Crude Unit Corrosion Guide

A Manual for Plant Operators, Process Engineers, Metallurgists, Maintenance Engineers, Inspectors, and Equipment Specialists

By Joerg Gutzeit

NACE INTERNATIONAL

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Revised 3rd Edition

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NACE International
The Worldwide Corrosion Authority

Printed in the United States of America

ISBN: 978-1-57590-330-9

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Preface to the Revised 3rd Edition

The *Crude Unit Corrosion Guide* was written for plant operators, process engineers, metallurgists, maintenance engineers, inspectors, and all others who deal with corrosion and fouling issues on a daily basis. In the past, most refineries also employed corrosion engineers. That position has all but disappeared as the experienced practitioners moved on, retired, or were replaced by engineering contractors, equipment builders, and process additives suppliers.

Like the earlier editions of the *Guide*, the Revised 3rd Edition is based primarily on the author's experience dealing with all aspects of corrosion and fouling in crude units. The *Guide* also reflects the Industry's consensus experiences reported at past meetings of the NACE[1] STG34 Committee on Petroleum Refining and Gas Processing (formerly T8 Committee on Refining Industry Corrosion) and the API[2] Subcommittee on Corrosion and Materials. Diluent recovery units (DRUs) and vacuum distillation units (VDUs) of bitumen upgraders are quite similar to crude units with similar corrosion and fouling issues and are now included in the discussions where appropriate. In addition to corrosion and fouling issues with the usual 3 or 4 crude types, the *Guide* now covers various bitumen-derived crudes, including synthetic crude, dilbit crude, synbit crude, and shale crude all of which have come to market in recent years.

In many ways, refinery corrosion and fouling control remained more "Art than Science." Despite college-level courses in corrosion and materials science and ongoing efforts by NACE, API, and ASM[3], few resources for practical training on plant corrosion and fouling control are available. In recent years, process simulation (PS) and risk-based inspection management (RBIM) software has been very helpful for identifying and ranking critical components on which to concentrate future inspection and maintenance efforts. However, a certain amount of expertise is still required to facilitate reliable data input and assessment. The *Guide* attempts to present in compact form what the author considers the most important aspects of corrosion and fouling control in the atmospheric and vacuum sections of crude units and the corresponding sections in bitumen upgraders. Various chapters deal with general corrosion characteristics of different feedstocks; materials of construction (metallurgy); corrosion and fouling monitoring; feedstock preparation by tank settling, desalting, and caustic injection; and the types of damage seen in major components. Other chapters cover specific topics, including preheat exchanger fouling; high-temperature corrosion and fouling by organic sulfur compounds and naphthenic acids in fired heaters, transfer lines, and distillation columns; low-temperature corrosion and fouling by inorganic chlorides in the top of columns and in overhead systems; organic chloride problems; and various issues with neutralizer, corrosion inhibitor, and water injection systems.

While the *Guide* is not a formal literature review per se, important reports, research papers, and monographs published during the past 60 years or so are cited in the text, or listed at the end of each chapter. Many are out of print, but worth pursuing in university, public, or corporate libraries. All data and illustrations are by the author, unless otherwise credited. NACE members are reminded that they can obtain, at no charge, copies of conference proceedings, reports, and standards published by NACE since 1996. Also, the discussions on refinery corrosion and fouling issues during the biannual NACE STG34 (formerly T8) *Technical Information Exchange* were recorded since 1957 and are available up to 2008 on a searchable CD disk.[4] Annual updates can be downloaded from NACE.

January 2016
Joerg Gutzeit

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1. NACE International (formerly National Association of Corrosion Engineers), Houston, TX.
2. American Petroleum Institute, Washington, DC.
3. ASM International (formerly American Society for Materials), Metals Park, OH.
4. *REFIN•COR Vers.10.0*.

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1.1 First Glance

Crude oil (commonly called "crude" in singular or plural form) originated from organic matter in marine and other aquatic deposits over a period of many thousands to millions of years. The oil migrated from the deposit sites to geological traps or reservoirs. During this process, the oil composition changed: the oil matured (aged) and became heavier, while evolving gases, such as methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and water (H_2O) vapor.[1] Crudes range in consistency from waterlike liquids to tarlike solids, and in color from clear to black. Since the nature of the original deposits and the subsequent aging processes varied from reservoir to reservoir, crude compositions varied accordingly. The principal components of crude are aromatic, naphthenic, paraffinic, and asphaltic hydrocarbon species; aromatic or naphthenic ring structures make up the bulk of crude.

1.2 Crude Sources

Crudes are usually named after the reservoir, geographic area, or country where they are produced. In practice, a crude source may encompass several different fields: Arabian Light, for example, comes from numerous wells in an area covering hundreds of square kilometers (square miles). However, the name by itself does not guarantee a product of constant composition or properties; crude from any given reservoir is bound to change over time. In addition, there can be major differences between individual crude cargoes to a refinery, depending on how the crude was produced, recovered, treated, and shipped. When purchasing crude, many plants still rely on crude assays obtained years ago instead of insisting on up-to-date crude analyses. As a result, crude unit operators are often surprised to find that processing, corrosion, or fouling characteristics have changed even though a given crude slate (at least in name) has remained the same. Overall, crudes have not only become heavier, but also more corrosive. Over 70% of the world's estimated crude reserves now have API gravities below 20, including heavy crude, extra heavy crude, and bitumen.

1.3 Processing and Corrosion Characteristics of Crude

Other than source, important crude characteristics affecting corrosion and fouling properties and therefore purchasing decisions and price include API gravity, UOP characterization factor K, sulfur content, total acid number (TAN), and salt content.

1.3.1 API Gravity. °API (commonly called API gravity) defines crude in terms of weight per unit volume and is useful, because crudes are sold on the basis of volume delivered, while pumping cost, freight rates, and tanker cargoes are determined on the basis of weight. More important, however, API gravity also defines the processing, corrosion, and fouling characteristics of crude. As a general rule, the lower the API gravity, the less desirable and less expensive crude is for several reasons: Pumping costs increase inversely with API gravity and heat and various chemicals have to be applied to aid pumping and reduce the amount of water accompanying all crudes. Water not only represents useless cargo, but also increases corrosion, fouling, and maintenance costs of pipelines, tank farms, and tanker cargo holds. At the refinery, low API gravity crudes are more expensive to process, because of increased tank settling and desalting costs and increased corrosion, fouling, and maintenance costs of preheat exchangers (PHEs), fired heaters, columns, and overhead systems.

API gravity is a dimensionless[2] number and is usually measured with a hydrometer as detailed in *ASTM[3] D-287 Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)*. The hydrometer has a modified Baumé scale designed so that most crudes fall between 10 and 70 degrees. API gravity of crudes ranges from less than 12 (specific gravity over 0.986) to more than 30 (specific gravity below 0.875) and higher, as shown in Table 1-1. By definition, API gravity is a measure of how light or heavy crude is compared to water. In comparison to crude, water has an API gravity of 10 (specific gravity of 1.000). If the API gravity is greater than 10, the crude is lighter than water and floats on top of water. If the API gravity is less than 10, the crude is heavier than water and settles out at the bottom of separators, tanks, and piping. Thus API gravity determines how difficult it is to separate water from a crude in order to meet pipeline BS&W[4] specifications. With high API gravity (light) crude, water can be readily removed in upstream and midstream operations in simple water-settling drums or tanks. With low API gravity (heavy) crude, heater-treaters and desalters have to be deployed along with water-settling drums or tanks.

In downstream operations, API gravity determines primarily the ease of water and salt removal in the crude receiving tanks. Most, if not all, crudes require additional desalting at the plant, and API gravity determines the optimum desalting, dewatering, and solids removal efficiencies (in %) obtainable with single or double desalting. Since API gravity determines the amount of entrained salt left in crude, API gravity also affects the extent and severity of low-temperature corrosion and fouling in preheat exchangers, flash drums, and flash columns upstream of the fired heater and, by extension, the severity of low-temperature corrosion and fouling in the top and overhead system of the atmospheric and vacuum columns downstream of the fired charge heater.

1.3.2 UOP Characterization Factor K. The UOP (or Watson) characterization factor K defines crudes in terms of the predominant hydrocarbon species. While primarily of interest from a processing point of view[5], it can also affect corrosion-related decisions. UOP K factors for various types of crude normally range from approximately 10 to 13. K factors at the high end of the range (12.5 to 13) characterize crudes containing primarily paraffinic species, K factors in the mid range (11.5 to 12.5) characterize crudes containing primarily aromatic species, K factors at the low end of the range (11 to 11.5) characterize crudes containing naphthenic species, while K factors below 11 characterize crudes containing asphaltic species.

TABLE 1-1 API GRAVITY OF VARIOUS CRUDES

API Gravity	Specific Gravity	Weight/BBL, kg (lb)	Type	Examples
>30	<0.875	<139 (305)	Light and ultralight crude	Alaska North Slope, Edmonton Lt. Sour, ND Bakken Shale Crude, TEF Shale Crude
20 - 30	0.875 - 0.935	139 - 148 (305 - 325)	Intermediate crude	East Texas Medium, Lloydminster Hvy Sour, Athabasca Oil Sands Synthetic Crude, Synbit
12 - 20	0.935 - 0.986	148 - 156 (325 - 343)	Heavy, low resid crude	Venezuela Mesa, Athabasca Oil Sands Dilbit, Orinoco Tar Sands Merey
<12	>0.986	>156 (343)	Extra heavy crude	Athabasca Oil Sands Bitumen, Orinoco Tar Sands Bitumen

1.3.3 Sulfur Content. Sulfur content expressed as % S (or % total S) characterizes crudes in terms of potential high-temperature sulfidic corrosion (HTSC) by various organic sulfur compounds above approximately 230 °C (450 °F)[6]. As a general rule, the higher the sulfur content, the less desirable and less expensive crude is. High-sulfur crudes require alloy upgrading of many high-temperature circuits in refineries and bitumen upgraders. Aside from corrosion considerations, high-sulfur crudes tend to be heavy crudes and can be expected to be more difficult to transport, store, and desalt compared to low-sulfur crudes. They also require additional and often expensive downstream processing in order to yield products that meet sulfur and emission specifications.

1.3.4 Total Acid Number. Total acid number or TAN expressed as mg KOH/g crude characterizes crudes in terms of potential naphthenic acid corrosion (NAC) above approximately 230 °C (450 °F)[7]. As a general rule, the higher the TAN, the less desirable and less expensive crudes are. High-TAN crudes usually require alloy upgrading of many high-temperature circuits in refineries and bitumen upgraders beyond that required for high-sulfur crudes. High-TAN crudes may also require alloy upgrading of column tops and overhead systems to control corrosion by light organic acids, such as acetic acid (CH_3-COOH), formic acid (H-COOH), or proprionic acid (CH_3CH_2-COOH). These acids can form when naphthenic acids [R-$(CH_2)_n$–COOH] decompose in the fired heaters of the atmospheric and vacuum sections. Aside from corrosion considerations, high-TAN crudes are often more difficult to desalt and dewater than low-TAN crudes because sodium coordination complexes (“naphthenate soaps”), such as $[R-(CH_2)_n-COO]_2-Na$ or $[R-(CH_2)_n-COO]_6-O-Na_3$ tend to form and cause foaming in the desalter.

1.3.5 Salt Content. Inorganic salt content (expressed as mg/L or PTB[8] chlorides) characterizes crudes in terms of potential corrosion and fouling below approximately 230 °C (450 °F). Inorganic chloride salts in crude include sodium chloride (NaCl), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$) that originate with formation water[9], production brines, water floods, surface waters, and tanker ballast from upstream production and midstream treating and transportation operations. Upon passing through the hot preheat exchangers (HPE)[10] and fired crude heater, magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) partially hydrolyze to hydrogen chloride (HCl). Subsequent reaction of HCl with ammonia (NH_3) or liquid organic neutralizers then yields ammonium hydrochloride (NH_3•HCl) or neutralizer hydrochlorides (R-NH_2•HCl), respectively, and leads to a variety of corrosion and fouling issues in column tops and overhead systems. As a general rule, the higher the salt content, the less desirable and less expensive crudes are, because crude desalting by water extraction becomes more critical. Often, extended tank settling, double desalting, and caustic addition are required to sufficiently lower chloride levels. Alloy upgrading of many low-temperature circuits, including the upper distillation columns and the overhead systems in refineries and bitumen upgraders, often becomes necessary and injection of various process chemical additives is often necessary.

1.4 Hydrocarbon Components of Crude

Crude consists of relatively few homologous series of hydrocarbon molecules containing 84-87% carbon (C), 11-14% hydrogen (H), 0-6% sulfur (S), and up to 2% each of nitrogen (N) and oxygen (O). The blend of hydrocarbon molecules may include from 1 to 70 or more carbon atoms and crude properties depend primarily on the number and arrangement of the carbon and hydrogen atoms in the molecules. For example, hydrocarbons containing less than 4 carbon atoms are usually in the form of gases, those with 5 to 19 carbon atoms are usually liquids, and those with over 20 carbon atoms are solids. The relative amounts and types of the major constituents of crude are listed in Table 1-2; unsaturated olefins (R–C=C-R) are rarely found in crude.

TABLE 1-2 HYDROCARBON COMPOSITION OF CRUDE

Category	Type	Chemistry	Amount, wt%
Alkanes, paraffins, asphalts	Saturated n-alkanes and iso-alkanes	To C_{78}	15 - 60
Aromatics	Unsaturated structures with one or more aromatic nuclei	C_nH_m	3 - 30
Waxes	Unbranched n-alkanes	To C_{30}	?
Naphthenes	Cycloparaffins or cycloalkanes	C_nH_{2n}	30 - 60
Hydrocarbon gases	Methane butane, propane	CH_3 to C_3H_8	?
Unsaturated olefins	?	R-C=C-R	Rarely
Heteroatomic compounds	Organic sulfur, nitrogen, and oxygen compounds	Many types	Balance

1.5 Principal Crude Types

As far as corrosion and fouling in crude refineries are concerned, the six principal types of crude charged are sweet crude, sour crude, acidic crude, bitumen-derived crude, shale crude, and opportunity crude. Bitumen upgraders receive primarily diluted bitumen (dilbit) for conversion into crude.

1.5.1 Sweet Crude. The term "sweet crude" originated from the fact that a low level of organic sulfur provides crude with a mildly sweet taste and pleasant smell. Crude traders designate crude with less than 0.4% S as sweet. From a corrosion point of view, the term usually describes any low-sulfur crude with less than 0.6% S as opposed to high-sulfur or "sour crude" with more than 0.6% S. Sweet crude may also contain small amounts of free[11] hydrogen sulfide (H_2S) and dissolved carbon dioxide (CO_2). High-quality, light sweet crude is the most sought-after crude as it contains a large hydrocarbon fraction that can be directly distilled into gasoline (light naphtha), kerosene, diesel, and various gas oil fractions without additional processing. *West Texas Intermediate (WTI)* crude contains approximately 0.25% S and is traded on the New York Mercantile Exchange (NYMEX) as a benchmark for crude pricing, while *North Sea Brent* crude with approximately 0.35% S is traded as a benchmark on the London ICE Futures Europe Exchange for refining in Northern Europe.

1.5.2 Sour Crude. The term sour crude refers to crudes that contain significant amounts of free hydrogen sulfide (H_2S) regardless of organic sulfur content. As originally defined, sour crudes contain and evolve more than $4 \cdot 10^{-4}$ m^3/100L (0.05ft^3/100gal) free H_2S. The industry currently uses the term sour crude simply to designate any crude with more than 0.6% S. While sour crude has an obnoxious odor, free H_2S presents no high-temperature corrosion issues until the crude contains and evolves at least 10 times that amount, or $4 \cdot 10^{-3}$ m^3/100L (0.5ft^3/100gal). In contrast to H_2S, organic sulfur compounds in crudes can attack components fabricated from carbon and low-alloy Cr-Mo steels at temperatures above approximately 230 °C (450 °F). The resultant complex iron sulfide scales can become pyrophoric when exposed to the atmosphere during shutdown.