Corrosion in the crude distillation unit overhead line: Contributors and solutions

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Abstract

This study is about corrosion found in the overhead line of a crude distillation tower. To understand the reasons for the observed degradation and to derive appropriate conclusions, a comprehensive review of all relevant parameters was conducted. The most important process parameters such as throughput, temperature or dew-point and data from injection of neutralising and filming amines were recorded during one year. Also, crude desalter efficiency and process water quality in the overhead accumulator vessel (regarding pH, chlorides, ammonium and iron content) were considered. Furthermore, corrosion data from ER probes (electrical resistance), UT sensors (ultrasonic testing) and weight-loss coupons was analysed for the same period. The comparison of all parameters suggested corrosive amine salts as main contributor to the observed corrosion where amine hydrochloride salts appear to be dominant. The involvement of NH_4Cl salts was predicted by a simple model to be unlikely. Also, the variation of the neutralising amine injection rate did not influence pH significantly. Finally, a chloride limit for the overhead system was calculated for the conditions present to limit the corrosion rate in carbon steel equipment.

Keywords

Crude distillation unit, CDU overhead, ammonium salts, amine hydrochloride salts, HCl corrosion, NH_4Cl corrosion, corrosion inhibitor, neutralising amine, corrosion monitoring.

Introduction

Corrosion and/or fouling issues in the overhead system of crude distillation units (CDUs) are a well-known and well-described phenomenon in the petrochemical industry. The most important degradation mechanisms are 1) aqueous corrosion owing to hydrogen chloride that origins from hydrolysis of inorganic chlorides in crude pre-heat and furnace, 2) corrosion due to ammonium and/or hydrochloride salts that absorb moisture and start corrosion somewhere above the aqueous dew point, and 3) fouling of heat exchanger or air cooler tubes by such salts. Mitigation of these degradation mechanisms always involves several parts of the unit (crude tanks, desalter, injection points, overhead system etc.) and a combination of different approaches is needed such as optimisation of the desalter performance, injection of chemical agents or dew point control in the overhead system. This complexity makes an overhead system one of the most vulnerable parts of each distillation unit. It also explains why corrosion/fouling in CDU overheads is still nowadays frequently observed, resulting in unplanned and expensive unit outages. This study provides a comprehensive review of process, chemical and corrosion data gathered during one year in one of three CDUs in Shell Rheinland Refinery. The conclusions suggestions drawn from this analysis are currently realised in order to minimise the observed corrosion.

Background

1) Corrosion mechanisms

The most important corrosion mechanisms that can appear in the CDU overhead can be summarised as follows:

- HCl corrosion: Corrosion due to dilution of HCl vapour into liquid water. Especially the first water droplets formed during condensation can be very acidic and can provoke localised but heavy corrosion at very low pH. HCl is mainly formed by hydrolysis of naturally occurring inorganic chloride salts when crude oil is heated up in the pre-heat train and in the CDU furnace. Most HCl is produced by heat-unstable salts such as $MgCl_2$ and $CaCl_2$ that start to hydrolyse at much lower temperatures than e.g. NaCl does. NaOH injection into crude oil helps to minimise salt hydrolysis, see below.

- Ammonium chloride (NH_4Cl) corrosion: HCl tends to combine with NH_3 to form ammonium chloride (NH_4Cl) [1]. NH_3 can origin 1) from hydrocarbon streams that are blended into crude oil, 2) from the desalter's wash water that often comes from other refinery units where NH_3 is formed or 3) it is even injected intentionally into the CDU overhead vapours to neutralise liquid HCl (i.e. for pH control). The re-sublimation of solid NH_4Cl salt depends upon the partial pressure of both HCl and NH_3 vapours; the product of these partial pressures is the K_p value. NH_4Cl salts usually form above the aqueous dew point and they remain dry and non-corrosive as long as the process temperature is sufficiently above the dew point. A typical suggestion for this temperature difference is minimum 20 to 25 Kelvin. The reason for this limit is that NH_4Cl is very hygroscopic and can absorb moisture, even if water has still not condensed [1]. If NH_4Cl salt deposits become wet, they can be very corrosive to many kinds of materials provoking localised under-deposit corrosion. Also, excessive salt formation can cause fouling, particularly in overhead heat exchangers and air coolers. Typical approaches to prevent NH_4Cl corrosion are 1) reduction of NH_3 and HCl levels and thus salt formation temperature by optimising the crude oil desalter and by adding NaOH, 2) temporary water wash in the overhead line to remove salt deposits or even continuous water wash to avoid salt deposition, 3) reduction of intentionally injected NH_3 to a minimum and 4) increase of the process temperature in the overhead line (if feasible from an economic standpoint regarding product yields).

- Amine hydrochloride salt corrosion: HCl can also combine with amines to form hydrochloride salts that behave similarly to NH_4Cl. Some hydrochloride salts can even be liquid and thus corrode a larger surface [1]. Amines can origin 1) from amine solutions that are injected into the overhead line for pH control as more effective alternative to NH_3, 2) from desalter wash water carry-over (as for NH_4Cl), 3) from upstream facilities where amines are frequently injected e.g. as H_2S scavengers, and 4) from imported residues or synthetic crude feedstocks that are used for blending and that can contain amines from corrosion inhibition on other sites. Such amines that are brought from externally into the refinery are often referred to as "tramp amines" [2].

- Wet H_2S damage: Under wet conditions and if sufficient H_2S is present, blistering and/or cracking can occur, dependent upon water pH, cyanide content, plate metallurgy and welding procedure (mainly regarding post-weld heat treatment). The different cracking mechanisms will not be discussed further in this study, which focuses on corrosion due to HCl and salts.

2) Minimisation of overhead corrosion

The most common approaches to generally minimise the above-mentioned corrosion mechanisms are as follows [3]:

- Blending: One of the most common techniques for corrosion control is blending corrosive crudes with less-corrosive crudes, dependent upon refinery configuration and crude flexibility.
- Crude oil de-watering: Most salts are diluted in the water phase why the crude oil's water content should be minimised, e.g. by draining crude oil storage tanks. A typical H_2O limit for desalted crude oil is max. 0.5 wt.-%.
- Crude oil desalting: Crude oil is mixed with wash water to remove most of inorganic contaminants (e.g. salts) and solids, typically at temperatures between 100 and 150°C and water contents of approx. 5 vol.-%, including injection of chemicals such as de-emulsifiers to avoid emulsion formation or chemicals to control pH of the desalter water. Oil and water phase are separated in the desalter where most salts and sediments leave the vessel together with the water phase.
- Caustic injection: To minimise hydrolysis and thus HCl in the overhead. Diluted NaOH is typically dosed into crude oil downstream of the desalter. Caustic will then convert most of the unstable chloride salts (such as $MgCl_2$ and $CaCl_2$) and/or already formed HCl into NaCl that leaves the distillation column through the bottom. The exact mechanism of how NaOH reacts with chlorides is still under debate [1].
- Injection of chemical agents: NH_3 or amines are often used to neutralise HCl and to control pH in the condensing water phase by e.g. injecting them into the overhead vapour. Note that, as indicated above, amines such as e.g. ethylene diamine (EDA) or monoethanolamine (MEA) are more effective in stabilising the pH of the first water drops condensing. The disadvantage of ammonia (NH_3) is that it dissolves into water much slower than HCl and most amines do [4]. Hence, NH_3 has a comparably poor ability to influence pH at the point of first condensation. Typical pH limits are 5.5 to 6.5 to avoid increased corrosion at lower pH and salt formation (and possibly fouling) at higher pH. Also, organic corrosion inhibitors are injected to reduce corrosion. They are commonly called "filmers" as they attach to the internal surface protecting it to some degree from corrosion by acidic solutions.
- Water washing: As mentioned above, water washing is an important tool to 1) dilute low pH water phases at dew point conditions and to 2) wash out salts from overhead piping and heat exchangers / air coolers.
- Materials selection: The application of CRAs (corrosion resistant alloys) is restricted, due to chlorides present, mostly to ferritic steel, (super-) duplex steel or (comparably expensive) Ni base alloys. For this reason, unalloyed carbon steel is still likely the most common material used in CDU overhead piping and vessels.

Procedure

This study is about one of three crude distillation units that exist in Shell Rheinland Refinery. The corresponding CDU has a one-step overhead system as shown by Figure 1. The overhead vapours leave the atmospheric distillation column over the top. In the following horizontal part of the DN 800 overhead line there are injected two chemical agents, both via a typical injection quill. Four chemicals are injected via an injection quill on different locations:

- Neutralising amine into the overhead line (aqueous solution without dilution into slip stream, average injection rate is approx. 3 l/h and adjusted continuously by the chemical vendor on pH, chloride and iron content of process water ex overhead accumulator vessel)
- Filming corrosion inhibitor into the overhead line (diluted with Naphtha slip stream, constant injection rate of approx. 0.5 l/h)
- Filming corrosion inhibitor injected into the (Naphtha) top cyclic reflux (TCR, constant injection of approx. 0.4 l/h)
- Aqueous NaOH solution (5 wt.-%) diluted with a crude oil slip stream and injected into crude right after the crude desalter (not shown in Figure 1). This NaOH dosing is practiced since 2012. This explains why the overhead condensers were originally made from a corrosion-resistant alloy, see below.

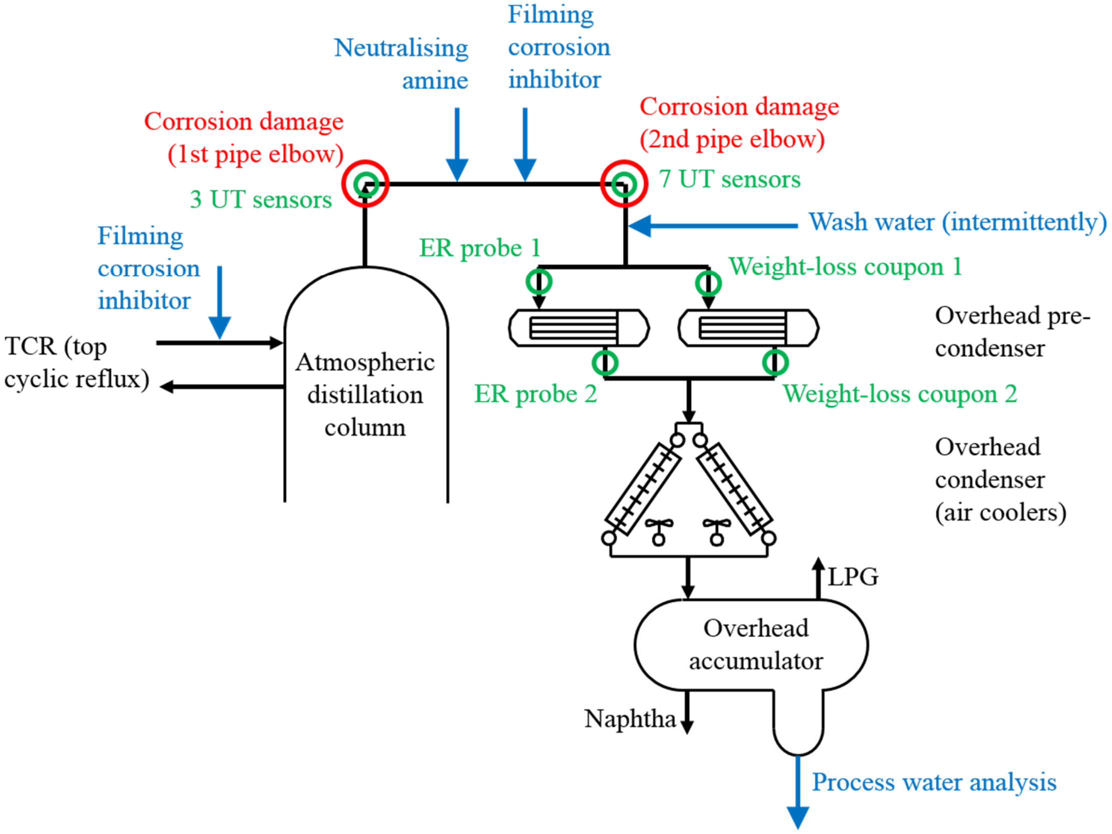

Figure 1: Crude distillation overhead setup.

The vapours are routed downwards and cooled / condensed in two steps (two parallel heat exchangers and afterwards in air coolers) before entering the overhead accumulator vessel where Naphtha is separated from light hydrocarbons and process water. Wash water is injected intermittently into the overhead line (approx. once per month for 2-3 hours) to wash heat exchangers and air coolers / prevent fouling. Continuous corrosion monitoring is done in the overhead system by

- 2 intrusive electrical resistance (ER) probes that determine online a corrosion rate. They are installed upstream and downstream of one heat exchanger to monitor corrosion under dry conditions (upstream) and after partial condensation (downstream).
- 2 intrusive weight-loss coupons in a similar position close to the other heat exchanger. They are removed /renewed every approx. 3-4 months
- 10 wireless Permasense® UT (ultrasonic testing) sensors that measure twice a day local wall thickness on the first and on the second elbow, see Figure 2. Sensor installation and technique are described in detail elsewhere [5].

Most piping and vessels located in the overhead system are made from (unalloyed) carbon steel, including ER probes and weight-loss coupons. Only the air cooler tubes as well as the header boxes are made of the super-austenitic alloy 904 L. Furthermore, one of two heat exchanger bundles was upgraded recently from carbon steel to Alloy 59 (NiCrMo). Overhead line and heat exchangers suffered increased corrosion in the past. Accordingly, parts of the overhead line such as nozzles (where salt deposition and water condensation are more likely) had to be replaced due to increased wall thinning. Also, both heat exchanger bundles are designed to be replaced regularly due to water condensation that initiates in these bundles. Severe pitting corrosion and scaling on the external surface of the tube bundles and in the bottom of the shell seems to be most likely caused by corrosive salts.

Figure 2: UT sensor arrangement on 1st (left) and 2nd (right) pipe elbow of overhead line.

In spring 2016 there was found during a major turnaround severe wall thinning in the first two elbows of the overhead line, see Figure 1 and Figure 2. It should be emphasised that the appearance of this wall thickness reduction was very uniform (no pitting or non-uniform distribution at all); it was even difficult to visually detect this thinning after demounting and observing both elbows from the inside. As one consequence, the second elbow was replaced and the above-mentioned 10 UT sensors were installed on both elbows to start monitoring wall thickness and thus corrosion rates on these locations. After one further year, in spring 2017, all available measuring data from the last year was gathered and analysed in detail. The corresponding results and conclusions are summarised below.

Results and Discussion

1) UT sensor measurements

The wall thickness data recorded by the wireless UT sensors from Figure 2 was converted into corrosion rates that are shown in Figure 3. Note that, due to legal reasons, all corrosion rates in this study are normalised values being called "relative corrosion". This means that absolute values (in mm/y) were transformed by a simple multiplication with a constant factor into relative values (in %). This normalisation was applied consistently to all corrosion rates calculated from different devices (ER probes, UT sensors and weight-loss coupons) te ensure comparability.

In Figure 3, each black line represents one UT sensor; there are some differences between different sensors but in general they describe similar and significant ups and downs of corrosion over time. On the one hand, this emphasises a good repeatability of these sensors if they are located close to each other. One conclusion from this data was that the number of sensors per piping element (such as elbows as in this case) can be limited to 2-3 sensors. On the other hand, the average corrosion varied between zero and more than 0.8. This is a clear indication that corrosiveness in the overhead line varied significantly during this period of time. The lack of data in between (indicated in Figure 3) was caused by coating and insulation works why the sensors had to be removed for approx. two months and by some antenna outages (later in time).

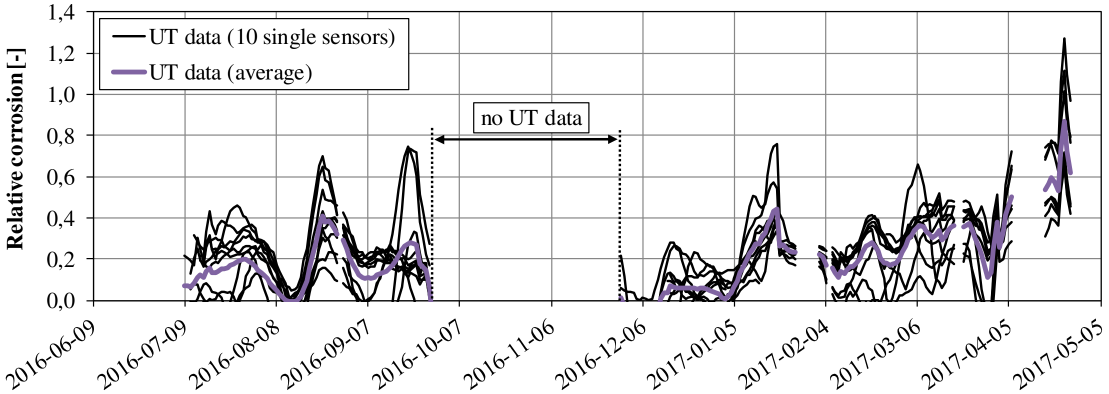

Figure 3: Corrosion measured by wireless UT sensors on overhead line.

2) Comparison of all relevant parameters

For a thorough and comprehensive corrosion analysis all parameters that might influence corrosion in the overhead system were recorded during approx. 11 months and their trends are shown is Figure 4. For purposes of clarity, all diagrams are plotted one upon the other to allow comparison of different data. Figure 4 can be summarised as follows:

- The desalter performance (Figure 4a) is indicated by the contents of remaining water and NaCl after the desalter that should be as low as possible. Accordingly, the water content was almost always below a typical threshold value (0.5 wt.-%) but increased NaCl contents up to 22 ppmw reveal frequent desalter issues. NaCl is here not an issue due to its low tendency for hydrolysis but it indicates that other, more instable chlorides may also remain in the desalted crude oil (not measured at this location).

- The same diagram (Figure 4a) shows the NaOH concentration of the crude oil right after the desalter / at the NaOH injection point. The NaOH injection rate is adjusted automatically on the crude feedstock rate, which explains rather constant concentrations between 4 and 5 ppmw with drops if the crude feed to the distillation tower dropped, too. Typical limits for CDUs with desalter are maximum 11 to 14 ppmw [1], which suggests some space to higher rates. Anyway, the NaOH concentration should be as low as possible to minimise sodium contents in residues and related issues with increased coking or poisoning of catalysts.

- Figure 4b shows three important process parameters for the overhead line: Throughput, flow velocity (directly derived from throughput for DN 800), and pressure. These parameters are in a typical range for such an overhead line with some ups and downs due to process variations.

- An important question is if condensation must be expected in the overhead line, which is treated by Figure 4c. Therefore, the dew point was calculated on an empirical basis dependent upon water content / partial pressure. The process temperature of the overhead vapours was quite constant at around 130 °C. The calculated dew point for the column's top and the overhead line was in average 51 Kelvin and always not less than 39 Kelvin below the process temperature, see the distance between black and blue line. This is for sure a comparably large distance between temperature and dew point, which makes condensation in that location very unlikely, even at "cold spots" such as e.g. nozzles or uninsulated parts. A more conservative approach is to look at the difference between calculated dew point and the TCR temperature right before the TCR enters the upper part of the distillation column: This delta T was in average 25 K, see green line in Figure 4c. NACE [1] suggests 1) the dew point to be min 14 K above the salt point and 2) the process temperature to be further min 14 K above the dew point. This would ensure the presence of free water in advance to salt formation. The salt point is, however, unknown because the salt composition is unidentified. Furthermore, it should be noted that formed salts are very hygroscopic and start absorbing moisture at temperatures somewhere above the dew point. For these reasons, higher limits are usually applied such as min 28 K [1] or min 22 K (within Shell, see dotted line in Figure 4c). In this study, the 22 K limit was not exceeded in most of the time (column top) or not at all (overhead line). Consequently, both dew point corrosion (due to diluted HCl) and corrosion by water-absorbing ammonium / amine hydrochloride salts appear from this data to be rather unlikely for the overhead line.

- The ambient temperature (daily average) varied seasonally between + 27 °C and - 4 °C and was also considered because the overhead line was not fully insulated during a certain period due to maintenance works. The data (see yellow line in Figure 4c) suggests, however, no significant impact on process temperature (black line) and thus on condensation on the process side.

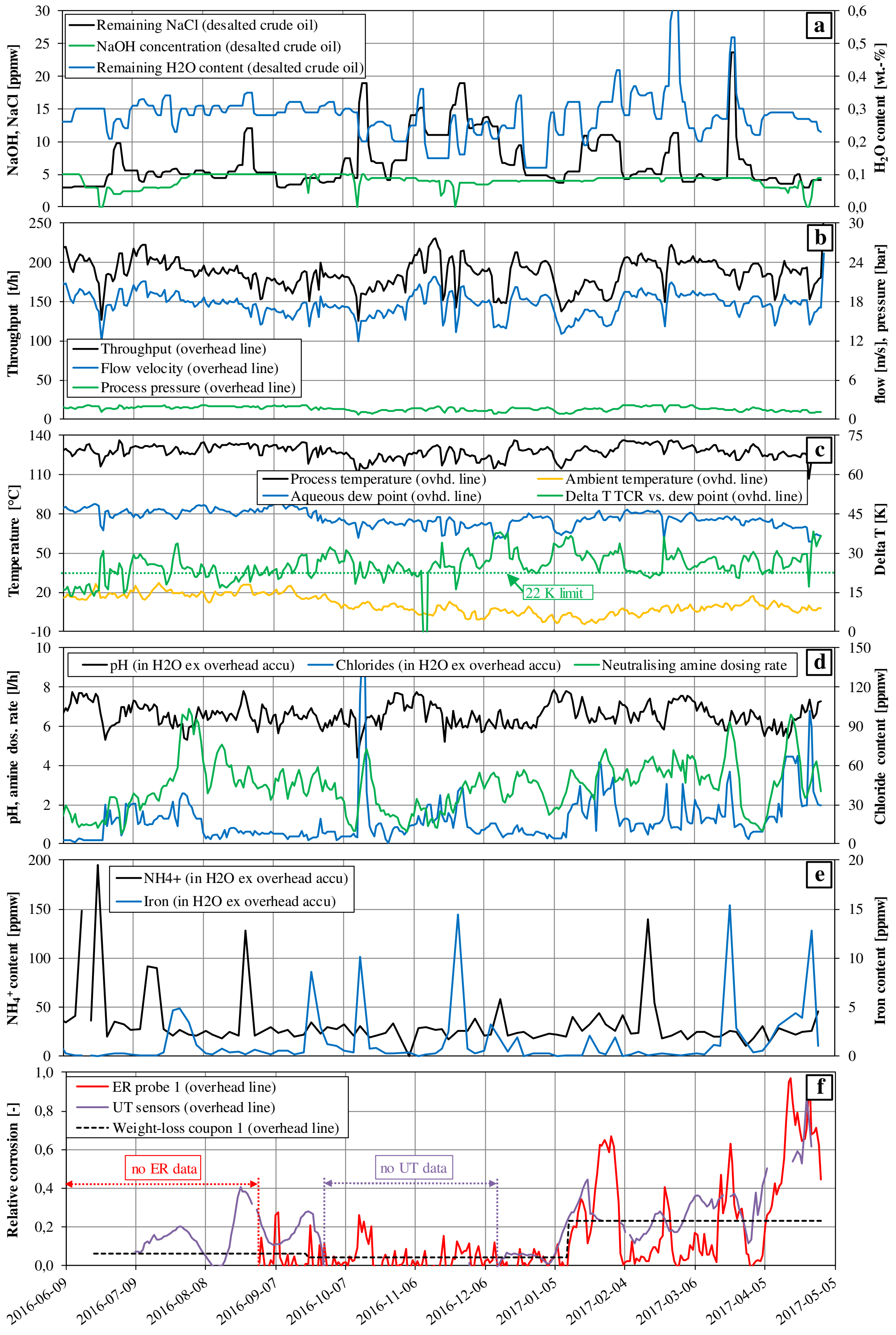

Figure 4: Process, chemical injection and corrosion data between 2016-06 and 2017-04.

- Very important to check is, of course, the process water quality from the overhead accumulator, see Figure 4d. The often-used chloride limit of max 10 ppmw was exceeded in 60% of the time with 5 peaks at even > 50 ppmw. The average chloride content was 18 ppmw, which clearly suggests increased corrosion, particularly for the carbon steel equipment. Interestingly, the corresponding pH (black line) was in average 6.6, being in 44% of the time within the typical range (5,5 to 6,5), only few times (2%) too low, but many times (54%) too high with peaks up to 8. High chloride levels together with increased pH can be explained by the following hypothesis: HCl vapours are not diluted in the water phase (to immediately form aggressive hydrochloric acid) since there is no liquid water in the overhead line due to the large distance between process temperature and dew point, see above. Hence, the gaseous HCl present might react (at least partially) with (tramp) amines to form hydrochloride salts. The formation of pH-decreasing salts (when being diluted in water during condensation) such as e.g. NH_4Cl seems to be unprobable because of the comparably high pH during the year. Further reasons for elevated pH can be excessive NaOH and/or amine dosing.

- The intention for adding neutralising amine into the overhead line is to limit the water pH to a minimum, which again limits the corrosion rate. Consequently, the above-mentioned comparably high pH values either a) challenge the need for neutralising amine or b) even indicate overdosing of neutralising amine and/or filmers (that generally increase pH). Furthermore, the actual amine dosing rate was varied significantly over time (see green curve in Figure 4d, in average 2.9 l/h); but it does not seem to have a large influence on the water pH in the overhead accumulator. This is discussed further below.

- The filming amine corrosion inhibitors used in TCR and overhead line are further sources of amines for possible reactions with HCl to form amine and/or amine hydrochloride salts. However, they usually tend to be less reactive with HCl than neutralising amines owing to their different chemical composition [1].

- Two further parameters are measured twice a week in the water phase from the overhead vessel, see Figure 4e: Ammonium (NH_4^+) that reflects the salt formation potential but it also includes all injected amines, which makes interpretation difficult. Moreover, the iron content is determined to check for active corrosion. Both parameters reveal sharp peaks that coincide rather well with chlorides in desalted crude oil and chloride peaks measured in the same water phase. The observed average ammonium content (34 ppmw) is argued to be in a typical range for CDU overhead systems [6] whereas the average Fe content (1,5 ppmw) was comparably low. Low Fe contents together with increased corrosion rates suggest more localised than generalised corrosion.

- The corrosion measuring data from all three techniques is shown by Figure 4f. Note that from both ER probes and weight-loss coupons only data from the probes upstream of the pre-condenser is considered for purposes of comparison. The measuring data looks very similar: All techniques reveal an increased tendency for corrosion during the whole period, even the weight-loss coupons with their very low "measuring frequency" (approx. 3.5 months) compared to ER and UT probes. Furthermore, single peaks in corrosion coincide quite well for ER and UT probes, which confirms both techniques as appropriate techniques for corrosion monitoring in such a CDU overhead system. Interestingly, ER probe 1 shows a higher variation in corrosion and seems thus to be more sensitive than UT wall thickness sensors; on the other hand, ER data seems to be "delayed" by approx. 5 days. The reasons for this different behaviour might be linked to the different location: ER probes are intrusive and located in the centre of the pipe whereas UT sensors detect corrosion / wall thinning directly on the internal pipe surface.

Note that the sensitivity of the wireless wall thickness sensors used in this study is comparably high at approx. ± 0.01 mm [5]. Moreover, the process conditions should be similar at both locations. Also, it was found a rather clear correlation of corrosion data with the chloride content of the water phase from the overhead accumulator (Figure 4d). This finding is discussed further in the next section.

The data further showed that wash water injected intermittently did not have any noticeable effect on the data presented in Figure 4.

3) Further discussion

a) Neutralising amine dosing

The neutralising amine injection was further compared in detail to pH and corrosion data, see Figure 5 (data from Figure 4d/f). As discussed already above, neutralising amine is used to increase pH but Figure 5a suggests the injected amine to be rather ineffective. Accordingly, the pH varied mostly between 5 and 8, irrespective of the large variation of the amine dosing rate between 0 and around 10 l/h. A simple linear data fit would even slightly suggest a decrease in pH with increasing dosing rate (not included in the diagram). One may argument that it takes some time for injected amine to adjust pH. The general appearance of Figure 5a does, however, not change if one compares dosing rates with pH from a later time (e.g. from one day afterwards).

Figure 5b reveals a similar picture: Corrosion measured by probes/sensors that are downstream from the amine injection point does not correlate with the amine dosing rate. This is surprising since amine dosing is eventually intended to reduce corrosion, at least indirectly by controlling pH. Figure 5 is hence generally questioning the need for dosing neutralising amine for the conditions as presented in this study. Furthermore, it should be noted that dosing rates should always be as low as possible to avoid overdosing. Injected amines (especially for neutralisation and, to some degree, as filming corrosion inhibitor) can be generally counterproductive because they can form corrosive salts together with HCl. This results at the end of the day in corrosion and/or fouling [1,7].

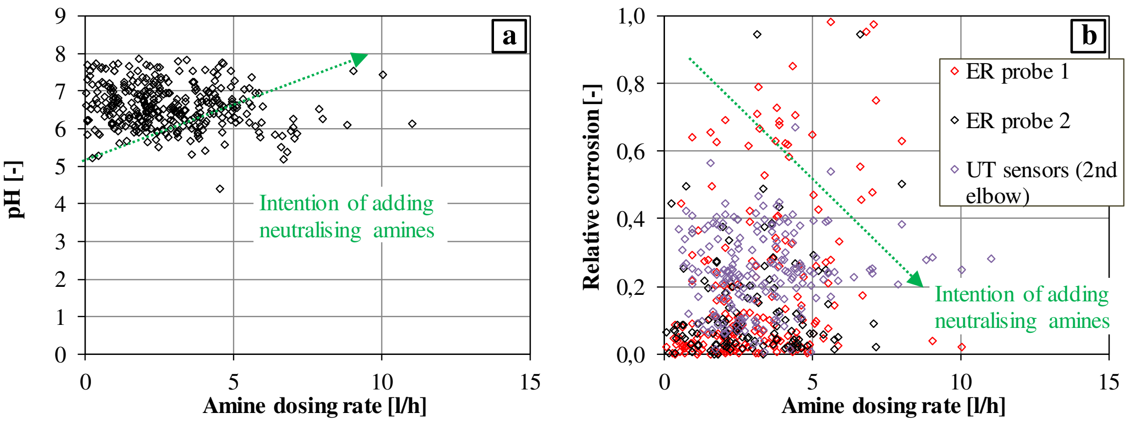

Figure 5: Relationship between pH (a) / corrosion data (b) and neutralising amine.

b) Influence of chlorides on corrosion

The above-mentioned correlation between chlorides in the overhead water and corrosion (from Figure 4d/f) is presented in Figure 6. The diagram clearly shows how increasing chloride contents increase the tendency for corrosion in the overhead system, which is not very surprising since it confirms well-known knowledge [1,7].

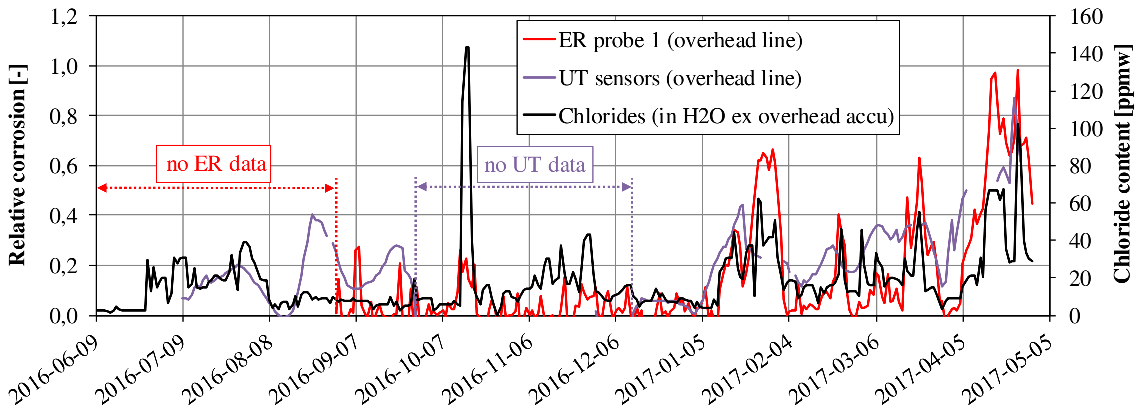

Figure 6: Effect of chloride content on corrosion.

The relation between both parameters was plotted again for ER probe 1 in Figure 7 (not shown for UT sensors whose date appears similarly). The data was fitted with the green curve that is the graph of the power function given in equation (1). The constant parameters c_1, c_2 and c_3 were calculated with the method of least squares regarding the chloride content. Note that three data points at chloride contents > 110 ppmw were excluded from this calculation because they represent most likely a measurement error during probe sampling.

$$Relative\ corrosion = c_0 + c_1 \cdot chloride\ content^{c_2} \qquad \ldots(1)$$

From the fit one can derive a suggestion for the maximum chloride content. The resulting limit was determined to be max 17 ppmw. This should limit corrosion for carbon steel equipment to a typical design corrosion rate that gives a lifetime of 20 years, see horizontal dotted black line in Figure 7. 17 ppmw fits very well into the range between the widely-used limit of 10 ppmw and other suggestions such as 15 ppmw [6] or, even less conservative, 20-25 ppmw [1].

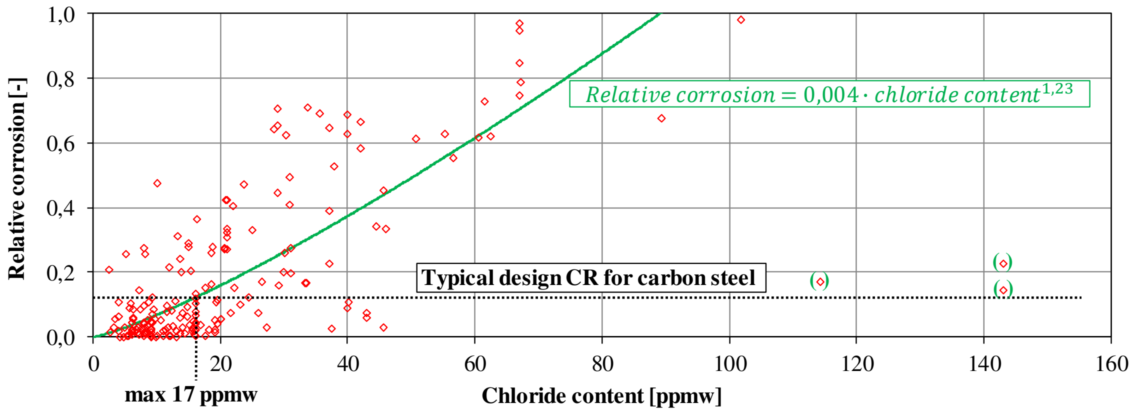

Figure 7: Corrosion prediction based on corrosion data (ER probe 1) and chloride content.

Note that the empirical corrosion prediction from measurements of 1) corrosion and 2) chloride content in the overhead process water does not consider at all in which form the chlorides are present when corrosion starts. Also, consider that it represents the process conditions as represented for the CDU overhead of this study.

c) Prediction of NH_4Cl salt formation

One uncertainty remains the question which salts form in the overhead system presented in this study. This question cannot be answered easily since the composition of salt forming amines present is unknown, too. Nevertheless, one typical salt that is usually expected in CDU overhead systems and that is suggested as main contributor to corrosion is ammonium chloride (NH_4Cl) [1]. The related corrosion mechanism was outlined in the background section above. It should be further noted that one reason for the frequent appearance of NH_4Cl-related corrosion issues, not only in CDUs but particularly in hydroprocessing units, is its low salt point compared to other ammonium salts, see Figure 8. The diagram shows that the partial pressures of NH_3 and HCl needed to allow re-sublimation of solid NH_4Cl salt are significantly lower than for other ammonium salts. Also, as known from literature and practice, higher temperatures allow higher concentrations / partial pressures to avoid salt formation, being indicated by the curvature of the curves.

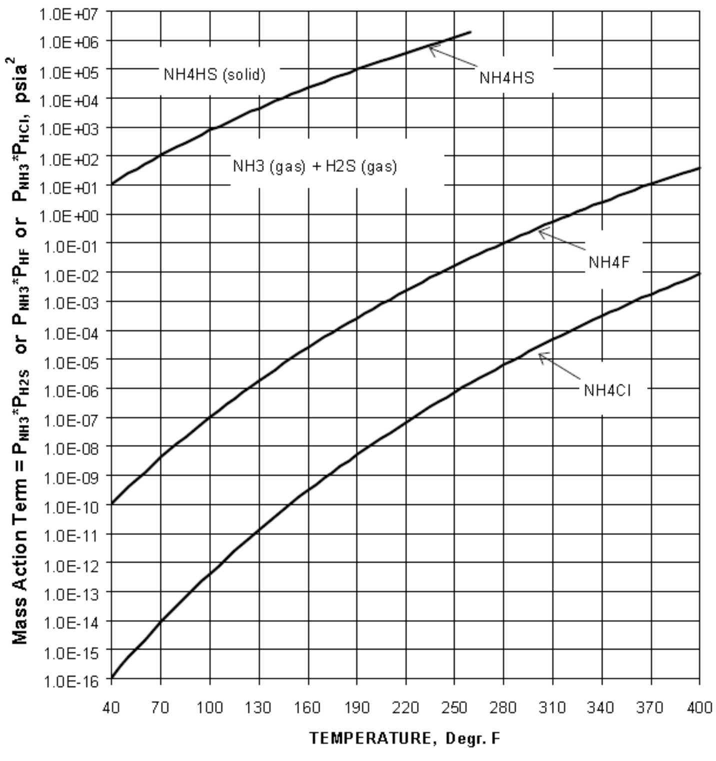

Figure 8: Ammonium salt deposition curves [8].

The mass action term K_p (product of NH_3 and HCl partial pressures) for NH_4Cl formation was determined from Figure 8 for an average temperature in the overhead line of 130 °C (= 290 °F) to be $2.76 \cdot 10^{-7}$ bar². This value coincides well with other salt point diagrams in literature [1]. On the other hand, the actual mass action term was estimated from equations (2) and (3). p_{total} and ρ_{total} are live pressure and average density of the overhead vapour, V_m is the ideal gas molar volume (assuming for purposes of simplicity ideal gas conditions in the overhead line), and M_{NH3} and M_{HCl} are the (constant) molar masses of ammonia and (gaseous) HCl. It was further assumed that ammonia (NH_3) is diluted in the accumulator's water phase to fully form ammonium ions (NH_4^+). For purposes of simplicity, the NH_4^+ content was assumed to be the average value from above (34 ppmw, recall Figure 4e) because NH_4^+ was determined only twice per week. The chloride content in equation (3) comes from daily live values, see the results above (Figure 4d). All constant parameters are summarised in Table 1.

$$\frac{p_{total}}{p_{NH_4}\cdot p_{HCl}} = \frac{p_{total}}{K_p} = \frac{n_{total}}{n_{NH_4}\cdot n_{HCl}} \qquad \ldots(2)$$

$$K_p = p_{total}\cdot \rho_{total}\cdot V_m\cdot \left(\frac{x\%\cdot NH_4^{+}content)}{M_{NH_3}}\cdot\frac{y\%\cdot chloride\ content)}{M_{HCl}}\right) \qquad \ldots(3)$$

The amount of NH_4^+ and HCl that may form NH_4Cl is unknown. Also, the amount of NH_3 is unknown that is finally measured in the form of NH_4^+ in the accumulator's process water. Therefore, different curves for K_p were produced assuming different amounts of NH_4^+ and HCl being involved in NH_4Cl formation, see Figure 9. This allowed to check the sensitivity of the model to varying NH_4^+ / HCl contents. Thus, the analysis showed that the critical partial pressure product K_p is hardly reached in the overhead line, even if 100 % of the measured NH_4^+ and HCl are assumed to fully form NH_4Cl; and this assumption seems to be unrealistic because at least some part of the ammonium measured was likely bound in other chemical compounds, e.g. in amine hydrochlorides. Furthermore, injected amines are also affecting the measured NH_4^+ value.

Table 1: Constant parameters for NH_4Cl salt point calculation.

Parameter	Description	Value
K_p ($p_{NH3}\cdot p_{HCl}$)	Threshold partial pressure product for NH_4Cl salt re-sublimation	$2.76\cdot 10^{-7}$ bar² (at 130 °C)
ρ_{total}	Average density of overhead vapour	6,29 kg/m³
V_m	Molar volume for ideal gases	0,02241 m³/mol
M_{NH3}	Molar mass of NH_3	0,01703 kg/mol
M_{HCl}	Molar mass of HCl	0,03646 kg/mol

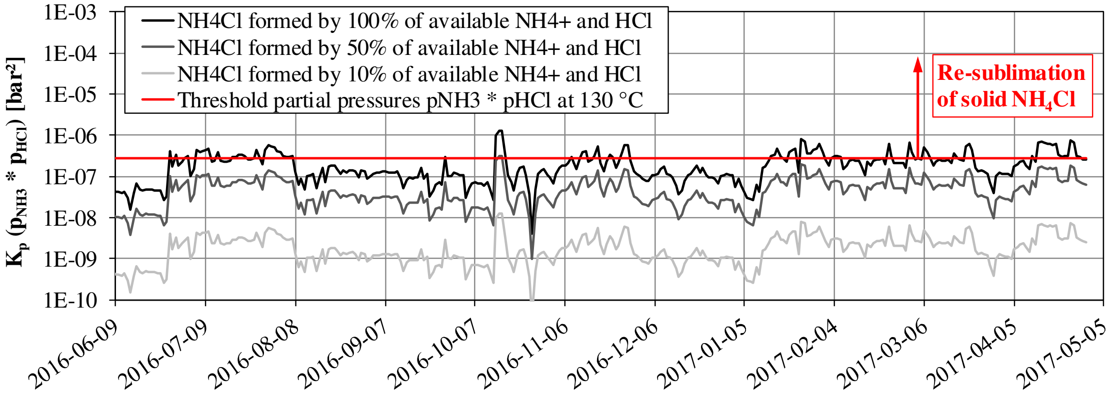

Figure 9: Prediction of NH_4Cl salt re-sublimation based on NH_4^+ and HCl content.

Nevertheless, under the conditions present in this study and with the assumptions made, NH_4Cl formation in the overhead line is unlikely. This finding together with the above-described high chloride – high pH observation leads to the following conclusion: Both (aqueous) HCl and NH_4Cl corrosion seem to be of secondary importance. Instead, corrosion by amine hydrochloride salts can be carefully suggested as main contributor to the observed, increased corrosion in overhead line and heat exchangers. The above, described very uniform wall thinning in the first two elbows of the overhead line further suggests liquid amine hydrochlorides as main contributor.

Conclusions and suggestions

The following conclusions can be derived step by step from the results and for the process conditions presented above:

- Dew point corrosion was found to be unlikely in the CDU overhead line owing to a comparably large distance of (in average) 25 K between process and TCR temperature.
- Aqueous HCl corrosion in the overhead line is hence unlikely, too. This is supported by the comparably high water pH. It further increases the probability that the corrosion observed was primarily caused by ammonium and/or hydrochloride amine salts.
- Measured corrosion (by ER probes, UT sensors and weight-loss coupons) revealed a clear correlation between chloride content and corrosion rate.
- An empirical limit of max 17 ppmw was defined for the process conditions present in this study to keep corrosion in carbon steel equipment below a design corrosion rate that allows 20 years of lifetime.
- A simple model predicted the NH_3 and HCl partial pressures present as too low to form significant amounts of NH_4Cl. Thus, NH_4Cl as well-known corrosion contributor can be mostly excluded from the group of possibly contributing ammonium / amine hydrochloride salts.
- These findings and the recent corrosion appearance in the overhead line`s first two elbows (very uniform, no localised pitting) suggest liquid hydrochloride amine salts as one likely reason for the degradation found. Such compounds work as electrolytes promoting electrochemical corrosion without the need for liquid water.

Further conclusions are:

- The origin of liquid hydrochloride amine salts is unclear. Possible origins range from the crude oil diet itself over tramp amines from e.g. blended residues or condensates to the chemicals injected (amines and NaOH).
- The neutralising amine injection rate varied significantly over time being adjusted on measuring values from the overhead process water. The injected amine showed, however, no impact on pH that is actually intended to be controlled by the injection. Also, corrosion was not reduced by the injected amine.

These conclusions lead to the following suggestions:

- The 4 injected chemicals (NaOH, neutralising amine and both amine filming inhibitors) should be checked in a parameter study for their influence on the particular parameter that they are designed for to control. On this basis, each injection should be reduced carefully to a minimum necessary. Switching to other amines can also be a reasonable option. The (possibly positive) impact of NaOH on the (suggested) formation of liquid hydrochlorides should be checked separately by a comparison of NaOH injection vs. corrosion data during a certain period.

- Computer modelling / ionic modelling should be applied to calculate more reliably salt formation temperatures. This will also provide 1) water condensation rates and 2) salt deposition rates as further corrosion indicators.
- The refinery`s crude oil diet (including distillation into side streams) should be analysed for nitrogen levels as rough indicator for nitrogen compounds such as ammonia or amines.
- The planned extension of the above-described CDU by replacing the currently used flash vessel by a pre-flash fractionating column should be realised and would relieve the current CDU overhead system.
- The number of (Permasense®) UT wireless wall thickness sensors can be reduced to approx. 3 sensors per pipe elbow to have a sufficiently high repeatability, even on pipes with large diameters such as DN 800 as described in this study.

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