralizers and corrosion inhibitors. What is not always sufficient to maintain is the appropriate pH and low corrosion rates over slack periods, as observed in January (average of 70 ppm chloride).

**Figure 4.** Data of iron values in the overhead accumulator drum of the tower for Train A.

The iron level in the water was also monitored. Iron can be another indicator of corrosion in the overhead system. In Fig. 4, the measurements from 2013 are shown; conditions exceeded the maximum value of 1 ppm over the year. Also, we can observe that the iron content was below the recommended limit 4 of the 10 months evaluated. These results vary greatly over the month, with standard deviations above the mean values; the data is not included in Fig. 4. Intakes of neutralizing solutions and corrosion inhibitors also represent relevant data on analyzing control parameters in the overhead system. Figs. 5 and 6 show the injection rates for neutralizers and inhibitors for Train A in 2013.

The mass balance at the tower overhead is shown in Fig. 7. It is known that the chloride content measured in the top accumulator is directly linked to the presence of HCl formed from the hydrolysis of salts present in the feed. Thus, it is possible to set base values for neutralizing agent flowrates. From the condensate analysis in the overhead drum, several periods were selected in which the chloride content was close to 80 ppm, or 50% of this, 40 ppm. On the same dates, the average flowrates of the neutralizing solution and pH were recorded, as listed in Table 3.

**Figure 5.** Data of neutralizer amine Flowrates at overhead pipe in the atmospheric tower for Train A

**Figure 6.** Data of inhibitor flowrates at overhead pipe in the atmospheric tower of Train A

**Figure 7.** Mass balance of the atmospheric tower overhead system Train A
With the pH near the equivalence point, if we consider only the presence of HCl, neutralizer and water, the result is salt formation, N2Cl, which dissociates. We can determine the resulting pH; the reactions are

\[ \text{N}_2\text{Cl} = \text{N}_2^+ + \text{Cl}^- \]  
\[ \text{N}_2^+ + \text{H}_2\text{O} = \text{N}_2\text{OH} + \text{H}^+ \]

From the salt concentration, it is possible to determine the expected pH:

\[ K_a = \frac{[N_2OH] \cdot [H^+]}{[N_2^+]} = \frac{[H^+]}{[N_2^+]} = 5.8 \times 10^{-5} \]

As Ka is very low, the salt concentration \( C_s = [N_2^+] \)

\[ [H^+]^2 = C_s \cdot \frac{K_w}{K_b} \quad \iff \quad 2 \log[H^+] = \frac{1}{2} \log K_w - \frac{1}{2} \log K_b + \frac{1}{2} \log C_s \iff \]

\[ pH = 7 - \frac{1}{2} \cdot \log K_b - \frac{1}{2} \cdot \log C_s \]

There are many other contaminants in the overhead system, such as H2S, ammonia (NH3), sulfur oxides (SOx) and others that can alter conditions and force changes on the predicted pH values. We cannot establish a direct relationship between the chlorides (Cl\(^-\)), flowrate and pH neutralizer from field results. However, we can determine the salt concentration (N2Cl) from the N2 solutions, as described in Table 4, and compare it with the expected resulting pH. Table 4 lists the results; observing that, in a few cases the values coincide, as in D1, D3, D4 and D5, and the neutralizing added on top is extremely diluted into the total water solution (264,000 l).

At the VB unit presented in this study, various problems caused by corrosion are sourced to low operating efficiencies in the crude desalting unit, which is initiated at the storage tanks. Checking field data and literature to find benchmark values for evaluating the effectiveness of existing desalters can help maximize salt-removal efforts. Also, leakages observed in pipelines in Train A were mainly caused by deficiencies in pH control. This is the main control parameter in the tower overhead, and it must be kept within the range with the minimum possible deviation. We could not associate a neutralizer type to observed failures.

The results showed that even with a stable pH behavior over the study period, corrosion increased. The standard deviation observed during 2012 was 0.54, with daily routine measurements. This value is consistent with observed deviation cited in the literature, equal to 0.78, when gaseous ammonia was used as a neutralizer in the same unit. The literature shows that low pH values lead to high corrosion rates on mild steel, even though the presence of inhibitors may be insufficient to alleviate this problem. Conversely, a pH too high can also bring negative consequences.
Using excess neutralizing solutions, based on amine or ammonia, favors the occurrence of deposits, leading to localized corrosion with extremely fast kinetics.

In stream containing H₂S, such as the CDU, stability of the protective iron-sulfide film is compromised while increasing its solubility, thus accelerating corrosion.

We can analyze a phase diagram for H₂O-HCl and correlate it to the overhead corrosion process. It is possible to observe a temperature range of approximately 100°C to 102°C, in which an average concentration observed in the field (0.7% HCl), and in which two phases are present in equilibrium conditions: vapor (rich in water) and liquid (rich in HCl). At the temperature where condensation begins, the HCl concentration in the liquid is 10 times higher than vapor phase. Only below 100°C, in equilibrium condition, the steam is fully condensed, and the final concentration of the liquid is reached.

To increase the process data analysis, the measured consumption of neutralizing amine in the overhead during 2012 were compared with values originally estimated by the supplier data presented in Figure 5. The comparison was done in a period in which the main process variables, such as pH and chloride content in the overhead drum, did not suffer interference from typical discontinuities, such as high levels of base sediment and water in oil. The selected period was the months of January 2012 to March 2012, in which the corrosion rate was below the recommended target of 0.09 mm/yr, as shown in Figure 6.

Application of neutralizing amine can be varied for many reasons, such as incorrect pH measurement, which interferes directly in injection flowrate. If the quality of the crude is kept almost constant, the product amount injected into the overhead stabilizes. This is the condition studied in the chosen period optimum injection to compare the predicted with the far field. From Figure 5, the relationship between the measured and predicted consumption of neutralizer is doable.

For a maximum chloride content of 50 ppm at the overhead using data of steam injection background and specific consumption provided by the manufacturer, the amount of amine provided at the top would be 60 l/d, while in practice, keeping variables under control, the measured consumption was 120 l/d. We can conclude that the predicted flowrate for the neutralizing solution can be a guide for the process, but only constant pH monitoring (preferably online) can promote adequate control for amine injection.

Corrosion rates are directly proportional to pH. Accordingly, field monitoring uses weight loss coupons to validate the quality of process parameters control. Measurements were made from 2008 until early 2013, when only 35% of cases were below the limit 0.13 mm/yr. Throughout 2008, the weight loss was framed in only 30% of the months monitored. Comparing these results with inspections by thickness measurement, we realized that the difference between the rates obtained with both techniques was short only at the second decimal number.

Among the available neutralizing solutions, we should use the one that provides the best efficiency, coupled with the cost benefit for each unit, while considering environmental aspects from waste generation and final treatment. There are pros and cons associated with each neutralizer. The results showed that the type of neutralizer used on the CDU atmospheric tower overhead was not the determining factor in minimizing corrosion. Only a good control of process parameters, especially the desalting efficiency (low chloride level at the overhead accumulator drum), can increase equipment service life. We can also establish a direct relationship between the historic data of the process parameters (chloride level, pH, temperature and pressure) and the expected thickness loss of the equipment and pipes. Monitoring weight-loss coupons is essential to validate the quality of the process parameters’ control. The rates obtained with the coupons were compared to results from inspections by ultrasonic thickness measurement, where only a small difference in the second decimal number (0.02 mm to 0.07 mm) was observed. With these low rates and constant monitoring, the likelihood of failure is minimized, and it becomes possible to predict damage to equipment and avoid unplanned shutdowns due to equipment failures by corrosion. Plant results and literature data indicate that there is an optimal pH control range for the CDU overhead system. The main process parameter, defined in terms of two main corrosion mechanisms are:

• At low pH (pH below 5.5) the HCl causes severe corrosion in the mild steel
• At high pH (pH above 6.8), due to the presence of H₂S, there is an increase in the uniform corrosion rate due to the breakdown of the iron sulfide layer, and localized corrosion under deposit is also more likely to occur because of the salts formed. For each system, an optimal range should be specified. It will depend on the chemical composition of the final solution obtained in the accumulator drum. It is important to note that pH stability is dependent on system automation. More reliable online information enables low deviations if there is an instrumented injection control fed by online pH measurement. From this study, it was observed that the average chloride concentration was 10 ppm to 30 ppm in accumulator overhead drums. Chlorides are generated from some salts contained in the crude oil that is processed in the CDU; thus HCl is formed. Regardless of the neutralization technique applied, the pH is lower than the dew point of water. This adds more challenges in measuring pH.
when condensation occurs; this is the preferred region for the corrosion process to begin. One concern for neutralization is the difficulty of controlling the ammonia or amine flowrates, which depend on the varying HCl levels in the CDU.

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