The origins and fates of chlorides in hydrotreating units

A step-by-step roadmap to identifying and managing the negative effects of chlorides in hydrotreating units

STEVEN A TREESE
Becht Engineering

This article in three parts explores the impacts chlorides may have on hydrotreating units (hydrotreaters and hydrocrackers). It will provide a methodical approach to identifying the typical effects that point toward chlorides, the sources of chlorides in process feed streams, chloride induced failure mechanisms, methods for identifying chlorides, strategies for chloride control, and a step-by-step process outline for dealing with a problem. Some of the approaches and impacts here can also be applied to other halogens in hydrotreaters, such as fluoride.

Part 1: Recognising the problem

Problems caused by chlorides are often missed or misdiagnosed in a refinery. They impact not only the hydrotreating units, but other units as well. Sometimes the methods used to manage chlorides in upstream units, such as corrosion inhibitors, merely move the problem on downstream. Partial solutions in hydrotreating units may, in turn, just pass problems on to other units. Comprehensive solutions require a wider understanding of the problem.

Locating a chloride root source is made more difficult if a problem has gone unrecognised or has been allowed to persist for a few months. The chlorides will propagate throughout a refinery in multiple streams and in multiple forms to obscure the original source. There may be multiple sources. Someone may have introduced the chlorides into a system without realising it or without realising the impacts.

The amount of material required to create a significant chloride problem is often very small. To get 1 wppm PERC in the feed (0.0055 vol% of the stream). Introducing a barrel of PERC into the naphtha stream can contaminate it for several days.

So how can you approach a chloride problem? Methodical application of the steps below is suggested. The balance of this article provides the background to execute the steps:

1. **Recognise the problem** Recognise the chloride problem from the impacts observed in the plant. Where is the problem? Are other units seeing problems?

2. **How big is the problem?** How much material are you looking for? Calculate or estimate the amount.

3. **Identify the source(s)** Identify potential sources for the chlorides, both organic and inorganic. Look especially at reformers and isomerisation units where concentrated organic chlorides are present. Use analyses to narrow down the possible sources. For organic chlorides, determine specifically what chloride compound(s) you are looking for (speciation). If all you find is PERC, for instance, then you need to suspect the reformer, the isomerisation unit, or solvent dumping.

4. **Manage the chlorides** This may include physical changes or correcting practices and procedures. You may need to use higher metallurgy in some equipment. You may need to adopt a coping strategy rather than a complete solution.

Chlorides and/or their effects can be successfully controlled, once they are identified and understood.

We will begin by looking at how to recognise a problem rooted in chlorides.

**Step 1: Recognise the problem**

Chloride as a possible issue can be identified from its typical effects on hydrotreating units. There will likely be impacts in other units also which can serve to support your identification.

Figure 1 illustrates several areas to look for indications of chloride impacts in a hydrotreating unit. Impacts are sometimes seen in other units of the refinery.

Referring to Figure 1, the most common issues indicative of chlorides include:

- **Deposition of salts in reactor preheat exchangers and charge heater (A)** Deposits of white salt in exchangers when opened often indicate a chloride problem. This is seen
in cokers and crude units, as well as hydrotreating units. If there is any entrained water in the hydrotreating unit feed or chloride salts above saturation are present, there will be fouling of the feed preheat exchangers. The salts will simply lie down on the exchanger tubes as their solubility dictates. If the tubes are austenitic stainless steel, stress corrosion cracking may occur. Under-deposit corrosion is also a likely result. In any event, there would be a loss of heat transfer and, eventually, high pressure drop.

- **Reactor fouling (C)** Chloride containing salts that reach the reactors will decompose or hydrolyze at reaction conditions, releasing HCl and leaving metals fouling the catalyst. If, somehow, sodium chloride is present in the feed, it will deposit directly in the catalyst bed without decomposing, forming a hard rind and causing high pressure drop. Fortunately, most catalysts today are fairly resistant to poisoning, so the metals may not hurt much. The HCl probably does not harm the catalyst and, in the case of hydrocracking, may even help catalyst activity a little. More importantly, the HCl moves into the effluent train.

- **Reactor effluent fouling and corrosion (B, E)** Heat exchanger tube and shell thinning or pitting, especially in reactor effluent exchangers, is often seen. The most common corrosion location of concern is the reactor effluent side of the feed/effluent exchangers where ammonium chloride salts (NH₄Cl) deposit in the exchangers, especially when wash water practices are inadequate. If austenitic stainless steel is present, chloride stress corrosion cracking presents an additional metallurgical challenge.

Fouling or high pressure drop in effluent exchangers at higher temperatures than ammonium bisulphide laydown occurs (say over 250°F, 120°C) also points toward ammonium chloride deposition.

In the reactor effluent train, ammonium chloride will deposit below the temperature indicated by:

\[
T_{dep} = 523 \times \exp(0.0507 \times \ln(K_{sp})).
\]

Where \( T_{dep} \) = deposition temperature, °F

\( \frac{P_{NH_3}}{P_{HCl}} \) = ammonia partial pressure, psi

\( P_{HCl} \) = Hydrochloric acid partial pressure, psi.

Note that the feed nitrogen is just as important in this equation as the chlorides. The use of amines upstream to control corrosion or scavenge H₂S will aggravate a chloride problem. Once deposited, the ammonium chloride increases pressure drop, reduces heat transfer, and causes tube damage by under-deposit corrosion. This effect is intensified as water begins to condense in the reactor effluent. The first drop of water will be rich in acid gas and very corrosive. Ammonia generated from feed nitrogen or injected with wash water can help reduce the pH impacts, but ammonia is not as soluble at high temperatures as HCl, so the HCl tends to control the pH.

- **Stripper/fractionator feed preheat (A)** Some of the most difficult exchanger conditions are presented when fractionator or stripper feed is preheated by high pressure reactor effluent. The fractionator feed has a small amount of residual free water that is carried into the fractionator/purge exchangers. This water contains dissolved ammonium chloride. As the stream is heated, the water eventually evaporates, leaving ammonium chloride salt deposits on the tubes where it evaporates. The exchanger where you can expect trouble can be identified using flash calculations, if you can estimate the water slip out of the upstream separators.

The deposit insulates the tubes, raising the temperature on the underside of the deposit until the ammonium chloride breaks down into ammonia and hydrochloric acid. The presence of trace amounts of water in the hygroscopic ammonium chloride deposit promotes acid attack of the tubes in the form of pitting.

Dry attack under deposits is also
possible as a corrosion cell is set up between the clean and the fouled metal surfaces. Attack is, again, in the form of pitting.

- **Stripping and fractionation impacts (D, G, H)** Corrosion of the upper trays in a hydroprocessing unit stripper or fractionator may indicate a problem. Crude units will see essentially the same effects from chlorides. Wet H₂S can also show a similar effect. Testing for corrosion products and pH wherever water collects downstream of a suspected problem may help. Deposits of iron sulphide will be observed in product rundown coolers and tanks when chloride is active in a system. The metallurgist frequently helps sort out these effects.

  In the fractionation system, chlorides will follow the water and ammonia, just as they do in the crude units. Expect to see corrosion anywhere a liquid water phase may be present. Problem areas frequently include upper trays, tower walls, and overhead condensers. Chloride salt deposition in draw lines and exchangers has also been observed. This laydown follows the equation presented above, although application of the equation is difficult because it is hard to determine partial pressures for ammonia and acid.

- **Compressor issues (F)** Make-up hydrogen compressors and recycle compressors will experience chloride salt deposition on machine surfaces. In reciprocating compressors, valve deposits form, resulting in high valve failure rates. Centrifugal compressors will experience loss in efficiency.

- **Impacts observable in other systems and units:**
  - **Amine systems** Several hydrotreating units have high pressure amine scrubbers to remove H₂S from recycle gas. These scrubbers also effectively remove chloride from the gas. While the hydrotreater may not have problems, the amine regenerator tower and overhead system may suffer accelerated corrosion.
  - **Fuel gas systems** Chlorides have been detected in fuel gas streams where fouling and corrosion are issues. These are believed to be active in promoting corrosion of the fuel gas piping.
  - **Reformer water/chloride balance problems** Reformers that do not need chloride make-up to maintain a residual are probably getting chlorides through the feed. This may or may not be a problem, depending on the unit.

  As a general comment, chloride issues are often missed because evidence may come in the form of iron sulphide (FeS) deposits in equipment, which may be attributed to sulphidic corrosion. The FeS may actually come from wet NH₃Cl under-deposit corrosion via the reaction route shown below:

\[
\text{NH}_3\text{Cl}(s) \rightarrow \text{NH}_3(g) + \text{HCl}(g)
\]

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

\[
\text{FeCl}_2\text{aq)} + \text{H}_2\text{S} \rightarrow \text{FeS(s) } + 2\text{HCl(g)}
\]

Once you realise you have a chloride issue, you need to determine the magnitude and find the source(s) of the chlorides. These are the subjects addressed in Part 2.

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**Part 2: Magnitude and source(s) of the problem**

Part 1 introduced the symptoms of a chloride problem in a hydroprocessing unit. In this part, we will explore how to interpret the symptoms by determining how much chloride containing material we are looking for and identifying the possible or likely source(s) for this amount of material, embodied in steps 2 and 3 of the problem analysis.

**Step 2: How big is the problem?**

It is very helpful to know the magnitude and type of the chloride problem before you go looking for a possible source. Start by chemically analysing selected streams for chlorides. Be sure your operators use good industrial hygiene practices (for instance, chemical gloves) in sampling streams for chlorides since most chloride compounds are hazardous, even in the low concentrations we are testing.

**Analyse the hydroprocessing unit feed**

Determine the total chloride content of the feed and the split between inorganic and organic chlorides. There are multiple methods available for determining feed chlorides:

- X-rays can be used to determine the chloride content of most hydrocarbon streams down to less than 3 ppm. This method is useful and fast for normal chloride analyses.
- Wet chemical methods based on potentiometric titration with methanol and ion chromatography are also available. These are accurate to less than 1 ppm, but require considerably longer to run than the x-ray.
- Newer instrumental analysis methods are continually improving chloride determination. Methods for determining individual chloride compounds down to less than 0.01 ppm in feedstocks are available.
- The split between inorganic and organic chlorides can be determined by water washing the feed. Then analyse the wash water and the remaining oil for chloride separately.

- Detailed speciation of the organic chlorides is available. This is a huge help in finding or eliminating possible sources. This service is available from several of the common third-party labs.
- Analyse the feed for bottom sediment and water (BS&W) to get an idea of how much inorganic salts may be entering.

**Analyse the sour wash water**

Determine the chloride content of the spent sour wash water from the high pressure separator and the stripper overhead, if used.

**Analyse the chlorides in the crude unit**

Crude assays indicate salt content of the crude in pounds per thou-
sand barrels. This is a good starting point. The crude salts are usually determined by a simple device like the ‘Nalcometer’ based on conductivity using a calibration reference. For more detail, look at the inorganic and organic chlorides in the crude before and after the desalters. Look at the chloride contents of any slops or recovered oil streams sent to the crude unit. Detailed organic chloride speciation and analysing for sodium, calcium, and magnesium may help here. If the chloride problem is in a specific boiling range, you can make a rough heart-cut of that boiling range of the crude and look at the chlorides in that cut specifically.

**Analyse the chlorides in the make-up hydrogen**

Test for HCl in the make-up hydrogen. Normally, this is done using a Dräger tube or similar test method. This may not be accurate if your chloride adsorbers are saturated, in which case you need to use another method to look for organic chlorides (or, better yet, change your adsorbents).

From the feed analysis results and known or estimated flow rates, you can estimate the amount of chloride coming into the hydroprocessing unit. Consider a 50 000 b/d diesel hydrotreater with a 40ºAPI feed containing 5 ppm organic chloride. The total incoming organic chloride is:

\[
50\ 000 \text{ bpd} \times 288.6 \text{ lb/bbl} \times 5 \times 10^{-6} \text{ parts Cl} = 72 \text{ lb/day chloride.}
\]

Using the spent wash water analyses, suppose you have 50 gal/min wash water (once through) to our 50 000 b/d diesel hydrotreater. The concentration expected in the spent wash water would be about:

\[
(72 \text{ lb/day Cl}) / (50 \text{ gal/min} \times 1440 \text{ min/day} \times 8.34 \text{ lb/gal}) \times 10^6 = 120 \text{ wppm Cl in water}
\]

If you recycle water for phase control or use stripped sour water, you need to account for any chloride coming in with the water when making the above calculations. You could also get an estimate of how much material you are looking for by taking the 72 lb/day chloride and assuming it was PERC. This would imply a PERC contamination of about 6.2 gal/day.

Looking at the hydrogen make-up stream analyses, you can estimate how much chloride is entering from this source fairly easily using the concentration of chlorides (usually in volppm) and the make-up gas rate. If you have 1.5 volppm chloride in 700 scf/bbl reformer hydrogen make-up at 50 000 bpd, the make-up hydrogen is bringing in:

\[
50\ 000 \text{ bpd} \times 700 \text{ scf/bbl} \times 1.5 \times 10^4 \text{ ppm HCl} = 52.5 \text{ scf/day chloride}
\]

52.5 scf/day = 379.45 scf/mol x 35.5 lb/mol = 4.9 lb/day chloride

For deposits of chlorides in exchangers or the reactors, you can estimate the mass of chloride in the deposits from the analyses. You then can make some assumptions about how much mass of deposit that represents. Note that for ammonium chloride deposits, both the chloride and nitrogen are needed. So, for instance, if you have a naphtha with 5 ppm chloride, but only 1 ppm nitrogen, the amount of deposit possible is limited by the nitrogen, not the chloride; 1 wppm nitrogen can make, at most, 3.8 ppm NH4Cl deposit before running out of nitrogen. In fact, you will not get even that much as deposition occurs and partial pressures drop. The excess chloride will go on to
lower the pH of any effluent water. You get some effluent fouling, along with a corrosion bonus.

From observations and experience, the density of the fouling deposits tends to be in the order of 20-30 lb/ft³, regardless of what the foulant is. Suppose we have our diesel hydrotreater with 72 lb/day of chloride and it has more than enough nitrogen for all the chloride to deposit as a NH₄Cl in the effluent. The amount of deposit expected would then be about:

\[ 72 \text{ lb Cl/day} \times 53.5 \text{ lb NH}_4\text{Cl} / 35.5 \text{ lb Cl} = 25 \text{ lb/ft}^3 \text{ (avg)} = 4.3 \text{ cft/day of NH}_4\text{Cl deposits.} \]

Another approach to determining the amount of material you are looking for is to perform chloride balance around the upstream units. This can be one of the best tools for identifying the source and magnitude of a chloride problem at the same time. Pay particular attention to the desalters and reforming and isomerisation units. Develop a good material balance and sample all streams for chlorides. With attention to detail, an acceptable (+/-2%) chloride balance is achievable.

Once you have an idea of how much chloride you are looking for, you can begin considering possible sources for the material.

**Step 3: Identify the sources**

As you could surmise from the analytical testing above, chlorides in hydroprocessing units enter generally via two routes:

- **Feedstock**
- **Reformer hydrogen make-up**

We now have an idea of how much material we are looking for, so we can start looking at the possible sources in more detail. From experience, the most common source(s) for chloride problems are internal to a refinery. Outside crude contamination can still occur occasionally, however, so do not rule it out too early.

**Feedstock chloride sources**

Naphtha reforming and isomerisation units

Chloride is used in both reformers and isomerisation units to maintain catalyst activity. We are going to focus here on how chloride can get into a hydroprocessing unit liquid feed from one of these units. We will talk later about the reformer hydrogen route.

Chloriding agents are used to provide the necessary chloride to a reformer or isomerisation unit. The agents are mixed with naphtha and injected into the unit. Agents which have been used include trichloroethylene (TCE, C₂HCl₃), perchloroethylene (PERC, C₂Cl₄), and carbon tetrachloride (CCl₄). PERC is most common and carbon tetrachloride is no longer used due to toxicity. PERC has also been used for dry cleaning and equipment cleaning. These materials normally convert completely to yield HCl in processes. Key properties of some of these chemicals are listed in Table 1.

Chloriding agents can enter hydroprocessing unit feedstocks by several, unintended routes. Observed contamination routes from reformer and isomerisation operations have included:

- Leaks or drainings from chloriding agent storage drums or systems
- Overflow of chloriding agent drums to sewer or flare
- Poor chloriding agent receiving practices (such as draining residual material from a truck into the sewer)

The agents that reach the sewer or flare end up in the slopes or recovered oil systems and are charged back to the crude unit. They then normally distill into the naphtha heading to the reformer pretreater.

**Crude oil**

Salt is a natural part of crude oil. A certain amount of brine is co-produced with crude. The brine is separated in the field and the relatively dry crude oil is sent to the refinery. Chloride introduced into a well during a workover or well stimulation effort will also appear in the produced crude. During transportation, brine can enter crude oil from seawater. Regardless of the origin, the crude salts can be a source of chlorides in hydroprocessing unit feeds. The salts consist primarily of sodium, magnesium, and calcium.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Perchloroethylene</th>
<th>Trichloroethylene</th>
<th>Carbon Tetrachloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickname</td>
<td>PERC</td>
<td>TCE or Trice</td>
<td>CCl₄</td>
</tr>
<tr>
<td>Formula</td>
<td>C₂Cl₄</td>
<td>C₂HCl₃</td>
<td>CCl₄</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>165.8</td>
<td>131.4</td>
<td>153.8</td>
</tr>
<tr>
<td>Boiling point, °F</td>
<td>250</td>
<td>189</td>
<td>170</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1.622</td>
<td>1.46</td>
<td>1.5867</td>
</tr>
<tr>
<td>Density, lb/gal</td>
<td>13.5</td>
<td>12.2</td>
<td>13.2</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>0.15 g/L</td>
<td>1.28 g/L</td>
<td>0.81 g/L (25°C)</td>
</tr>
<tr>
<td>Wt% chlorine</td>
<td>85.6</td>
<td>81.1</td>
<td>92.3</td>
</tr>
<tr>
<td>Health effects</td>
<td>Toxicity moderate to low</td>
<td>Carcinogenic</td>
<td>Very toxic</td>
</tr>
<tr>
<td>NFPA ratings, H-F-R</td>
<td>2-0-0</td>
<td>2-1-0</td>
<td>3-0-1</td>
</tr>
</tbody>
</table>

**Table 1**

![Figure 2](https://www.eptq.com)
chlorides. As a rule, the less polar the salt, the less soluble it will be in water and the more soluble it is in the crude. The crude will tend to hang on to magnesium and calcium chlorides, even through desalting. Sodium salt removal by desalting is usually complete. Fortunately, the normal levels of magnesium and calcium chlorides in crudes are low. But some crude have more than others.

As crude is processed through the primary crude unit, vacuum unit, and coker, residual magnesium or calcium chlorides will begin to hydrolyse in the presence of trace water, releasing HCl.\(^1\) The hydrolysis relationship to temperature is illustrated in Figure 2, with data published by Petrolite.\(^2\) Sodium chloride will not decompose to any significant extent. HCl generated from the magnesium and calcium salts will move upward in the distillation columns until it finds ammonia or amines to combine with, or until a liquid water phase forms, or until the HCl gets drawn into a product. There the chlorides effects will be evident in the columns or exchangers for the crude, vacuum, and/or coker units.

A key control on crude unit inorganic chlorides is desalting efficiency. Most desalters can remove 90-95% of the salts from the incoming crude in a single stage. This salt will mostly be sodium chloride. A lot of the magnesium and calcium chlorides stay in the desalted crude. For a crude with 20 lb per thousand barrels salt, the product salt will be less than 2 lb per thousand barrels. This is not really a problem level. If the crude salt level rises to 200 lb per thousand barrels, however, and the crude has more magnesium and calcium salts, the desalter may only produce 20 lb per thousand barrels product. This is a lot of salt to leave in the crude unit charge, even when only some is Mg and Ca.

Organic chlorides are not naturally present in crude oils. A crude organic chloride source that has been frequently observed is the blending of organic solvents (for instance, PERC dry cleaning solvent) into the crude for disposal. This is often difficult to trace back to a specific crude source. Some refiners have set specifications for maximum organic chlorides in crude (or in the naphtha fraction of crude) that they are willing to purchase. Such solvents would usually distill into the naphtha streams and react in the naphtha hydrotreaters to release HCl.

Other upstream units

Residual chlorides from upstream units often end up in hydproprocessing unit feeds. For instance, chlorides in a coker fractionator will be present in every product stream. Depending on the operating conditions for a given column, chlorides will distribute across the full range of distillation products. A chloride balance around each upstream unit, although difficult, helps indicate where a problem condition exists. These chlorides may include various organic compounds resulting from the reaction of HCl with olefins.

Water and nitrogen play roles in determining where chlorides come out of fractionation units. Most chlorides are very soluble in water, so any chloride formed by decomposition in a still will move up a column until liquid water forms. Some of the chloride will partition to the oil, in equilibrium with the water phase. While we might usually ignore HCl dissolved in oil, when you are worried about parts per million of chloride, the solubility is important. Nitrogen compounds, such as amines, also hold on to chloride, acting as bases. Some nitrogen compounds are specifically designed to pull inorganics into the oil phase. Crudes high in nitrogen will tend to produce gasolins high in nitrogen, which will carry chloride into downstream hydproprocessing systems.

Even within the upstream units, operating conditions for columns can increase or decrease chloride contents of streams. Manipulating column pressures, temperatures, and reflux rates can greatly affect how the chlorides will partition among the product streams.

In some instances, very heavy crudes may be charged directly to a coker. These heavy crudes are generally not desalted and have not been separated well from production brines. Crude chlorides are thus introduced directly into the coker, often at the fractionator. The resulting coker products have concentrations of chloride and will even contain organic chlorides formed from reactions between HCl and olefins in the coker products.

Potentially major sources (or accumulation locations) for organic chlorides within a refinery are the recovered oil and slops systems. These streams are often charged to the crude unit to save the hydrocarbon value of the streams. Organic chlorides can enter these systems from many sources, including:

- Reformer or isomerisation unit chloriding agents as previously described
- Skimmings from the sour water drums or tanks from a contaminated system
- Spent maintenance solvents sent into the system
- Receiving solvents from an outside source for disposal
- Wastewater treatment plant recovered oil or sludge.

When recovered or slop oil contaminated with organic chlorides is re-run in the crude unit, the organic chlorides distribute into the products according to their boiling points. It can be extremely difficult to identify the source(s).

Contamination of a refinery sewer system with organic chlorides can be a particularly difficult issue to identify. Because the compounds involved are not very water soluble, are only mildly volatile, and are heavier than water, they can lay in the sewer seal boxes and other low point, quiescent locations until high flow rates entrain the material out of the low points or a hydrocarbon dissolves them out. They may then show up at once or in spikes. Similar issues can make identifying a chloride source difficult when the materials are moving through the sour water or flare systems.

Reformer hydrogen make-up

The most common gaseous source of chloride in hydproprocessing units is naphtha reformer hydrogen. There is always a trace of chloride (as HCl) in any naphtha reformer or isomerisation unit net hydrogen.
production. When this offgas is introduced into a hydroprocessing unit as make-up hydrogen, the chloride goes too.

The chloride level in reformer hydrogen is normally very low — about 1-3 volppm. It is often managed by passing the net reformer hydrogen through a chloride adsorber. When the adsorbent is spent, it will allow chloride to slip, but the resulting material released is an organic chloride polymer (‘green oil’, not HCl). This was alluded to in the analytical discussion above.

An isomerisation unit maintains a higher level of HCl in the treat gas than a reformer; but the small amount of purged net gas leaving the isomerisation unit is treated in a caustic absorber so that almost no chloride escapes. If the absorber is mismanaged, of course, chloride can get out.

For perspective, it is helpful to consider the potential magnitudes of the different chloride sources and their impacts. We often worry about chlorides from the reformer hydrogen make-up because we know it always contains chloride (without an adsorber), but compare the amount of chloride introduced into a hydrotreater from the reformer gas with the impact of chloride in a liquid feed. Suppose we have a 50 000 b/d naphtha hydrotreater and we run once-through reformer hydrogen at 500 scf/day rate. One volppm chloride in the gas will be about 2 lb/day of chloride, whereas 1 wtppm chloride in the feed will be about 13 lb/day. We need to be a lot more concerned about feed chloride content than make-up hydrogen chloride, in general.

Also, do not assume chlorides are eliminated by upstream processing. Chlorides do get through FCC feed pretreaters and end up in the FCC slurry and cycle oils, for instance. Coker streams almost always have some chlorides. The levels in these streams are generally low, but they can be elevated if there is a problem. Consider all feed and recovered oil streams when looking for chloride sources.

Table 2 provides a checklist for many of the possible chloride sources in feeds to a hydroprocessing unit. It contains the most common sources people have seen, as well as a few less common ones. Is it all inclusive? Probably not; you have to think through your specific case, but the table is a starting point.

You can systematically work your way through the list. Be sure to actually consider and prove or disprove each possible source. From experience, most locations that have had a problem that they thought was from an outside source, actually had internal problems they did not recognise. Do not make assumptions and eliminate sources too quickly or without proof. Be sure you understand the actual practices being used in handling any chloride chemicals, not just what the refinery has on paper. Verify procedure against practice.

Part 3: Managing the chlorides

Parts 1 and 2 of this article provided a methodical approach to identifying a chloride problem in a hydroprocessing unit, determining the size of the problem and narrowing it down to a likely source or sources. This final part will address approaches to dealing with the source(s).

Step 4: Manage the chlorides

Now that you have a clue about the magnitude of chlorides present and where they might be coming from, you can address the problems. There are three fundamental strategies or options for controlling chlorides in a hydroprocessing unit:

- Keep chlorides out
- Intercept what gets through
- Design and monitor for chlorides.

By the application of these strategies, individually and in combination, chlorides have been effectively controlled in many units.

Keeping chlorides out

As a general rule, target to have much less than 2-3 ppm chlorides in feed and less than 0.5 ppm in make-up reformer hydrogen to a hydroprocessing unit. In eliminating chlorides from the feeds, consider the following:

- What potential sources were implicated using the Table 2 checklist? Run the sources to ground.
- If possible, select crudes that have
low salt content, or at least a salt content within a range you can tolerate. Eliminate any crude source that has demonstrated high organic chloride contents or penalise that crude’s value consistent with its impacts. Crude pricing may make this option difficult to implement.

- Dry the crude as much as possible before it reaches the crude unit. Keep the crude warm in tankage to maximise water separation. Water draw the crude tanks regularly. Consider using one of the materials marketed by treatment chemical suppliers to accelerate separation.
- Pay attention to desalter performance and consider a second stage of desalting. Where single stage desalting removes 90-95% of the salts; two stage desalting will remove 98-99% of the salts. The second stage targets the magnesium and calcium chlorides more. This may be enough to avoid problems.
- Caustic can be injected into the desalted crude to neutralise HCl released in the crude unit by hydrolysis. This can help reduce crude unit corrosion and intermediate product chloride levels; however, caustic may negatively affect the vacuum and coker units downstream.
- Run designed experiments on your crude, vacuum, and coker towers to identify the operating conditions that minimise chlorides in the hydroprocessing feeds.
- Dry hydroprocessing unit feeds are essential. Upstream systems should ensure good water separation and feed tanks should be regularly water-drawn to keep salts out of processing units. It is a good practice to use swing-line draws from your tanks where possible. Dry stripping (reboiling) feeds is preferable to steam stripping (which guarantees a wet feed).
- For chlorides present in reformer hydrogen, installation of a cold chloride adsorbent (alumina) bed ahead of the make-up hydrogen compressors will eliminate most of the chloride. Alumina beds can take up, perhaps, 10-15% chloride. This is a proven technology. If you already have a chloride adsorber on make-up gas, be sure it is working correctly. Calculate the expected bed capacity and life. Change the bed when you calculate that it would be spent; do not wait until you detect breakthrough.

Intercept what gets through
Your second line of defence against chlorides is to control what gets through into the hydroprocessing unit feed. One ppm of chlorides in 50 000 b/d gasoil is about 16 lb/day or about 3 t/y. Options for controlling the chloride slip within a unit include:
- Wash the effluent exchangers with condensate. Meet the same rate, water quality, and design configuration requirements defined in API RP 932, as applied to an ammonium chloride case. Inject condensate upstream of the first exchanger where chlorides may deposit as determined by the equations
presented earlier. There must be enough condensate for about 25% to remain free liquid at the injection point. Allow enough downstream piping for the condensate to mix well (perhaps 30 diameters) or install an inline mixer (which will not block flow if it fails); otherwise, the condensate droplets will damage the downstream piping or exchanger by erosion or erosion/corrosion.

- If the chloride and nitrogen levels in the feed are low enough, condensate injection can be intermittent. This frequently works in naphtha and jet hydrotreaters. It may even be worth dropping unit pressure and temperature for a good, intermittent wash every few months. Sample and analyse the wash water to determine the length and frequency of washing. The required time is longer than you might think. You cannot leave any salt deposit or it will be more corrosive. Wash water pH can be moderated by ammonia or non-volatile amine injection, but avoid contaminating the product with nitrogen if it is reformer feed.

- Where chloride deposits in fractionation towers or draw systems, periodic or continuous water wash is also useful. Water washing for 4-12 hours every 2-6 months has been used to remove deposits with success. Again, be sure all the salts are removed during the water wash.

- For fractionator preheat exchanger problems, the quality of water separation ahead of the exchangers is crucial. To aid in separation, keep your high pressure separator temperature above 90°F (32°C), but not over 105-110°F (40-43°C). Separation of water and oil must be better than 99% efficient. You need to remove enough water so that all the remaining water evaporates in a relatively cool exchanger, thereby reducing the risk of corrosion.

- You may be able to simply raise separator oil level and help yourself. A review of residence times and separator configurations, along with a water balance, should indicate if improvements are needed here. Rate increases over time often defeat a separator that used to be adequate at lower rates. Water coalescing and separation seem to be as much art as science. A combination of coalescing pads and horizontal plate separators have been fairly effective in difficult cases.

**Design and monitor for chlorides**

If you cannot keep the chlorides out and you cannot make them go where you want, you will have to otherwise cope with their presence. A few techniques that have been successful are:

- Expect increased corrosion in the areas described earlier. Plan to increase metallurgical inspection, and plan on more frequent retubes and replacements of bundles and shells.

- Select metallurgies that are resistant to chloride attack. Exchangers where corrosion may be most aggressive may require alloy tubes (for instance, Inconel 625 for tube-side reactor effluent), but the lower pressure shells (fractionator feed) may still use carbon steel with large corrosion allowances. AL6XN and 2205 have been used with limited success where corrosion was moderate. In crude units, titanium has been successful when chlorides are present.

- Avoid creating dead spots and cold zones in susceptible exchangers. Keep the exchangers insulated well and review your baffle arrangements. Wet NH4Cl deposits on the shell are troublesome, since they can result in shell corrosion. Thermography of the shell can help spot potential problem temperature zones.

- Corrosion inhibitors may help resist damage in the fractionation and effluent systems in cooler zones. In naphtha reformer pre-treater service, however, they may send unwanted nitrogen to the reformer.

- Review your fractionator or stripper relief system design for tube failures in preheat exchangers. API Recommended Practices 520 and 521 contain published guidelines for tube failure scenarios.

- Establish good chloriding agent receiving practices. Never put any chloriding agent to the sewer, flare, or recovered/slop oil. If there is extra agent after filling your chloride agent drum, send it back and accept the restocking charge.

- Monitor, monitor, monitor. Watch for chloride deposits and damage when the unit is down for turnaround. Track feed chlorides by frequent sampling. Track chlorides in your wash water. Watch for losses in heat transfer in exchangers where chlorides may deposit. Chloride balance your reformers and isomerisation units. Watch your recovered/slop oil organic chloride content. Watch your sour water skims for organic chloride.

**Conclusions**

Chlorides can enter a hydrosprocessing unit via several routes. They will adversely affect unit reliability. The primary keys to controlling the adverse effects centre around elimination of the incoming chlorides, intercepting the chlorides that do enter, and controlling the effects of the remaining chlorides.

By applying the principles discussed here, you can successfully steer clear of the pitfalls posed by chlorides in hydrosprocessing units.

**References**


Steven Treese is a Hydroprocessing Consultant with Becht Engineering in Gig Harbor, Washington with 45 years’ industrial experience. Email: streese@becht.com