



This Technical Committee Report has been prepared by NACE International Task Group 274 on Refinery Corrosion and Fouling—Effect of Nondesaltable Halogens: Report*

Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling

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Foreword

Recently, an increasing number of refineries have experienced extreme corrosion and fouling in crude distillation unit overheads and/or naphtha hydrotreating units. The root causes were traced to severe spikes in the chloride levels. The spikes were unexpected because most of the chlorides in the incoming crude oil are usually removed by the desalter and the remaining chlorides are measurable by commonly used test methods. During the spikes, the chlorides passed through the desalter and were difficult to detect. Therefore, the industry coined the term “phantom chlorides” to describe them.¹ A number of possible sources of phantom chlorides are discussed later in this report. The source affects the expected location of problems, the best test methods for detection and concentration measurement, and the possible corrective actions. Other terms often used synonymously with phantom chlorides are “nonextractable chlorides,” “nondesaltable chlorides,” and “rogue halogens.” Henceforth, this report primarily uses the term *nonextractable chlorides* when referring to these species.

The purpose of this technical committee report is to increase awareness of the problem of nonextractable chlorides on refinery equipment and to document the lessons learned to date. Because information is still being developed by the industry, it is not possible to provide detailed descriptions of all “phantom chloride” sources or definitive solutions to prevent all potential problems. This report lists sources determined to date, includes details on test methods to measure the levels of chlorides, and lists solutions various refiners have used for their specific conditions.

This report is intended as a technical resource for materials and corrosion specialists at oil refining, oil production, chemical-treatment suppliers, and other companies involved in analyzing and preventing corrosion at refineries.

The topics included in the scope of this report are:

- Description of extractable vs. nonextractable chlorides,
- Known sources of nonextractable chlorides,

* Chair Cathleen A. Shargay, Fluor Corporation, Aliso Viejo, California.

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- Test methods,
- Case histories of problems in crude distillation units (CDUs) and naphtha hydrotreaters (NHTs), and
- Possible solutions used to date.

Not included in the scope are:

- A complete description of mechanism, or

- Complete solutions for predicting or solving problems.

This technical committee report was developed by Task Group (TG) 274 on Refinery Corrosion and Fouling—Effect of Nondesaltable Halogens: Report. This TG is administered by Specific Technology Group (STG) 34 on Petroleum Refining and Gas Processing. This report is issued by NACE under the auspices of STG 34.

NACE technical committee reports are intended to convey technical information or state-of-the-art knowledge regarding corrosion. In many cases, they discuss specific applications of corrosion mitigation technology, whether considered successful or not. Statements used to convey this information are factual and are provided to the reader as input and guidance for consideration when applying this technology in the future. However, these statements are not intended to be recommendations for general application of this technology, and must not be construed as such.

Section 1: Introduction

Most chloride salts in the crude oil coming into a refinery are inorganic (sodium, magnesium, or calcium chloride) and are effectively removed by the desalter. The nonextractable chlorides are not removed in the desalter, but can break down from downstream heating and processing to form hydrochloric acid (HCl). They sometimes cause corrosion and fouling problems. The forms of these chlorides are still being determined, but probably include organic chlorides (either natural or added via treatment chemicals or by the disposal of slops into the crudes); inorganic chlorides encapsulated in high-melting-point waxes or asphaltenes; or chlorinated solvents used in upstream operations.

The primary locations of problems to date have been in CDUs and NHTs. Within this report, the term CDU includes atmospheric and/or vacuum distillation units. Some types of nonextractable chlorides break down (by hydrolysis and pyrolysis), primarily in the CDU atmospheric and/or vacuum heaters, causing corrosion problems in the tower

overheads. With other types, only a very small percentage break down in the CDU and most of the chlorides go downstream to the NHT. There are also reports of nonextractable chlorides found in gas oils going into the applicable downstream units.

Even with as little as 1% of the nonextractable chlorides breaking down in the CDU, a major increase in the atmospheric tower overhead HCl and chloride levels can occur and cause severe corrosion and fouling problems. One refinery had new overhead condenser tubes fail in less than 14 hours with a corrosion rate of about 1,000 mm/y (40,000 mpy). All incoming chlorides are converted to HCl by the hydrotreating reaction in NHT units. One refinery with nonextractable chloride corrosion in the NHT experienced 5 to 30 mm/y (200 to 1,200 mpy) rates on the tubes and shell of the feed/effluent exchangers, reducing the service life of the exchangers to 33 days.

Section 2: Extractable vs. Nonextractable Chlorides

Chlorides in crude oils fall into two major categories: those that can be removed by extraction into an aqueous phase and those that cannot be extracted by water.

Extractable Chlorides

Crude oils are usually contaminated with inorganic salts. These salts are dissolved in the produced water, which is appropriately referred to as *brine*. The predominant cations are sodium, calcium, and magnesium. There are many different anions, but the acidic condition resulting from the hydrolysis of chloride salts is the primary cause of corrosion. The calcium and magnesium chloride salts (CaCl_2 and MgCl_2) hydrolyze during the crude distillation process to form hydrogen chloride gas, while sodium chloride (NaCl) goes into the reduced crude or residuum streams. The hydrogen chloride gas passes up the distillation towers to the point at which water starts to condense. There it readily dissolves in the water and forms HCl that is extremely corrosive to many metallurgies. Various corrosion

mechanisms can occur and an array of control methods are used to minimize these overhead corrosion concerns.²

At various steps in the crude production and handling process, some of the brine solution is normally removed in the oil field in order to meet limits set by contract. This separation and removal is often facilitated by the use of chemical, thermal, electrical, and mechanical means before the crude reaches the refinery. However, there is typically enough emulsified brine to cause serious corrosion problems. Refiners usually address this problem by washing the crude with cleaner water and applying electric fields and/or chemicals such as surfactants and emulsion breakers. This is typically done to heated crude in the CDU in a vessel called a *desalter*.

The function of the desalter is to extract the water-soluble inorganic salts into the water layer. This water layer is usually discarded to the refinery's effluent system. This water-washing process typically removes more than 90% of the inorganic salts associated with the crude oil. Because

this removal efficiency has an impact on the integrity of the CDU, plant operators and chemical vendors usually measure the extractable chloride levels of the incoming crude and desalted crude. Some units use two desalters in series (double desalting) to achieve higher removal efficiencies.

Historically, the discussion of chloride-related corrosion, as well as the testing and analysis, was based on the assumption that all the chloride found in the CDU was derived from inorganic, and therefore water-extractable, salts.

Nonextractable Chlorides

By contrast, nonextractable chlorides are not dissolved in emulsified water, removed by desalters, or reflected in extractable chloride measurements. Some solvents may be able to extract these chlorides, but for the purposes of this report, the term *nonextractable* applies to *nonextractable in water*.

Nonextractable Chlorides Known to Date

One form of nonextractable chlorides is organic solvents that have at least one carbon-to-chlorine (or other halogen) bond. This bond is not easily broken, but the conditions in a CDU can cause substantial hydrolysis or possibly some thermal breakdown that can result in considerable amounts of HCl in the overhead system. The remaining nonhydrolyzed chlorides from these sources typically go into the naphtha. These solvents are extremely oleophilic and cannot be removed or extracted by water. One common source is chlorinated solvents.

Nonextractable Chlorides—Unconfirmed Structures and Types

In the early 1990s, several deposits high in chlorides were found in CDUs, hydrocrackers, and hydrotreaters that

processed gas oils. Nonextractable chlorides were found in residuum. This was a major change from the previous chloride “behavior”—the chlorinated solvents and hydrolyzed chlorides went into the overhead, while the sodium chloride salts stayed in the reduced crude/residuum. The presence of nonextractable chlorides in gas oils and residuum appears to be a recently reported phenomenon. There is no definitive evidence identifying the cause of chlorides in gas oils and residuum.

At a refinery in which the atmospheric residuum is sent to a residuum desulfurizer (RDS), the following chloride levels have been measured:

Sample Point	Extractable Chlorides (ppmw)	Nonextractable Chlorides (ppmw)
1. Crude Oil Feed	4 to 10	1 to 8
2. Desalted Crude Oil	0.4 to 1.7	2 to 5
3. Atmospheric Residuum	0.4 to 1.4	1 to 2

This unit injects caustic upstream from the crude heater and has 80 to 200 ppmw chlorides in the atmospheric tower overhead water. Various chloride corrosion problems are occurring in both the CDU and RDS. The source of the nonextractable chlorides has not yet been determined.

In general, there have been several chemicals or conditions proposed to explain this phenomenon (see also Section 4). These are listed in Table 1.

Table 1: Potential Sources of Nonextractable Chlorides and Other Halogens

Chemical ^(A)	Possible Source	Desaltable?
Oil-wetted inorganic salt crystals	Natural	Yes
Filming amine hydrochlorides	Production and refinery corrosion inhibitor	Unknown; unlikely
Neutralizing amine hydrochlorides	Production and refinery corrosion inhibitor	Yes
Alcohol amine hydrochlorides	Production and refinery waste	Yes
Asphaltene hydrochlorides	Natural	Unknown
Amine chloride polymer (cationic polymer)	Refinery flotation and emulsion breakers	Unknown
Treatment chemicals (cold-flow improvers)	Production	Unknown; unlikely
Quaternary amine chloride compounds (production treatment chemicals)	Production	Unknown
Waste-chlorinated oils (polychlorinated biphenyls [PCBs])	Illegal dumping	No
HF acid-soluble oil (ASO)	HF alkylation units	Unknown
Alumina treater spent alumina	Refinery	No
Fire-retardant polybrominated biphenyl (PBB)	Waste dumping/disposal	No
Catalytic reformer hydrogen from modified alumina-based chloride traps with alumina that is at end of run	Refinery (export hydrogen is used in hydrotreating units)	No

^(A) Some of these chemicals can be desaltable, but in some units are added downstream from the desalter.

Section 3: Sources of Nonextractable Chlorides

Chlorinated Solvents Used in Upstream Operations

The occurrence of organic chlorides in crude oil has often been the result of chemical cleaning solvents used in the oil production field. Solvents such as carbon tetrachloride, 1,1,1 trichloroethylene, various chlorofluorocarbon (CFC)-based solvents, and perchloroethylene (PERC) have been used in the past to dissolve deposits in production facilities. Typical uses were to clean industrial equipment or remove paraffin, wax, or tar deposits from crude gathering lines, tanks, pipelines, or similar equipment. These practices have been banned by most oil-producing countries. However, localized cases of “dumping” have been reported.

Other sources of organic chlorides are typically the result of biocide application downhole or in pipelines. Halogenated biocides, such as 2,2-dibromo-3-nitrilopropionamide (DBNPA) and chlorinated cyanurates, have been injected into oil-bearing formations and pipelines. Chlorine dioxide has also been used as a downhole biocide and can form chlorinated organics. The quantities being processed—quantities that typically cause problems, decomposition temperatures, etc.—are not all known at this time.

Organic chloride solvents have also been used as a fracturing fluid for well stimulation.

The oleophilic (oil-affinity) nature of these solvents and other chemicals causes them to stay with the crude oil throughout the upstream and terminal crude processing operations. At temperatures of 160°C (320°F) or higher these solvents begin to hydrolyze, forming HCl. However, the hydrolysis is not complete in the CDU, and these chlorinated solvents have been found in the naphtha cuts, causing processing problems in NHTs.

Refinery, Chemical, or Production Field Slops (Especially Those Containing Cationic Polymers)

Cationic polymers from oilfield and refinery use are typically sent to slops processing and are often added to the crude oil. Possible sources of slops that sometimes contain chlorine-containing organic chemicals include:

- Emulsion breaker,
- Desalting chemicals,
- Induced-air flotation or dissolved air flotation (DAF) wastes,
- Flocculation chemicals,
- Some biocide chemicals (not all biocides contain chlorides),
- Catalyst-chloriding chemicals,
- Alumina liquid,
- Chemical plant waste oils,
- Lube unit waste,

- Tank-cleaning chemicals or sludge,
- Tank-bottom solids, and
- Laboratory solvents.

These hydrocarbon liquid-waste streams are sometimes known as “black oil” or “red oil.”

Feeds Contaminated en Route to the Refinery by Ships Loading Slops

Ships in certain ports-of-call have been found to load up on slops. This can contaminate a batch of crude oil with nonextractable chlorides. One refiner measured incoming shipments of fuel oils and found one shipment out of seven was extremely contaminated with chlorides.

Crude Oils Consistently Containing Organic Chlorides (or Forming Them During Normal Production Steps)

Some crude oils consistently show relatively high levels of organic chlorides. There is debate as to whether any crude oils naturally contain measurable amounts of organic chlorides. For the crude oils consistently showing problems it is possible that the chloride compounds regularly form during production operations, or are the result of consistent contamination. The organic chlorides typically form as a result of water flooding, steam flooding, fire flooding, drilling, etc.

In an unpublished forum, one refiner reported that a certain crude oil was found to have 9 ppm nonextractable chlorides. This caused corrosion problems. Another refiner reported that they have measured up to 100 ppm chlorides in the same crude oil. A second problem crude oil had up to 60 ppm chlorides. One crude oil was mentioned as having consistently high levels of nonextractable chlorides for years.

Blending of Incompatible Crude Oils

Naphthenic acid is reported to increase the hydrolysis of sodium and calcium chloride. Therefore, the blending of crude oils containing naphthenic acids sometimes

contributes indirectly to the problems with nonextractable chlorides by destabilizing asphaltenes (causing fouling) or promoting the formation of HCl from asphaltene (or other) chloride salts. Another possible source is that some crude blending combinations may result in the formation of asphaltene-encapsulated inorganic chlorides. These compounds would not be effectively removed by desalting.

Recycled Transformer and Lube Oils

There have been instances of recycled lube oils (with additives that can form organic chlorides in service or when heated) being dumped into crude oil gathering systems, especially offshore pipelines. This has caused severe upsets in desalter operations and fouling in the CDU atmospheric tower overhead system and downstream NHT and fluid catalytic cracking unit (FCCU).

Another possible example of intentional waste disposal involves halogenated oils such as PCBs from transformer oils. This dumping is illegal in most countries. There has been speculation that these streams have been disposed of in crude oil. One refiner reported corrosion in the CDU after processing various pipeline transport mixes (transmix). The exact source and shipping history of these small batch “recycle” oil feedstocks are highly variable and suspect. Some have been found to contain up to 500 ppm chlorides.

Catalytic Reforming Unit Hydrogen

In catalytic reforming units with modified alumina-based chloride traps on the export hydrogen, there is a possibility of forming organic chlorides as the alumina is approaching its end of life. This possible source has not been fully tested yet. There is a concern that the hydrogen is being monitored for HCl only, but the organic chlorides may begin to form prior to the HCl being out-of-specification. The hydrogen, which may contain periodic high organic chloride content, may be injected into hydrotreating units. A solution used by some has been to monitor for organic chlorides and to replace the alumina earlier. This area would benefit from further testing and compilation of industry experience.

Section 4: Test Methods for Measuring Chlorides in Crude Oils

Introduction

Crude oils are typically analyzed for inorganic chloride salts because of their impact on corrosion and fouling in both the CDU and downstream processing units.

Determining inorganic extractable chloride in crude oils is a common practice, and a method frequently employed typically involves water extraction followed by quantification of the chloride salts extracted into the water. However, with crude oils containing substantial amounts of nonextractable chloride compounds, this traditional chloride measurement can sometimes understate the potential corrosion impact. Analytical techniques to determine organic chloride in crude

oil exist. One common approach is to first use water extraction to separate the chloride into:

- Extractable chlorides—water-soluble chloride compounds (NaCl, MgCl₂, and CaCl₂) that dissolve in the water, and
- Nonextractable chlorides—chloride compounds that do not easily extract into water and remain in the oil

Both the water and oil phases are analyzed for chlorides, and these two values are added to determine the total chlorides. Special techniques are generally employed to deal with interferences such as from sulfides.

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Analysis for chloride in crude oils typically involves the following steps, each of which is described in more detail below.

- Sample preparation,
- Water-extraction methods,
- Determination of the water-extractable chloride, and
- Determination of the nonextractable chloride content in the oil after water extraction.

Sample Preparation

The crude oil sample contains some water, a portion of which settles (over time) to the bottom of the sample container. This water can contain a substantial portion of the chloride and, as such, the water is normally mixed with the crude oil to obtain a representative sample for chloride determination. There are several methods available to mix the oil and water. Two common methods use either a high-speed shearing mixer or rely on vigorous shaking.

The high-speed shearing mixer has been shown to be an effective approach. The vigorous shaking approach is typically done either manually or with a mechanical shaker. The effectiveness of the vigorous shaking method depends, in part, on how long the sample has been allowed to settle. After a long settling time it becomes more difficult to fully homogenize the oil/water mixture and obtain a representative sample.

If the sample is properly mixed the same chloride result can be found in samples from the top, middle, and bottom of the container. This is a method sometimes used to validate the sample-preparation step.

Water-Extraction Methods

Four methods typically used in water extraction can be found in Appendix A. Some examples of results using multiple extractions are shown in Figure 1.

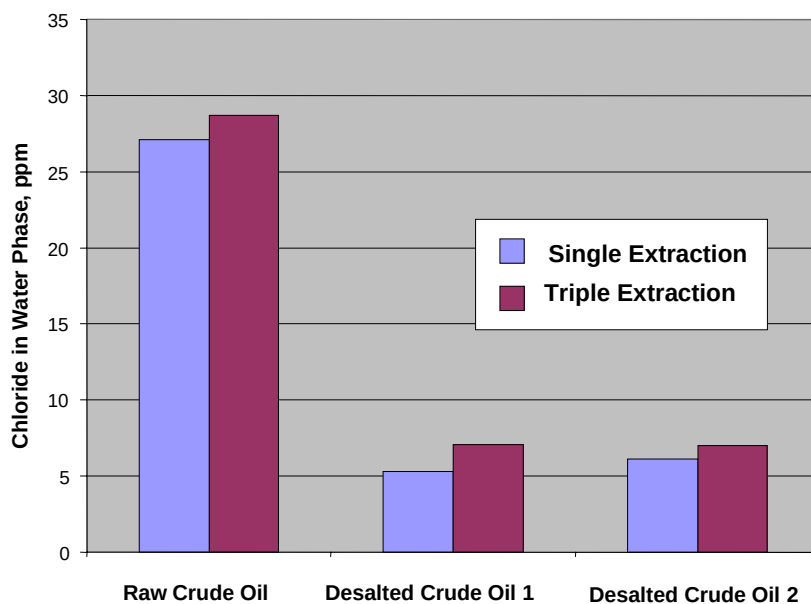


FIGURE 1: Comparisons of Single vs. Triple Extraction Methods

Additional heat and a demulsifier are sometimes used to better separate the water from the crude oil after the extraction process. When the extraction process is complete, samples of the crude oil and extract water are often analyzed for chloride.

Determination of Water-Extractable Chlorides

A number of methods for determination of chloride in water samples are available. For the low levels typically encountered in desalted crude oil samples, ion chromatography (IC) is generally accurate and reliable.

However, for locations not equipped for IC, potentiometric titration methods give satisfactory results. Two commonly used titrants are silver nitrate (AgNO_3) and mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$). Tables 2 and 3 contain comparative data on chloride results for IC and for titration using AgNO_3 and $\text{Hg}(\text{NO}_3)_2$. Table 2 compares IC versus $\text{Hg}(\text{NO}_3)_2$ for laboratory-prepared standard solutions. Both methods give very good results compared to the standards; however, the $\text{Hg}(\text{NO}_3)_2$ titration is typically not as accurate as IC at very low concentrations of chloride. This is more easily seen by average results for both methods.

Table 2: Standard Concentration vs. IC and Hg(NO₃)₂ Titration Results

Standard	Standard Concentration		IC Results		Hg(NO ₃) ₂ Titration Results	
	g/L as NaCl	lb/1,000 barrels [PTB] as NaCl	mg/L as NaCl	PTB as NaCl	mg/L as NaCl	PTB as NaCl
A	3.4	1.2	3.4, 3.9, 3.9, 3.7, 3.7 Avg. 3.7 ±0.3	1.2, 1.4, 1.4, 1.3, 1.3 Avg. 1.3 ±0.1	4.3, 5.7, 4.8, 4.8, 2.8 Avg. 4.5 ±1.7	1.5, 2.0, 1.7, 1.7, 1.0 Avg. 1.6 ±0.6
B	9.8	3.5	9.4, 9.4, 9.8, 9.8, 9.8 Avg. 9.6 ±0.2	3.3, 3.3, 3.5, 3.5, 3.5 Avg. 3.4 ±0.1	12.3, 10.5, 12.3, 9.7, 11.4 Avg. 11.2 ±1.5	4.3, 3.7, 4.3, 3.4, 4.0 Avg. 3.9 ±0.5
C	65.9	23.1	65.9, 70.0, 65.9, 65.5, 65.3 Avg. 66.5 ±3.5	23.1, 24.5, 23.1, 23.0, 22.9 Avg. 23.3 ±1.2	66.4, 73.6, 69.3, 69.6, --- Avg. 69.7 ±3.9	23.8, 25.8, 24.3, 24.4, --- Avg. 24.6 ±1.2
D	197	69.2	187, 199, 196, 196, 196 Avg. 195 ±8	65.5, 69.9, 68.8, 68.6, 68.6 Avg. 68.3 ±2.8	193, 201, 202, 196, --- Avg. 198 ±5	67.5, 70.4, 71.0, 68.7, --- Avg. 69.4 ±1.9

Table 3 contains data comparing IC with AgNO₃ titration on field-water samples. The AgNO₃ titration results agree at lower chloride concentrations, but at higher concentrations

the AgNO₃ titration gives higher values than those obtained by IC.

Table 3: IC vs. AgNO₃ Titration Using Field-Water Samples

Laboratory Number	Chloride by IC (ppm)	Chloride by AgNO ₃
		Potentiometric Titration (ppm)
MA1	134	160.6
MB2	2	2.2
MD4	13.1	13.0
MG7	310	330.4
MI9	1.7	1.7
MN14	72	78.7
MO15	1.8	1.8

Table 4 compares AgNO₃ and Hg(NO₃)₂ titration results. AgNO₃ titration gives chloride values that are generally

higher than those obtained by Hg(NO₃)₂ titration.

Table 4: $\text{Hg}(\text{NO}_3)_2$ vs. AgNO_3 Titration

Sample ID	mg/L (PTB) by $\text{Hg}(\text{NO}_3)_2$ Titration	mg/L (PTB) by AgNO_3 Titration
7830	148 (51.8)	161 (56.6)
7831	139 (48.9)	189 (66.4)
7832	148 (51.8)	153 (53.6)
7833	230 (80.5)	254 (89.2)
7834	656 (230)	556 (195)
7835	62.4 (21.9)	70.1 (24.6)

The data presented here show IC has been the preferred approach. When IC has not been available, titration using $\text{Hg}(\text{NO}_3)_2$ has provided good results. If mercury-based reagents are not allowed, AgNO_3 is often used, with the understanding that the chloride results obtained are probably higher than actual.

Determination of Nonextractable Chlorides

The next analysis step is typically to subject the crude oil sample obtained from the extraction process to analysis for chloride concentration. This method typically involves the following three steps:

- (1) A combustion process to pyrolyze all chloride to HCl,
- (2) Scrubbing the gases in a caustic solution to capture the HCl, and
- (3) Measuring the chloride by microcoulometry.

Experience shows this method produces satisfactory results, even at low chloride-concentration levels. There are other methods that follow similar approaches. These include:

- Total chlorine by sodium biphenyl reduction and titration,

- Total chlorine by bomb oxidation and titration,
- Total chlorine by neutron activation,
- Inductively coupled plasma (ICP), and
- Fluorescent indicator adsorption (FIA).

An alternative that some refiners use is ASTM⁽¹⁾ D 4929.³ This method typically involves the following three steps:

- (1) A crude oil sample is distilled up to 204°C (400°F), condensing and capturing a naphtha cut,
- (2) The naphtha cut is washed with caustic and with water to remove hydrogen sulfide and inorganic chlorides, and
- (3) The washed naphtha cut is then analyzed by a total chlorine method as previously described.

The result is called organic chlorine but could be better described as “volatile organic chlorine.” The downside to this method is that the distillation leaves behind any inorganic chloride (both water-extractable and nonextractable), plus any higher-boiling compounds that contain chloride (polymeric chloride quaternary amines, asphaltene-hydrochlorides). As such, the method sometimes misses some of the nonextractable chloride in the crude oil, thus giving an underestimate of the true chloride content.

Section 5: Experience in Crude Distillation Units

This section describes the details of three recent cases of rapid corrosion as a result of problems with nondesaltable chlorides.

Case 1

The CDU overhead condenser in a Far East refinery experienced accelerated corrosion while processing feedstock heavily contaminated with organic chlorides.¹

Some new carbon steel (CS) condenser tubes failed in less than 14 hours. This is equivalent to a corrosion rate of about 1,000 mm/y (40,000 mpy). A downstream NHT in the same refinery experienced severe fouling with ammonium chloride (NH_4Cl) deposits. The feedstock contained greater than 3,000 ppm organic chlorides. Table 5 illustrates the spike in chloride levels and the resulting low pH values during the excursion.

⁽¹⁾ ASTM International (ASTM), 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.

Table 5: Process Conditions During Normal Operation and Upset Conditions

CDU	Total Cl in Feed, ppm	Atmospheric Tower Overhead Accumulator Sour Water	
		pH	Cl (mg/L)
Normal	<1	5.5 to 7	<10
Problem	3,730	1 to 2	~ 6,000

Case 2

This CDU started having problems in 1999-2000, while processing West African crudes (up to 30% of the crude oil slate) and some North Sea crudes. The unit has an undersized overhead drum and there was water carryover in the reflux. It was limited to two-year runs because of fouling in the tower. Corrosion occurred on the UNS⁽²⁾ N04400 (alloy 400) trays. The downstream solvent deasphalting (SDA) unit, which receives the vacuum bottoms from the CDU, also experienced corrosion caused by chloride attack. UNS S41000 (Type 410 SS) packing and the CS shell corroded in an area that was about 150°C (300°F).

Case 3

A series of sudden tube leaks in four first-stage overhead exchangers of a CDU atmospheric tower on a major Gulf Coast refinery was attributed to repeated contamination of the crude oil charge with organic chlorides.⁴ Corrosion in these exchangers increased to a point at which the remaining life was used up in a matter of weeks. The contaminated crude oils were traced back to a single supplier that had dumped organic-chloride-containing hydrocarbon waste streams into one of the refinery's pipelines over a period of 10 months or longer. The organic-chloride content of the contaminated crude oils ranged from approximately 3 to 3,000 ppm. The total crude oil charge contained at least 50 ppm at the time when most leaks occurred, and possibly as much as 255 ppm.

Additional case histories are listed in Appendix B.

Section 6: Experience in NHTs

Two types of organic chloride are typically identified at NHT inlets:

- Nondesaltable organic chloride, such as light chlorinated solvents (e.g., tetrachloroethylene, tetrachloroethane, trichloroethylene, trichloromethane, dichloromethane), and
- Water-soluble amine-hydrochloride salts entrained with water in the naphtha from the CDU overhead accumulators.

Naphtha-soluble filming amine-hydrochloride salts are sometimes found in the rare cases of filming amine overdosage and high concentration of HCl. The following discussion primarily deals with the first type of organic chloride compounds.

Under normal operation without high organic-chloride levels, the amount of ammonia (NH₃) resulting from the denitrification of the nitrogen-containing compounds (including organic nitrogen compounds and corrosion inhibitors) and the HCl, which is typically sourced with the hydrogen treat gas, form dry NH₄Cl in the high-pressure fin-fan air coolers at temperatures of 50 to 80°C (122 to 176°F)

or higher, depending on the partial pressures. The deposition rate is normally limited by the small amount of HCl present in the effluent stream relative to the amount of NH₃. NH₄Cl salts are not corrosive in the absence of water. Because of the salt build-up and subsequent increase in pressure drop (delta P), refineries typically inject water on an intermittent basis to reduce the pressure drop. However, when the HCl content of the NHT effluent increases, the deposition of NH₄Cl in the feed/effluent heat exchangers is normally massive. This is because of similar and high mass flow rates of NH₃ and HCl in the deposition temperature range, which is increased to 100 to 160°C (212 to 320°F). Because of these conditions, the last two to three feed/effluent heat exchangers are typically subjected to a continuous water wash. This water wash, if not neutralized or of insufficient quantity, often leads to high corrosion rates caused by a very low pH at the injection point (pH 2 to 3.5) and throughout the system to the high-pressure separator (pH 4 to 5).

In the presence of organic chloride, if the ratio of nitrogen-to-organic-chloride content in the feed (in ppm) is generally lower than 0.4, normally taken actions cope with and avoid probable corrosion problems. With 2 ppm of nitrogen in the feed, a limit of 3 ppm of organic chloride in the feed is

⁽²⁾ Metals and Alloys in the Unified Numbering System (latest revision), a joint publication of ASTM International (ASTM) and the Society of Automotive Engineers Inc. (SAE), 400 Commonwealth Drive, Warrendale, PA 15096.

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typically considered as a maximum value to avoid problems with intermittent water washing. Above this limit, water washing is generally switched from intermittent to continuous and more detailed monitoring and controls are established. Two factors are typically addressed for corrosion control:

- The water-injection technique: Water injection points between feed/effluent heat exchangers are typically designed to achieve adequate mixing and HCl neutralization kinetics.
- The neutralization demand at the injection point (type and concentration of neutralizing amine): A neutralizing

amine with a low salt-forming tendency but high vapor pressure and lowest solubility in naphtha is normally sought. Rather than focusing on the pH of the high-pressure separator water, the required amount of neutralizing amine is typically calculated from the chloride content of the separator water.

Table 6 gives an indication of the critical level of organic chloride contamination of the NHT feed. However, this table does not account for the ratio of water injected/throughput.

Table 6: Levels of Organic-Chloride Contamination of NHT Feeds

Feed Organic Cl mg/kg [ppmw]	Sour Water Cl mg/kg [ppmw]	Iron in Sour Water mg/kg [ppmw]	Comments
4 (normal)	98	0.2 to <1.0	
<1 (normal)			No water injection
<3			Intermittent water wash
9	189	11	Neutralized and continuous water wash
10	227	2.2	
17	325	--	Neutralized water wash
25	580	--	Neutralized and continuous water wash
38.9	775	508	

Filming amine is not normally used in an NHT ahead of a catalytic reforming unit because of potential chloride entrainment (as a hydrochloride salt) in the naphtha feed to the catalytic reforming unit. One side effect of the neutralizing amine is a slight solubility in the naphtha that increases the nitrogen content of the feed to the catalytic reforming unit.

Some case histories include:

Case 1: Organic-chloride contamination (up to 30 ppm) of the crude oil feed during a 4- to 6-week period caused a heat exchanger shell in the NHT of a Louisiana refinery to suddenly rupture. Estimates of the short-term corrosion rates that occurred just prior to the failure are as high as 25 mm/y (1,000 mpy).¹

Case 2: Two European refineries experienced severe fouling and corrosion problems in their NHT units. In both instances, the culprit was organic chloride contamination of pipelined crude oil from Eastern Europe. The contamination produced leaks in the piping to and from the reactor-effluent high-pressure separator and in the pressure let-down valve from the separator. Corrosion rates as high as 8 mm/y (300 mpy) were measured.¹

Case 3: An NHT in a U.S. refinery experienced severe corrosion (5 to 30 mm/y [200 to 1,200 mpy]) on both the tubes and shell of the feed/effluent exchangers, reducing the service life of the exchangers to 33 days. The source of the problem was the presence of 100 to 170 ppm organic chlorides in the naphtha from a thermal cracker that processed chemical slops.¹

Additional case histories are listed in Appendix B.

Section 7: Possible Solutions

Because there are still many unknowns regarding the exact nature of the nondesaltable chlorides, this section only presents solutions to this elusive problem that have been attempted or considered. These possible solutions are indicated in **bold type**.

One solution to corrosion and fouling caused by nondesaltable chlorides is **source control**. However, this typically involves extensive chemical analysis in a very complex crude oil logistics system. Source control, in most cases, is costly and impractical. The solutions used thus far by various refiners have been a combination of source control, chloride analysis, crude purchase, and blending management. Some crude blends may lead to nonextractable chloride problems by forming asphaltene-encapsulated chlorides. This is typically managed by crude compatibility testing and strategic blending to avoid this problem.

The organic-chloride limits sometimes vary based on different unit designs and other factors. An explanation is given in this excerpt from a paper by Joerg Gutzeit:⁴

“When organic chloride contamination of crude oil became a problem in the past, most pipeline operators and refineries established stringent limits on organic chloride content.^{5,6,7} Some companies called for 5 ppm, while others called for 0 ppm organic chlorides. Typically, most companies called for from 1 to 3 ppm. From a corrosion point of view, the upper limit of 3 ppm is too high—a more realistic limit is 1 ppm. Even with only 1 ppm organic chlorides in the crude charge, the amount of hydrogen chloride formed in the crude heater is doubled, assuming the crude charge is normally desalted to 2.32 mg/L, or approximately 4 ppm inorganic salts. Some pipeline companies and petroleum companies have allowed higher limits only on a case-by-case basis, and then only when they receive sufficient advance notice. Other companies flatly reject any and all crude oils containing organic chlorides in any amount.”

Effective responses to incidents of nondesaltable chlorides typically depend on the ease of hydrolysis of the chlorides in question. If the chlorides are easily hydrolyzed, they affect primarily the CDU atmospheric tower and overhead and are amenable to one set of remedies. However, if the chlorides are not easily hydrolyzed and are not volatile, they affect primarily the CDU vacuum tower and overhead and somewhat different remedies are typically applicable. Finally, if the chlorides are not hydrolyzable but are volatile under the conditions typical of CDUs, they affect primarily the NHT. From an equipment-reliability and consequence-of-failure perspective, this is a serious case. A rapid response to identify and remove the source of nondesaltable chlorides normally reduces unacceptable risk of equipment failure.

If the source and quantity of the nondesaltable chlorides are known from prior experience, **setting a charge rate limit** for the crude oil or rerun stream in question is sometimes effective. This is commonly referred to as “trickle feed” or “dilution by blending.” The basis for the charge limit is often an ammonium or amine salt deposition temperature or initial dew point pH caused by the higher partial pressure of HCl in the affected unit. Usually, this limit is based on simulation of the process or experience under a controlled set of conditions.

Chlorides that are hydrolyzable exist in the chloride (anion) form and as such are theoretically amenable to extraction by water. They are easy or difficult to extract depending on the associated cation (various inorganics or organics) or physical form (e.g., oil-coated salts). Typically, the first step in dealing with nondesaltable-chloride problems is having an **effective method to measure** salt in the desalted crude oil. Without this, the desalter performance usually cannot be effectively optimized. Depending on the source of chlorides, multiple or more rigorous extraction techniques are typically used. With the tools to **optimize desalter performance**, the amount of inorganic chlorides in the desalted crude oil can be minimized.

Once the desalting operation is optimized, maximizing inorganic-chloride removal—the process of detecting and dealing with the remaining hydrolyzable chlorides—is normally begun. Detection is typically enhanced by frequent chloride or pH measurements by unit operators or continuous pH analyzers. If compatible with downstream processing, **caustic injection** into the desalted crude oil (primary neutralization) might further reduce chlorides in the CDU atmospheric tower overhead system. Care is typically taken in the design of a caustic injection system to reduce the potential for caustic corrosion and stress corrosion cracking and to ensure effectiveness. If caustic injection is not feasible, **increasing neutralizer to the overhead** (secondary neutralization), **institution of a water wash**, or **adjustment to filmer dosage** can sometimes reduce corrosion caused by the increased chloride loading. The increased chloride loading typically necessitates the relocation of the injection point of any or all of these means of corrosion control.

The species responsible for excessive chloride evolution and salting problems in the CDU vacuum distillation section have not been well defined. Adequate responses to proactively solve these problems have not been developed.

As mentioned above, a critical unit with regard to nondesaltable-chloride contamination is the NHT. In many cases, these units do not have a continuous water wash because chloride loading is low enough that NH_4Cl does not form continuously and the concentration of aqueous ammonium bisulfide (NH_4HS) is not a corrosion issue. In such cases, frequent monitoring of the naphtha feed for total chlorides can be done. In units with a continuous

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water wash, frequent monitoring of the inorganic chloride in the sour water has been conducted.

Once it is detected that a feed- or sour-water chloride limit has been exceeded, the **source of the chlorides can be identified**. This generally involves an analysis of all NHT and upstream CDU feed streams for total chlorides and observations of any water entrainment. If the source is an organic chloride compound in a particular crude oil source or rerun stream, the stream **is normally removed from the feed** until means to deal with it are formulated. The typical responses are either **to limit the charge rate based on the NH_4Cl deposition temperature relative to the water injection location and/or to move the water-injection location (and adjust the water rate to meet the injection criteria)** to deal with the increased NH_4Cl deposition temperature.

The source is sometimes entrained water from the CDU atmospheric tower overhead accumulator, which contains NH_4Cl or amine hydrochlorides from secondary neutralization. These instances are usually episodic in nature and result from equipment limitations (e.g.,

inadequate settling time, poor level control) or are induced by the filmer because of its emulsification tendency or a higher than typical dosage. A root cause analysis has sometimes been used to determine the cause and serve as the basis for potential solutions.

Another possible source to be investigated is **alumina-based HCl scrubbers** in catalytic reforming units. When at their “end-of-life,” these scrubbers generate chlorinated hydrocarbons that have been found in both the produced hydrogen, which is exported to hydrotreating units, and in the liquid “knock outs,” which are treated as slop and sent to CDUs. Proper scrubber maintenance helps avoid chloride contamination in hydrogen exported to downstream units.

Changes in operating and inspection procedures and strategies to deal with the conditions imposed by the responses to nondesaltable chlorides are often employed to ensure that long-term improvement reliability is attained and maintained. If changes in feedstocks, process limits, and operating procedures are inadequate to resolve the problem, **materials upgrades** are another option to meet reliability constraints.

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Appendix A: Typical Methods Used in Water Extraction

Four methods have been utilized for carrying out the water extraction. Each involves combining the crude oil with deionized water. Some methods include the addition of xylene to lower the viscosity of the mixture, thus enhancing water-oil contact and improving the efficiency of the extraction.

Each of the methods involve a sample mixing vessel, a means of contacting/mixing, and a means to obtain samples

of the extract water and the crude oil for analysis. Descriptions of these methods are provided here as examples.

Method 1: Using a 100-mL centrifuge tube, combine 30 mL of the crude oil with 30 mL of deionized water and 40 mL of xylene. Use boiling deionized water for best results. Place the mixture on an orbital shaker for about 30 minutes, then centrifuge the sample for about 20 minutes at a fairly high

speed. Remove samples of the crude oil and water layers with a syringe. The times given here for shaking and centrifuging have been shown, with most crude oils, to recover the majority of the extractable chloride salts. Longer times can be used if higher efficiency of extraction is required.

Method 2: Using a 500-mL separatory funnel, combine 100 mL of the crude oil with 100 mL of xylene (use the xylene to rinse out the graduated cylinder used to measure the crude oil, then add it to the separatory funnel). Add 100 mL of very hot deionized water and shake about 200 times. Again, longer shaking times yield a more effective extraction.

Method 3: Use a mechanized piston/cylinder device. A sample of the crude oil and deionized water, in equal volumes, are placed inside the cylinder and exposed to

repeated piston motion that shears the crude oil and water together for good mixing. After mixing, transfer the crude oil/water mix to a separatory funnel to allow separation. For more viscous crude oils, an equal volume of xylene can be used to improve crude oil-water contact.

Method 4: Distillation with reflux method. A crude oil/deionized water mixture, with equal volumes of each (and possibly with an additional co-solvent) is refluxed for at least an hour with good stirring to help dissolve water soluble species. This is typically the most efficient extraction method, but is also the most time-consuming.

With all of these methods, a double or triple extraction normally gives better results, although the improvement is typically minor. The mixing process can form a stable emulsion. This emulsion typically needs to be broken in order to separate the crude oil and water.

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Appendix B: Case Histories Reported in REFIN•COR^{8(A)}

REFIN•COR PARAGRAPH NO.	CRUDE/ LOCATION	SOURCE OF ORGANIC CHLORIDE	AMOUNT OF ORGANIC CHLORIDE IN FEED	CORROSION PROBLEM	OTHER COMMENTS
71F4.1-01	From distribution pipeline with primarily Louisiana delta crudes	Slop chemicals accidentally mixed with crude	300 to 400 to as high as 900 ppm (sometimes total Cl)	Leak in CDU atmospheric tower overhead piping (fire)	Unable to add enough ammonia to control CDU atmospheric tower overhead pH; tried adding carbonate to crude oil feed; caused heavy sodium chloride deposition in preheat exchangers and feed heater.
71F4.2-02	From distribution pipeline with primarily Louisiana delta crudes				Two other refiners received part of same shipment, but were forewarned and managed to control it.
87C7.1-18		Use of organic solvents to clean out wax deposits in production fields	Typically 30 to 50 ppm (implied that this level is not a problem and contamination results in higher levels)	Major problems in CDU in the past	Typical solvents are chloroethane or carbon tetrachloride.
87C7.1-19	Some Pennsylvania crudes	Can also be from slops or other crude oil recycle sources			
87C7.1-20	Middle East (intermittently)	Also from refiners adding slops with cleaning solutions		Hydrotreater piping leak and major fire	Italian refinery

REFIN•COR PARAGRAPH NO.	CRUDE/ LOCATION	SOURCE OF ORGANIC CHLORIDE	AMOUNT OF ORGANIC CHLORIDE IN FEED	CORROSION PROBLEM	OTHER COMMENTS
87C7.1-21	German refinery	In crude oil	10 ppm (sometimes total Cl)	Hydrotreater furnace experienced stress corrosion cracking (SCC) of UNS 30400 (type 304 SS) tubes	Dry NH ₄ Cl deposits formed during the run. SCC occurred from water washing during a shutdown; failed on startup.
87C7.1-25	Montana refinery	Slugs		Hydrotreater condenser downstream from hot reactor effluent coolers	Lost 9.5 mm (0.37 in.) in four weeks (125 mm/y [5,000 mpy]); added a corrosion probe; when it goes up, they inject neutralizing amine.
96C5.9-03 99C5.2-47	California refinery	Use of cationic polymers for cleaning		Found evidence in deposit from a vacuum gas oil (VGO) line.	Examples are quaternary amine chloride; could be used with slops or in the oil field.
99C5.2-36	California oil field	Cleaning water in a flotation process adding cationic polymer; putting all slop back into the crude oil.			Oil producers were selling water to agriculture.
99C5.2-37			Problems occur with 1 to 2 ppm in feed.	Accelerated HCl corrosion in CDU atmospheric tower overhead.	They were using an inadequate test method that was only detecting down to 30 ppm.
99C5.2-46				CDU and NHTs	Measurements showed that 25 to 75% of organic chlorides break down in the CDU and remainder (~50%) stays in the naphtha.

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REFIN•COR PARAGRAPH NO.	CRUDE/ LOCATION	SOURCE OF ORGANIC CHLORIDE	AMOUNT OF ORGANIC CHLORIDE IN FEED	CORROSION PROBLEM	OTHER COMMENTS
99F5.3-13	Californian (naphthenic)	Theories were air flotation units in the oil field, or from desalting problems with naphthenic-acid- containing crude oil.	35 ppmw in gas oil feed to FCCU.	None reported.	A hard brittle dark scale was found in the top VGO cut that was highly water-soluble and 13% Cl.
2000F5.8-01		May be hydrogen from catalytic reforming unit.	2 ppm in naphtha (<100 ppmw water)	Pitting failures on titanium tubes in the NHT effluent cooler (shell and tubes).	Due to dry NH ₄ Cl at 121 °C (250 °F). They plan to install a chloride trap in the feed stream.
2001F5.2-20		Fire-retardant chemical injected in the well.			They had to selectively blend this high-chloride crude oil into the feed at low charge rates.
2001F5.2-34		Slop from chemical plants.	Slop was very high in organic chlorides.		Blended 80 m ³ /d (500 bpd) of slop into a 20,700 m ³ /d (130,000 bpd) CDU. They saw higher than normal chlorides in the atmospheric tower overhead and the NHT.

^(A)Testing was addressed in REFIN•COR paragraphs 87C7.1-23, 87C7.1-24, 99C5.2-36, 99C5.2-37, 99C5.2-38, 99C5.2-39, 99C5.2-41, 99C5.2-45, and 2000F5.2-24.