Crude Unit Corrosion and Corrosion Control

Authors: Ara Bagdasarian, Chevron Research and Technology; Jim Feather, Exxon Research and Engineering; Bob Hull, Marathon Oil; Ray Stephenson, Lyondell-Citgo Petrochemical; Russell Strong, GE Power & Water

Abstract

This paper reviews fundamental corrosion issues concerning the Crude Unit process. It is, in concise form: a description of the process and major equipment found in the Crude Unit; types of corrosion and where they occur; corrosion monitoring and inspection advice; and a list of related references for further reading. Keywords: Crude Unit, Atmospheric Column, Vacuum Column, desalting, inorganic salts, sulfur compounds, organic acids, organic chlorides, naphthenic acid, caustic addition, pH control, corrosion inhibitor, water washing, corrosion rate measurement

Crude Unit Process Description

In the petroleum refining process, the Crude Unit is the initial stage of distillation of the crude oil into useable fractions, either as end products or feed to downstream units. The major pieces of equipment found on crude units will vary depending on factors such as the assay of the design crude, the age of the refinery, and other downstream units. The unit discussed in this paper has all of the major pieces of equipment found on crude units including double desalting, a preflash section, an atmospheric section, a vacuum section, and a stabilization section.

Cold crude from storage is transferred from tankage by the unit charge pump and is preheated in a series of heat exchangers. It then passes through the desalters and another series of heat exchangers. The operation of the desalter is special enough to warrant a separate section following this crude unit process overview description.

There may be a flash drum in the middle of the desalted crude preheat, which will allow lighter vapors and water to be removed from the crude and sent into the upper part of the crude tower. This design helps to prevent accumulation of water hardness on the preheat tubes as a precursor to fouling. If there is no flash drum, at 450°F to 550°F (230°C to 280°C) the crude may enter a Preflash Column. The Preflash Column typically has no reboiler section or bottoms stripping steam, so with no upward moving vapors from any source other than the crude preheat, the crude will enter below the bottom tray. In the Preflash Column, most of the light naphtha and all of the lighter components are removed from the crude oil, yielding a “flashed crude.” Preflashing the crude unloads the top of the Atmospheric Column and the Crude Heater, thus increasing throughput and reducing heater coking. A Preflash Column will often operate at a temperature low enough that condensation of water can occur inside the tower, which often leads to corrosion of the tower internals. Some units process a crude heavy enough that they do not have a Preflash Column, and crude is directly fed to the Atmospheric Column following the preheat and crude heater.

In a Preflash Column, butane and lighter fractions will go overhead. Liquids which distill overhead are most often sent to a Debutanizer and the gases are sent to the Saturate Gas Plant or plant fuel gas. Light naphtha may be drawn off the side of the Preflash Column, or taken overhead, depending on the refinery configuration. The light
naphtha and naphtha from the atmospheric column overhead may be combined and sent to a Naphtha Splitter. On units which do not include a Preflash Column or Flash Drum, it is common for the unit design to include a Stabilizer Column which will remove pentane and lighter material from the Atmospheric Column naphtha product.

The flashed crude from the bottom of the Preflash Column or Flash Drum is passed through a series of heat exchangers and enters the Atmospheric Heater at about 500°F to 550°F (260°C to 285°C). Leaving the heater at 650°F to 720°F (345°C to 380°C), it enters the Atmospheric Column flash zone. Naphtha vapors off the top of the tower are condensed and the naphtha liquid may combine with either a light or heavy naphtha and then go to the Splitter. The flow plan shown in Figure 1 shows a simplified single stage overhead system with one set of condensers and a reflux drum. The tower top temperatures of this type of system are typically in the range of 250°F to 280°F (120°C to 140°C). While somewhat uncommon, there are units with the Atmospheric Column top temperature near or below the water dew point and hence water condensation occurs in the tower. Some units have a two stage overhead system with tower top temperatures above 285°F (140°C). Often, these two-stage systems will condense part of the naphtha in the first stage and the remaining naphtha plus the water in the second stage. The first stage of such a unit may have problems related to shock condensation, due to low tube-wall temperatures, and salt deposition in the absence of a bulk water phase. The second stage of a two-stage system has similar types of corrosion problems to a single stage overhead. To maximize heat recovery, some units may have a more complex three or four stage condensation scheme. The process and design variations described above make universal corrosion control schemes impractical.

Kerosene is drawn off the upper part of the column, sent to a stripper and then to hydrotreating or #2 fuel oil product storage. Diesel is drawn off the middle of the column, sent to a stripper, and then to hydrotreating, Hydrocracker feed, or diesel or #2 fuel oil product storage. Atmospheric gas oil is drawn off the lower portion of the column, stripped, and sent to Fluid Catalytic Cracking (FCCU) feed or Hydrocracker feed. The atmospheric residuum from the bottom of the column is sent to the Vacuum Heater.

The residuum enters the Vacuum Heater 15°F to 30°F (10°C to 20°C) below the temperature that crude enters the Atmospheric Column, leaves at about 700°F to 740°F (370°C to 395°C), and is fed to the flash zone of the Vacuum Column. The vapor off the top of the column goes to a series of vacuum condensers which provide the necessary vacuum for column operation. Light vacuum gas oil is drawn off the upper portion of the column and goes to FCCU feed or Hydrocracker feed.
Heavy vacuum gas oil is drawn off the lower part of the column, is combined with the light vacuum gas oil, and sent as feed to the Cat Cracker. The column bottoms residuum is sent to a Coking Unit or to plant fuel oil. Vacuum towers may also be used to produce feedstocks for lube oil plants.

In the stabilization section, the Naphtha Splitter bottoms go to the Catalytic Reformer and the overhead liquid to the Debutanizer Column. From the Debutanizer Column, the overhead liquid goes to the Saturate Gas Plant or to plant fuel and the bottoms to the Isomerization Unit.

**Crude Desalting**

Crude oils are complex mixtures obtained from many parts of the world, and all crudes contain varying degrees of impurities. These impurities consist of naturally occurring water, salts, solids and metals as well as added contamination from well stimulants, gathering methods, storage and transportation. Adverse effects of these impurities are excessive corrosion, fouling and unit upsets. These effects can result in shortened unit run lengths and reduced equipment reliability. To minimize these effects, the refiner often washes the crude oil with water, and uses a desalting vessel to remove the added water and most of the inorganic contaminants from the crude prior to distillation in the crude unit. Common desalter types and a brief description of them are given below:

- Electrical desalting - an electric field is induced by AC or DC current in the oil and water mixture to enhance water coalescence.
- Chemical desalting - surfactant chemicals are used to aid water coalescence
- Chemical and electrical desalting - a hybrid of electrical and chemical methods
- Gravitational separation - typically a large tank or drum which allows water and water borne contaminants to separate due to density difference between the water and oil phases.

The type, size and series stages of desalting facilities chosen is dictated by the individual refiner based on refinery specific requirements and limitations. The fundamental functions of desalters are the following:

1. Remove chloride salts, typically calcium, magnesium, and sodium to minimize corrosion in the crude unit overhead system. This corrosion is caused by hydrochloric acid which is formed by hydrolysis of the magnesium and calcium salts during the distillation process.
2. Remove solids and sediment that cause erosion or abrasion of equipment. Deposition of solids in the preheat exchanger train can lead to plugging of tubes or fouling which results in reduced heat transfer and higher energy consumption.
3. Minimize unit upsets by preventing water slugs from tankage to be charged directly to the distillation column.

A detailed description of how desalters operate is beyond the scope of this paper. However, a summary of the major variables and their expected effect on the desalter operation follows:

- Crude oil properties - Because desalters rely on the density difference between oil and water, lower gravity (higher density), higher viscosity crudes make it more difficult to separate water from the crude, and hence more difficult to desalt.
- Desalting temperature and pressure - Generally desirable desalting temperatures are in the range of 250°F to 300°F (120°C to 260°C). The upper temperature limit is to avoid vaporization of the crude oil in the desalter, or to prevent damage to the electrical grid insulator bushings.
- Residence time - Adequate residence time is essential for oil-water separation. Heavier crudes require longer residence time because the gravity difference between the oil and water is reduced. For low gravity crudes, the required water residence time can be two hours. Chemical emulsion breaker selection may have a significant effect on oil undercarry in the water which is caused by inadequateresidence time.
- Wash water quality and rate - Variables in water quality, particularly pH can affect the effectiveness of desalting and the transport of water and ammonia into the crude or oil into the desalter brine water. Sufficient added
water must be provided to ensure good coalescence of the water in the crude.

- Wash water mixing - To ensure the added water is dispersed well so that it can be available to combine with the contaminants in the crude, a controllable mixing is required. This is typically accomplished by a mixing valve with adjustable pressure drop. Location of the wash water injection may vary, normally into one or more places between the raw crude charge pump and the mix valve. Injecting desalter water into the suction of a crude pump is not recommended because this mixing can not be controlled. Over mixing can prevent adequate water coalescence.

Some of these items are discussed in more detail in the paragraphs which follow.

The source of desalter wash water is governed by the refiner’s needs, environmental requirements, and availability of reusable process waters. However, the purer the water, the easier it is to wash the crude. The volume of water can be from 3 - 10% with typical usage at ~5% based on total crude charge. Lowering the washwater rate below 3% of total charge reduces the rate of coalescence and often makes water removal more difficult. A low water rate in conjunction with high mixing energy will likely further degrade desalter performance.

For the wash water to be effective in removing the impurities from the crude, it must make good contact with the crude. Controlled mixing is achieved most often by use of a mixing valve which permits varying degrees of water/oil contact. The higher the pressure drop \( \Delta P \) across the mix valve, the greater the mixing energy. However, if the \( \Delta P \) is excessive, a tight emulsion will form which cannot be easily resolved in the desalter. Poor water separation increases the BS&W (Basic Sediment and Water) carryover with the crude and high oil entrainment in the effluent brine. If the \( \Delta P \) is too low, the crude/water contact will be insufficient for good desalter efficiency. Typical mixing valve \( \Delta P \) is 10 to 20 psi. The only sure method for determining the optimum \( \Delta P \) for operation is by testing and adjusting while monitoring the desalter. Many variables dictate mixing valve \( \Delta P \) requirements and must be considered before adjustments are made.

To minimize fouling in the raw crude preheat train from the deposition of salts in the crude, it is advisable to utilize a portion of the wash water for injection immediately downstream of the crude charge pump. This water is referred to as “primary” water. While testing and adjusting to find and maintain the optimum primary water rate is advisable, a good starting point is an even split. For example, 5% (v) wash water would be split into 2.5% each for primary and secondary locations, with an injection at the desalter mix valve as the most common secondary location. Tighter control on mixing valve adjustments is required while in this mode of operation.

Another item that may improve desalting is wash water pH control. Chemical desalters are more efficient with high pH water, somewhere around 8.0 to 9.5. While electrical desalters function much better in the 5.5 to 7.0 pH range. Low pH’s result in excessive corrosion while high pH permits ammonia to migrate into the crude. Excessively high pH can aid in stable emulsion formation. Typical pH control, if required, is done with sulfuric acid or caustic into the water as far upstream as possible, with pH controllers monitoring results. Quills for injection of the acid or caustic are necessary to avoid mix point corrosion. Spent acids and caustic are not advisable. They may return impurities to the crude stream that can promote equipment fouling and corrosion.

Chemical assistance is extremely important for the desalting operation. Chemicals, when properly applied, will not only enhance the speed of separation, but will assist residence time, improve solids removal, minimize water carryover/oil undercarry, and reduce the emulsion layer (cuff, or rag) to a manageable thickness. The chemicals used are termed emulsion breakers, wetting agents, and/or demulsifiers. They can be oil soluble, water soluble, or water/oil dispersible and in varying forms of chemistry. However, they all serve a common goal, to enhance separation of impurities from the crude. The chemicals are surfactants which migrate to the oil/water interface to rupture the stabilizing film around the water droplets that allows them to merge and coalesce.

Chemical usage rates vary widely with crude type, equipment and operating parameters. It is usually in the range of 1 pint (3 vppm) to 1 gallon (25 vppm) per thousand barrels of crude. Several
test methods are available for chemical selection on a cost/performance basis. Chemical vendors are best equipped to assist with these evaluations, as refinery laboratories are not normally equipped for these tests.

For the chemical to be effective, it must be well dispersed before it arrives in the desalting vessel. The oil soluble/dispersible types are normally injected into the crude charge pump suction or upstream of the wash water inlet point. Water soluble/dispersible chemistry injection is preferred with the wash water, in the wash water pump suction, or before the flow controller.

**Materials of Construction**

The majority of the equipment in a Crude Unit is made of carbon steel regardless of whether the crude slate is “sweet” or “sour.” The term sour refers to the release of H₂S, but is often applied to a crude oil based on its sulfur content, with less than 0.5 wt% sulfur called “sweet” or greater than 1.0% called sour. This use of carbon steel is possible because at temperatures below about 450°F (230°C), except for the preflash and atmospheric column overhead systems, the streams are essentially non-corrosive to carbon steel. Where temperatures exceed 450°F (230°C), problems with high temperature sulfur attack and naphthenic acid corrosion may begin. In the overhead system, the formation of acidic deposits of condensates occurs below about 250°F (120°C) and often necessitates the use of one or more highly alloyed materials.

The purpose of this section is to point out where problems occur in major equipment and systems, and to discuss the materials commonly used to alleviate those problems.

**Columns**

In a Crude Unit designed to process “sweet” crude, the Preflash Column will typically have UNS 04400 cladding in the top zone which operates near or below the dew point. The remainder of the shell will be bare carbon steel. This Ni-Cu alloy will be corroded by sulfur compounds above about 350°F (177°C). Since the inlet temperature is about 500°F (260°C), crude units typically have a 12% chrome lining in the bottom to protect against sulfur corrosion.

The Atmospheric Column is commonly lined more extensively than the Preflash Column because the feed, at about 690°F (365°C), is not only hotter, but also contains larger amounts of HCl and H₂S. The top of the column is often lined with UNS 04400 to protect against condensing HCl. Even though the top temperature may be above the water dew point, the addition of “cold” reflux can cause localized condensation and conditions extremely corrosive to carbon steel.

Typically, the lower 2/3 to 3/4 of the column will be lined with 12% chrome cladding to protect against high temperature sulfur corrosion.

In the area of the feed inlet, or flash zone, Type 316 stainless steel may be required in those plants processing crudes high in naphthenic acid content.

It is important to make sure that the nozzles in each area are lined with the same material as the shell. After exposure to service, the shell immediately above and below the cladding should be closely monitored for wall loss. It is not uncommon to find that the original clad areas need to be extended.

In the absence of naphthenic acids, the Vacuum Column is typically lined with 12% chrome, with the exception of the top few feet and head. The flash zone is often one of the worst naphthenic acid problem areas. For highly naphthenic crudes, Type 316 or 317 stainless steel cladding may be required in all areas of the column operating above 450°F (230°C).

In sweet crude plants, the side-stream strippers are usually unlined even though the diesel and atmospheric gas oil feeds are 550°F (285°C) and 650°F (345°C). In plants running sour crude, these hot strippers might require a 12% chrome lining. The Naphtha Splitter and Debutanizer are normally not lined.

**Exchangers and Piping**

Heat exchanger metallurgy varies with stream composition and temperature. The majority of the exchangers are 100% carbon steel. In fresh water cooled exchangers, admiralty brass tubes have been used to prevent water-side fouling and corrosion. Due to the cost of the brass bundles and improvements in cooling water treatment, many
brass bundles are being replaced with carbon steel. Where sea water or brackish water are used, admiralty brass, cupro-nickel, UNS 04400, titanium, and some of the super ferritic (e.g., 26 Cu-1 Mo) and duplex stainless steels have been used successfully where carbon steel failed to perform. The use of austenitic stainless steels has been limited in water service due to their susceptibility to chloride stress cracking and under-deposit pitting.

In hot hydrocarbon service, the use of 5% chrome materials in heat exchangers is common. As the sulfur content in the crude increases, the use of high chrome tubes and 12% chrome shell and channel linings becomes necessary. Austenitic stainless steels are also used to great advantage in this service.

Generally, the most severe corrosion problems are in the areas of initial condensation in the atmospheric column and preflash column overhead systems. This may include the top of the column, the overhead vapor line, the naphtha exchangers, coolers and interconnecting piping. As was mentioned previously, these are the areas where HCl vapor, formed by the hydrolysis of the magnesium and calcium chloride salts in the preheat, dissolves in the condensing water to form hydrochloric acid. HCl, along with hydrogen sulfide which is also present, creates a very corrosive environment. Usually the UNS 04400 lining and trays in the tops of the columns are effective in resisting the acid attack unless chloride salt deposits form. The overhead vapor line, which is typically carbon steel, can be severely attacked if unneutralized condensate is present. A good pH control program in conjunction with corrosion inhibitors can be very effective in protecting the bare steel line.

The chlorides in the overhead receiver water should be kept below 25 WPPM, which can usually be accomplished with effective desalting of the crude oil and judicious use of caustic addition to the desalted crude. This will go a long way toward solving the acidic condensate corrosion problems. However, if the chlorides exceed about 30 PPM (mg/L), the solution to the problem may be quite difficult. It is sometimes necessary to install a UNS 04400, or UNS 04400 clad, vapor line. The heat exchangers closest to the point of initial condensation or chloride salt deposition may require alloy tubes, ranging from admiralty brass to titanium. Where chloride salt fouling and corrosion occurs, titanium exchanger tubes have worked well. The unlined carbon steel exchanger shells may be strongly attacked, particularly around the inlet nozzles. This may require UNS 04400 cladding or weld overlay in this area. If the pH of the system is well controlled, as measured at the overhead receiver, and inhibitors are properly used, the remainder of the piping and exchangers downstream can be carbon steel with few serious problems.

The overhead vacuum condensers may have admiralty brass tubes and Type 316 stainless steel lined shells and Type 316 SS outlet lines. The stainless steel may be needed because of CO₂ and H₂S in the condensing vapors. However, carbon steel is often used successfully. Sometimes 90-10 or 70-30 copper-nickel tubes are used in the vacuum condensers as part of standard vendor steam ejector packages. In some case, 90-10 can experience accelerated corrosion since copper-nickel alloys are not highly resistant to H₂S. Materials such as Admiralty or Aluminum brasses may be considered.

**Fired Heaters**

The fired heaters have corrosion and material problems due to the elevated temperatures experienced both on the process side and in the fire-box. The Atmospheric Heater receives flashed crude at about 500°F (260°C) and sends it to the Atmospheric Column at about 690°F (365°C). For sweet crude, the radiant tubes and lower rows of convection tubes are typically 5% chrome with carbon steel in the upper rows of the convection section. In the Vacuum Heater, with a 680°F (360°C) inlet and 720°F (380°C) outlet the radiant tubes and convection tubes would be 5% chrome for sweet and 7 - 9% chrome for sour crudes. Some plants running very sour crudes have Type 316 austenitic stainless steel radiant tubes. This material would also be used where naphthenic acid attack is severe.

High fire-box temperatures of >= 1500°F (815°C) also create materials problems. Tube supports and hangers suffer excessive oxidation and premature failure if they are not sufficiently alloyed. Historically, HH casting alloy (25% chrome - 12% nickel) was the industry standard. This material did well in the cooler convection section, but
failed in the radiant section. The substitution of HK alloy (25% chrome - 20% nickel) added extra life in the hot areas. Higher nickel materials give excellent service where low sulfur fuel is burned. However, where sulfur is high, these alloys suffer from sulfidation. This is also true for the high nickel welding electrodes commonly used to fabricate or repair the Cr-Ni castings. Units which burn fuel oil high in sodium and vanadium may have refractory lined HK alloy or solid 50 Cr-50 Ni supports to resist fuel ash corrosion.

The transfer lines from the heaters to the columns are usually alloyed much the same as the heater tubes. The vacuum heater outlet piping and transfer line may be severely attacked by naphthenic acid, requiring the use of Type 316 stainless steel.

**Materials and Corrosion Problems**

Crude oil is a mixture of many different chemical compounds, generally combinations of carbon and hydrogen, all with their own unique physical properties. Crude oil as such is not considered to be corrosive to carbon steel. However, crude oils all contain some impurities, several of which can be extremely corrosive under crude unit operating conditions. The more common of these potentially damaging impurities are:

1. Inorganic salts
2. Sulfur compounds
3. Organic acids
4. Organic chlorides

**Inorganic Salts**

Inorganic salts are present in brine produced with the crude oil or picked up as a contaminant from tanker ballast. The bulk of the salts present in the water are sodium chloride (NaCl), magnesium chloride (MgCl₂) and calcium chloride (CaCl₂), commonly reflecting the composition of sea water (≈85%, 10%, 5%, respectively). However, these ratios can vary widely. The total salt content by weight can vary from less than three pounds per thousand barrels of crude oil (PTB) to 300 PTB or more.

When the crude oil is preheated, most of the MgCl₂ and a small amount of the CaCl₂ begin to hydrolyze at about 250°F (120°C) and form hydrogen chloride (HCl) vapor. At 700°F (370°C), approximately 95% of the MgCl₂ and 15% of the CaCl₂ have hydrolyzed. The chemical reaction is:

\[
\text{MgCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{MgO} \quad (1)
\]

A similar reaction occurs for the CaCl₂. The NaCl, being more temperature stable, does not hydrolyze to any appreciable extent.

The HCl vapor thus formed is not corrosive at temperatures above the water dew point. For this reason, there is no corrosive acid attack in the preheat system where no liquid water is present. However, in the preflash and atmospheric columns, the HCl is carried up the columns with the hydrocarbon where, being highly water soluble, it dissolves in the condensing water to form hydrochloric acid. This highly corrosive acid can create severe corrosion problems in the top of the column, the overhead line, the overhead exchanger and condensers. The source of the condensing water can be the crude oil, stripping steam, or carryover from the desalters. The resulting corrosion reaction with steel is:

\[
\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2 \quad (2)
\]

The presence of H₂S (which will be covered later) keeps the reaction going as follows:

\[
\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow 2\text{HCl} + \text{FeS} \quad (3)
\]

The formation of additional HCl thus perpetuates the cycle.

Above the water dew point, HCl can also react with NH₃ to form solid ammonium chloride (NH₄Cl). The temperature at which NH₄Cl forms is dependent upon the partial pressures of HCl and NH₃. NH₄Cl is hygroscopic so may absorb moisture even though water is not condensing. Wet NH₄Cl is highly corrosive to many materials. Ammonia is often added to neutralize HCl. Other sources of ammonia include carry-over from desalter wash water and streams imported from hydrotreating units. NH dependent upon the partial pressures of HCl and NH₃. NH₄Cl deposition can occur in the tops of the columns as well as in overhead and reflux piping and overhead condensers. Some chloride salt characteristics of commonly used neutralizing amines can be found in the Corrosion Control Measures discussion on Overhead pH control.
Sulfur Compounds

Some forms of sulfur are found in virtually all crude oils. Sulfur contents up to 6 wt% are not unusual, but most crudes fall within the range of 0.5 - 3.0 wt%. The most important sulfur related corrosion problems are caused by hydrogen sulfide (H₂S), both below the water dew point (aqueous) and above 500°F (260°C). While small amounts of naturally occurring H₂S may survive the journey to the crude unit in some crudes, the bulk of the H₂S present in the unit is the result of the thermal decomposition reactive organic sulfur compounds which occurs in the heaters between 500°F (260°C) and 900°F (480°C).

It is difficult to predict the corrosivity of a crude oil based entirely on its sulfur content. Generally, the dividing line between non-corrosive and corrosive crudes lies somewhere between 0.5% and 1.0%. However, the determining factor is quite often not the amount of sulfur compounds, but rather the extent to which these compounds thermally decompose to form H₂S. This phenomenon requires evaluating each crude individually.

At temperatures in excess of about 500°F (260°C), H₂S reacts with iron to form iron sulfide scale. The rate at which this reaction occurs is dependent on the H₂S concentration, the temperature, the stream velocity, and the composition of the material. Generally, an increase in sulfide concentration, temperature, or velocity will increase the rate of metal loss. An increase in the chromium content of the material will decrease the rate, with 5% chromium being a practical minimum threshold level required for corrosion protection. Lower chrome alloys like 1-1/4 Cr - 1/2 Mo and 2-1/4 Cr - 1 Mo do not have significantly enhanced corrosion resistance to justify their increased cost over carbon steel. High temperature sulfur attack is a serious problem in the hot portions of the atmospheric column, preflash column, the vacuum column, fired heater tubes, hot heat exchangers and associated piping. The problem is alleviated by the use of proper alloy materials, as discussed previously.

Aqueous phase H₂S corrosion is widespread in the predominantly carbon steel equipment where water can condense. While a specific mechanism to cover all situations is not available, it is known that three important variables in determining its severity are pH, chloride ion concentration, and sulfide ion concentration. The types of corrosion control programs described in the discussion on inorganic salts also apply to corrosion control in H₂S containing sour water.

Organic Acids

Many crude oils contain organic acids, but seldom do they constitute a serious corrosion problem. However, a few crudes contain sufficient quantities of organic acid, generally naphthenic acids, to cause severe problems in those parts of the crude unit operating over 450°F (230°C). Thus, naphthenic acid attack often occurs in the same places as high temperature sulfur attack such as heater tube outlets, transfer lines, column flash zones, and pumps. In sour crude units a crude TAN (Total Acid Number) of 1.0 (mg KOH/g) is sufficient to be concerned about potential naphthenic acid corrosion. In sweet units, a TAN of 0.5 may be high enough to cause corrosion. Both high temperature sulfur and naphthenic acid mechanisms are strongly affected by velocity. Whereas sulfur corrosion is characterized by a smooth surface with a sulfide scale deposit, naphthenic acid corrosion results in sharp edged, smooth grooves, gouges, or holes with no corrosion scale or deposit. Those materials commonly used to prevent high temperature sulfur corrosion, primarily 5% to 12% chrome steels, can be severely attacked by naphthenic acid. The most commonly used material is type 316 stainless steel, which does well because of its molybdenum content. Type 304, which contains no molybdenum, has some resistance to lower levels of naphthenic acids, but in most cases it is no better than carbon steel.

Organic Chlorides

Organic chlorides constitute a contaminant in crude oil, often resulting from the carry-over of chlorinated solvents which are used in the oil fields. They can also be picked up by the crude during transportation in contaminated tanks or lines. Organic chlorides are not removed in the desalters. Some of them can decompose in the heaters, forming HCl, causing erratic pH control and accelerated corrosion in the crude unit overhead system as well as in downstream units.
Corrosion Control Measures

The crude unit overhead system can benefit from corrosion control measures other than materials selection as described earlier. Several steps can be taken to reduce the severity of acid attack in the crude unit overhead circuit:

1. Blending
2. Desalting
3. Caustic addition
4. Overhead pH control
5. Use of corrosion inhibitors
6. Water washing

Blending

Perhaps the most commonly used technique for corrosion control is the blending of problem crudes with non-problem crudes. Sometimes the flexibility may not exist, or blending may not provide enough reduction of the problems, and in those cases more attention needs to be placed on the following options.

Desalting

As the name implies, the primary purpose of a desalter is to reduce the amount of salt in the crude oil, less than 3 ppm (1 PTB) being a commonly targeted level. Removal of the salt reduces the amount of HCl produced from hydrolysis in the preheat and flash zone of the crude tower. In addition to salt removal, the desalting process also removes entrained solids such as sand, salt, rust, and paraffin wax crystals which may be present in the crude. Removal of these contaminants helps decrease plugging and fouling in heaters and preheat exchangers.

Caustic Addition

The addition of small amount of dilute caustic (NaOH) to the desalted crude is often an effective way to reduce the amount of HCl released in the preheaters. The caustic converts the HCl to thermally stable NaCl, thus reducing the amount of free HCl produced. While the results of caustic addition can be quite beneficial, there is a risk of crude preheat train fouling, accelerated atmospheric, vacuum, and visbreaker or coker coking, caustic stress corrosion cracking, and catalyst contamination problems in downstream units if it is not controlled properly. A typical limit for avoiding coking problems in furnaces is to inject no more than necessary based on downstream chloride (20 to 30 ppm [mg/L] in the Atmospheric Column overhead water) or sodium limits (20-50 ppm in the Vacuum Tower bottoms).

Fresh caustic is preferred over spent caustic for two major reasons. Spent caustic tends to have variable amounts of “free” or available NaOH to neutralize the HCl formed. As a result, proper control is very difficult. Also, spent caustic, depending on its source, can be a significant promoter of preheat exchanger fouling.

To minimize the negative effects of caustic injection and maximize its efficiency, thorough mixing is necessary. To achieve good mixing, the caustic is often added to suction of the crude booster pumps after desalting. Some refineries will mix by injecting the dilute caustic into a slipstream of desalted crude oil prior to its injection into the main process. Injection of caustic upstream of the desalters is not recommended because high desalter water pH can result in the formation of emulsions and can drive ammonia into the crude. Also, the caustic will be unavailable to react where the salt hydrolysis takes place since it will typically be removed in the desalter brine. For units without a desalter, to minimize potential for caustic cracking, if possible caustic should be added to the preheat train at or about desalter outlet temperature.

Overhead pH Control

The desired result of an overhead pH control program is to produce an essentially non-corrosive environment by neutralizing the acidic components in the overhead liquid. This is done by injecting ammonia, an organic neutralizing amine, or a combination of the two. The desired pH control range depends on the concentrations of the various components of the corrosive environment.

Usually, this range is 5.5 to 6.5. However, it is important to recognize that neutralizers may have only a different effect on the pH at the initial condensation point. At this point, the pH could be higher or lower, depending on the product selected. A pH above 8 must be avoided if brass alloys are used in the overhead system as they
are vulnerable to stress corrosion cracking and accelerated corrosion at high pH.

The preferred injection point for the neutralizer is the subject of some debate. In single overhead drum systems, some chemical vendors advocate injecting the neutralizer into the column reflux stream to help protect the tower internals. Others discourage this practice because neutralizer-chloride salts, similar to ammonia salts, that form in the tower may be corrosive especially to copper bearing alloys such as Monel, and may be trapped in a section of the tower. Because stability of neutralizer-chloride salts vary depending on the type of neutralizer used, the various options and their risks should be discussed with the chemical vendor prior to implementing a chemical treatment program.

In two-stage overhead systems, the neutralizer or ammonia (or both) is normally injected upstream of the second stage condensers. Generally neutralizers are not used in the first stage if it operates without water condensation due to concerns with forming corrosive neutralizer-chloride salts which may also be refluxed to the tower. Wet first-stage systems, however, may benefit from neutralizer addition if there is a continuous water draw from the first stage drum. Neutralizers are sometimes used in vacuum tower overhead systems as well, using an application point that minimizes or eliminates the possibility of introducing neutralizer-chloride salts into the tower.

A variety of neutralizers and blends of neutralizers are available for pH control. Some neutralizer components in widespread use today include ammonia (NH₃), morpholine, ethylene diamine (EDA), monoethanolamine (MEA), and methoxypropylamine (MOPA). All of the neutralizer salts are water soluble. MOPA and MEA form liquid neutralizer salts with chlorides at elevated temperatures. NH₃, morpholine and EDA form solid salts. Liquid salts may be less prone to fouling, but they may also flow better and result in more widespread salt corrosion if they are returned to the atmospheric tower.

**Corrosion Inhibitor**

Most overhead corrosion control programs include the injection of proprietary film forming organic inhibitors, commonly referred to as “filmers.” These inhibitors establish a continuously replenished thin film which forms a protective barrier between acids in the system and the metal surface underneath the film. For maximum results, proper pH control of the system is essential.

Filming inhibitor injection rates will vary with time and between refineries. There is a surface adsorption/desorption steady state established which varies based on the aggressiveness of corrosion in the system, and the inhibitor concentration. Factors which affect inhibitor solubility in the liquids, such as pH, and affect the inhibitor’s ability to adsorb onto the surface, such as temperature, will affect the effective dosage for a given situation. A typical injection rate is of the order of 3 to 5 vppm for normal operations. During startups or unit upsets, injection rates may be temporarily increased to levels such as 12 vppm to help establish or re-establish the protective film. Inhibitors also could have a cleaning effect so they may remove some iron sulfide deposits, particularly at the higher injection rates.

Because these inhibitors have high molecular weights, they are non-volatile and will follow the path of other liquids present following their injection. Therefore, they must be independently injected into both stages of a two-stage overhead system. Filming inhibitors should normally not be injected in concentrated form. Inhibitors are non-corrosive to equipment at treatment dosage dilutions, but near 100% concentration they may be corrosive to injection equipment. This should be kept in mind when designing an injection system. Typically, naphtha dilution is provided to help the dispersion at the injection point.

In the feed to the Atmospheric and Vacuum Columns, as well as in the columns themselves, naphthenic acid corrosion can occur. There has been some success with the use of corrosion inhibitors purported to be effective in the 500°F (260°C) to 700°F (370°C) temperature range and for this type of corrosion. These inhibitors may offer some economic advantage over alloy when the acidic crudes are charged intermittently, but their effectiveness is hard to determine. Additionally, most of the inhibitors available contain phosphorus, which may be considered to be a poison to some hydrotreating catalysts.
Water Washing

Since the products of the above discussed neutralization reactions, ammonium chloride or amine chloride, can be highly corrosive and also cause fouling, it is common practice to recirculate water from the overhead receiver back into the column overhead vapor line. Stripped sour water and/or other water condensates are also by some refineries. Water which contains dissolved oxygen, however, can dramatically accelerate corrosion and should be avoided. Water washing can be quite effective, but must be carefully engineered to prevent the creation of more corrosion problems and cause significant loss of heat exchange in the overhead naphtha coolers.

Water washing the vapor line can prove to be beneficial or disastrous. Too little water can just add to the acid making process, and too much can cause grooving of the line. The path of the grooves can be unpredictable and difficult to locate with normal U.T. surveys. A proper spray nozzle is necessary to prevent impingement corrosion of the pipe downstream of the injection point. When the wash water is injected directly upstream of the condensers, a good distribution system is necessary to ensure evenly divided flow among the different banks of exchangers. An intermittent wash is difficult to optimize, may be neglected, and may actually increase corrosion of otherwise dry and non-corrosive salts. Therefore, use of water on an intermittent basis should be considered only when a continuous wash is not possible due to process constraints, or when a continuous wash has been shown to create erosion problems.

The ideal water injection rate is 5% to 10% of the overhead stream. Excessive water rates, however, can result in poor water separation in the overhead drum. Poor separation can result in water being returned to the tower in the reflux and resultant corrosion both in the tower and the overhead line. With the proper mechanical design and chemical balance, the water wash can be an important part of the overhead corrosion control program.

Corrosion Monitoring

Several methods of evaluating the effectiveness of crude unit corrosion control programs are employed as follows:

1. Water analyses - for pH, metals, chlorides, and hardness
2. Hydrocarbon analyses - Inhibitor residual and metals
3. Corrosion rate measurement by:
   a. Electrical resistance probe
   b. Weight loss coupon
   c. Linear polarization resistance probe
4. On stream non-destructive examination by UT or RT

Water Analyses (Overhead Corrosion Control)

The most important monitoring parameter for good overhead corrosion control is receiver pH. The system pH can shift from an acceptable pH to an aggressively corrosive pH in a matter of minutes, so the overhead receiver pH should be measured as frequently as possible on the Atmospheric Column. The Preflash Column and Vacuum Column pH will usually not shift as rapidly. Continuous pH monitor reliability is poor relative to most other instruments used in refining, and so most refineries still rely on manual readings. Although pH measurements can capture a corrosive event and prevent extended damage, even holding the pH in an acceptable range does not always assure the lowest possible corrosion rate. See the section on Corrosion Control Measures, Overhead pH Control for more information.

Routine analysis of the overhead receiver water for metals can be of value in some cases, particularly when used in conjunction with other methods of measurement. Iron, copper and zinc are typically measured, but this depends on the materials used in the overhead system. If no brass, copper, nickel, or UNS 04400 alloys are used, for example, there is little value in determining copper, nickel, or zinc concentrations. Much reliance has been put on the iron content of the water, and very often the results are misleading. Since iron solubility is quite dependent on pH, the iron concentration in the receiver water may not be indicative of the amount of iron going into solution somewhere upstream where the pH may be
lower. The only source of copper and zinc in a typical system would be brass or UNS 04400 exchanger bundles. If their levels increase in the water (particularly zinc in brass-containing systems), there probably is a corrosion problem. This has been seen very dramatically in the FCCU and cokers.

Overhead receiver water chlorides are a very useful parameter to measure. Since aqueous corrosion is almost always related to the quantity of hydrochloric acid or chloride salts, measuring chlorides can help to confirm when a corrosion event began, and how long it was sustained. A regular measurement of chlorides can also be used to optimize caustic addition or blending of crudes which result in minimum corrosivity.

An often overlooked measurement which can be useful for corrosion control measurement is hardness. The hardness of water condensing in an overhead should be zero. If any hardness is detected, it generally will mean that a leak has occurred in a cooling water exchanger. If a recycled water wash is in use, a cooling water leak means that oxygenated water is being recycled. Oxygen can accelerate corrosion. Additionally, the hardness from the water can precipitate when the water is injected into the overhead, causing severe fouling. If hardness is detected, it is possible that adjustments will need to be made to the corrosion control program, and that repairs need to be scheduled.

**Hydrocarbon Analyses**

For filming inhibitors used in an overhead to control aqueous corrosion, depending on the inhibitor formulation, it is sometimes possible to run a "residual test" on a stream to detect the presence of the corrosion inhibitor. As mentioned earlier, there is an adsorption/desorption steady state which is affected by the environment. There must be sufficient inhibitor present to continuously replenish the film. This is often seen as a residual of 3 to 5 ppm (mg/L). However, for many inhibitors the nearest available test is total nitrogen which is not specific enough to quantify inhibitor residual.

For naphthenic acid corrosion control measurement, sometimes the only tool for measuring the aggressiveness of the environment is metals analysis of the oils. For this measurement, historical data is very useful as a check on current conditions. The absolute value of the metals content will change when naphthenic crudes are processed. Some of that metal comes from “tramp” metals in the crude oil. Some of these metal-naphthenates will distill, which can make even a relative determination of the rate of corrosion difficult. The ratio of iron to nickel has been used with some success as a relative measure of the effectiveness of naphthenic acid corrosion inhibitors. In most systems, the presence of nickel is from “tramp” sources, because the nickel alloys which are used corrode very little. The measure of iron will include both the tramp iron and the iron from active corrosion. If the iron/nickel ratio declines, it is then assumed to be due to inhibitor effectiveness. What cannot be determined using this technique is the uniformity of the protection, and localized corrosion zones remain a concern.

**Corrosion Rate Measurement**

Electrical resistance corrosion rate probes are widely used but with varied success. These devices measure the change of cross section of the measuring element by measuring the change in resistance to electric current flow. It is necessary to take a series of readings over a period of time to establish a curve, the slope of which is indicative of the corrosion rate. This device is used with good success in many instances. However, like all such devices, it is only indicating the corrosivity of the measured stream at the point where the probe is located. It is not always possible to relate the probe readings to a pipe wall or the condensing surfaces of exchanger tubes. They lend themselves well to the evaluation of a corrosion control program which changes the environment through pH control and inhibitor injection. They have the advantage of being read on stream. Also, they can be designed to be retracted through a packing gland and replaced onstream. Electrical resistance probes are most commonly used in the tower overhead systems. They are often used at both the inlet and outlet of overhead exchangers and may also be installed in the bulk sour water draw-off from the overhead drum.

There are high temperature electrical resistance probe designs which have been used to measure naphthenic acid corrosion. The same limitations with location exist for these probes. The biggest impediment to their use is the serious safety
issues related to inserting and extracting an instrument at the temperatures and pressures involved.

Weight-loss coupons yield a calculated corrosion rate based on initial surface area and weight. They lend themselves to visual examination as well as giving rate data. They have a disadvantage in that they must be removed to give information, and they can not represent heat transfer surfaces. They can often be replaced on stream and are used in high temperature sections of crude units with the same safety concerns as for electrical resistance probes. They are commonly used in overhead systems.

Linear polarization resistance probes give an instantaneous corrosion rate based on a measurement of the probe element corrosion current. This type of probe will work only in a conductive medium. It is for on-stream measurements and lends itself well to bulk water systems like cooling water streams. Applications in the overhead receiver water drum are limited but feasible. These probes can be made retractable through a packing gland and replaced on-stream.

**Onstream non-destructive examination by UT or RT**

NDE is normally not used for extensive routine corrosion monitoring because of its cost. It is most often used on-stream on an exception basis, when there is a confirmed or suspected problem which is being watched closely. Since NDE is often used as an inspection tool, its use on and off line is detailed in the next section.

**Inspection**

Whenever possible, corrosion rate information should be verified by direct measurement of equipment. This may not be possible on-stream for items like tube bundles, but piping and vessels can be checked for changes in wall thickness using ultrasonics (UT) or radiography (RT).

UT readings can be taken easily and quickly on most surfaces which can be reached by the inspector. These readings are accurate and reproducible when taken on clean, relatively smooth surfaces. Readings can be taken on-stream at metal temperatures as high as 750°F (400°C). This method allows the monitoring of a particular spot over a period of time, providing good data for corrosion rate calculations at that point. In this manner, the routine monitoring of a relatively few representative points in a large piping system will yield an accurate picture of that system. UT readings are the most important on-stream data obtainable on a plant-wide basis. The selection of representative UT points must consider differences in flow rates, turbulence and fouling tendencies which affect corrosion.

Scanning UT methods are limited to lower temperatures than spot, manual UT measurements. However, they permit making a permanent record for future comparisons. These methods are particularly well suited to areas where localized corrosion can occur such as at high turbulence areas in the hot or overhead systems or in areas of the overhead system vulnerable to under-deposit corrosion or impingement.

While sometimes limited by accessibility and geometry, RT is also an important on-stream inspection tool. It can be used to measure wall thickness, indicate the presence of pitting, and under some circumstances, show thickness of deposits on pipe walls. RT provides as permanent visual record, unlike some of the other measuring methods.

Another useful on-stream inspection method is the use of infrared to measure temperatures of heater tubes, vessel shells, electrical equipment heat exchangers, insulation damages, etc. The ability to perform reliable remote temperature measurement is extremely important both from the standpoint of equipment reliability and economy of energy.

When the unit is shut down and equipment opened up, visual inspection can be performed. This includes not only “looking.” but also checking the depths of pits with pit gauges, caliperining the O.D. and I.D. of exchanger tubes, looking for cracks using dye-penetrant or one of the several magnetic particle methods, plus extensive use of UT and RT methods.

Since heat exchanger tubes, due to their geometry and arrangement in bundles, do not lend themselves to visual inspection along their full length, several inspection tools have been devised. The
simplest is the borescope which allows visual examination along the I.D. of a tube. Since no measurement can be made, this is of limited value. Eddy-current equipment allows a record to be made of the ID of the tube wall, indicating cracks, pitting and general wall thickness. Equipment based on ultrasonic principles is also used for this purpose.

Ultrasonic wall thickness measurements should be routinely made at predetermined points on all piping systems in the unit. UT measurements should also be taken at a number of representative points on vessel shells and nozzles, exchanger shells and nozzles and at one or more points along the length of each heater tube. If coking of heater tubes is a problem, radiographic techniques can be developed to evaluate this.

While not as common as with FCC light ends, there have been reports that equipment in the overhead systems of the Preflash, Atmospheric Vacuum, and light ends towers may be vulnerable to wet H₂S cracking. Therefore this equipment should be included in a wet H₂S inspection program.

Bibliography
1. NACE Group Committee T-8 Minutes.