



CORROSION CONTROL IN HEAT EXCHANGERS OF CRUDE OIL REFINING PLANTS: MECHANISMS, PREVENTION APPROACHES, AND THE CONTRIBUTION OF CORROSION INHIBITORS

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Abstract. Heat exchanger units rank among the refinery components most susceptible to corrosion damage, since they operate under a combination of elevated temperatures, thermal differentials, dual-phase streams, and corrosive contaminants present in crude oil. The present study examines the principal corrosion pathways affecting shell-and-tube exchangers as well as air coolers installed in atmospheric-vacuum distillation (AVT) facilities. Among these pathways are high-temperature sulfidic corrosion and hydrogen sulfide attack, hydrochloric acid corrosion within condensation regions, under-deposit corrosion caused by ammonium chloride and ammonium bisulfide, and erosion-corrosion phenomena.

The work further surveys prevention strategies that complement one another: desalting of crude feedstock, neutralization of overhead vapor streams, appropriate material selection, process parameter control, and the dosing of film-forming corrosion inhibitors. Particular emphasis is placed on the nitrogen-based film-forming inhibitor KAFN-2024, which was formulated by the author. Industrial-scale trials demonstrated protection levels of 94.6-95.1% at dosages of 75-100 ppm, thermal stability reaching 200 °C, and satisfactory performance across a pH window of 6.5-9.8. Findings indicate that a combined strategy - wherein a site-specific inhibitor works alongside desalting and neutralization measures - is capable of prolonging heat exchanger service life and lowering reliance on foreign-supplied chemicals.

Keywords: oil refinery, heat exchanger, air cooler, hydrogen sulfide corrosion, hydrochloric acid corrosion, ammonium chloride, under-deposit corrosion, corrosion inhibitor, KAFN-2024, atmospheric-vacuum distillation.

The refining sector of the Republic of Uzbekistan is undergoing modernization, and the dependability of processing equipment directly influences the economic performance of refineries. Corrosion-related damage continues to be a leading cause of unscheduled plant shutdowns. Based on international assessments, a significant portion of maintenance expenditure in refining is linked to corrosion of stationary equipment, with heat exchange apparatus responsible for a substantial share of these breakdowns [1, 2].

Heat exchangers hold a particularly important position in this context. Within an AVT facility, crude feedstock travels through an extended preheat train composed of shell-and-tube exchangers prior to reaching the furnace. Subsequently, overhead vapours from the



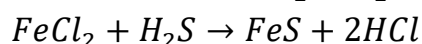
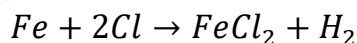


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atmospheric column are cooled and condensed within air coolers and water-cooled condensers. In every one of these installations, the metallic surface contacts media whose composition and temperature vary along the apparatus length. This gives rise to regions where water condenses, salts accumulate, and acidic constituents become concentrated.

The refining of sour and high-sulfur crude oils, which has expanded in recent years, exacerbates the problem. Sulfur-containing compounds break down upon heating and generate hydrogen sulfide, which participates both in low-temperature electrochemical corrosion and in high-temperature sulfidation of steel [3]. Magnesium and calcium chlorides that persist in the oil following desalting undergo hydrolysis inside the furnace and liberate hydrogen chloride, which converts into hydrochloric acid at the dew point of the overhead system [2, 4]. Tube failures in a heat exchanger lead to product contamination, diminished heat recovery, increased fuel consumption and, under the most severe circumstances, fire hazards. Substituting a tube bundle necessitates shutting down the unit. Consequently, developing dependable and economically sound corrosion prevention approaches for heat exchangers constitutes an urgent scientific and practical objective. The purpose of this study is to systematize corrosion mechanisms occurring in refinery heat exchangers and to justify an integrated protection strategy incorporating a domestically manufactured corrosion inhibitor. Corrosion processes in heat exchangers are governed by the apparatus location within the process flow diagram. Four categories of mechanisms are of greatest significance for AVT units [2, 3].

1. Hydrochloric acid corrosion in condensing zones. Hydrogen chloride generated through the hydrolysis of remaining chloride salts is carried along with the overhead vapours. At the location where the initial water droplets begin to condense, the acid becomes highly concentrated, potentially driving the pH down to values below 2-3. Carbon steel exposed in this region undergoes rapid corrosive degradation, and the damage typically concentrates at the entrance section of air coolers and condensers. This process is further intensified by the presence of H_2S , since iron sulfide layers that develop under HCl-containing conditions lack protective properties.



These two reactions form a cycle in which hydrochloric acid is regenerated, so even a small amount of HCl can cause continuous metal loss.

2. Hydrogen sulfide corrosion. Within the aqueous medium, H_2S undergoes dissociation and behaves as a weak acid. When it contacts carbon steel, it generates iron sulfide layers in the form of mackinawite, troilite and pyrrhotite. The degree to which these layers provide protection is governed by temperature, pH level and flow velocity [3]. Atomic hydrogen liberated during the cathodic reaction is capable of penetrating into the steel structure, giving rise to hydrogen blistering, hydrogen-induced cracking and sulfide





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stress cracking. On account of this, the provisions of ISO 15156 (NACE MR0175) are applied to materials intended for service in wet H_2S environments [5].

3. Ammonium salt and under-deposit corrosion. When ammonia or amine compounds coexist with HCl and H_2S , the result is the formation of ammonium chloride (NH_4Cl) and ammonium bisulfide (NH_4HS). Ammonium chloride is capable of precipitating from the vapour phase as a solid salt at temperatures above the water dew point. Owing to its strongly hygroscopic nature, a highly concentrated acidic solution develops beneath the deposit, leading to severe pitting attack [4, 6]. Deposits of NH_4HS are commonly encountered in air coolers within hydrotreating facilities, although they may also emerge in overhead systems whenever neutralizers are dosed improperly.

4. High-temperature sulfidic corrosion and erosion-corrosion. Within the hot section of the preheat train, at temperatures of approximately 230-400 °C, sulfur-bearing compounds interact directly with steel in the absence of an aqueous phase. The reaction rate is governed by the total sulfur concentration, the operating temperature and the chromium content present in the alloy. Under conditions of elevated flow velocity, particularly when solid particles are present or when two-phase flow occurs, protective scales are mechanically stripped away. Consequently, erosion-corrosion manifests at tube entrances, around baffles and within U-bend sections [2].

Under real operating conditions, these mechanisms do not act in isolation but rather in combination. Fouling deposits, for instance, simultaneously impair heat transfer, generate crevices that promote under-deposit corrosion, and entrap chlorides. For this reason, any prevention strategy must account for the entire set of contributing factors rather than addressing a single mechanism in isolation.

Corrosion control in refinery heat exchangers is based on several levels of protection that complement each other [1, 2, 6].

Level	Method	Mechanism addressed	Limitation
Feed preparation	Electric desalting, caustic dosing to crude	HCl formation from chloride hydrolysis	Cannot remove all chlorides; excess caustic causes fouling
Process control	Wash water injection, keeping metal temperature above salt deposition point	NH_4Cl and NH_4HS deposits	Requires accurate dew-point calculation and good water distribution
Neutralization	Ammonia or amine neutralizers to the overhead	Low pH at the dew point	Overdosing forms amine hydrochloride salts





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Level	Method	Mechanism addressed	Limitation
Materials	Cr-Mo steels, stainless steels, duplex, titanium, Ni alloys	High-temperature sulfidation, chloride attack	High capital cost; risk of chloride stress cracking in austenitic steels
Inhibition	Film-forming inhibitors	Electrochemical H ₂ S and HCl corrosion	Needs correct dose and continuous monitoring
Monitoring	Coupons, ER probes, analysis of Fe and Cl in boot water	Assessment of all measures	Indirect data; requires regular sampling

The initial protective measure involves maintaining the residual salt concentration in desalted crude at the lowest feasible level. The second measure consists of elevating the pH of the first condensate through the application of neutralizers. The selection of neutralizers must be carried out in such a way that their hydrochloride salts do not precipitate at the operating temperature of the overhead system [4].

Although upgrading tube materials represents an effective option, it is associated with considerable expense. Within the hot preheat train, 5Cr-0.5Mo and 9Cr-1Mo steels exhibit superior resistance to sulfidation compared with carbon steel. In overhead condensers, titanium or high-alloy materials are occasionally employed; however, for the majority of existing units, carbon steel continues to serve as the primary material, and its protection depends on chemical treatment [2].

The injection of inhibitors constitutes the most adaptable approach, since it does not necessitate reconstruction of the equipment. Organic inhibitors that incorporate nitrogen, sulfur or oxygen atoms become adsorbed onto the metal surface via the lone electron pairs of heteroatoms. The hydrocarbon portion of the molecule creates a hydrophobic layer that isolates the metal from the aqueous corrosive phase [7]. The adsorption behavior of such inhibitors is typically characterized by the Langmuir isotherm:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Here C is the inhibitor concentration, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant. The protective efficiency Z is calculated from the corrosion rates without (K_0) and with (K_1) inhibitor:

$$Z = \frac{K_0 - K_1}{K_0} \cdot 100\%$$

The KAFN-2024 inhibitor. As part of the author's doctoral investigation, a nitrogen-based film-forming inhibitor designated KAFN-2024 was synthesized for the purpose of suppressing hydrogen sulfide and sulfurous corrosion in AVT operations. Its performance





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was assessed through both gravimetric and electrochemical techniques. During gravimetric experiments, an H_2S -containing environment was produced via the reaction between aluminium sulfide and water, while the inhibitor dosage was adjusted across a range of 20-100 mg/l. The degree of protection rose as concentration increased and eventually levelled off, a trend consistent with monolayer adsorption described by the Langmuir model.

In industrial-scale trials conducted at CHILON LUBRICANTS LLC, KAFN-2024 was evaluated alongside the imported counterparts DODIGEN-481 and PS-40. The inhibitor delivered 94.6-95.1% protection at a dosage of 75-100 ppm, maintained stability at temperatures reaching 200 °C, and retained its efficacy within the pH interval of 6.5–9.8. This pH window corresponds to the conditions prevailing in the overhead condensing system following neutralization. Owing to its thermal stability, the inhibitor is well suited to the condensing section as well as the low-temperature portion of the preheat train, where electrochemical corrosion predominates. For heat exchanger applications, the recommended injection point for the inhibitor is the overhead vapour line positioned upstream of the air coolers, where it should be introduced together with the neutralizer and wash water. The dosage ought to be regulated based on the iron and chloride concentrations measured in the accumulator boot water, as well as on data obtained from corrosion probes.

Conclusion. Corrosion in refinery heat exchangers arises from the simultaneous influence of hydrochloric acid at the water dew point, hydrogen sulfide, ammonium salt deposits and elevated-temperature sulfidation; the most aggressive deterioration is observed in overhead air coolers and condensers belonging to AVT units.

Complete protection cannot be achieved through any single measure. Dependable operation is attained by means of an integrated scheme encompassing deep desalting, proper neutralization together with wash water injection, judicious material selection, continuous dosing of a film-forming inhibitor, and routine corrosion monitoring.

Film-forming inhibitors represent the most adaptable and cost-effective component of this scheme, as they safeguard existing carbon steel equipment without requiring reconstruction.

The domestically produced inhibitor KAFN-2024 delivered 94.6-95.1% protection at 75-100 ppm, thermal stability reaching 200 °C and effectiveness across the pH range 6.5-9.8, which is on par with the imported counterparts DODIGEN-481 and PS-40. Its deployment in the condensing sections of heat exchangers is capable of prolonging their run length and diminishing the reliance of Uzbek refineries on imported reagents.





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