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Corrosion Problems and Solutions in Oil Refining and Petrochemical Industry

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Chapter 2
Physicochemical Properties of Crude Oils

> *The great aim of education is not pure knowledge but its application.*
>
> Herbert Spencer (1561–1626), an English philosopher.

Abstract Physicochemical properties and components of crude oils affecting their corrosiveness are described. Corrosiveness of crude oils is defined by water and salt content, total sulfur content, total acid number, microorganisms, and conditions (temperature, flow regime, etc.). Not all sulfur compounds and acids are corrosive to metals. Hydrogen sulfide is most corrosive among sulfur substances. The corrosiveness of crude oil containing water can be determined by a combination of three properties: the type of emulsion formed between oil and water, the wettability of the steel surface, and the corrosiveness of aqueous phase in the presence of oil. A case study with analysis and solution is given.

In order to understand corrosion problems and solutions in oil refining and petrochemical industry, we will describe physicochemical characteristics of crude oils and their corrosiveness. Other media, such as water (cooling water, boiler feed water, extinguishing water), steam, different gases and chemicals also can participate in corrosion of equipment at refining and petrochemical units. Crude oil types and their physicochemical properties are described in Appendix B. First, we will describe constituents of crude oils and components related to their corrosiveness.

2.1 Physicochemical Composition of Crude Oils

Crude oil is a mixture of numerous liquid hydrocarbons containing dissolved gases, water, and salts. Crude oils vary widely: from almost solid and heavy that sink in water up to light materials that float on water. Crude oils are, in fact, emulsions—drops of aqueous solution dispersed throughout the continuous hydrocarbon phase. Interstitial or connate water is always present in crudes. These water drops vary from almost fresh to saturated aqueous solutions of salts and are the main cause of

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Table 2.1 Crude oil constituents [2, 3]

Constituent	Chemical type
Hydrocarbons:	
Paraffinic (Alkanes)	Straight chain; branched chain
Naphthenic	Alkyl cyclopentanes; alkyl cyclohexanes
Aromatic	Alkyl benzenes; aromatic naphthenic fluorenes; polynuclear aromatics
Dissolved gases	Nitrogen (N_2); carbon dioxide (CO_2)
Sulfur compounds	Elemental sulfur (S_8), hydrogen sulfide (H_2S)[a], mercaptans; organic sulfides, disulfides and polysulfides; thiophenes and benzothiophenes; sulfones
Organic nitrogen compounds	Pyridine, quinoline
Organic oxygen compounds	Carboxylic acids (including naphthenic acids)[b], alcohols, phenols[b], aldehydes, ketones, esters, ethers, oxyacids
Organic metallic compounds	Porphyrins
Colloidal particles	Asphaltenes; resins; paraffin waxes
Surfactants	Sulfonic acids, sulfonates, sodium napthenates
Metals	Vanadium, nickel[c], iron[c], aluminum, sodium, potassium, calcium, copper
Water (S&W[d] or BS&W[d])[e]	Fresh or saline
Solids	Sand, dirt, silt, soil dust, mud, corrosion products (metals' oxides, sulfides, salts)

[a] Hydrogen sulfide is present as dissolved gas
[b] They are surfactants
[c] They are present in porphyrins
[d] S&W—sediment and water; as previously called BS&W—bottoms sediment and water [2]
[e] Microorganisms can be present in crude oils

crude corrosiveness. Crude oils in addition to hydrocarbons can include also compounds containing sulfur (S), nitrogen (N), oxygen (O), and metals (Table 2.1). All these contaminants may be present in crude oils as dissolved gases, liquids and solids or distinctive phases. Microorganisms also can be present in crudes in active or dormant state. Every crude contains about the same kinds of compounds, but in different proportions. As a result, crude oil differ by their corrosiveness.

2.2 Corrosiveness of Crude Oils

Chemistry of crude oils is so complicated and there are so many factors influencing corrosiveness of crudes that it is difficult and even in most cases impossible to predict their corrosiveness according to physicochemical composition. Usually corrosiveness of crude oils is defined by total acid number (TAN), total sulfur content, water and salt content, and microorganisms. The combination of these parameters and components influences corrosion by different manner and differently at stages of preparation, transportation, storage, and processing crude oils at refineries. Both TAN value and total sulfur content do not always define corrosiveness of crudes. For instance, H_2S and alkanethiols are corrosive to carbon steel, while thiophenes are not corrosive. Therefore, it was suggested speciation of corrosive (H_2S and alkanethiols) and non-corrosive (thiophenes) organic sulfur compounds in crudes using physicochemical analytical methods with the aim to define potential corrosiveness of crudes [1]. The problem is complicated by the fact that H_2S and alkanethiols reacting with iron form iron sulfide scale which under particular conditions can be protective (see Fig. 3.1).

Sometimes crudes containing relatively high water content can inhibit corrosion and, vice versa, crudes may be corrosive at relatively low water concentrations. Only experiment can respond on the question about corrosiveness of crudes. Usually crude oils are not corrosive under pipeline transportation conditions. However, water can drop-out and accumulate at low velocities and under stagnant conditions. As a result, corrosive contaminants in crude are dissolved in separate liquid aqueous phase and cause corrosion of inner surface of pipelines. It is possible to use model for determination the velocities at which water could drop out of crude oil as a function of the crude oil density and viscosity [4]. Water is less likely to drop out at lower velocities when entrained in heavier crudes compared to light crudes. These velocities are well below normal operating velocities on most transmission pipelines. The deposition of sediments and water are minimized in highly turbulent flow.

The low corrosiveness of most crude oils (including oil sands) in transmission pipelines is due to the fact that corrosive (water, dissolved salts) and erosive (sand, mud) constituents are largely removed before transportation [5]. Quality specification for crude oil transporting in pipelines requires that basic sediment and water (BS&W) content should be <0.5 vol% because most corrosion problems are caused by dropping out the above mentioned corrosive contaminants of the crudes [6–10]. Corrosive sulfur compounds (excluding H_2S) and organic acids (including naphthenic acids) do not cause corrosion in pipelines at operating temperatures of transportation, usually at 5–50 °C. They can cause corrosion under refinery processing conditions at temperatures >190 °C (naphthenic acids) and >230 °C (sulfur compounds).

Water, salts, H_2S and microorganisms containing in crudes as contaminants can cause corrosion during storage in tanks or transportation in tankers. In the absence of water, the crude oil is noncorrosive in tanks and tankers, even some types of crude oils possess inhibitive properties. It is not easy to predict an extent of crude oil corrosiveness because of many complicated factors. The methods of determination of crude oil corrosiveness were developed and they will be considered in the next section.

2.3 Determination of Crude Oil Corrosiveness

The corrosiveness of crude oil containing water can be determined by a combination of three properties:

(a) The type of emulsion formed between oil and water (the emulation of the oil and water).
(b) The wettability of the steel surface.
(c) The corrosiveness of aqueous phase in the presence of oil.

These three properties are described below.

(a) The type of emulsion formed between oil (O) and water (W). Water and oil are immiscible but they can form emulsion under certain conditions. There are two kinds of emulsion: O/W and W/O. W/O emulsion (in which oil is the continuous phase) has low electric conductivity and is thus less corrosive; whereas O/W (in which water is the continuous phase) has high electric conductivity and, hence, can be more corrosive. The percentage of water at which W/O converts to O/W is known as the emulsion inversion point (EIP). EIP can be determined by measuring the electrical conductivity of the emulsion. At and above the EIP, a continuous (separate) phase of water or free water is present. Therefore, there is a potential for corrosion.
(b) The wettability of the steel surface. Whether water phase can cause corrosion in the presence of oil depends on whether the surface is oil-wet (hydrophobic) or water-wet (hydrophilic). Because of higher electrical resistance, an oil-wet metal surface is not susceptible to corrosion, but a water-wet surface is. It is important also the geometry type of metal surface on which water droplets are separated from crude oils: horizontal, sloping, or vertical. Horizontal metal surfaces, on which water droplets tend to be retained, are more prone to corrosion than sloping or vertical surfaces [11].
(c) Influence of impurities in oil phase on corrosiveness of aqueous phase. Dissolution of corrosive contaminants (H_2S, chloride salts, HCl—see Sect. 2.3.1, light organic acids) from crude oils may alter the corrosiveness of the aqueous phase. Crude oils can be classified as corrosive, neutral, or inhibiting crudes. This classification is based on the corrosiveness of the aqueous phase in the presence of crude oil [12–14].

Corrosion problems related to crude oils in addition to low velocity flow and stagnation conditions, can occur later in oil refineries if desalters do not function properly.

It is important to emphasize that crude oil supply patterns are often changing as production from traditional supply basins decline and new sources of supply come on-stream. Corrosiveness of crudes can also change respectively. Sometimes groundless allegations appear in mass media, for instance, about increased corrosiveness of new unconventional crudes. In this case, it is important to prove by means of experiment that these new crudes do not represent increased corrosion risk compared to conventional crudes. For instance, the bitumen produced in oil sands operations must be processed or mixed with lighter hydrocarbons for transport in pipelines. Some bitumen is upgraded to synthetic crude oil and called *synbit*. Bitumen mixed with light Canadian condensate is referred to as *dil*uted *bit*umen, or *dilbit* (see Appendix B). Mixtures of the two are sometimes referred to as *syndilbit* [15]. Corrosion rates of steel used for pipelines (API 5L X-65) in different types of crudes (dilbit, synbit and conventional crudes) changed in 0.001–0.03 mm/year (so low values!) both in aqueous and oil phases [15]. There was no correlation between physicochemical properties of crudes (TAN, sulfur and water content) and corrosiveness. Weight loss (WL) method of determination of corrosiveness of crudes has long exposure time and low reproducibility. Coupons (used in WL method) can sometimes gain weight due to adhesive product buildup. Radioactive tracer technology was used to measure high temperature crude corrosiveness with very high sensitivity during 1 h to avoid thermal degradation of organic acids [16]. The disadvantage of radioactive method is that it requires complicated equipment and skillful personnel.

Example of corrosion problems described above concerning crude oil at oil refinery is shown in the following case study.

2.4 Case Study

Conditions. Crude oil after desalter flowed in the shell at 140–190 °C and 12 bar.

Material of construction. Carbon steel A516 Gr.70. Wall thickness of the shell—12.5 mm.

Service period before the failure: 2 years. The heat exchanger was filled with crude oil and has not been worked during 8 months among 2 years of service.

Visual examination and findings. Deposits and pits of 6–7 mm in deepness were found on inner surface of the lower part of the shell (Fig. 2.1).

Corrosion pitting rate growth was 3–3.5 mm/year. Analysis of salt content in crude oil after the desalter showed that during 2 years these values changed in the range 2–6 ptb when allowable maximum concentration is 1 ptb.

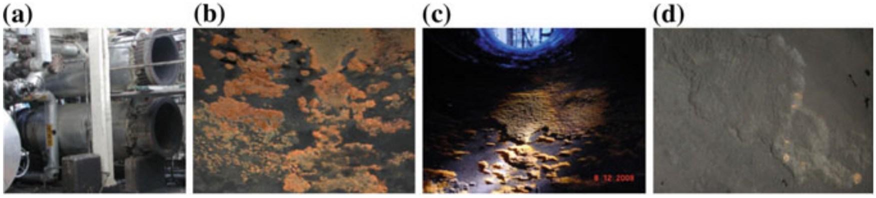

Fig. 2.1 **a** General view of failed two heat exchangers. **b–d** Inner surface of corroded heat exchanger shell

X-ray fluorescence (XRF) analysis. The deposits formed inside the shell of the heat exchanger contained Fe, S, Ca, Na, Si, and Cl.

Chemical analysis. Deposits (inorganic part) mostly consisted of FeS and $Fe_2(SO_4)_3$.

Failure phenomenon: *Under deposit acid corrosion* [17].

Cause of failure and its explanation. Crude oil was in stagnation and did not flow 8 months through the heat exchanger. Deposits from the crude precipitated on the lower part of the heat exchanger shell. Hydrogen sulfide contained in crude oil reacted with iron forming iron sulfide. Ingress of air (oxygen) into the shell caused oxidation of sulfides to sulfates. Presence of water in crude oil resulted in hydrolysis of ferric sulfate $Fe_2(SO_4)_3$ salts and as a result pH decreased to 1–2 (reactions 2.1 and 2.2):

$$Fe_2(SO_4)_{3(aq)} \xrightarrow{\text{Water}} 2Fe^{3+}_{(aq)} + 3SO^{2-}_{4(aq)} \tag{2.1}$$

$$Fe^{3+}_{(aq)} + H_2O_{(l)} \rightarrow H^{+}_{(aq)} + (FeOH)^{2+}_{(aq)} \tag{2.2}$$

Thus, corrosion occurred under acid deposits of ferric sulfate salts.

Solutions and recommendations.

(a) In no case not to leave crude oil without flow in heat exchanger shell. To fill shell with gas oil for the stand-by period.

(b) To repair pits by welding.

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